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Small molecule activation using electropositive metal N-heterocyclic carbene complexes

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Declaration

The work described in this thesis is entirely my own, except where I have either acknowledged help from a named person or given reference to a published source. Text taken from another source will be enclosed in quotation marks and a reference given. This thesis has not been submitted, in whole or in part, for any other degree.

Signature: Date:

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Finally, for J.C.. I just couldn't have done it without you...

Abbreviations

General

°	degrees
°C	degrees Celsius
Å	angstrom
Ad	adamantyl
AIM	Atoms-in-molecules
Am	amylate, CMe_2Et
Ar	generic aryl group
Ar^F	pentafluorophenyl, C_6F_5
atm	atmosphere
9-BBN	9-borabicyclo[3.3.1]nonane
Bn	benzyl, $CH_2C_6H_5$
Bn'	*o*-aminobenzyl, 1-CH_2-2-NMe_2-C_6H_4
^{i}Bu	*iso*-butyl
^{n}Bu	*n*-butyl
^{t}Bu	*tert*-butyl
ca.	*circa*, about
cat	catecholate = 1,2-O-C_6H_4
C.N.	coordination number
cot	cyclooctatriene
Cp	cyclopentadienyl, C_5H_5
Cp*	pentamethyl cyclopentadienyl, C_5Me_5
Cy	cyclohexyl
d	day(s)
Dipp	2,6-^{i}Pr-C_6H_3
dme	dimethoxyethane
dmpe	$Me_2PCH_2CH_2PMe_2$
DFT	Density Functional Theory
Flu	fluorenyl, $C_{13}H_9$
g	grams(s)
GC	Gas Chromatography
GPC	Gel Permeation Chromatography

h	hour(s)
HOMO	Highest Occupied Molecular Orbital
Ind	indenyl, C_7H_9
IR	infrared
K	Kelvin
$kJmol^{-1}$	kilojoules per mole
L^D	$OCMe_2CH_2(1\text{-}C\{NCH_2CH_2NDipp\})$
Ln	lanthanide
LUMO	Lowest Occupied Molecular Orbital
MBO	Mayer Bond Order
Me	methyl
Mes	mesityl, 2,4,6-Me-C_6H_2
mL	millilitre(s)
mmol	millimole(s)
µmol	micromole(s)
MS	Mass Spectrometry
N'	$N(SiHMe_2)_2$
N''	$N(SiMe_3)_2$
N'''	$N(SiMe_3)_3$
NAO	Natural atomic orbital
NHC	N-heterocyclic carbene
Np	neopentyl, CH_2CMe_3
PDI	Polydispersity Index
Ph	phenyl
pin	pinocolate, $(OCMe_2)_2$
^iPr	*iso*-propyl
q_x	partial charge on atom x
rac	racemic
rt	room temperature
R	generic alkyl group
s	second(s)
SQUID	Superconducting Quantum Interference Device
tacn	1,4,7-triazacyclonane
thf	tetrahydrofuran
tmeda	tetramethyldiamine

Nuclear Magnetic Resonance spectroscopic data

$^{13}C\{^{1}H\}$	proton decoupled ^{13}C NMR experiment
$^{1}H\{^{1}H\}$	proton decoupled ^{1}H NMR experiment
app.	apparent
δ	chemical shift in ppm
br.	broad
d	doublet
dd	doublet of doublets
^{x}J	coupling constant over x bonds
Hz	Hertz
m	multiplet
MHz	Megahertz
NMR	Nuclear Magnetic Resonance
ppm	parts per million
s	singlet
t	triplet
tt	triplet of triplets
COSY	2D correlation spectroscopy

Mass spectroscopic data

EI	Electron Impact
FI	Field Ionisation
m/z	mass to charge ratio
M^{+}	molecular ion

Infrared spectroscopic data

br.	broad
cm^{-1}	wavenumber
IR	Infrared
m	medium
s	strong
w	weak

Abstract

The versatility of N-heterocyclic carbenes (NHCs) is demonstrated by numerous practical applications in homogeneous transition metal catalysis, organocatalysis and materials science. There remains a paucity of electropositive metal NHC complexes and so this chemistry is poorly developed with respect to that of the late transition metal and main group elements. This thesis describes the synthesis of new alkoxy-tethered NHC proligands, their use in the synthesis of reactive metal amide and metal alkyl complexes, and finally small molecule activation using these complexes.

Chapter One introduces NHCs and discusses their use as supporting ligands for early transition metal and f-block complexes. Small molecule activation using organometallic complexes is examined alongside the use of electropositive metal NHC complexes in catalysis.

Chapter Two contains the synthesis and characterisation of new alkoxy-tethered NHC proligands and a variety of electropositive M^{II} (M = Mg and Zn), M^{III} (M = Y, Sc, Ce and U) and M^{IV} (M = Ce and U) amide complexes. X-ray diffraction studies and a DFT study are used to probe the extent of covalency in the bonding of the M^{IV} complexes.

Chapter Three investigates the reactivity of the amide complexes prepared in Chapter Two. The M^{II} complexes are shown to be initiators for the polymerisation of *rac*-lactide into biodegradable polymers. The M^{III} complexes are used to demonstrate addition-elimination reactivity of polar substrates across the M-$C_{carbene}$ bond which allows the formation of new N-E (E = Si, Sn, P or B) bonds. Treatment of the U^{III} silylamide complex $U(N\{SiMe_3\}_2)_3$ with CO results in the reductive coupling and homologation of CO to form an ynediolate core $^{-}OC{\equiv}CO^{-}$ and the first example of subsequent reactivity of the ynediolate group. The M^{IV} complexes are used to examine the potential for forming M^{IV} cationic species and alkyl complexes.

Chapter Four examines the synthesis of M^{III} (M = Ce and Sc) aminobenzyl complexes and M^{III} (M = Y, Sc and U) neosilyl and neopentyl alkyl complexes. The addition-elimination reactivity discussed in Chapter Three is extended to include C-E bond formation (E = Si, Sn, P, B, I or C).

Chapter Five provides overall conclusions to the work presented within this thesis.

Chapter Six gives experimental and characterising data for all complexes and reactions in this work.

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Chapter Two: Synthesis of metal amide complexes

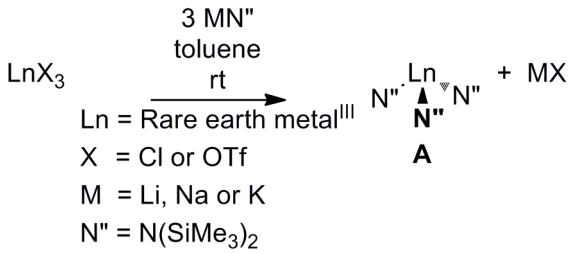
Chapter Three: Reactivity of metal amide complexes

Introduction

1.1 Neutral metal silylamide complexes

1.1.1 Yttrium, scandium and the lanthanides

The homoleptic *tris-bis*(trimethylsilyl)amido M^{III} complexes **A**, MN''_3 (M = Y, Sc or Ln, N'' = $N(SiMe_3)_2$) are extremely useful synthetic precursors in rare earth chemistry and have been prepared for the entire series (excluding Pm) (Equation 1). Typically, the treatment of 1 equivalent of MCl_3 with 3 equivalents of MN'' (M = Li, Na or K) affords MN''_3. The use of Na or K reagents avoids the potential problem of salt incorporation, as have been observed by the isolation of $[YN''_3Cl][Li(thf)_4]$[1] and $NdN''_3(\mu\text{-}Cl)Li(thf)_3$.[2] An alternative method of synthesis involves reaction of 1 equivalent of $M(OTf)_3$ (OTf = OSO_2CF_3, M = Ce, La, Nd, Sm, Er) with 3 equivalents of NaN''.[3] This has resulted in a significant improvement of the yield of CeN''_3.



Equation 1: Synthesis of homoleptic rare earth M^{III} *tris-bis*(trimethylsilyl)amido complexes

MN''_3 have been most commonly utilised in protonolysis reactions with protic ligands of the general form HA to afford M-A bonds and eliminate HN''. This strategy, the "silylamide route",[4] is effective for a range of HA given that HA is more acidic than HN'', but is susceptible to steric effects. For example, reaction of the complexes $M(N\{SiHMe_2\}_2)_3(thf)_2$ (M = Y, Nd) (which use a less bulky silylamide ligand) with 3 equivalents of HOC^tBu_3 afforded the corresponding alkoxide compound $M(OC^tBu_3)_3(thf)$[5] whereas the same reactions with MN''_3 only afforded the homoleptic alkoxide $M(OC^tBu_3)_3$ for the larger metal cation, Nd^{III}.[6]

Cerium is the only lanthanide with a readily accessible +4 oxidation state. The synthesis of Ce^{IV} complexes is often challenging due to large dependence on the choice of reaction solvent, temperature and oxidant. There have only been a small number of Ce^{IV} amide complexes reported to date.[7-18] Scott and co-workers reported the oxidation of the triamidoamine complex Ce(L) (L = $N\{CH_2CH_2NSi^tBuMe_2\}_3$) with molecular halogens to

afford **B**, Ce(L)X (X = I, the first structurally characterised Ce^{IV} amide) and the mixed valence Ce^{III}/Ce^{IV} species **C**, $(Ce\{L\})_2(\mu\text{-}X)$ (X = Br or Cl) (Figure 1).[9] Lappert and co-workers described the oxidation of CeN''_3 in low (24 % – 30 %) yield to **D**, CeN''_3X (X = Br or Cl) using TeX_4 or PBr_2Ph_3 in thf or diethyl ether respectively (Figure 1).[7,19] Reaction byproducts were also characterised as $(CeN''_2\{\mu\text{-}Cl\}\{thf\})_2$ and $CeBr_3(thf)_4$. The use of molecular halogens, which are stronger oxidising agents, resulted in no reaction and it was suggested that the ability of $TeCl_4$ and PBr_2Ph_3 to dissociate into more electrophilic halogenium ions $TeCl_3^+$ and $PBrPh_2^+$ solution may have facilitated the oxidation.

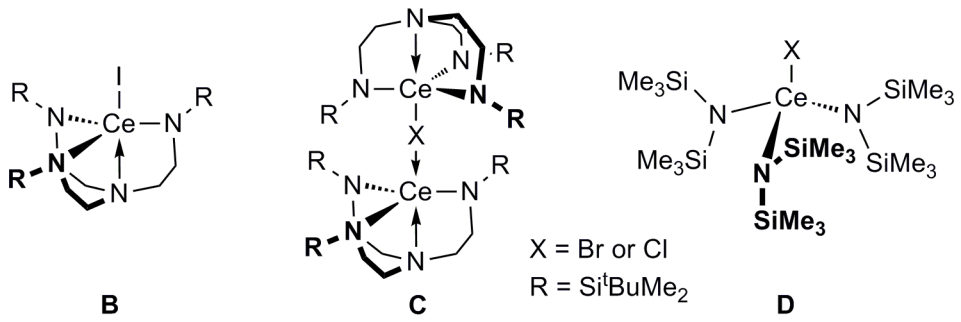
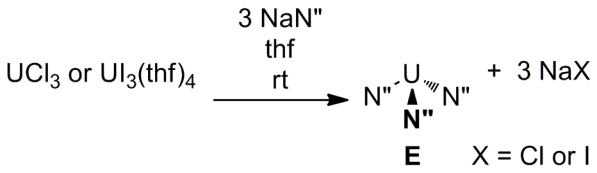


Figure 1: Ce^{IV} amides

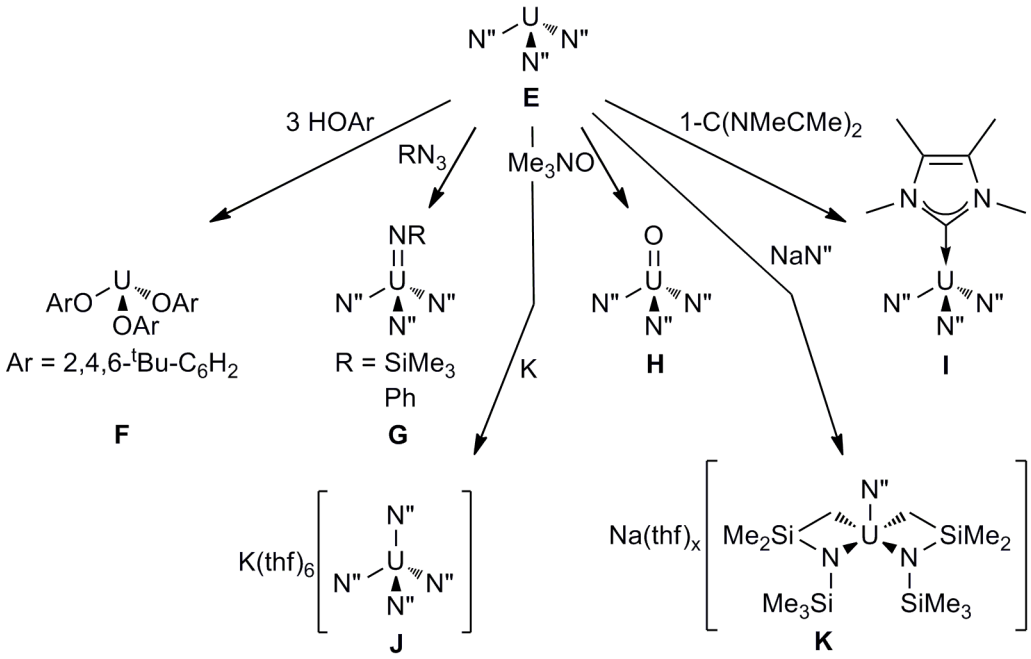
1.1.2 Uranium in the +3 and +4 oxidation state

Andersen reported the synthesis of the first U^{III} amide, the homoleptic *tris-bis*(trimethylsilyl)amide U^{III} complex **E**, UN''_3 (N'' = $N(SiMe_3)_2$). Originally prepared using 1 equivalent of UCl_3 and 3 equivalents of NaN'' in thf, the synthesis was improved by the use of $UI_3(thf)_4$ (Equation 2).[20]



Equation 2: Synthesis of the first U^{III} amide, UN''_3

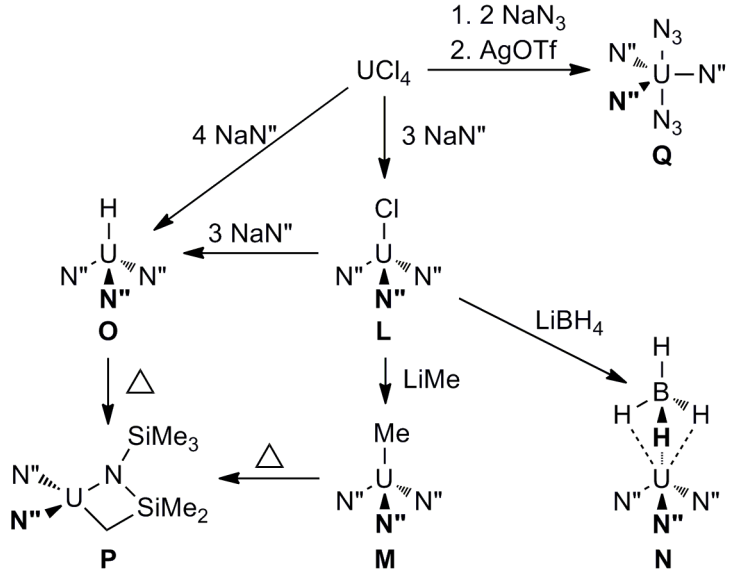
UN''_3 has proved an extremely useful starting material for U^{III} chemistry and undergoes a range of reactivity (Scheme 1).



Scheme 1: Some selected reactions of UN"$_3$

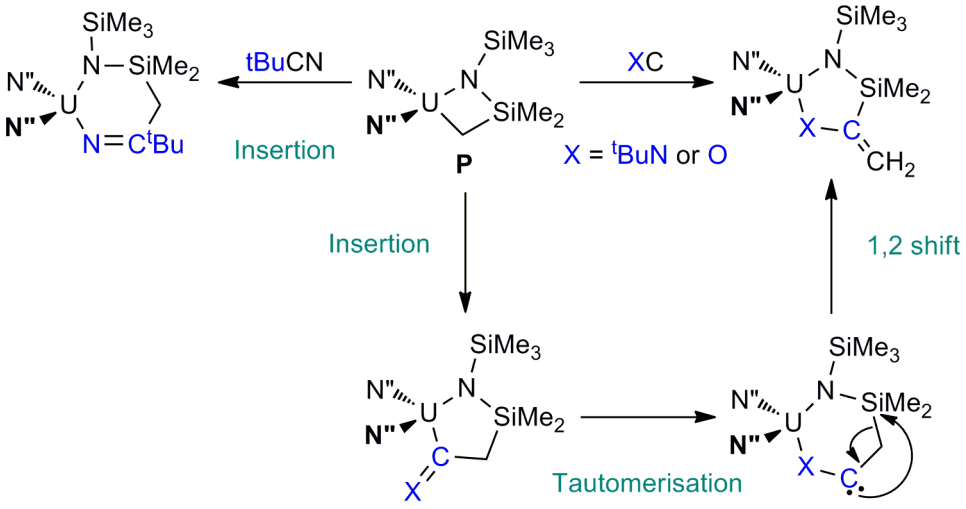
For example, Sattelberger *et al.* described the synthesis of the *tris*(aryloxide) **F**, U(OAr)$_3$ (OAr = O-2,4,6-^{t}Bu-C$_6$H$_2$) by protonolysis of UN"$_3$ with 3 equivalents of HOAr.[21] Oxidation of UN"$_3$ was achieved with alkyl and aryl azides RN$_3$ (R = SiMe$_3$[22] and Ph[23,24]) to afford the U^V imido species **G**, UN"$_3$(=NR) and by oxidation with Me$_3$NO or molecular oxygen to give the *mono*(oxoamide) **H**, UN"$_3$(=O).[25] Despite the initial report that UN"$_3$ "has no coordination chemistry", Meyer and co-workers reported the synthesis of the N-heterocyclic carbene (NHC) adduct **I**, U(L)N"$_3$ (L = 1-C(NMeCMe)$_2$) from the reaction of 1 equivalent of UN"$_3$ with 1 equivalent of L in excellent yield (91 %) (see 1.4.2 also). The U^{III} ion is large enough to accommodate four bulky silylamide ligands; Evans and co-workers reported that the 'ate' complex **J**, [UN"$_4$][K(thf)$_6$] was obtained by treating UN"$_3$ with 1 equivalent of elemental potassium in thf.[26] Ephritikhine and co-workers recently described the synthesis of the *bis*(metallacyclic) U^{III} 'ate' complexes **K**, [M(thf)$_x$][UN"(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] (M = Li or Na) which could be prepared by treatment of UN"$_3$ with 1 equivalent of LiCH$_2$SiMe$_3$ or NaN".[27] The reaction to form the metallacycles most likely proceeds through γ-CH activation with elimination of H$_2$. The U^{III} ion has undergone one electron oxidation in the process to U^{IV}. (Scheme 1).[28] Another route into U^{III} silylamide chemistry is through salt metathesis chemistry. For example, (UCp*N")$_2$(μ-η^6:η^6-C$_6$H$_6$) was prepared by Evans *et al.* by the treatment of (UCp*$_2$)$_2$(μ-η^6:η^6-C$_6$H$_6$) with 1 equivalent of KN".[29]

The first U^{IV} silylamide compounds **L** – **N**, $UN"_3X$ (X = Cl, Me or BH_4) were reported by Andersen and co-workers (Scheme 2).[30] The chloride **L** was prepared by reaction of UCl_4 with 3 equivalents of NaN" in thf. **M** and **N** were synthesised from **L** in salt metathesis with the appropriate lithium salt. The hydride **O**, $UN"_3H$ was made by the treatment of UCl_4 with 4 equivalents of NaN".[31] Pyrolysis of **M** or **O** (or decomposition of other $UN"_3X$ (X = Et or CH_2SiMe_3) resulted in the formation of a metallacyclic species **P**, which was proposed to be the key intermediate of H/D exchange for the hydride species (Scheme 2). Hayton and co-workers reported the first example of a U^V azide by the salt elimination reaction of $UN"_3Cl$ with NaN_3 followed by oxidation with AgOTf (OTf = OSO_2CF_3) to afford **Q**, $UN"_3(N_3)_2$.[31-33]



Scheme 2: Synthesis of the first U^{IV} silylamide compounds $UN"_3X$

The metallacyclic species **P** was shown to undergo insertion reactions with ^{t}BuCN, ^{t}BuNC and CO, and formation of a simple coordination complex with Me_3SiN_3.[34] The insertion reactions with ^{t}BuNC and CO were proposed to take the following pathway: coordination to the metal centre, insertion into the U-C bond and tautomerisation to a carbene species which inserts into the Si-C bond (Scheme 3). **P** has been employed by Dormond *et al.* for the methylenation of carbonyl compounds, in a process that was shown to be essentially quantitative and stereoselective,[35] in addition to the synthesis of ketones from nitriles.[36] Numerous protonolysis reactions of **P** have also been reported.[37]



Scheme 3: Insertion of ^{t}BuNC and CO into the metallacycle **P**

1.2 Metal alkyl complexes

The emphasis here is placed on σ-bound alkyl complexes of yttrium, scandium and the lanthanides and actinides. Several general reviews[38] and those on metal arene-,[39,40] cyclopentadienyl-,[41-44] non-cyclopentadienyl-based[45-47] and cationic complexes[48,49] have been published.

1.2.1 Yttrium, scandium and the lanthanides

Homoleptic rare earth alkyl compounds are extremely useful starting materials for the synthesis of alkyl compounds through alkane elimination but they are hampered by a lack of reliable general synthetic methodology, suitable combinations of alkyl groups and metal centres and potential thermal instability. Most require the presence of thf as a donor solvent for stabilisation.

Early reactions of MCl_3 with 3 equivalents of MeLi by Hart and co-workers afforded products whose formulation could not be identified. Methyl 'ate' complexes of the form $[Li(D)_3]_3[M(CH_3)_6]$ (D = tmeda or dme), **R**, were originally isolated by Schumann and co-workers for almost the entire series of rare earth metals (the Eu^{III} metal centre was instantly reduced to Eu^{II}) by treatment of MCl_3 with 6 equivalents of MeLi (Figure 2).[50] Similarly, the *tert*-butyl 'ate' complexes **S**, of the form $[M^{t}Bu_4][LiL_x]$ (M = Sm, Er, Lu, Tb or Y, L = Et_2O, thf or tmeda, x = 2, 3 or 4),[50,51] were prepared from the reactions of MCl_3 or $M(O^{t}Bu)_3$ with 4 equivalents of $Li^{t}Bu_4$ (Figure 2).

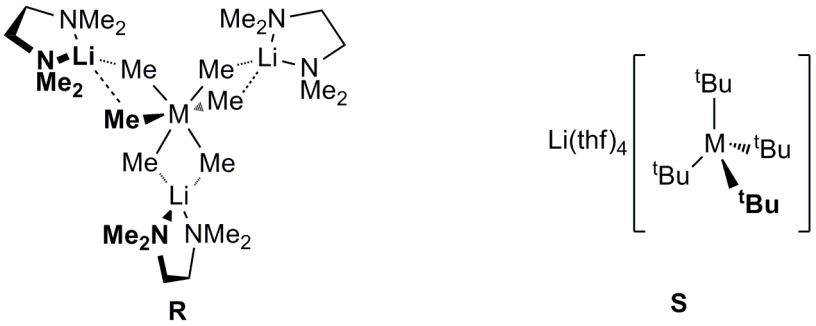


Figure 2: Rare earth MMe_6 and M^tBu_4 'ate' complexes and polymeric $[MMe_3]_n$

Only recently, Anwander and co-workers reported the first synthesis of $[MMe_3]_n$ (M = Y or Lu) as polymeric materials.[52] $[MMe_3]_n$ were synthesised by the "donor induced cleavage" of the homoleptic tetraalkylaluminates $M(AlMe_3)_4$ using thf or Et_2O as the donor solvent. Their formation was shown to be reversible; addition of 3 equivalents of $AlMe_3$ reformed $M(AlMe_3)_4$. The yttrium derivative has already been demonstrated to undergo a range of reactivity including alkane elimination, addition to ketones and Lewis acid-Lewis base reactions.[53]

The thermally sensitive *tris*(silylalkyl) metal complexes $M(CH_2SiMe_3)_3(thf)_x$ (M = Y or Sc, x = 2 or 3) have found the most use in alkane elimination reactions. They were first prepared by Lappert and co-workers through reaction of the anhydrous metal chlorides with 3 equivalents of $LiCH_2SiMe_3$.[54] In the same paper, the synthesis of the neopentyl derivatives $M(CH_2CMe_3)_3(thf)_2$ was also reported. Following this initial report, a range of $M(CH_2SiMe_3)_3(thf)_2$ (Gd, Tm, Dy, Ho, Tb, Er, Yb, or Lu) and $Sm(CH_2SiMe_3)_3(thf)_3$ have also been prepared.[55,56] However, the salt elimination reaction scheme can lead to the formation of undesired 'ate' complexes; for example, $[Li(thf)_4][M(CH_2SiMe_3)_4]$ (M = Y, Er, Tb, Yb) and $[Li(tmeda)_2][Ln(CH_2SiMe_3)_4]$ (Ln =Y, Er, Yb, Lu) are obtained in the presence of donor solvents to solvate the lithium cation.

The use of the bulkier $CH(SiMe_3)_2^-$ ligand can also result in 'ate' complexes; treatment of MCl_3 (M = Y, Er, Yb or La) with 3 equivalents of $LiCH(SiMe_3)_2$ in a donor solvent (Et_2O, thf or $MeN(CH_2CH_2NMe_2)_2$) yielded **T**, $[Li(D)_x][M(CH\{SiMe_3\}_2)_3Cl]$ (M = Y, D = Et_2O, x =4; M = Er or Yb, D = thf, x = 4; M = La, D = $MeN(CH_2CH_2NMe_2)_2$, x = 1) (Figure 3).[57] To avoid salt incorporation, the homoleptic $M(CH\{SiMe_3\}_2)_3$ (**U**, Figure 3) are prepared by treatment of the bulky *tris*(aryloxide) $M(OAr)_3$ (M = Y, Sc, La, Ce, Pr, Nd, Sm, Er, Yb or Lu, OAr = O-2,6-^{t}Bu-C_6H_3 or O-2,6-^{t}Bu-4-Me-C_6H_2) with 3 equivalents of $LiCH(SiMe_3)_2$ in a non-polar solvent such as hexanes or pentane (Figure 3).[58,59]

$M(CH\{SiMe_3\}_2)_3$ complexes are isoelectronic and isostructural with the *tris*(silylamide) complexes $M(N\{SiMe_3\}_2)_3$, adopting a pyramidal geometry in the solid state.

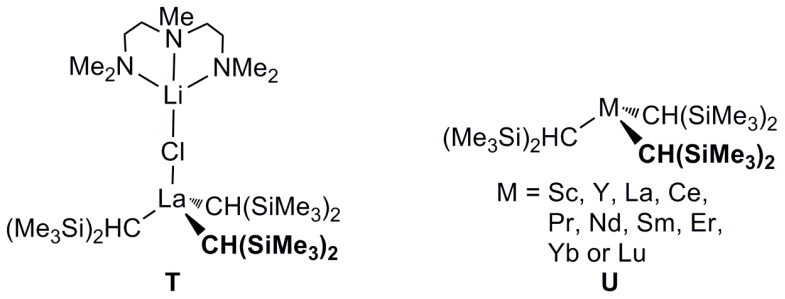


Figure 3: Neutral and 'ate' complexes of the $CH_2(SiMe_3)_2^-$ ligand

Cerium complexes provide the rare examples of organometallic lanthanide complexes where the metal ion is in the +4 oxidation state. The first crystallographically characterised example was the *tris*(cyclopentadienyl) supported Ce^{IV} alkoxide **V**, $CeCp_3(O^tBu)$[60] reported by Evans *et al.* (Figure 4) following the synthesis of the *iso*-propoxide analogue by Marks and co-workers.[61] Arnold and co-workers demonstrated the synthesis of **W**, $Ce(L)_4$ (L = $OCMe_2CH_2(1\text{-}C\{NCHCHN^iPr\})$) (see 1.4.1 also).[62,63] The Ce^{IV} ion is supported by two bound and two unbound unsaturated backbone NHC ligands and is the only example of a Ce-C two electron σ bond. Cloke and co-workers described the preparation the Ce^{IV} pentalene sandwich complex **X**, $Ce(1,4\text{-}Si^iPr_3\text{-}C_8H_6)_2$ *via* oxidation of the Ce^{III} analogue with $AgBPh_4$.[64] While K-edge XANES measurements indicated that the charge on the cerium ion was closer to +3 than +4, DFT studies identified that the ground state was likely to have a contribution from a configuration where an f-electron is antiferromagnetically coupled to a hole in the ligand shell; the data suggests that regardless of the real metal charge, the nature of formally Ce^{III} and Ce^{IV} compounds is distinct . The synthesis of **Y**, $Ce(cot)_2$[65] (cot = cyclooctatetraene) (Figure 4) and related complexes,[64,66,67] combining a highly oxidising metal cation with a reducing anionic ligand, has led to intensive study and debate into assignment of the M^{IV} oxidation state.[16,68-72]

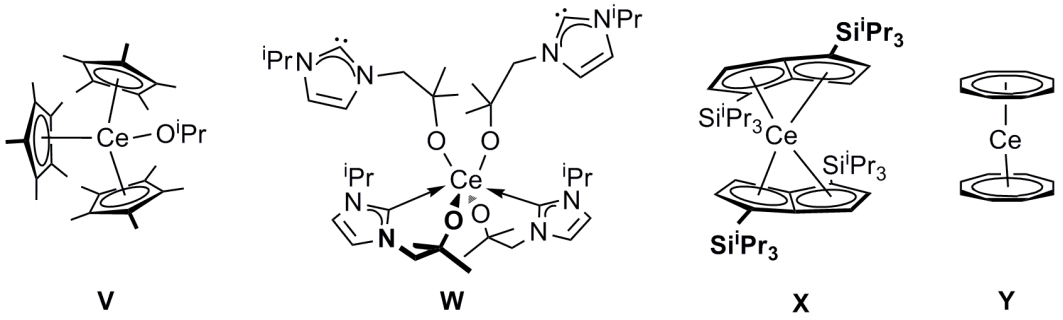
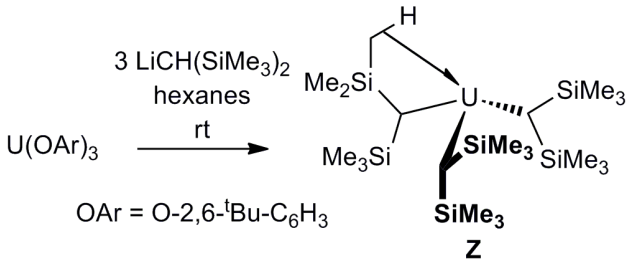


Figure 4: Organometallic lanthanide complexes in the +4 oxidation state

1.2.2 Uranium in the +3 and +4 oxidation state

In contrast to the alkyl chemistry of yttrium, scandium and the lanthanides, to date the only neutral homoleptic alkyl complex of U^{III} of known structure is the *tris*(silylalkyl) complex **Z**, $U(CH\{SiMe_3\}_2)_3$ reported by Sattelberger *et al.*.[73] **Z** was synthesised in 40 % yield by treatment of 1 equivalent of $U(OAr)_3$ (OAr = O-2,6-^{t}Bu-C_6H_3) with 3 equivalents of $LiCH(SiMe_3)_2$ (Equation 3). **Z** was found to be thermally sensitive in solution, decomposing over a period of hours. The molecular structure of **Z** revealed a trigonal pyramidal C_3 symmetric geometry and three stabilising, symmetry-related γ-agostic interactions with U^{III}.



Equation 3: Synthesis of $U(CH\{SiMe_3\}_2)_3$. One of three agostic interactions is indicated

As for the lanthanides, the synthesis of homoleptic uranium alkyls is also prone to the formation of 'ate' complexes. For example, treatment of $UCl_3(thf)_3$ with 3 equivalents of $LiCH(SiMe_3)_2$ does not afford the expected *tris*(alkyl) complex but instead affords **AA**, $[Li(THF)_3][UCl(CH\{SiMe_3\}_2)_3]$, a product of salt incorporation (Figure 5). Wilkinson and co-workers, in an effort to prepare sterically saturated uranium alkyl complexes with good stability, reported the hexaalkyl complexes $Li_2UR_6.8D$ (R = Me, CH_2SiMe_3, Ph and D = thf or Et_2O) and $Li_2UR_6.7D$ (R = Me or CH_2SiMe_3, D = tmeda).[74] More recently, Hayton and co-workers described the synthesis of the a number of U^{IV} penta- and hexaalkylate complexes: **AB**, $[LiD_x][UR_5]$ (R = CH_2SiMe_3 or CH_2CMe_3, x = 3 or 4, D = thf or dme), $\{[K(thf)]_3[K(thf)_2][UBn_6]_2\}_x$ and **AC**, $[Li(tmeda)]_2[UMe_6]$ from the treatment of UCl_4 with 5 or 6 equivalents of MR (M = Li or K, R = CH_2SiMe_3, CH_2CMe_3, Me or Bn) (Figure 5).[75]

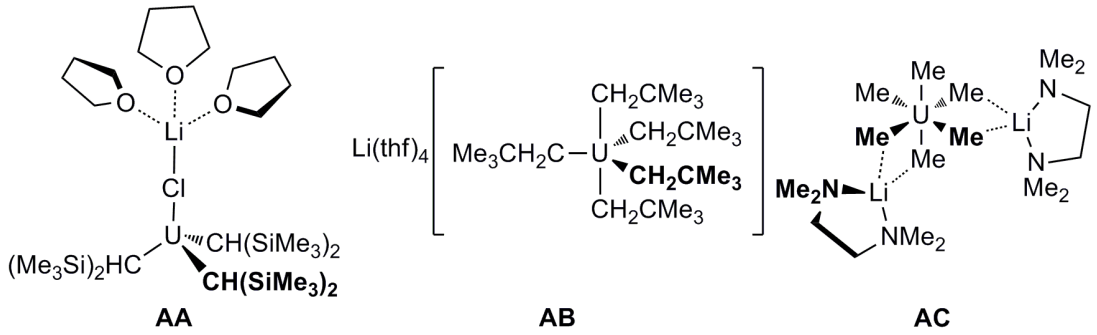


Figure 5: Examples of U^{III} and U^{IV} alkylate complexes

Apart from **Z**, there are no other examples of unsolvated U^{III} and U^{IV} homoleptic alkyls of the form UR_x (for example, R = Me, ^nBu, Et or CH_2SiMe_3, x =3 or 4) despite targeted research concerning their isolation; during the Manhattan project, such volatile uranium alkyl complexes were sought for uranium isotope separation. Marks *et al.* investigated the reactions of UCl_4 with 4 equivalents of lithium alkyl reagents and monitored the decomposition of the presumed tetraalkyl products that resulted.[76] It was found that these tetraalkyls decomposed *via* β-hydrogen elimination but that another mechanism was in operation when no β-hydrogens were present. Andersen and co-workers reported the stabilisation of the UMe_4 fragment by using chelating phosphine co-ligands to afford $UMe_4(dmpe)_2$ from the treatment of $UCl_4(dmpe)_2$ with 4 equivalents of MeLi.[77]

1.3 N-heterocyclic carbenes

1.3.1 Background

N-heterocyclic carbenes (NHCs) are two electron donors that contain a neutral, divalent and sp^2 hybridised carbon centre with a strongly nucleophilic lone pair. They have been shown to have extensive practical applications as organocatalysts,[78-80] ligands for metal complexes in homogenous catalysis[81-90] and materials science[91,92] and are a continuing source of academic interest. Complexes of all transition metals, many main-group elements and most rare-earth metals have been isolated to date.[93-96]

Free carbenes based on three- to seven-membered rings[94,97-99] have been isolated but the five-membered imidazolin-2-ylidene (unsaturated backbone) and imidazolidin-2-ylidenes (saturated backbone) are regarded as classical NHCs and will form the focus of this introduction. Normal binding to a metal centre is considered to take place through the C2 carbon though a number of abnormal carbenes have been isolated, binding through the C4 or C5 positions.[100] Increasingly, these abnormal carbenes, remote NHCs (with no N atom α to $C_{carbene}$) and those with reduced stabilisation (without two heteroatoms adjacent to $C_{carbene}$) are being reported and their use in homogeneous catalysis examined (Figure 6).[84]

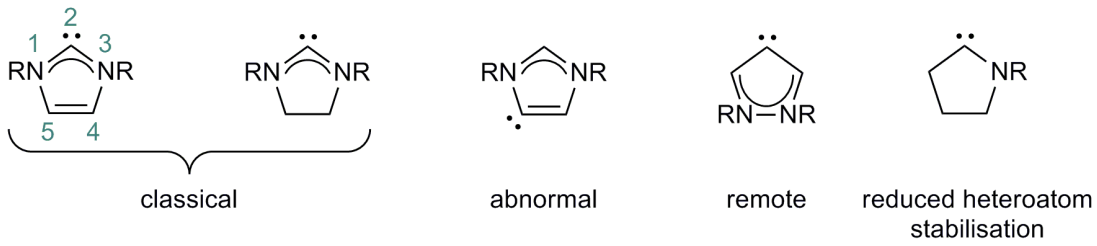
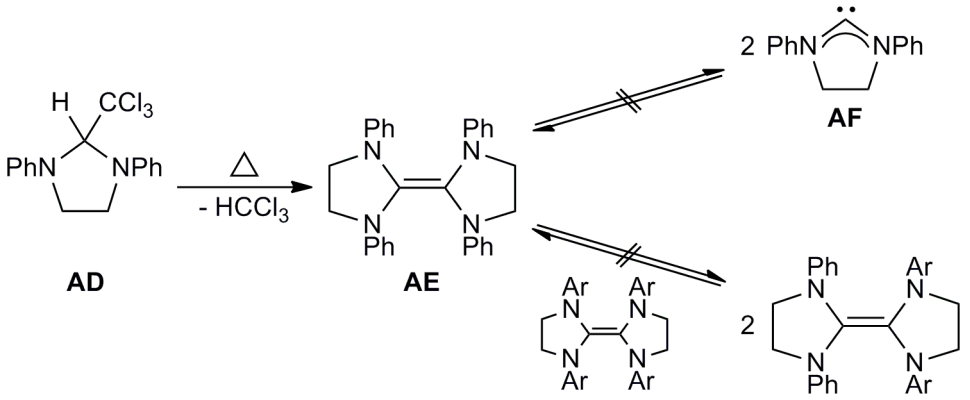


Figure 6: Structure, nomenclature and numbering scheme for N-heterocyclic carbenes

Following Wanzlick's observation of the α-elimination of chloroform from the imidazolidine **AD** to afford the dimeric enetetramine **AE**, the concept of N-heterocyclic carbenes was established.[101-103] Cross metathesis experiments established the absence of equilibrium between **AE** and the free carbene **AF**, which was never isolated (Scheme 4).[104,105]



Scheme 4: Wanzlick's initial exploration into imidazolidin-2-ylidenes

However, NHCs were trapped by metal ion complexation prior to the isolation of free carbenes. Wanzlick treated an imidazolium perchlorate salt with mercuric acetate to afford the corresponding mercury complex **AG**[106] and Öfele thermolysed an imidazolium hydridopentacarbonylchromate salt to eliminate H_2 and yield the chromium pentacarbonyl complex **AH**.[107] The first metal complex of the imidazolidin-2-ylidenes initially studied by Wanzlick was reported by Lappert and co-workers, the platinum chloride complex **AI** (Figure 7).[108]

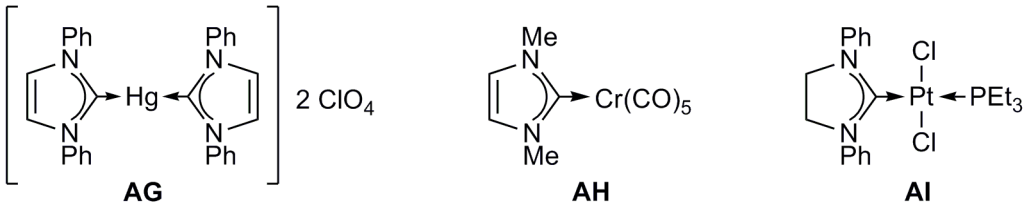
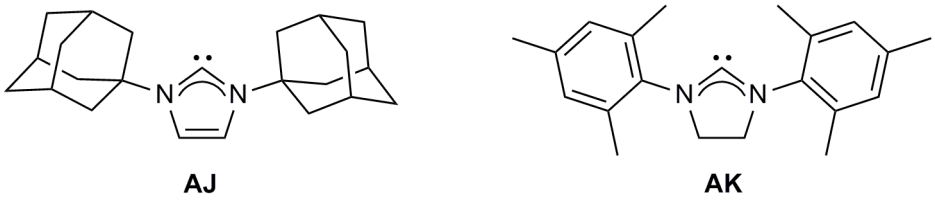


Figure 7: The first metal NHC complexes

In the search for free carbenes, investigation into the unsaturated imidazolin-2-ylidenes continued, with 6 π electron aromaticity initially predicted to be crucial to their stability. Despite achieving the first direct synthesis of a nucleophilic carbene metal complex, Wanzlick never isolated a free carbene. Arduengo *et al.* reported the first stable, crystalline free carbenes based on imidazolin- and imidazolidin-2-ylidenes, **AJ** and **AK** respectively (Figure 8).[109,110] Synthetic procedures for these types of classical NHCs are now well-developed and numerous.[94,96]



AJ **AK**

Figure 8: The first stable crystalline imidazolin- (**AJ**) and imidazolidin-2-ylidenes (**AK**)

1.3.2 Stereoelectronic considerations of the free carbene

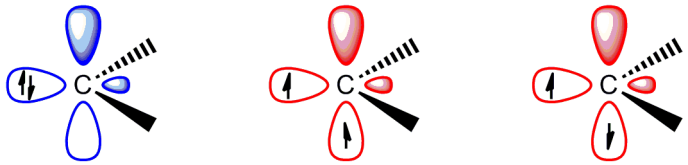


Figure 9: Singlet and triplet carbenes

A carbene can theoretically exist in a singlet or triplet form (Figure 9) but in the NHC, the singlet is strongly favoured by a combination of inductive electron withdrawal (stabilising sp^2 orbital $1a_1$, Figure 10 and Figure 11) and mesomeric electron donation (destabilising the anti-bonding orbital, $2b_1$, Figure 10 and Figure 11) by the α-amino substituents. Both effects serve to increase the HOMO-LUMO energy gap. The NCN unit can be formally regarded as a three centre-four electron fragment.

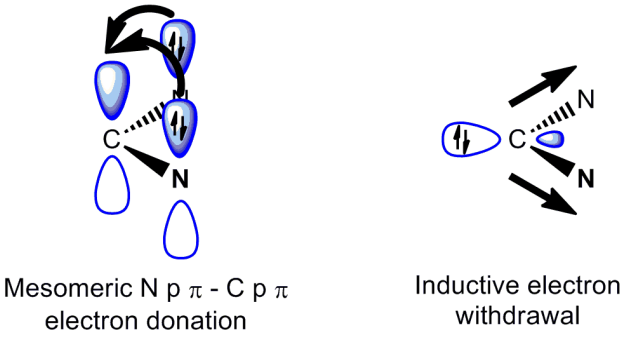


Figure 10: Mesomeric and inductive effects stabilising the triplet carbene form

The combination of N p π – C p π electron donation and mesomeric electron withdrawal is accepted as the main electronic contribution to stable NHCs with a limited 'aromatic effect' additionally stabilising imidazolin-2-ylidenes (singlet-triplet energy gap = 354 $kJmol^{-1}$) with respect to imidazolidin-2-ylidenes (singlet-triplet energy gap = 290 $kJmol^{-1}$).[111] The greater thermodynamic stability of imidazolin-2-ylidenes is supported by theoretical studies and its effect is readily observed in the decreased affinity for dimerisation of imidazolin-2-ylidenes to enetetramines (without considering kinetic factors).

According to quantum chemical calculations in a model system, Carter and Goddard reported that the C=C bond strength in an enetetramine can be estimated to be the C=C bond strength in ethylene minus the singlet-triplet energy gap for the carbenes involved.[112] Two mechanisms of the dimerisation process have been suggested; attack of the empty C p π orbital by the filled C sp^2 orbital or a proton-catalysed mechanism.[113]

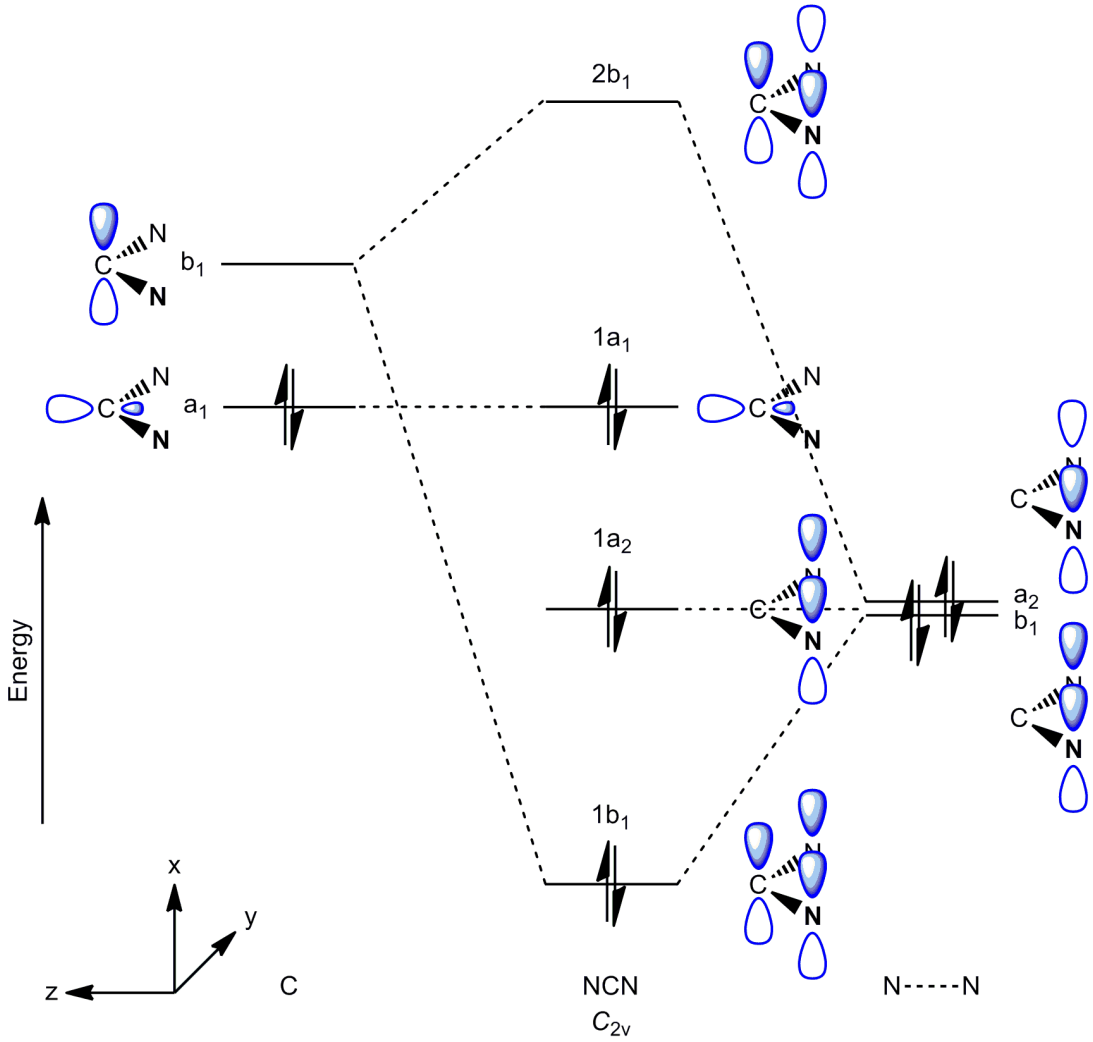


Figure 11: Fragment molecular orbital diagram of the NCN unit (C_{2v} symmetry)

Modification of the NHC wingtip substituents, ring substitution and ring size has been shown to have significant effects on the stereoelectronic nature of the ligand and offers potential to tune ligand properties.[81] Steric shielding by the wingtip substituents contributes to the kinetic stability of the free carbene and this is most important in the case of imidazolidin-2-ylidenes, which readily dimerise to enetetramines. The synthesis of cyclic alkyl(amino)carbenes (CAACs), where there is only one α-N, highlights that isolation of free carbenes is dependent on both steric and electronic factors (Figure 12).[84,114]

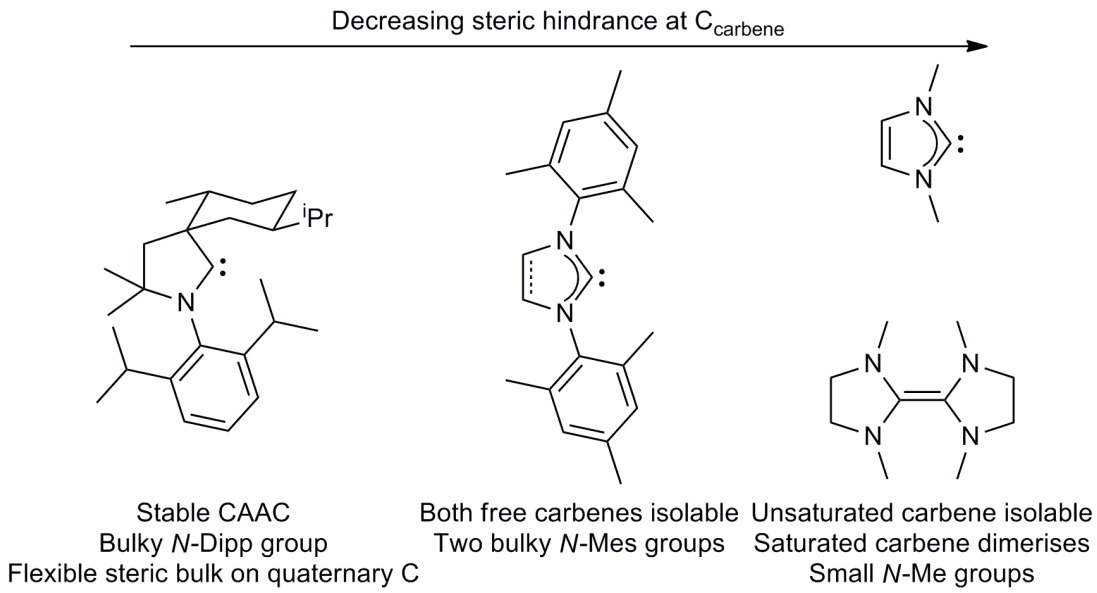


Figure 12: Effect of steric bulk on the isolation of free NHCs

1.3.3 Electronic considerations of the M-$C_{carbene}$ bond

There are three contributions to the M-$C_{carbene}$ bond to consider; σ and π donation from the carbene to the metal centre and π backdonation from the metal centre to the carbene (Figure 13).[115]

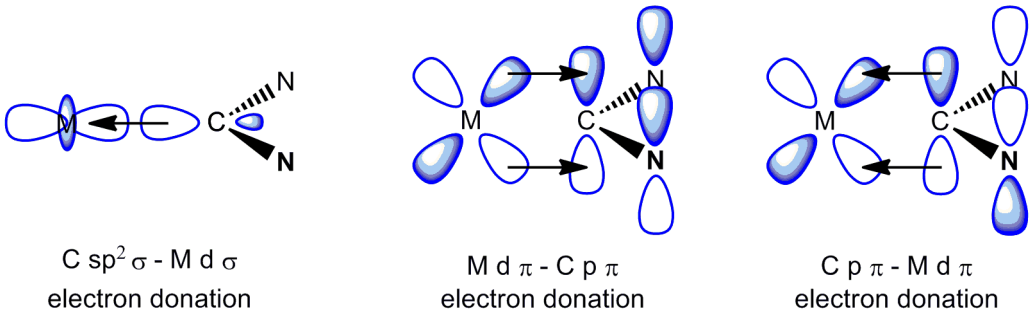


Figure 13: Electronic contributions to the M-$C_{carbene}$ bond

NHCs are σ donors that are stronger than even the most basic phosphine ligands, to which they are often compared.[86] The stereoelectronics of the M-$C_{carbene}$ fragment have been studied extensively in a number of model systems, commonly based upon a (NHC)M(CO) motif. In these cases, the σ donor ability can quantified through measurement of the carbonyl stretching frequency. σ donor ability has also been analysed through NMR spectroscopy, X-ray crystallography, DFT studies and photoelectron spectroscopy.[116-119]

The importance of the σ donation contribution to M-$C_{carbene}$ bonding is highlighted by the ready synthesis of complexes with main group, rare earth and transition metals in high

oxidation states which do not have electrons available for π back-bonding.[93,95] Arnold and co-workers reported the preparation of the amido-functionalised NHC compounds of the uranyl dication, **AL** and **AM**, $UO_2(L)_2$ (L = ^{t}BuNCH$_2$CH$_2$(1-C{NCHCHNR}), R = ^{t}Bu or Mes = 2,4,6-Me-C$_6$H$_2$) (Figure 14).[120]

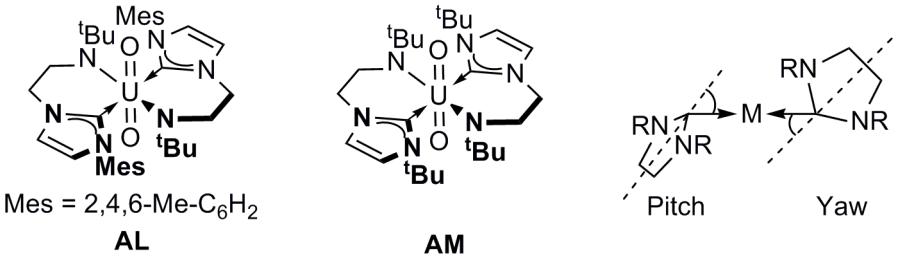
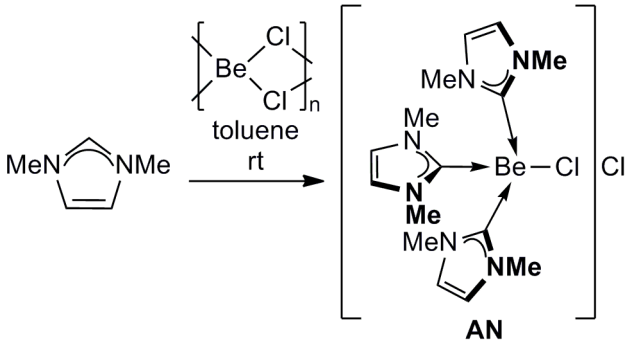


Figure 14: Uranyl dication NHC compounds (**AL** and **AM)** and the pitch and yaw angles

From an X-ray diffraction study, the NCN-M unit in **AM** was found to be severely distorted away from the ideal trigonal planar geometry in order to minimise the unfavourable interactions of the ^{t}Bu groups. There was no distortion in **AL** since the mesityl substituent is not so sterically demanding. This distortion can be defined and quantified though the terms of pitch (out of plane tilt) and (in plane tilt) yaw angles (Figure 14). Despite the differences in bonding geometry, the strength of the bond was inferred to be similar based on the FT-IR spectra, which show that the asymmetric ν_3 $[UO_2]^{2+}$ stretches in **AL** and **AM** are 933 cm^{-1} and 929 cm^{-1} respectively.

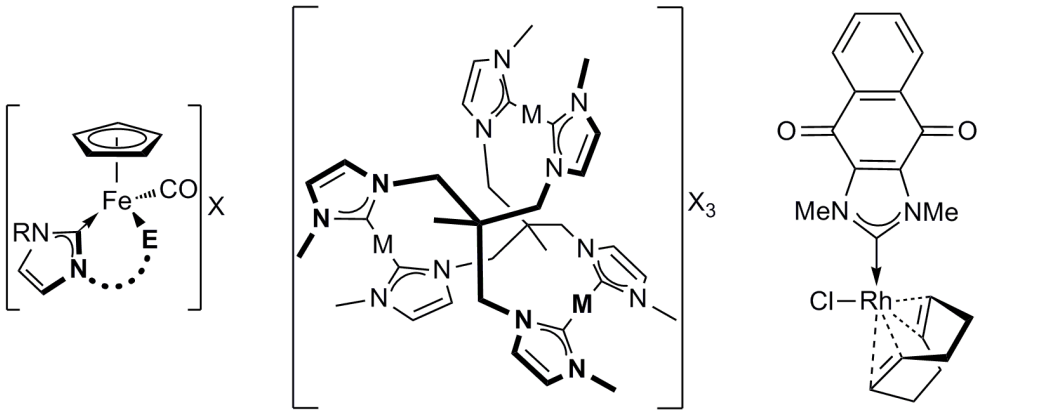
Herrmann *et al.* synthesised the Be^{II} chloride NHC compound **AN**, [Be(L)$_3$Cl]Cl (L = 1-C(NMeCH$_2$)$_2$) by treatment of $[BeCl_2]_n$ with 3 equivalents of ligand L (Equation 4).[121] Analysis of the bonding in the resulting ionic species showed that its stability is derived from electron population in the C p π orbital which can only be provided by N p π – C p π electron donation.



Equation 4: An ionic beryllium NHC compound stabilised by σ donation from the NHC

With an empty p-orbital centred on the $C_{carbene}$ perpendicular to the plane of the N-heterocyclic ring, π-backbonding is possible. The inclusion of this π-bonding component to the M-$C_{carbene}$ bond has been extensively studied and was a source of debate. While often negligible, this is not always the case and this π bonding contribution is dependent on the nature of the metal centre, carbene ligand and any co-ligands.[122-126]

Albrecht *et al.* examined a series of complexes based on the Fe^{II} piano-stool compounds **AO**, [Fe(NHC)(CO)(E)]X (E = secondary neutral donor, X = I^- or BF_4^-), using a combination of electrochemical, spectroscopic and DFT calculations to conclude that π bonding character was not negligible (Figure 15).[127] Through electrochemical analysis, the Lever parameter of an NHC (E_L = 0.29) was calculated to be similar to that of pyridine (E_L = 0.25), implying similar donor properties. Given that NHCs are stronger σ donors than pyridines, this infers that NHCs are also stronger π acceptors in order to achieve charge balance. DFT calculations indicated that when E = CO, the π contribution to the M-$C_{carbene}$ bond was 15.4 % and that this value increased, as expected, in the presence of an additional σ donor co-ligand (E = pyridine) to 28 %.



AO
Fe^{II} piano stool model
E = neutral 2 electron donor
R = Me, ^{i}Pr or Mes
X = I^- or BF_4^-

AP
Trimetallic Gp11 model
M = Ag, Cu or Au
X = PF_6

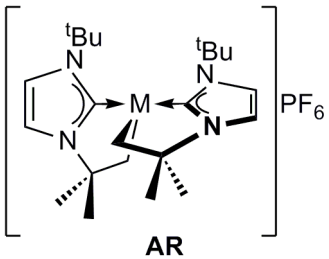
AQ
Rh^{II} model with IR, NMR and electrochemical probes

Figure 15: Model systems to probe the π backbonding interaction in the M-$C_{carbene}$ bond

Meyer and co-workers investigated the trimetallic complexes **AP** of the tripodal 1,1,1-*tris*[3-methyl(imidazolin-2-ylidene)methyl]ethane ligand (Figure 15) using DFT.[125] It was found that the metal based d_{xy} and d_{yz} orbitals interacted with hybridised π/π* orbitals of the NCN unit to create significant orbital overlap indicative of π bonding which contributed 15 % – 30 % of the total orbital interaction energy.

Bielawski and co-workers prepared **AQ**, Rh(L)Cl(cod) (cod = 1,5-cyclooctadiene) from which the cod group could be readily substituted with carbonyl groups (Figure 15).[128] L is designed to be used as an IR spectroscopic and electrochemical probe to study the π acceptor capability of the NHC. In **AQ**, the quinone carbonyl frequencies were lower and the reduction potentials higher than that in carbonyl compound $Rh(L)Cl(CO)_2$. Combined with solid state structural analysis, it was concluded that the π acceptor quality of ligand L was intermediate between an olefin and carbon monoxide.

C p π – M d π electron donation has been reported as a stabilising contribution in electron-deficient compounds. Nolan and co-workers isolated bare 14 electron Rh^{III} and Ir^{III} compounds **AR**, (Figure 16)[126] whose unusual stability was attributed to π electron donation from the supporting NHC ligands following X-ray structural analysis, DFT and reactivity studies.



AR
M = Rh of Ir

Figure 16: Electron poor metal centres stabilised by NHC π donation

An in-depth DFT study on d^0, d^4, d^6, d^8 and d^{10} metals showed that, though the overall π component to bonding increased on moving across the period, the π donation from the NHC to the metal centre also decreased in line with the metal centre becoming more electron-rich.[129]

1.3.4 Steric considerations of the M-$C_{carbene}$ bond

Nolan and Cavallo have described the steric profile of NHC ligands using the "percent buried volume" ($\%V_{bur}$).[130] This is defined as the percentage of the total volume of a sphere, centred on the metal ion and of defined radius (2.00 Å or 2.28 Å), that a ligand occupies (Figure 17). The volume of the sphere represents the coordination sphere of the metal centre. $\%V_{bur}$ is calculated using crystallographic data and the SambVca software developed by Cavallo and co-workers.[131] The "percentage buried volume" can be correlated to the Tolman cone angle θ[132] and extended to ligands other than NHCs.

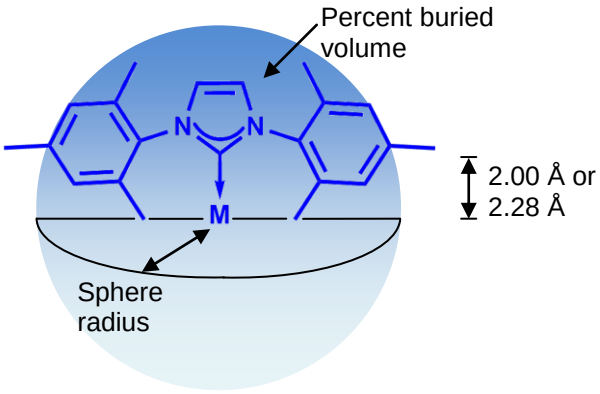


Figure 17: Representation of the "percent buried volume" measure of ligand steric bulk

The value of $\%V_{bur}$ was found to increase as the wingtip substituents became bulkier but that the effect of these substituents decreased with distance from the N atoms. For example, in the Au(L)Cl model (L = 1-C(NRCH)$_2$ where R = ^{i}Pr and cyclohexyl), the $\%V_{bur}$ = 27.4 % (2.00 Å) and 23.5 % (2.28 Å) for both *iso*-propyl and cyclohexyl substituted ligands. While the steric profile of *N*-alkyl NHC ligands changed little at the coordination environment, the *N*-aryl ligands showed a much greater variation. For the saturated ligand 1-C(NDippCH$_2$)$_2$, over a range of metal compounds, the $\%V_{bur}$ was found to be 38.7 % with a large standard deviation of 4.1. This demonstrates that the *N*-Dipp groups created a flexible ligand.

That the nature of the metal centre, coordination number and coordination geometry can influence $\%V_{bur}$ means that it must be used with caution. Saturated and unsaturated backbone NHCs show subtle differences in steric profile; if the N-heterocyclic ring is regarded as a simple wedge,[81] then two angles describe the width and height of this wedge. Saturated backbone imidazolidin-2-ylidenes are therefore expected to be more sterically demanding than the unsaturated analogues (the NCN angle in imidazolidin-2-ylidenes (105º – 106º) has been shown to be wider than in imidazolin-2-ylidenes (101º – 102º) through single crystal X-ray diffraction studies.[94] In the Au(L)Cl model (L = 1-C(NDippCH)$_2$ or 1-C(NDippCH$_2$)$_2$), the $\%V_{bur}$ shows an increase on saturating the ligand backbone. 44.5 % to 47.0 % (at 2.00 Å). However, when comparing these ligands across a range of metal compounds, M(L)Cl (M = Cu, Ag, or Au), saturating the ligand backbone resulted in a decrease of the $\%V_{bur}$ value in the case of Cu and Ag, which the authors cannot explain.

The importance of steric effects can be directly observed in structurally characterised metal NHC compounds. In the octahedral compounds, **AS**, M(L)$_2$Cl$_4$ (M = Zr or Hf, L = 1-C(N^{i}PrCH)$_2$), reported by Erker *et al.* (Figure 18), DFT studies were used to calculate the electronically preferred conformation on a model system where L = 1-C(NHCH)$_2$. This was

found to be when the NHC ligands were mutually perpendicular but each was aligned along a ClMCl unit. The solid state structures revealed that the preferred conformation was when the NHCs were co-planar and bisecting the ClMCl angle. Though the differences in the energy between the conformers were small (0.4 $kJmol^{-1}$ – 1.3 $kJmol^{-1}$), they had the expected inverse correlation with M-$C_{carbene}$ bond distance.

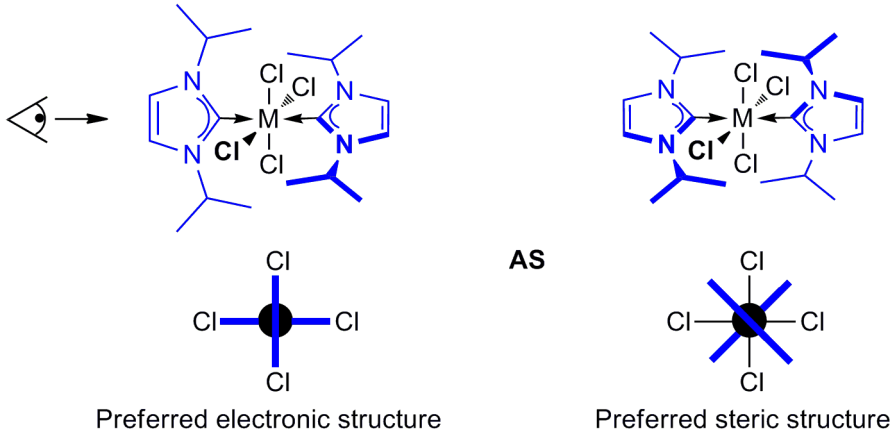


Figure 18: $M(L)_2Cl_4$ compounds where steric factors outweigh electronic factors in determining conformation

Similar effects are observed in trigonal bypyramidal and sawhorse compounds **AT**, $E(L)Cl_4$ (E = Si or S, L = 1-C(N^iPrCH)$_2$) (Figure 19).[133,134] The NHC has a greater effective electronegativity compared to Cl^- as a result of the inductive electron withdrawal of the α-N substituents. VSEPR theory implies that the carbene should occupy the axial position. However, the NHC is in the equatorial position for steric reasons in order to minimise unfavourable interactions with the other co-ligands.

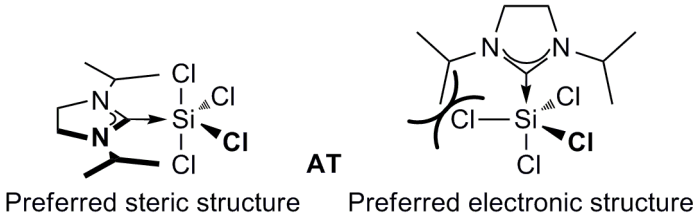


Figure 19: Deviation from VSEPR theory in $E(L)Cl_4$ compounds for steric reasons

A correlation between the steric profile of an NHC and the resulting M-$C_{carbene}$ bond strength has been examined in a number of cases. For example, in the Ru(L)Cp*Cl (L = 1-C(NRCHCHNR) or 1-C($NRCH_2CH_2NR$)) system, the bond dissociation energy was found to decrease with increasing $\%V_{bur}$. Saturation of the ligand backbone resulted in increased bond strength, though this was a small effect.[115,135]

1.3.5 Functionalised N-heterocyclic carbenes

Functionalisation of N-heterocyclic carbenes provides a way to tune the stereoelectronic properties. In particular, the incorporation of chirality is relevant to both organo- and transition metal mediated catalytic processes[79,80,136] and functionalisation can also be used to tether an NHC to a surface.[90] The first functionalised NHCs were based on neutral donors such as tertiary amines,[87] phosphines[137] and ethers.[138,139] (Figure 20).

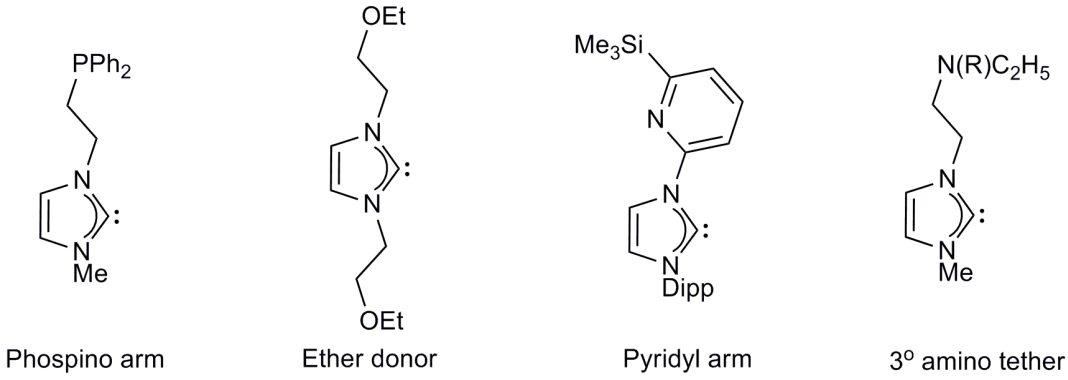
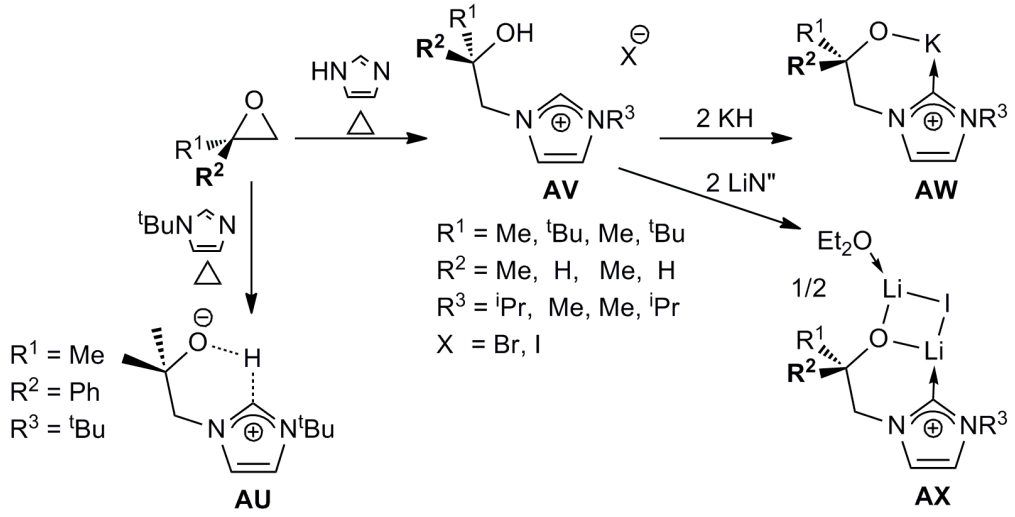


Figure 20: Examples of neutral and anionic O, N, P, C donor functionalised NHCs

New routes to incorporate donors bearing acidic protons have led to a range of anionic alkoxy-, amido-, enolate-, aryl-cyclometallated- and cyclopentadienyl-based arms.[140] Though NHCs possess a strongly nucleophilic lone pair, incorporation of the pendant anionic group facilitates binding to hard, electropositive metals (where bonding is primarily electrostatic in nature).[140,141] Such a tether also favours binding due to the chelate effect.

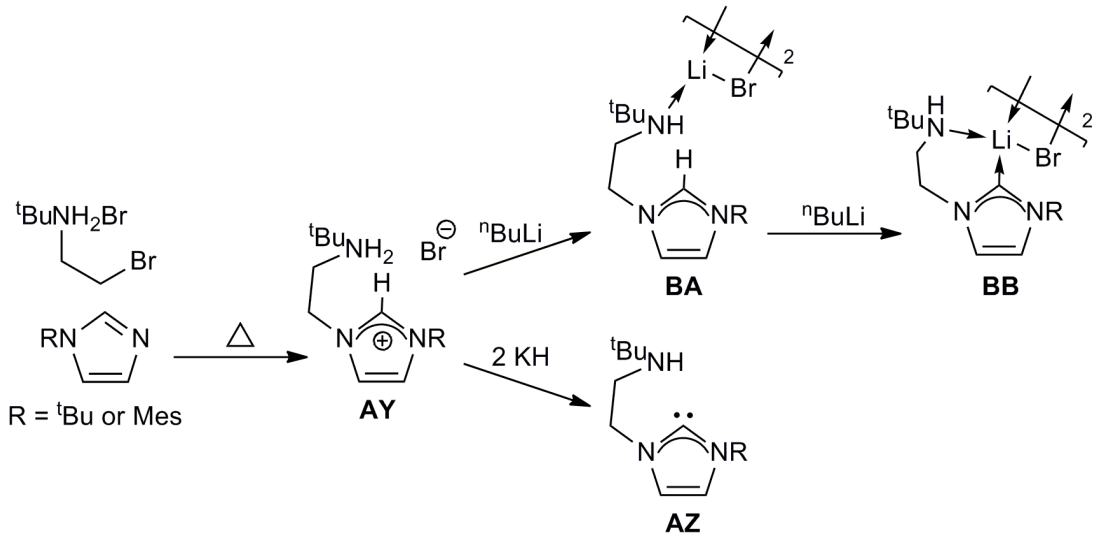
Arnold and co-workers reported the synthesis of alkoxy-tether NHC proligands through a modular synthesis combining an epoxide with an imidazole (Scheme 5).



Scheme 5: Synthesis of alkoxy-tethered NHC proligands, **AU – AX**

The high-yielding melt reaction of an epoxide with an *N*-substituted imidazole affords the zwitterionic **AU**, and the reaction of an epoxide with imidazole followed by subsequent quaternisation with an alkyl halide yields the imidazolium salt **AV** (Scheme 5).[142] This route is advantageous since it uses readily available epoxides; use of enantiomerically pure epoxides affords chiral ligands. **AU** and **AV** were transformed into alkali metal salts, **AW** and **AX**, through sequential deprotonation and these salts were proved to be excellent ligand transfer reagents.[142,143]

Arnold and co-workers also reported the first amido-tethered NHCs by reaction of $^{t}BuNHCH_2CH_2Br.HBr$ with an alkyl (^{t}Bu) or aryl (Mes = 2,4,6-Me-C_6H_2) imidazole to afford the imidazolium proligands **AY** (Scheme 6).[144] The free functionalised carbene **AZ**, was prepared by refluxing **AY** with 2 equivalents of KH in thf and could be converted to the lithium salt **BA** by treatment with 1 equivalent of $^{n}BuLi$. Deprotonation of **AZ** with 2 equivalents of $^{n}BuLi$ afforded the lithium bromide adduct **BB**, which has been used successfully in the synthesis of a number of f-block complexes.



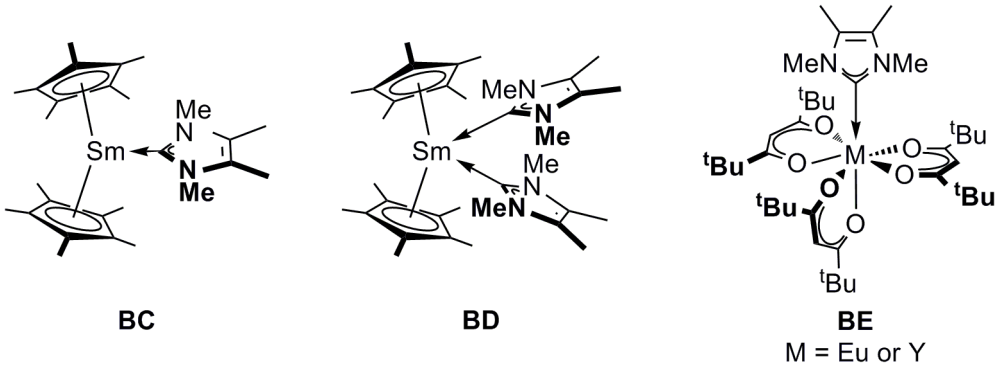
Scheme 6: Synthesis of amido-tethered NHC proligands, **AY – BB**

1.4 Early transition metal and f-block N-heterocyclic carbene complexes

A full review of all yttrium, scandium and f-block NHC complexes to 2009 was published by Arnold *et al.* and follows on from the brief review on the same subject in 2006.[93,141] Here, selected complexes are discussed in terms of their synthesis, physical properties and reactivity including catalysis.

1.4.1 Yttrium, scandium and the lanthanides

The first NHC complexes of yttrium and the lanthanides were reported by Arduengo *et al.*.[145] The *bis*(cyclopentadienyl) Sm^{II} complexes **BC** and **BD** were synthesised from reaction of $SmCp^*_2(thf)$ with 1 or 2 equivalents of ligand L (L = 1-C(NMeCMe)$_2$) respectively (Figure 21). The *mono*(carbene) adduct **BC** was used for the polymerisation of mesogenic methacrylates by Schumann *et al.* (see 1.4.3).[146,147]



BC **BD** **BE**
M = Eu or Y

Figure 21: The first yttrium and lanthanide NHC complexes

In the same communication, the preparation of **BE**, M(L)(thd)$_3$ (M = Eu or Y, thd = OC(^{t}Bu)CHC(^{t}Bu)O$^-$) was also reported (Figure 21). The $^{13}C\{^1H\}$ NMR spectrum of the yttrium analogue contained a high frequency resonance for the $C_{carbene}$ at 199.38 ppm which couples to the ^{89}Y it is bound to ($^1J_{YC}$ = 33 Hz). The single crystal X-ray diffraction study of **BE** showed that the M-$C_{carbene}$ bond lengths were longer than that of σ-bonded lanthanide alkyls.

Anwander and co-workers prepared the yttrium silylamide NHC adducts: **BF** Y(L)N"$_3$, **BG**, Y(L)(N{$SiHMe_2$}$_2$)$_3$ and **BH**, Y(L)$_2$(N{$SiHMe_2$}$_2$)$_3$ (L = 1-C(NMeCH)$_2$).[148] **BG** and **BH** were prepared through solvent displacement reactions of Y(N{$SiHMe_2$}$_2$)$_3$(thf)$_2$ (Figure 22).

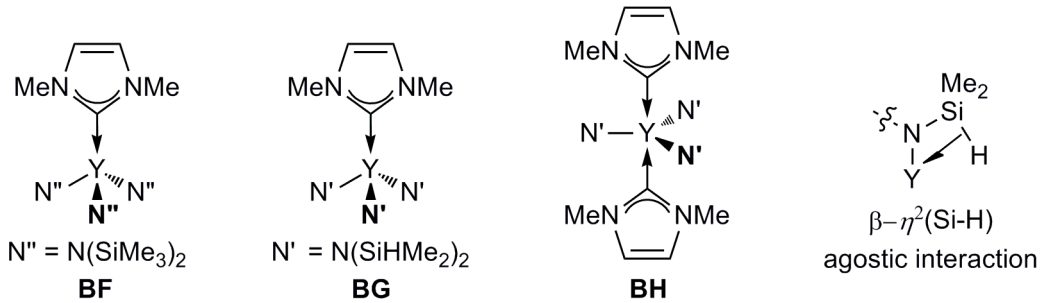
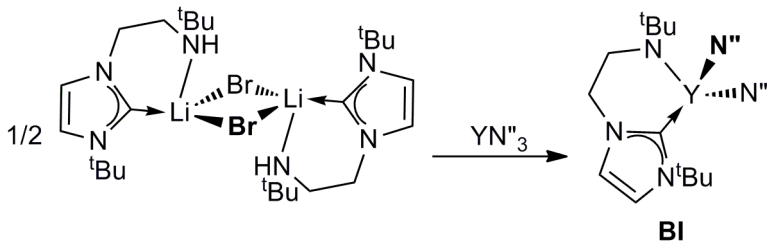


Figure 22: The first yttrium silylamide NHC adducts

The solid state structures of **BG** and **BH** displayed close contacts between the Si-H bond and the Y^{III} ion. The Y···Si distances are within the sum of the van der Waals radii and the asymmetric coordination of the silyl amide ligand implies the presence of β-η^2(Si-H) agostic interactions which help to stabilise the large Lewis acidic metal ion (Figure 22).

Arnold *et al*. described the synthesis of the first functionalised NHC complexes of Y^{III}, **BI**, Y(L)N"$_2$ (L = ^{t}BuNCH$_2$CH$_2$(1-C{NCHCHN^{t}Bu})) from the treatment of YN"$_3$ with 0.5 equivalents of the lithium bromide adduct [HL.LiBr]$_2$ (Equation 5).[144] The ^{13}C{^{1}H} NMR spectrum contained a diagnostic doublet at 186 ppm for $C_{carbene}$ ($^1J_{YC}$ = 55 Hz). This complex is an active catalyst for the polymerisation of *rac*-lactide (see 1.4.3).[149]

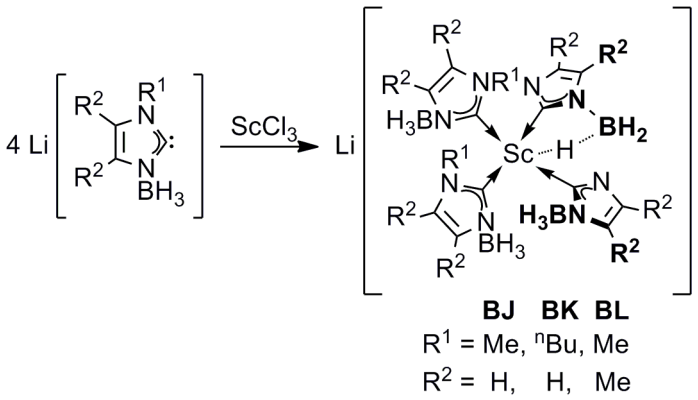


BI

Equation 5: Synthesis of the first asymmetric NHC lanthanide complex

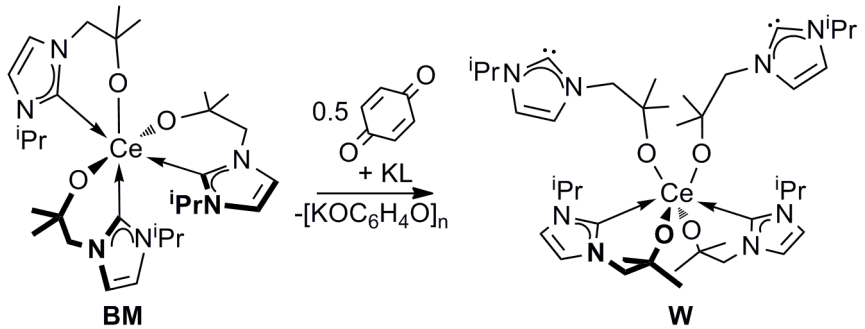
There are relatively few reports of scandium NHC complexes to date. Cui and co-workers prepared the *bis*(alkyl) complexes Sc(L)(CH$_2$SiMe$_3$)$_2$ (L = Ind-CH$_2$CH$_2$(1-C{NCHCHNMes}) or Flu-CH$_2$CH$_2$(1-C{NCHCHNMes})) and the CCC pincer *bis*(NHC) scandium dibromide Sc(L)Br(thf) (L = 2,6-[CH$_2$(1-C{NCHCHNMes})$_2$C$_6$H$_3$]). Their synthesis and applications to polymerisation of isoprene, ethylene and norbornene is discussed in detail later (see 1.4.3).

Siebert and co-workers described the preparation of the 16 electron Sc^{III} tetracarbene complexes **BJ** and **BK**, [Li(dme)$_2$][Sc(L)$_4$] (L = 1-C(N{BH$_3$}CHCHNMe) or 1-C(N{BH$_3$}CHCHN^{n}Bu) respectively) and **BL**, [Li(thf)$_4$][Sc(L)$_4$] (L = 1-C(N{BH$_3$}CMeCMeNMe)) from reaction of ScCl$_3$ with the corresponding Li(L) salt (Equation 6). Four-fold coordination of the NHCs was observed even when sub-stoichiometric quantities of Li(L) were used. An X-ray diffraction study of **BK** shows that the Sc^{III} ion is *pseudo*tetrahedrally coordinated to four carbenes but also has three centre-two electron Sc···H···B interactions with one H atom of each of the BH$_3$ (Sc···H distances = 2.17 Å – 2.39 Å).



Equation 6: Synthesis of tetracarbene Sc^{III} NHC complexes. Only one of the four Sc···H···B interactions is indicated for clarity

Arnold and co-workers synthesised **W**, $Ce(L)_4$ (L = $OCMe_2CH_2$(1-C{NCHCHN^{i}Pr})) which is an example of both the first Ce^{IV} NHC and Ce^{IV}-C dative bond.[62] **W** was first prepared from the Ce^{III} complex **BM**, $Ce(L)_3$ using 0.5 equivalents of benzoquinone as an oxidant and 1 equivalent of sacrificial K(L). Polymeric material of the form $[KOC_6H_4O]_m$ was extruded as a byproduct (Equation 7). Improved syntheses directly from $Ce(OTf)_4$ and $CeI_3(thf)_4$ were later reported.[63] The ^{1}H NMR spectrum of **W** contained one set of ligand resonances in the diamagnetic spectral region (Ce^{IV}: [Xe]$4f^0$) with a $C_{carbene}$ resonance at 212 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Variable temperature NMR spectroscopy supported the formulation of **W** with two bound and two free NHC ligands. At room temperature, a fluxional process exchanging free and bound carbenes is occurring which is fast on the NMR timescale. Cooling to 198 K saw three sets of ligand resonances in a 2:1:1 ratio which is expected for two magnetically equivalent free carbenes and two magnetically inequivalent bound carbenes. The free pendant carbenes could also be trapped through reaction with 2 equivalents of 9-BBN to afforded **W-9-BBN** $Ce(L)_2(L\text{-}9\text{-}BBN)_2$. Both **W** and **W-9-BBN** were also characterised in single crystal X-ray diffraction studies.



Equation 7: Synthesis of the first Ce^{IV} NHC complex (**W**)

1.4.2 Uranium

All low valent U^{III} NHC complexes to date have been simple *mono*(carbene) adducts of the ligand L (L = 1-C(NMeCMe)$_2$) (Figure 23).

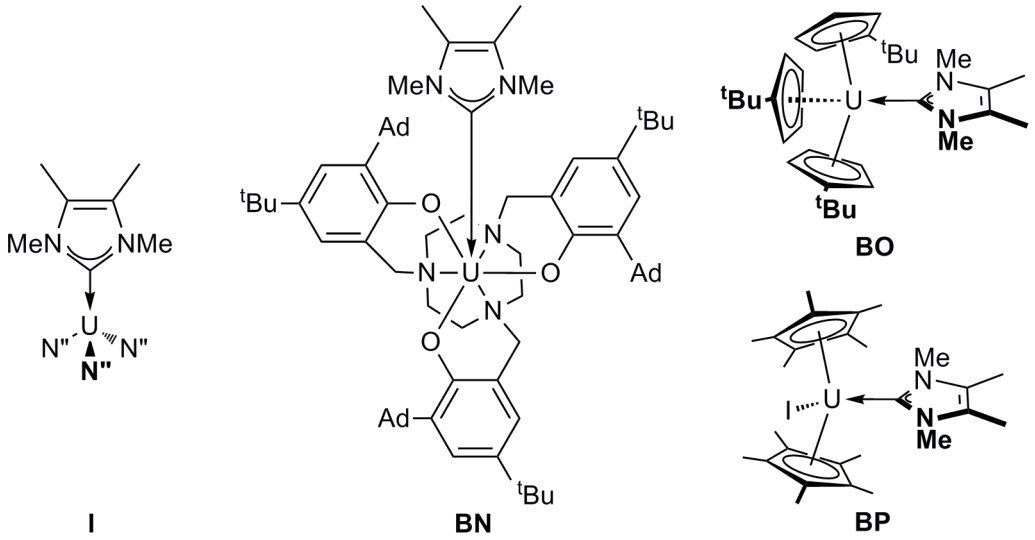
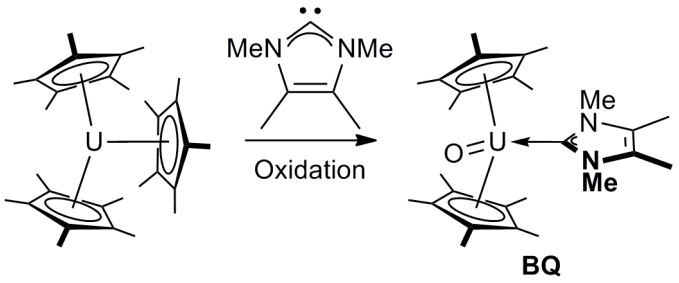


Figure 23: U^{III} NHC adducts

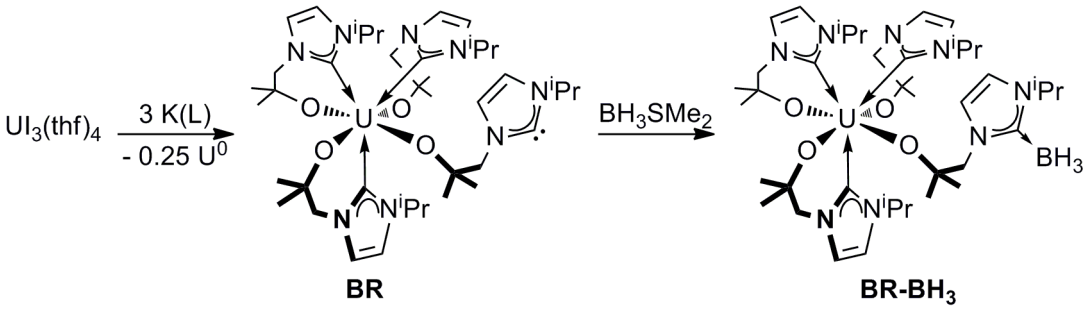
The first reports came from Meyer and co-workers of **I**, U(L)N"$_3$ (see 1.1.2 also) and **BN** U(L)(^{Ad}ArO)$_3$tacn (tacn = 1,4,7-triazacyclononane) (Figure 23).[28] The electronic absorption spectra and X-ray diffraction studies (M-$C_{carbene}$ in **I** = 2.672(5) Å), **BN** = 2.789(14) Å) were consistent with the stronger binding of L to the simple U^{III} amide. A DFT study was used to indicate that there was a π bonding contribution to the U-$C_{carbene}$ bond which involved the f-orbitals of the U^{III} ion. Ephritikhine and co-workers synthesised the *tris*(cyclopentadienyl) U^{III} NHC complex **BO**, U(L)(1-^{t}BuC$_5$H$_4$)$_3$ and the *bis*(cyclopentadienyl) U^{III} NHC iodide **BP**, U(L)Cp*$_2$I (L = 1-C(NMeCMe)$_2$) (Figure 23).[150] The molecular structures of **BO** and **BP** were compared to their cerium analogues (the first Ce^{III} NHC complexes) and the M-$C_{carbene}$ bond distances were *ca.* 0.03 Å shorter for the uranium complexes despite the larger ionic radius of U^{III} in the same coordination environment ($rCe^{III,\ 6C.N.}$ = 1.01 Å $rU^{III,\ 6C.N.}$ = 1.025 Å).[151] This was attributed to increased covalency between the more polarisable 5f metal ion and the soft carbene. NMR-scale competition reactions were used to confirm the stronger affinity of ligand L for U^{III} over Ce^{III}.

Evans *et al.* synthesised the first U^{IV} NHC complex **BQ**, U(L)Cp*$_2$(=O) (L = 1-C(NMeCMe)$_2$), afforded from the reaction of UCp*$_3$ with L which underwent an unexpected oxidation (Equation 8).[25] It is also a rare example of a terminal uranium *mono*(oxide).



Equation 8: Synthesis of the first U^{IV} NHC complex

Arnold *et al.* reported the synthesis of the tetracarbene U^{IV} complex **BR**, $U(L)_4$ (L = $OCMe_2CH_2$(1-C{NCHCHN^{i}Pr})) where there are three bound carbenes and one free carbene (Scheme 7).[152] Reaction of $UI_3(thf)_4$ with 3 equivalents of K(L) resulted in disproportionation to **BR** and 0.25 equivalents of uranium metal.



Scheme 7: Synthesis of the tetracarbene U^{IV} NHC complex **BR** and trapping the free carbene with BH_3SMe_2 to afford **BR-BH$_3$**

A variable temperature NMR spectroscopy study indicated that **BR** was fluxional in solution, exchanging the free and bound carbene groups. At room temperature, there were only two broad resonances 17 ppm and -6 ppm but the fluxional process was frozen out at 228 K, where four separate ligand environments were observed. The free carbene could be trapped with BH_3SMe_2 to afford **BR-BH$_3$**, $U(L)_3(L\text{-}BH_3)$. Comparison of **BR** with the cerium analogue **BR**, $Ce(L)_4$ clearly shows a dramatic difference in coordination despite the very similar ionic radii or Ce^{IV} and U^{IV} ($rCe^{IV,\ 6C.N.}$ = 0.87 Å , $rU^{IV,\ 6C.N.}$ = 0.89 Å; seven-coordinate ionic radii are not recorded in the Shannon lists).[151] It is energetically favourable for the carbenes to bind to the softer 5f metal centre, forming three U-C bonds and four strong U-O bonds, despite the increased steric congestion and unfavourable electrostatic interactions.

There are no reported U^{V} NHC complexes and all U^{VI} complexes are those of the uranyl dication, $[UO_2]^{2+}$. Oldham *et al.* reported the first examples **BS**, $U(L)O_2Cl_2$ (L = 1-$C(NMesCY)_2$, Y = H or Cl), prepared from solvent displacement reactions of $UO_2Cl_2(thf)_3$

(Figure 24).[153] X-ray diffraction studies and IR spectroscopy were used to show that the NHC was a poor ligand for the $[UO_2]^{2+}$. Arnold and co-workers prepared the first U^{VI} NHC complexes with a functionalised NHC ligand, **AL** and **AM**, $U(L)_2O_2$ (L = $^tBuNCH_2CH_2$(1-C{NCHCHNR}) where R = Mes or ^{t}Bu respectively), which were synthesised by the treatment of $UO_2N''_2(thf)_2$ with 1 equivalent of the free ligand HL (Figure 24).

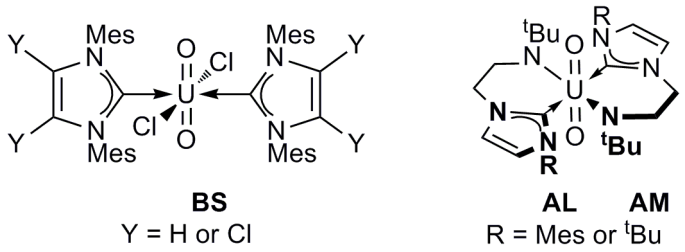


Figure 24: U^{VI} NHC complexes

1.4.3 Catalysis

Cui and co-workers reported the first rare earth *bis*(alkyl) complexes supported by an NHC ligand, **BT** and **BU**, $M(L)(CH_2SiMe_3)_2$ (M = Y, Sc, Ho or Lu, L = Ind-CH_2CH_2(1-C{NCHCHNMes}) and Flu-CH_2CH_2(1-C{NCHCHNMes}) respectively).[154,155] The imidazolium bromide salt $[H_2L]Br$ was first deprotonated with $LiCH_2SiMe_3$ to afford the carbene L, which was reacted *in situ* with the rare earth *tris*(alkyl) precursor $M(CH_2SiMe_3)_3(thf)_2$ to yield the Lewis base free $M(L)(CH_2SiMe_3)_2$ in good isolated yields of 62 % – 68 % (Figure 25).

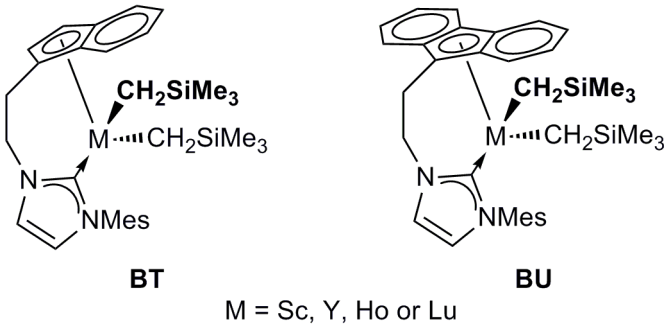


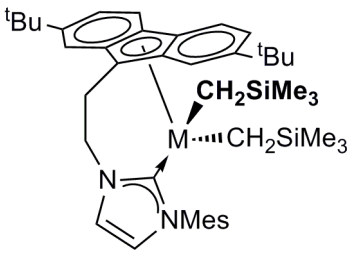
Figure 25: Indenyl- (**BT**) and fluorenyl- (**BU**) functionalised NHC complexes

On activation with $[Ph_3C][BAr^F_4]$ ($Ar^F = C_6F_5$), **BT** and **BU** showed low activity for the polymerisation of isoprene and were inert when Al^iBu_3 was used as a co-catalyst. Using a equimolar mixture of $[Ph_3C][BAr^F_4]$:Al^iBu_3, all except the scandium complexes were active. The active fluorenyl complexes showed high selectivity for polymerisation of crystalline 3,4-*poly*(isoprene) (as determined by ^1H and $^{13}C\{^1H\}$ NMR spectral analysis) and this selectivity increased with decreasing ionic radius of the metal centre (Y = 98 %, Lu = 99 %). The

polymerisation was living and produced polymer with narrow PDIs (M_w/M_n =1.06 – 1.38 over a range of conditions determined by Gel Permeation Chromatography) with good efficiency ($M_{n,\,calc}/M_{n,\,exp}$ × 100 % = 72 % – 91 %). This compares well with the rare earth alkyl complex $[Sc(L)CH_2SiMe_3]_2$ (M = Lu or Sc, L = 1-$SiMe_2$PHCy-C_5Me_4H) reported by Hou and co-workers which on activation with $[CPh_3][BAr^F{}_4]$ at -20 ºC – 25 ºC produced 3,4-*poly*(isoprene) with 99 % – 100 % selectivity.[156] The polymerisation was not living however and the active catalyst was found to decompose to inactive species in solution.

The polymerisation with **BU** could also be carried out at higher temperature (80 ºC) with little change in 3,4-selectivity and PDI. This implies that the active catalyst is thermally stable. The active indenyl-functionalised complexes showed lower 3,4-selectivity (91 % and lower) and, apart from the holmium complex, also showed considerably lower yields of polymer after 6 h (Y = 50 %, Ho = 93 % and Lu = 15 %) with respect to the fluorenyl-functionalised complexes under the same conditions. Overall, these results indicated that the greatest selectivity for 4,3-insertion of isoprene was achieved with the bulkier fluorenyl ligand and central metals of smallest ionic radius.

The related *tert*-butyl substituted fluorenyl complexes **BV**, $M(L)(CH_2SiMe_3)_2$ (M = Sc or Lu, L = 2,7-^{t}Bu-Flu-CH_2CH_2(1-C{NCHCHNMes}) have been prepared using an analogous procedure (Figure 26).[157]



BV
M = Sc or Lu

Figure 26: Rare earth *tert*-butyl substituted fluorenyl-functionalised NHC complexes

Alongside **BV**, the complexes **BT**, (M = Sc or Lu, L = Ind-CH_2CH_2(1-C{NCHCHNMes})) and **BU**, $M(L)(CH_2SiMe_3)_2$ (M = Y, Sc, Ho or Lu, L = Flu-CH_2CH_2(1-C{NCHCHNMes})) were evaluated as catalysts for both the homo- and co-polymerisation of ethylene and norbornene.

On activation by $[Ph_3C][BAr^F{}_4]$ (Ar^F = C_6F_5), all complexes showed low polymerisation activity. It is suggested that this low activity may be a result of impurities present in the polymerisation system or the instability of the active cationic species. On

activation with a 1:20 molar ratio of $[Ph_3C][BAr^F{}_4]$:Al^iBu_3, there was some catalytic activity towards the co-polymerisation of ethylene and norbornene, with the scandium complexes demonstrating high activity. Activity of the scandium complexes increased as the NHC ligand became less electron donating (indenyl ligand: 0.28 x 10^6, fluorenyl ligand: 2.37 × 10^6 copolymer g $mol_{Sc}^{-1}h^{-1}atm^{-1}$) but steric factors were also found to be important, with the *tert*-butyl fluorenyl ligand hindering the monomer insertion (^{t}Bu-fluorenyl ligand: 1.5 × 10^6 copolymer g $mol_{Sc}^{-1}h^{-1}atm^{-1}$). Under the same polymerisation conditions (40 ºC, 5 minutes [norbornene]/[ethylene] = 4.63, 100 mL toluene), the scandium complexes afforded polymers with 30 % – 37 % norbornene content and broad molecular weight distributions (M_w/M_n = 1.53 – 1.83). Variation of the activators to $[PhMe_2NH][BAr^F{}_4]$:Al^iBu_3 and $BAr^F{}_3$ also resulted in high activity. A more detailed study of the co-polymerisation catalysed by the fluorenyl-substituted scandium complex was completed and showed that the optimum temperature was 40 ºC. The resulting norbornene content decreased with increasing temperature (37 % at 40 ºC, 24 % at 50 ºC) and could be controlled by varying the feed ratio of ethylene to norbornene, as could the polymer microstructure (random to alternating).

The first reported example of rare earth catalysts reported to successfully co-polymerise ethylene and norbornene was the *bis*(alkyl) scandium system $Sc(L)(CH_2SiMe_3)_2(thf)$ (L = 1-$SiMe_3$-C_5Me_4, 1,3-$SiMe_3$-C_5H_3 or Cp*) from Hou and co-workers.[158] On activation with $[Ph_3C][BAr^F{}_4]$, the catalytic species was stable over a wide range of temperatures (0 ºC – 70 ºC) and, under optimised conditions, extremely active (L = 1-$SiMe_3$-C_5Me_4, 25 ºC, 5 minutes, 20 mmol norbornene, 1 atm ethylene, 40 mL toluene, activity = 25.2 × 10^6 copolymer g $mol_{Sc}^{-1}h^{-1}atm^{-1}$). The copolymerisation was alternating in nature with the polymers containing 36 % - 48 % norbornene.

Cui and co-workers also investigated the CCC pincer *bis*(NHC) rare earth dibromides, **BW**, M(L)Br(thf) (M = Y, Sc, La, Nd, Sm, Gd, Dy, Ho, Tm or Lu, L = 2,6-$[CH_2(1\text{-}C\{NCHCHNMes\})_2C_6H_3]$) with respect to isoprene polymerisation.[159,160] The complexes were afforded by the reaction of the imidazolium salt $[H_2L]Br.2HBr$ and anhydrous metal trichloride MCl_3 with 3 equivalents of ^{n}BuLi (Figure 27).

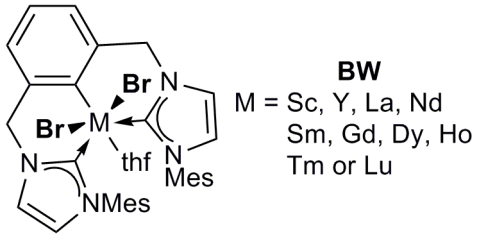


Figure 27: Rare earth *bis*(NHC) pincer dibromides for the polymerisation of isoprene

BW were evaluated as catalysts for the polymerisation of isoprene using the combination of AlR_3:$[Ph_3C][BAr^F{}_4]$ (R = Me, Et or ^{i}Bu) as an activator and chlorobenzene as a solvent. The catalyst activity was dependent on both the central metal ion and the steric profile of the AlR_3 ($AlEt_3$ > $AlMe_3$ >> Al^iBu_3 independent of metal ion). The neodymium, gadolinium and dysprosium complexes displayed the highest activity ahead of yttrium. The complexes with the smallest and largest metal ions (scandium, holmium, thulium and lanthanum) were inactive as was the samarium complex, which is assumed to have undergone reduction to an inactive Sm^{II} form on reaction with AlR_3. The active complexes were highly selective for *cis*-1,4-*poly*(isoprene) (Nd = 97 %, Gd = 99 %, Dy = 99 %, Ho = 100 % and Y = 100 %) and this was also the case at higher temperature. Under the same polymerisation conditions (AlR_3 = Al^iBu_3, 60 minutes, [isoprene]/[**BW**] = 1000, 5 mL C_6H_5Cl), the selectivity using the dysprosium analogue was 98.4 % (40 ºC), 98.0 % (60 ºC) and 97.6 % (80 ºC), though the yields were now found to be below 100 %. Analysis of the molecular structures gained from a X-ray diffraction study supported the observation of increased *cis*-1,4-selectivity on increasing steric encumbrance around the metal ion. The molecular weight distribution of the polymers produced was found to be variable (for example, PDI_{Nd} = 1.70 – 3.09) and broad in several cases, which was attributed to slow initiation *versus* fast propagation. Finally, NMR spectroscopy was used to probe the nature of the active species in the polymerisation and for the yttrium analogue, $Y(L)Br_2(thf)$ (activated with $2Al^iBu_3$:$[Ph_3C][BAr^F{}_4]$), this was proposed to be the yttrium hydrido aluminate species $[Y(L)(\mu\text{-}H)_2Al^iBu_2][BAr^F{}_4]$.

Schumann *et al*. reported the thermally stable Sm^{II} NHC adducts, **BC**, $Sm(L)Cp^*_2$ (L = 1-C(MeNCMe)$_2$)[146] (first prepared by Arduengo *et al.* from $SmCp^*_2(thf)$)[145] and **BX**, $Sm(L)Cp^*_2$ (L = 1-C(^{i}PrNCMe)$_2$),[145] which were synthesised by the treatment of $SmCp^*_2(thf)_2$ with the corresponding free carbene (Figure 28). **BC** and **BX** were used to catalyse the living polymerisation of a selection of mesogenic methacrylate monomers to afford liquid crystalline homo- and block co-polymers with a narrow PDI at room temperature.

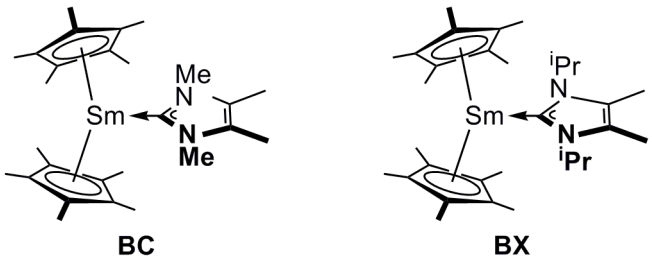


Figure 28: Sm^{II} NHC adducts for the polymerisation of mesogenic methacrylates

Baudry-Barbier *et al.* prepared the Sm^{III} NHC adducts, **BY**, $Sm(L)(1\text{-}^{t}Bu\text{-}C_5H_4)_2Cl$ and **BZ**, $Sm(L)(1\text{-}^{t}Bu\text{-}C_5H_4)_2(C_3H_5)$ (L = $1\text{-}C(^{i}PrNCMe)_2$), by direct reaction of the free carbenes with the *bis*(cyclopentadienyl) Sm^{III} allyl and chloride respectively (Figure 29).[161]

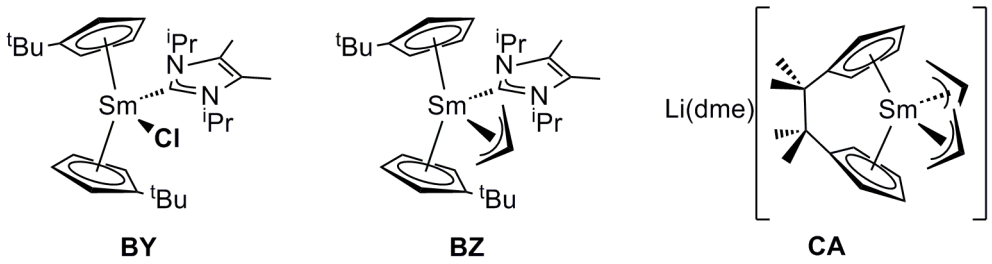


Figure 29: Sm^{III} NHC adducts for the polymerisation of isoprene

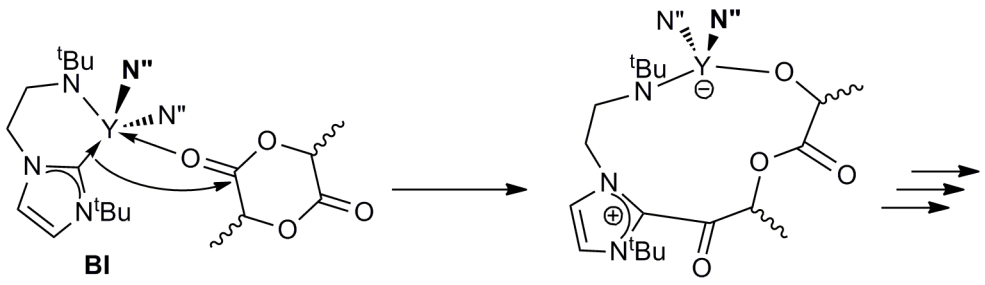
Both undergo partial rearrangement in solution to $Sm(1\text{-}^{t}Bu\text{-}C_5H_4)_3$ and, for $Sm(L)(1\text{-}^{t}Bu\text{-}C_5H_4)_2Cl$, the presence of a second NHC adduct $Sm(L)_2(1\text{-}^{t}Bu\text{-}C_5H_4)Cl_2$ was also identified. The equilibrium was a function of the solution concentration (Equation 9).

$$2\ Sm(L)(1\text{-}^{t}Bu\text{-}C_5H_4)_2Cl \rightleftharpoons Sm(1\text{-}^{t}Bu\text{-}C_5H_4)_3 + Sm(L)_2(1\text{-}^{t}Bu\text{-}C_5H_4)Cl_2$$

Equation 9: Concentration dependent solution equilibrium of $Sm(L)(1\text{-}^{t}Bu\text{-}C_5H_4)_2Cl$

BZ was examined as a polymerisation catalyst of isoprene but was found to have very low activity. The parent allyl complex, $[Sm(1\text{-}^{t}Bu\text{-}C_5H_4)_2(C_3H_5)]_n$ (believed to be oligomeric or polymeric), was completely inactive and it was suggested that while the strong donor properties of the NHC ligand allow the break up the polymeric starting material to create an active species, isoprene is not a good enough ligand to achieve this. The related samarium bisallyl 'ate' complex **CA**, $[Li(dme)][Sm(L)(C_3H_5)_2]$ (L = $Me_4C_2(C_5H_4)_2$ (Figure 29) was a more active catalyst (60 % yield after 12 h) and stereoselective for the production of *trans*-1,4-isoprene (> 95 %).

Arnold and co-workers investigated the amido-functionalised Y^{III} complex **BI**, $Y(L)N''_2$ (L = $^{t}BuNCH_2CH_2(1\text{-}C(NCHCHN^{t}Bu))$ (see 1.4.1) with respect to the polymerisation of *rac*-lactide (Scheme 8).[149]



Scheme 8: Amido-tethered NHC Y^{III} complex for *rac*-lactide polymerisation

BI was found to produce heterotactically enriched polymer with narrow polydispersities (cat:monomer = 1:100, 2 minutes, 75 % conversion, M_W = 77 000, PDI = 1.19) and remained active at very low concentration (cat:monomer = 1:10 000, 15 minutes, 85 % conversion, MW = 66 000, PDI = 1.47). End group analysis of the polymer using MALDI-TOF mass spectrometry showed that all chains were terminated by imidazolium groups. This indicates that the carbene is the sole initiator of the ring opening of the monomer but also that the NHC is catalysing undesirable transesterification side reactions.

The data suggest that **BI** acts as a bifunctional catalyst whereby the monomer first coordinates to the Lewis acidic Y^{III} centre before the Lewis basic carbene ring opens the monomer through nucleophilic attack and coordination insertion polymerisation continues. It is suggested that chain growth occurs through monomer insertion at the metal centre.

BI can be compared to other bifunctional catalysts for the polymerisation of polar monomers. For example, Waymouth and co-workers reported the use of thiourea amine catalyst **CB** for the living polymerisation of lactide using pyrenebutanol as an initiator (Figure 30)[162]. The *poly*(lactide) produced was of very low PDI (1.05 – 1.08) with 97 % conversion achieved after 24 h. Interestingly, and in contrast to **BI**, minimal transesterification was observed even after extended periods of time Control experiments with the thiourea and amine components of **CB** confirmed the bifunctional nature of **CB** since they did not polymerise lactide until combined.

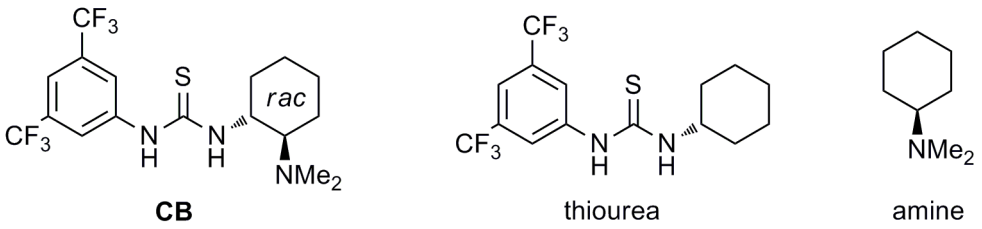


Figure 30: A bifunctional thiourea amine catalyst (**CB**) for lactide polymerisation

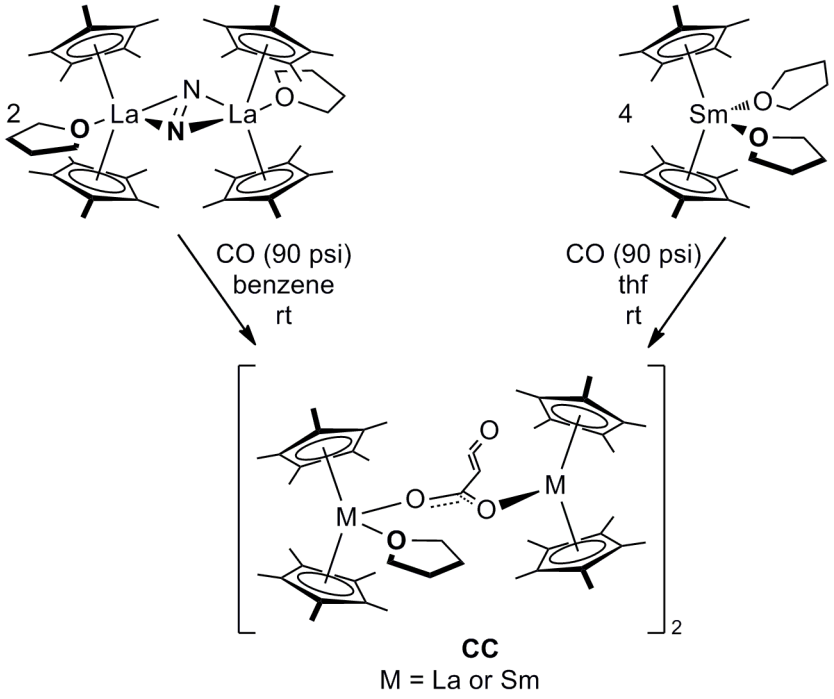
1.5 Small molecule activation by organometallic f-block complexes

1.5.1 CO

There are very few examples of direct reductive coupling and homologation of CO by f-block complexes and no examples of a catalytic process. This section focuses on this rare process but also examines a small number of examples of CO insertion reactions, which are more common.

Evans *et al.* described the synthesis of the ketenecarboxylate complex **CC**, $[Sm_2Cp^*_4(\mu\text{-}\eta^4\text{-}O_2CCCO)(thf)]_2$ from the reductive coupling of six molecules of CO at 90 psi

by $SmCp^*_2(thf)_2$ (Scheme 9).[163] Each samarium centre has undergone a one electron oxidation to Sm^{III}.

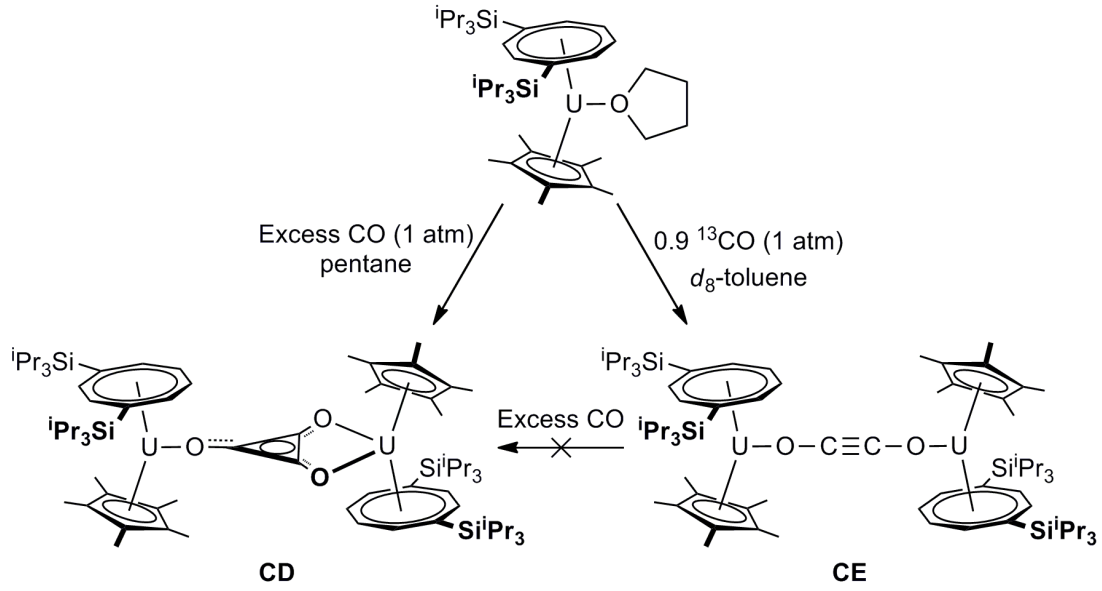


Scheme 9: Synthesis of ketene carboxylate complexes of Sm^{III} and La^{III}

The analogous La^{III} complex was prepared by the reaction of the dinitrogen complex $[LaCp^*_2(thf)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ with CO (90 psi) (Scheme 9).[164] The $^{13}C\{^1H\}$ NMR spectrum contained three doublets of doublets at 23.4, 129.7 and 167.2 ppm for the ketenecarboxylate group. The coupling constants and a ^{13}C-^{13}C COSY experiment allowed unambiguous assignment of these resonances.

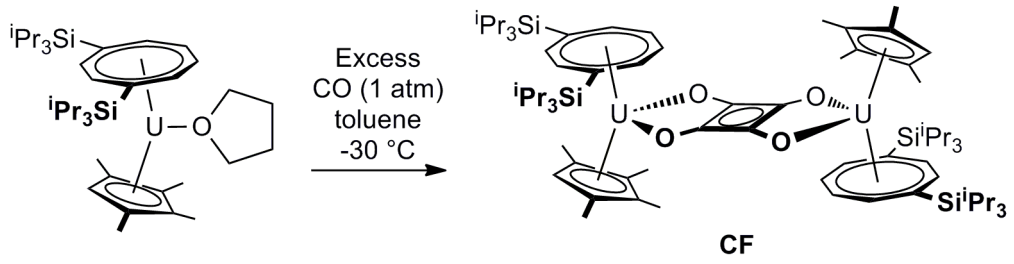
There are only two examples of f-block complexes that can reductively couple carbon monoxide at atmospheric pressure. Cloke and co-workers reported that treatment of pentane solutions (at -78 ºC and then warming to room temperature) of $UCp^*(1,4\text{-}Si^iPr_3\text{-}C_8H_6)(thf)$ with CO afforded **CD**, $[(1,4\text{-}Si^iPr_3\text{-}C_8H_6)Cp^*U]_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_3O_3)$ in 40 % yield (Scheme 10).[165] **CD** is the product of reductive coupling of three molecules of CO to the deltate dianion, $C_3O_3^{2-}$, between two U^{III} centres which undergo oxidation to U^{IV}. The molecular structure of **CD** revealed that the $C_3O_3^{2-}$ is distorted with one long C-C bond. A DFT study identified that this long bond was most likely due to a C-C agostic interaction with an f-orbital centred on the U^{IV} ion. Treatment of $UCp^*(1,4\text{-}Si^iPr_3\text{-}C_8H_6)(thf)$ with 0.9 equivalents of ^{13}CO afforded the ynediolate complex **CE**, $[UCp^*(1,4\text{-}Si^iPr_3\text{-}C_8H_6)](^{13}CO)_2$ and small amounts of deltate complex **CD** (Scheme 10).[166] IR spectra recorded immediately after ^{13}CO exposure contained a band at 1882 cm^{-1} (1920 cm^{-1} for the ^{12}CO analogue), which

decayed over time, consistent with the initial formation of a U^{III} monocarbonyl species. **CE** was isolated by fractional crystallisation; the $^{13}C\{^1H\}$ NMR spectrum contained a single diagnostic resonance at 313 ppm and the molecular structure indicated a short C≡C bond of 1.177(12) Å. **CE** did not react further with excess CO.



Scheme 10: Formation of U^{IV} deltate (**CD**) and ynediolate (**CE**) CO complexes

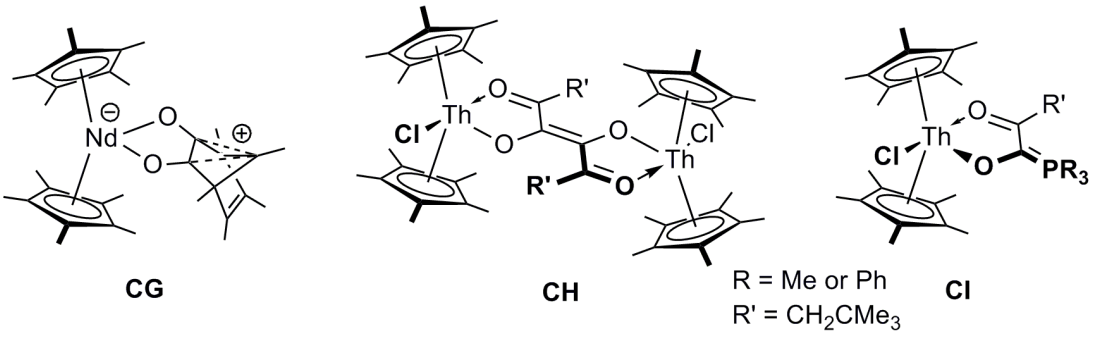
It was proposed that tuning the stereoelectronics of the ligand set could lead to the isolation of further CO homologues. Indeed, exposure the less sterically demanding $U(C_5Me_4H)(1,4\text{-}Si^iPr_3\text{-}C_8H_6)(thf)$ to CO (1 atm) at -30 ºC afforded the squarate complex **CF**, $[(1,4\text{-}Si^iPr_3\text{-}C_8H_6)(C_5Me_4H)U]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_4O_4)$ in 66 % yield (Equation 10).[167] The molecular structure of **CF** does not indicate any agostic stabilising interactions; the average O-C-C bond angle (127º) is much narrower compared to **CD** (159º).



Equation 10: Synthesis of a U^{IV} squarate complex

A DFT study into the mechanism of formation of the ynediolate, deltate and squarate complexes proposed that a relatively long-lived "zig-zag" intermediate containing two CO molecules is able to react further with CO to form higher homologues.

The insertion of CO into f-element amide, alkyl and hydride bonds is much more common. This is a distinct process compared to the examples of reductive coupling since CO insertion occurs without a change in the formal oxidation state of the metal ion or bound ligands; the electrons for reductive coupling may be provided by the metal centre or a ligand. For example, Evans and co-workers reported the synthesis of the nonclassical carbonium ion complex **CG**, $NdCp^*_2(O_2C_7Me_5)$ from the reaction of the *tris*(cyclopentadienyl) $NdCp^*_3$ with CO (20 psi) where CO has inserted into one Nd-Cp* bond (Figure 31).[168] The samarium analogue was also previously prepared.[169]



CG **CH** **CI**

Figure 31: Products of CO insertion in f-block complexes

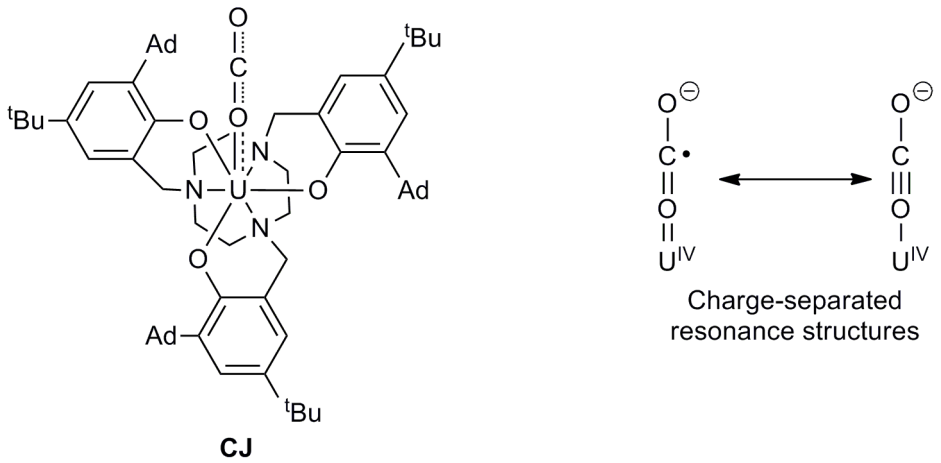
Marks and co-workers reported the reaction of $ThCp^*_2Cl(\eta^2\text{-}COCH_2CMe_3)$ (itself a product of CO insertion into the Th-C bond in $ThCp^*_2(CH_2CMe_3)Cl$) with CO ($\leq$ 1 atm) to form **CH**, $[ThCp^*_2Cl(OC\{COCH_2CMe_3\}CO)]_2$ in 40 % yield.[170] The molecular structure of enedionediolate **CH** revealed a planar $(OC\{COCH_2CMe_3\}CO)^{2-}$ central core. When the reaction with CO (1 atm) was carried out in the presence of PR_3 (R = Me or Ph), the formation of ylids **CI** occurred in quantitative yield (Figure 31). It was proposed that the phosphine reagent traps a ketene intermediate common to both the formation of **CH** and **CI**.

1.5.2 CO_2

Examples of well-characterised reactivity of f-block organometallic complexes with CO_2 are relatively limited. This section reviews CO_2 activation through a novel binding mode, insertion reactions and both the reductive coupling and splitting of CO_2.

Meyer and co-workers prepared the first example of linear oxygen-bound η^1-OCO CO_2 complex, **CJ**, $U(^{Ad}ArO)_3tacn(\eta^1\text{-}OCO)$ (tacn = 1,4,7-triazacyclononane) by exposing the U^{III} complex $U(^{Ad}ArO)_3tacn$ to CO_2 at ambient pressure and temperature (Figure 32).[171] An X-ray diffraction study confirmed the binding mode of CO_2 (U-O-C = 171.1(2)°, O-C-O = 178.0(3)°). Combined with IR, NIR and SQUID magnetisation data, it was proposed that the

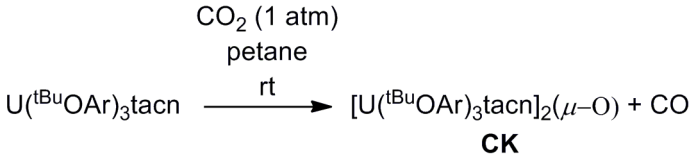
bonding was best described by charge-separated resonance structures in which the uranium centre is formally in the +4 oxidation state.



CJ

Figure 32: The first example of a linear bound CO_2 molecule

When a modified, less sterically demanding, *tert*-butyl substituted ligand was used in this system, exposure to CO_2 led to the formation of dimeric oxo-bridged $[U(^{tBu}ArO)_3tacn]_2(\mu\text{-}O)$, **CK** (Equation 11).[172] The reduction of CO_2 was accompanied by one electron oxidation of the uranium centres to U^{IV}.



CK

Equation 11: Reduction of CO_2 to afford an oxo-bridged dimer

An example of CO_2 insertion chemistry comes from Tilley and co-workers who demonstrated that reaction of the scandium silyl complexes $ScCp_2(SiR_3)(thf)$ (R = $SiMe_3$ or $^tBuPh_2$) with CO_2 immediately results in the formation of dimeric insertion products **CL**, $[ScCp_2(\mu\text{–}O_2CSiR_3)]_2$ (Figure 33).[173] The supersilyl analogue (R = $SiMe_3$) was characterised by IR spectroscopy (diagnostic $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ stretches at 1486 cm^{-1} and 1349 cm^{-1} respectively), NMR spectroscopy ($^{13}C\{^1H\}$ spectrum contained a resonance at 200.8 ppm for the carboxylate carbon) and an X-ray diffraction study which confirmed the proposed connectivity. Similarly, Schumann and co-workers reported an insertion of CO_2 into the alkyl bond of $YCp^*_2(CH_2CH_2CH_2NMe_2)$ to afford **CM**, $YCp^*_2(\eta^2\text{-}O_2CCH_2CH_2CH_2NMe_2)$.[174] The first example of CO_2 insertion in an $M(CH_2SiMe_2N\{SiMe_3\})$ metallacycle was reported by Ephritikhine and co-workers. CO_2 doubly inserted in the metal

amide bonds of **CN**, $[Na(thf)_x][UN"(CH_2SiMe_2N\{SiMe_3\})_2]$ to afford **CN** which was isolated as a pyridine adduct (Figure 33).[27]

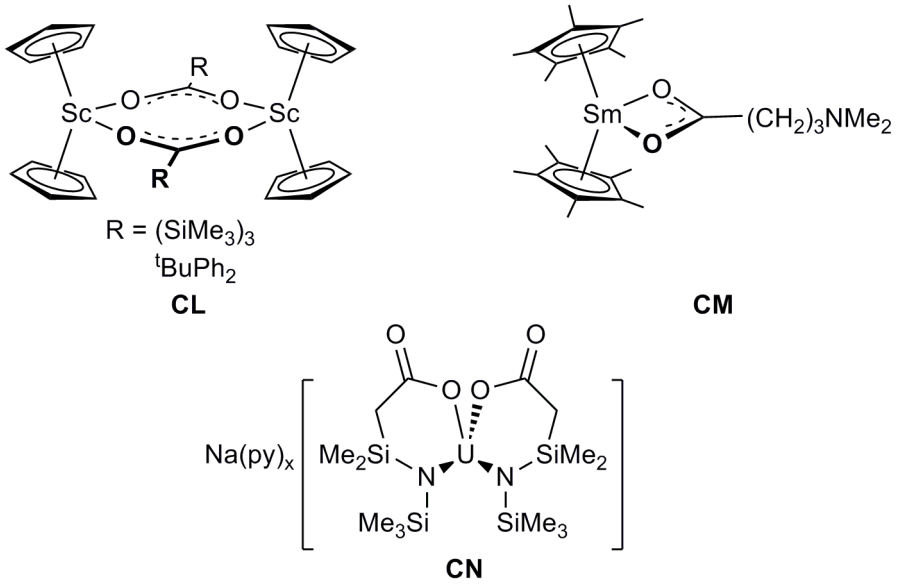
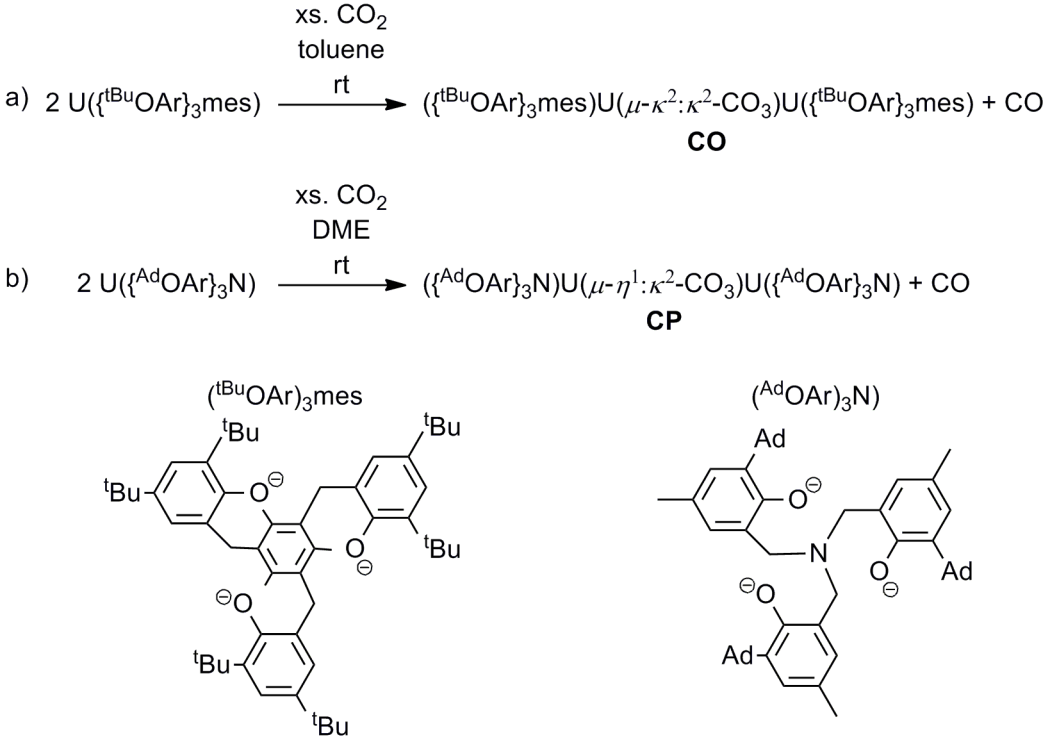


Figure 33: Products of CO_2 insertion into Sc-Si (**CL**) Y-C (**CM**) and U-N (**CN**) bonds

Evans and co-workers described the reductive coupling of CO_2 (1 atm) by the *bis*(cyclopentadienyl) complex $SmCp^*_2(thf)_2$ to form the oxalate complex $[SmCp^*_2]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2CCO_2)$ in 92 % yield.[175] The reaction was found to proceed cleanly at room temperature in thf but multiple products were observed in toluene or hexanes both at room temperature and at -78 ºC. The reaction mechanism was proposed to proceed through the formation of a CO_2 radical anion which coordinates to an oxidised Sm^{III} centre to afford $[SmCp^*_2(thf)_x]^+[CO_2]^{\bullet-}$ which dimerises at a faster rate than it is reduced by $SmCp^*_2(thf)_2$. This contrasts complex **CJ**, $U(^{Ad}ArO)_3tacn(\eta^1\text{-}OCO)$ which is readily isolated and the bound CO_2 molecule can be described by a resonance structure which is a radical anion (Figure 32).

A small number of cases of the reductive splitting of CO_2 to CO_3^{2-} and CO have also been reported.[176-178] The first example came from Gardiner and co-workers who reported the reaction of a Sm^{II} porphyrinogen (L) complex with CO_2 to afford the bimetallic carbonate complex $[Sm(L)](\mu_2\text{-}\eta^2\text{–O,O':}\eta^2\text{ –O,O"})$ where one electron oxidation to Sm^{III} has taken place.[178] The mechanism of reductive splitting was supported by headspace sampling which confirmed the presence of CO by high-resolution GC-MS. More recently, Meyer and co-workers undertook a mechanistic study on carbonate formation by using U^{III} complexes U(L) supported by two different chelating ligands (L = $(^{tBu}ArO)_3Mes$ or $(^{Ad}ArO)_3N$).[176] Reaction with excess CO_2 led to the carbonate complexes **CO** and **CP** (Equation 12a) and b)

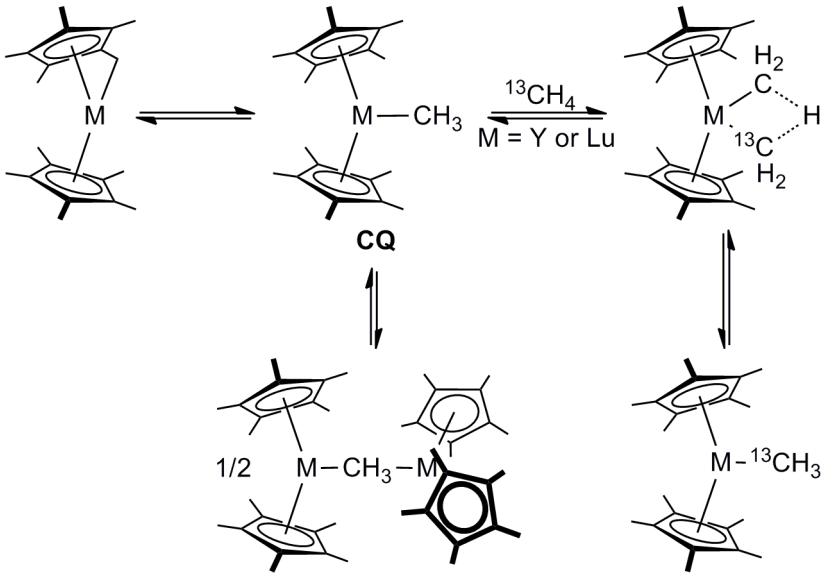
respectively). Treatment of U(L) with N_2O afforded the reactive (μ-O) bridged complexes which were shown to react with excess CO_2 to form **CO** and **CP**.



Equation 12: Reaction of U^{III} macrocyclic complexes to form carbonates

1.5.3 Alkanes

The reactivity of the yttrium, scandium and the f-elements is typified by three centre-four electron σ bond metathesis rather than oxidative addition/reductive elimination.

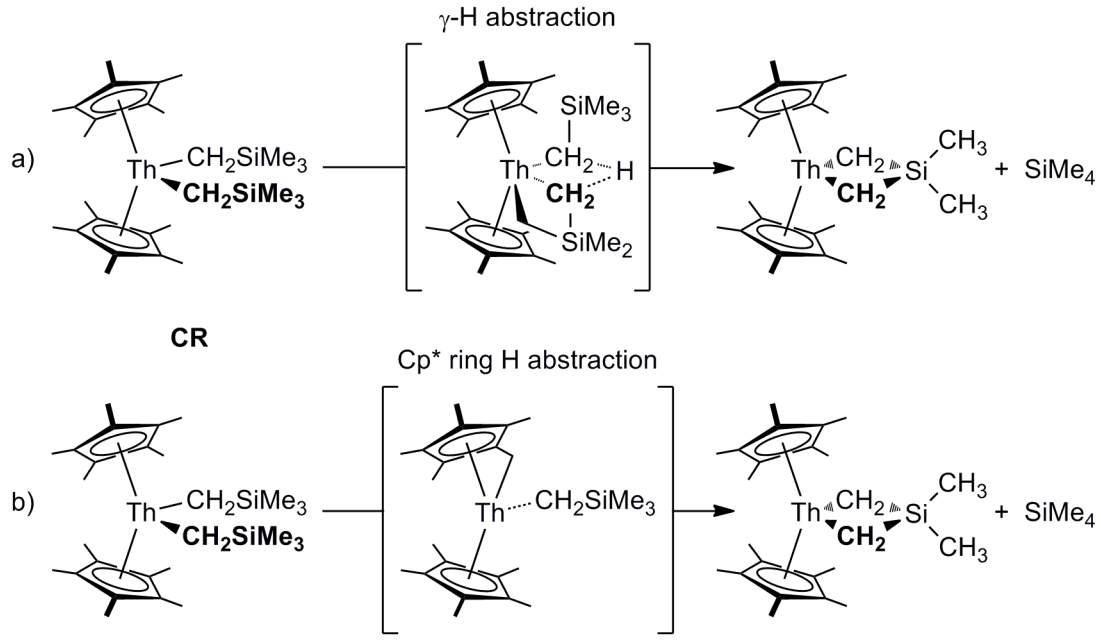


Scheme 11: The first example of methane activation by organometallic complexes

The first example of methane activation using an organometallic complex came from Watson using the *bis*(cyclopentadienyl) lanthanide complexes **CQ**, MCp^*_2Me (M = Y or Lu) (Scheme 11).[179,180] Treatment with ^{13}C-labelled $^{13}CH_4$ resulted in methane exchange. In solution, an equilibrium between monomeric and dimeric forms of **CQ** exists; the monomeric form is the active species. Equilibrium with a "tuck-in" metallacyclic product was also postulated. While ethane and propane were also observed to react with **CQ**, the products were assumed to decompose *via* β-hydrogen elimination.

The first structurally characterised example of a "tuck-in" complex, like that proposed to be relevant to the process of methane activation, was isolated by Evans and co-workers.[181] $UCp^*(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5Me_3\{CH_2\}_2)(\mu\text{-}H)_2UCp^*_2$, was formed by heating a mixture of the uranium hydrides, $[UCp^*_2H_2]_2$ and $[UCp^*_2H]_2$ to 110 ºC in toluene.

Marks and co-workers undertook a detailed mechanistic study on the cyclometallation process in *bis*(cyclopentadienyl)-supported thorium dialkyls which displayed high regioselectivity.[182] In a representative complex **CR**, $ThCp^*_2(CH_2SiMe_3)_2$ it was identified that there are two competing concerted mechanisms in operation which proceed through a four centre transition state; the first involves γ-hydrogen abstraction from the dialkyl group (Scheme 12a)) and second involves hydrogen abstraction from the cyclopentadienyl ring to afford a "tuck-in" complex (Scheme 12b)). Deuteration of **CR** to afford ***d*-CR**, $ThCp^*_2(CH_2Si(CD_3)_3)_2$ led to the second mechanism being favoured owing to a large kinetic isotope effect (k_H/k_D = 6.6(2) at 85 ºC and 5.0(1) at 115 ºC).



Scheme 12: Mechanistic pathways of metallacycle formation from thorium dialkyl **CR**

Metal-alkane complexes are thought to be key intermediate in alkane σ bond metathesis but they are almost always extremely short-lived; none have been isolated for d^0 metal complexes. Meyer and co-workers reported a series of alkane adducts U(L)R**.**R (L = ($^{t\text{Bu}}$ArO)$_3$tacn, R = cyclohexane and -pentane, methyl cyclo-hexane and -pentane and neo-hexane/cyclo-pentane) by treatment of pentane solutions of U(L) with 50 equivalents of the appropriate alkane R.[183] The adducts were characterised by single crystal X-ray diffraction studies which identified η^2-H,C coordination of the alkane and that that carbon proximal to the uranium centre showed a smaller thermal ellipsoid, relative to others of the coordinated alkane, as a result of coordination to uranium. The U-C bond distances (3.731 Å – 3.864 Å) were within the sum of the van der Waals radii for U-CH_2/U-CH_3 contacts and indicative of an orbital interaction. A DFT study of the U-R interaction showed it to be σ-based, with the main orbital contribution coming from the U f_{z^3} orbital.

1.6 Outlook

This thesis describes the synthesis of new alkoxy-tethered N-heterocyclic carbene (NHC) proligands and their amide and alkyl complexes of electropositive metals. A wide range of reactivity with small molecules will be examined. Depending on the conditions, the NHC can act both as a robust supporting ligand or as a labile ligand capable of delivering reagents to the electropositive metal centre.

1.7 References

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Synthesis of metal amide complexes

2.1 Introduction

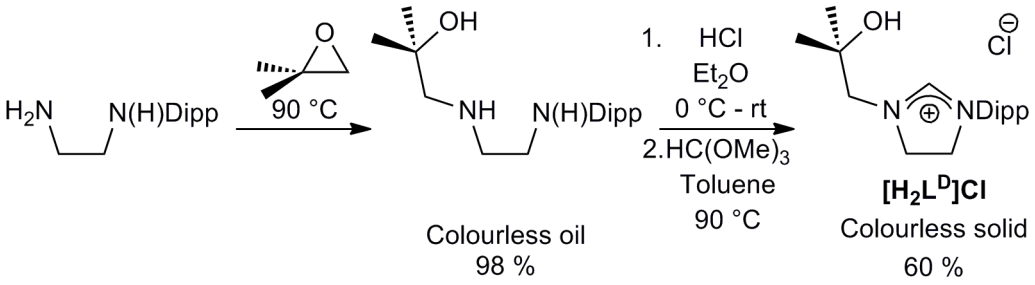
The versatility of N-heterocyclic carbenes (NHCs) is demonstrated by their numerous practical applications in homogeneous transition metal catalysis[1-3] and organocatalysis.[4,5] Within the Arnold group, a number of functionalised NHCs have been prepared. Their modular synthesis provides an attractive flexibility to ligand design, allowing the potential for the tuning of ligand stereoelectronic properties.

There remains a paucity of electropositive metal NHC complexes and so this chemistry is underdeveloped with respect to late transition metal and main group elements.[1,6] This chapter describes the synthesis and characterisation of a new NHC proligand and electropositive metal complexes.

2.2 Synthesis and characterisation of N-heterocyclic carbene proligands and s- and p-block complexes

2.2.1 Synthesis of N-heterocyclic carbene proligands

The imidazolinium salt $[H_2L^D]Cl$ (L^D = $[OCMe_2CH_2(1\text{-}C\{NCH_2CH_2NDipp\})]$, (D = Dipp = 2,6-^{i}Pr-C_6H_3) was synthesised *via* a modification of literature procedure.[7-9] The analogous *N*-mesityl-substituted (mesityl = 2,4,6-Me-C_6H_2) proligand had also been previously been made.[10] The pendant alkoxy arm was first incorporated in a melt reaction by the ring opening of the epoxide 1,2-*iso*-butylene oxide (CH_2CMe_2O) with the amine H_2N-Dipp. Acidification with HCl, followed by ring closure with the orthoester $HC(OMe)_3$ at 90 ºC led to $[H_2L^D]Cl$ as a colourless solid in 60 % yield. Alternatively, combination with NH_4Cl and $HC(OMe_3)$ at 120 ºC afforded the same product in 63 % yield (Scheme 1). $[H_2L^D]I$ was synthesised by treatment of $[H_2L^D]Cl$ with NaI in a simple anion exchange reaction in 73 % yield.



Scheme 1: Synthesis of $[H_2L^D]Cl$

The ^{1}H NMR spectrum of [H_2L^D]Cl illustrates the diagnostic resonances of the imidazolinium (9.47 ppm), backbone (4.44 and 4.14 ppm) and *iso*-propyl protons (2.88 ppm) (Figure 1).

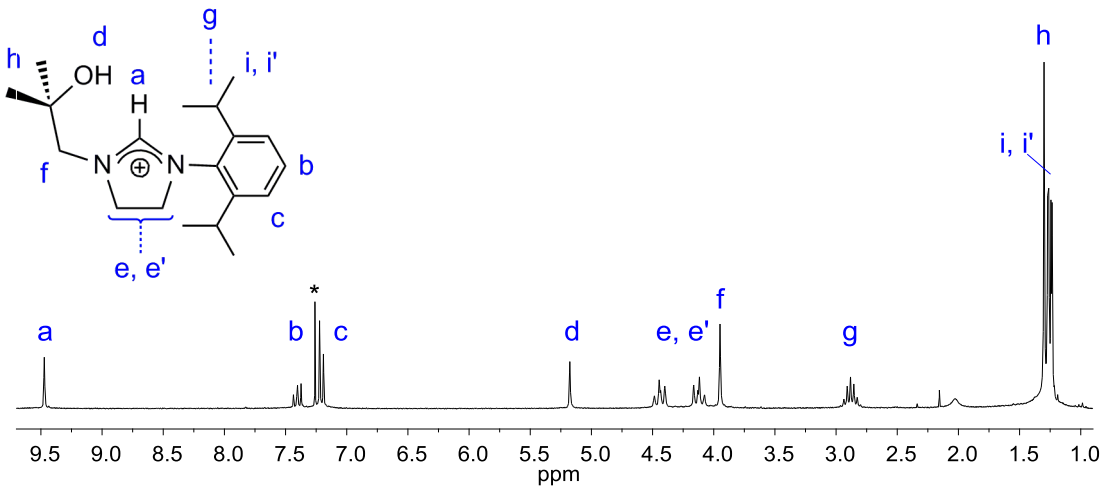


Figure 1: ^{1}H NMR spectrum (C_6D_6, 360 MHz, 298 K) of [H_2L^D]Cl
'*' denotes residual protio solvent

The typical imidazolinium resonance at high frequency reflects that this proton is bound to a sp^2-hybridised centre with a partially positive charge, further deshielded by two α-N atoms. Closely spaced doublets at 1.27 ppm and 1.24 ppm define the *iso*-propyl HC<u>Me$_2$</u> protons; the presence of two doublets is presumably due to restricted rotation about the **C-C**HMe$_2$ bond. In the ^{13}C{^{1}H} spectrum, the resonance at 160.4 ppm is diagnostic of the imidazolinium carbon and is at a higher frequency than imidazolium analogues.[1]

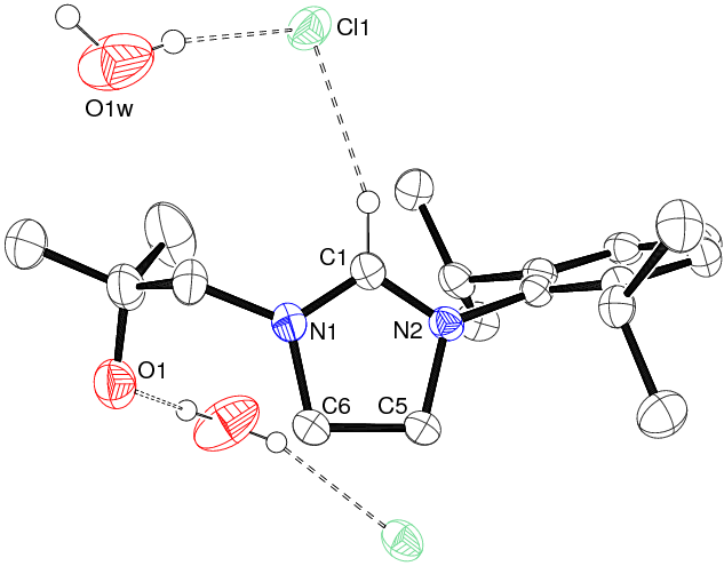


Figure 2: Displacement ellipsoid plot (50 % probability) for [H_2L^D]Cl
H atoms omitted for clarity (except for that bound to C1)

$[H_2L^D]Cl$ has been structurally authenticated in the solid state by X-ray crystallography. The displacement ellipsoid plot (Figure 2) and selected bond lengths (Å) and angles (º) are provided (Table 1).

Table 1: Selected bond lengths (Å), bond and torsion angles (º) for $[H_2L^D]Cl$

C1-N1	1.305(3)
C1-N2	1.317(3)
C5-N2	1.481(3)
C6-N1	1.479(3)
C5-C6	1.527(3)
C1-Cl1	3.438
O1-O1w	2.853
N1-C1-N2	113.7(2)
N1-C6-C5-N2	7.5(3)
C22-C21-N2-C1	75.6(3)

All bond lengths and angles are within standard ranges. The N-heterocyclic ring is in a twist-boat conformation, reflected by the N1-C6-C5-N2 torsion angle of 7.5(3)°. The C1-N1 and C1-N2 bond lengths are shorter than that of C6-N1 or C5-N2, indicative of partial double bond character of N1-C1-N2, where the bond angle of 113.7(2)° is typical of such an imidazolinium species. The *N*-Dipp substituent is staggered (C22-C21-N2-C1 = 75.6(3)°) relative to the N-heterocyclic ring in a conformation which minimises unfavourable steric interaction. Similarly, the *iso*-propyl groups are synclinal with respect to each other.

Examples of comparable molecular structures include the saturated backbone proligands: **A**, $[1\text{-}CH(NR^{BnOPinane}CH_2)_2]Cl$ and **B**, $[HOCMe^tBuCH_2(1\text{-}CH\{NCHCHNMes\})]PF_6$,[7,11] and the unsaturated backbone proligand **C**, $[HOCMe_2CH_2(1\text{-}CH\{NCHCHN^iPr\})]I$ (Figure 3).[12]

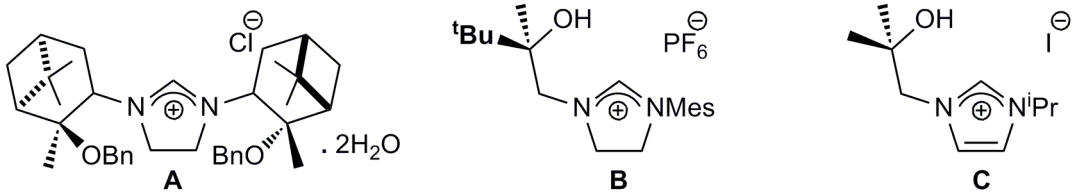
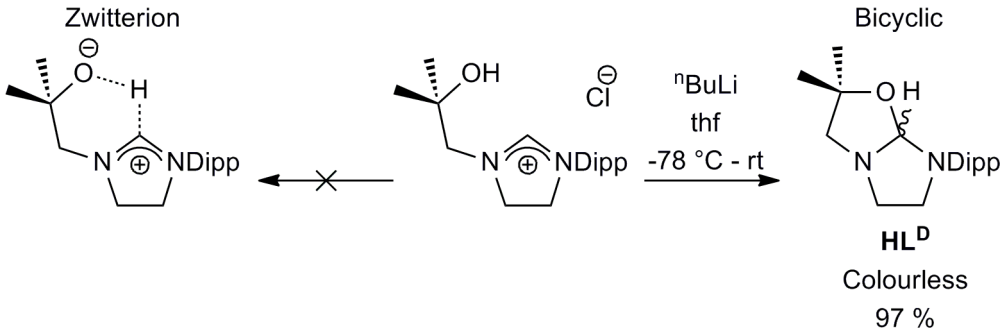


Figure 3: Structurally characterised complexes comparable to $[H_2L^D]Cl$

Bond lengths within $[H_2L^D]Cl$ are in good agreement with both **A** and **B**. In **A**, hydrogen bonding between the chloride counter-ion and a water molecule results in self-

assembly of an extended helical structure. In $[H_2L^D]Cl$, the hydroxyl group hydrogen bonds with a partial molecule of water present within the lattice and the imidazolinium proton bonds with the chloride counter anion. Compound **C** highlights some differences between proligands with saturated and unsaturated backbones; the five atoms defining the N-heterocyclic ring are co-planar as a result of their sp^2 hybridisation of all atoms and the C5-C6 backbone bond length (1.348(3) Å) is also consistent with double bond character, contrasting the longer 1.527(3) Å in $[H_2L^D]Cl$.

Single deprotonation of $[H_2L^D]X$ afforded the bicyclic product, HL^D. A variety of bases can be used (KAm where Am = amylate = $CHMe_2Et_2$, KBn where Bn = benzyl = CH_2Ph, KH, ^{n}BuLi) but reaction between $[H_2L^D]Cl$ and ^{n}BuLi proceeded cleanly in 97 % yield (Scheme 2). HL^D sublimes (55 °C, 10^{-5} mbar) in low yield and decomposed slowly on exposure to air.



Scheme 2: Synthesis of HL^D

The ^{1}H NMR spectrum of HL^D confirms that it does not adopt the anticipated zwitterionic form seen in unsaturated proligand analogues (Figure 4). Each proton is magnetically inequivalent, consistent with a rigid bicyclic structure formed where the alkoxy arm has bitten into the N-heterocyclic ring at the most electrophilic site. The diagnostic resonance at 5.78 ppm shows the sp^3 C2-bound proton. Two *iso*-propyl septets are observed at 3.37 ppm and 4.12 ppm and four closely spaced doublets between 1.00 ppm and 1.50 ppm represent the inequivalent *iso*-propyl $HC\underline{Me}_2$ group protons. There is geminal coupling (^2J = 11 Hz) between the $OCMe_2C\underline{H}_2$ protons, now part of an AB system. Multiplets associated with the backbone protons, as each proton in the ABMX system couples to each other, are complicated by overlapping resonances.

In the unsaturated zwitterionic proligand, HL (L = $OCMe_2CH_2(1\text{-}C\{NCHCHN^iPr\})$), the ^{1}H NMR spectrum is less complex as the molecular structure is no longer rigid as in HL^D. For example, the $OCMe_2C\underline{H}_2$ protons are magnetically equivalent and no coupling is

observed between them. A broad singlet at 7.77 ppm is attributed to the NCHN proton effectively bridging C_{NCN} and $O_{pendant}$ in an intermediate structure between an imidazolium alkoxide and free carbene alcohol.

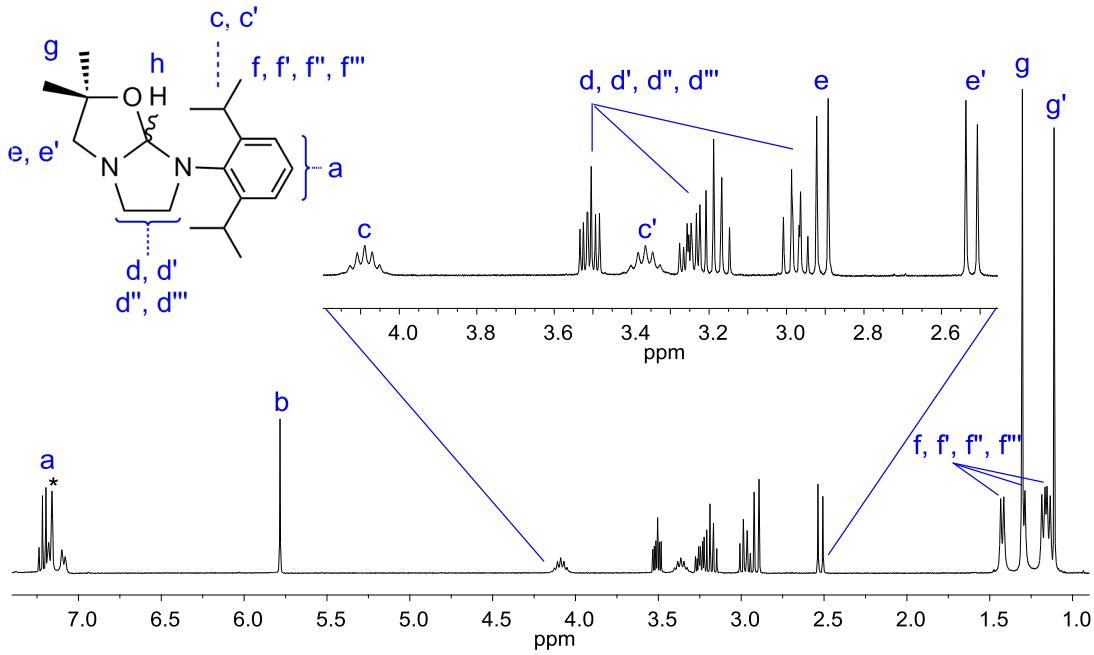
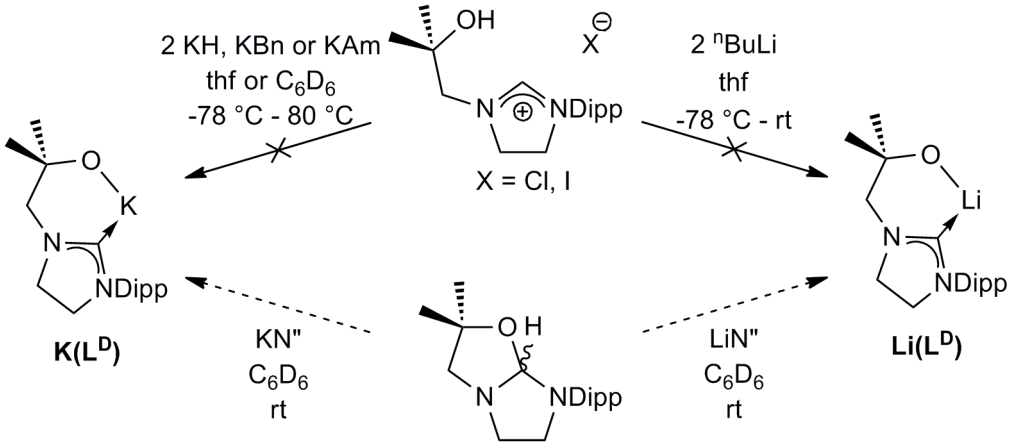


Figure 4: ^{1}H NMR spectrum (C_6D_6, 360 MHz, 298 K) of HL^D
'*' denotes residual protio solvent

2.2.2 Attempted synthesis of p- and s-block complexes

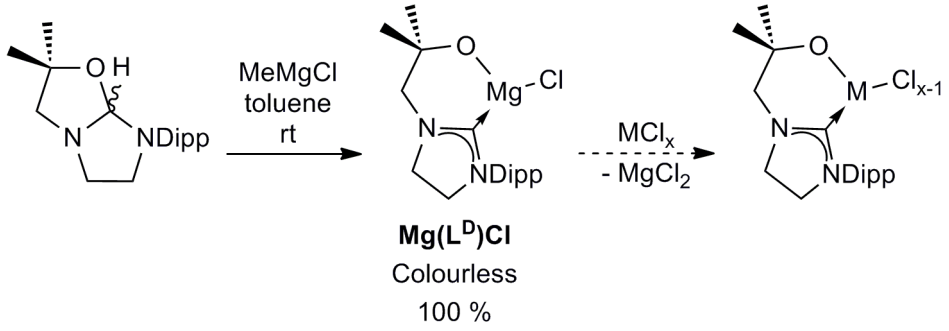
Syntheses of potassium, lithium and thallium salts were attempted in order to provide a route to new metal complexes through salt metathesis but HL^D is both thermally robust and unreactive with a number of bases. Indeed, attempted double deprotonation of proligands $[H_2L^D]Cl$ or $[H_2L^D]I$ yielded only HL^D and attempted direct deprotonation of HL^D with KBn, KH or ^{n}BuLi resulted in no reaction. Both NMR tube and preparative scale reactions between an excess of KN" or LiN" (N" = $N(SiMe_3)_2$) and HL^D at room temperature formed a new compound but pure material was not isolable (Scheme 3).

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra show only one major set of resonances for a coordinated ligand, which are no longer split as in the bicyclic HL^D spectra. The absence of a resonance in the ^{1}H NMR spectrum at 5.78 ppm indicates both that deprotonation has occurred and that the new compound is not a simple adduct of HL^D and MN" (M = Li or K). However, no high frequency $C_{carbene}$ resonance is observed in the $^{13}C\{^{1}H\}$ spectrum which would suggest a metal-bound NHC. Attempts to form the thallium salt, $Tl(L^D)$ *via* deprotonation of HL^D with TlCp (Cp = cyclopentadienyl) also resulted in no reaction.



Scheme 3: Attempted syntheses of M(L^D) (M = Li and K)

Reaction of HL^D with MeMgCl cleanly led to the formation of the poorly soluble Mg(L^D)Cl. Attempts to utilise this as a further ligand transfer reagent to synthesise new metal chloride species resulted in no reaction (Scheme 4).



Scheme 4: Synthesis of Mg(L^D)Cl and potential further reactivity

2.3 Synthesis and characterisation of M^{II} amide complexes

2.3.1 M^{II} amide complexes

The reaction of $MgN"_2(thf)_2$ or $ZnN"_2$ with 1 equivalent of HL^D proceeded cleanly at room temperature in toluene or benzene to afford colourless Mg(L^D)N" and Zn(L^D)N" in 86 % and 84 % yield respectively (Scheme 5). The ^{1}H NMR spectra of Mg(L^D)N" and Zn(L^D)N" are greatly simplified with respect to HL^D as a result of opening the rigid five-membered ring structure to form a more flexible six-membered metallacycle (Figure 5). All resonances are clearly shifted relative to HL^D and notable is the absence of the singlet at 5.78 ppm for the NCHN proton. For Zn(L^D)N", there is one singlet at 3.02 ppm for the $OCMe_2C\underline{H}_2$ protons, which are no longer geminally coupled. A singlet at 0.34 ppm defines the SiMe protons. In the $^{13}C\{^1H\}$ NMR spectrum, the $C_{carbene}$ resonance is at 196.1 ppm, a far higher frequency than for the imidazolium-type NCN unit.

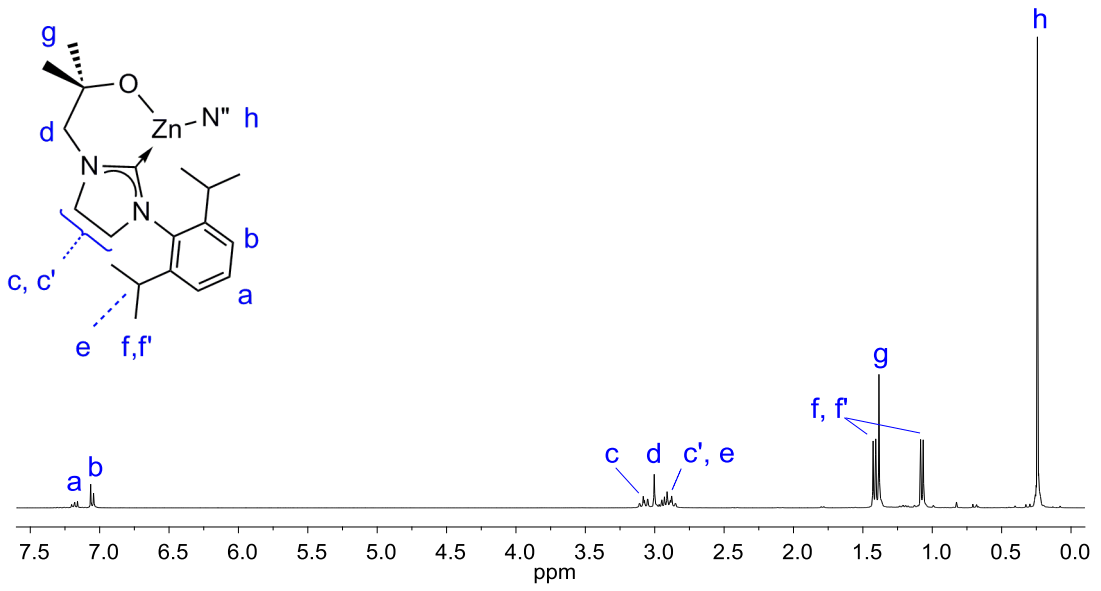
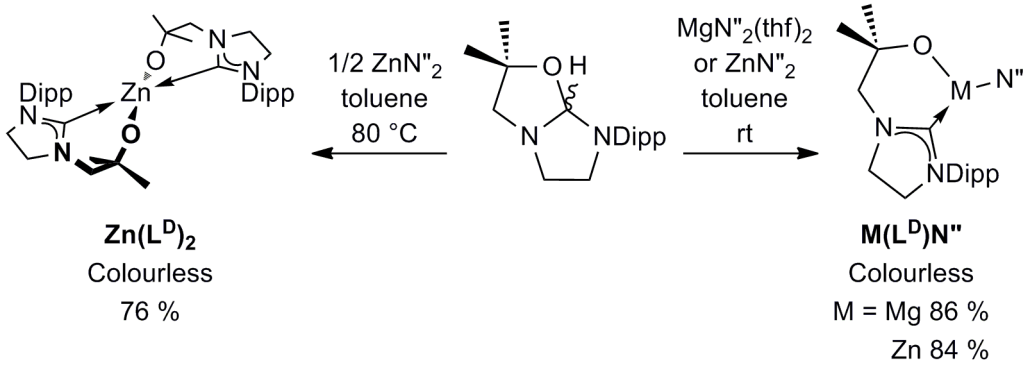


Figure 5: ^{1}H NMR spectrum (C_6D_6, 298 K, 360 MHz) of Zn(L^D)N"
'*' denotes residual protio solvent

Reaction of ZnN"$_2$ with 2 equivalents of HL^D initially formed the *mono*(ligand) compound Zn(L^D)N" but, on heating at 85 °C for 16 h in toluene, further reaction to form Zn(L^D)$_2$ occurred. The ^{1}H NMR spectrum indicates a rigid structure as it contains two sets of sharp resonances for two distinct ligand environments. As for HL^D, the protons in each ligand are magnetically inequivalent which is perhaps surprising as a C_2 symmetric tetrahedral structure is anticipated. The ^{13}C{^{1}H} spectrum contains a $C_{carbene}$ resonance at 201.3 ppm.



Scheme 5: Reactivity summary of HL^D with MgN"$_2$(thf)$_2$ and ZnN"$_2$

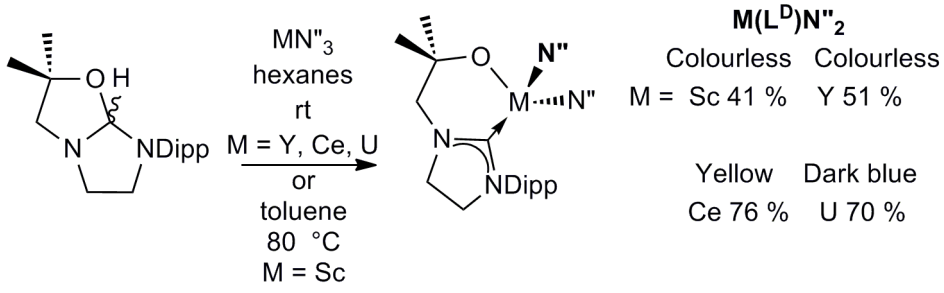
Despite the similar ionic radii of Mg^{II} and Zn^{II} ($rMg^{II,\ 4C.N.}$ = 0.57 Å, $rZn^{II,\ 4C.N.}$ = 0.60 Å; no data is provided for three-coordinate ionic radii in the Shannon lists)[13], the analogous Mg(L^D)$_2$ was not isolable (Scheme 5). Using the same procedure, after heating at 80 ºC, only an equal mixture of Mg(L^D)N", HL^D and HN" were visible in the ^{1}H NMR

spectrum. To achieve this transformation, $MgMe_2$ was also used as an alternative reagent but a single clean product could not be isolated. The weaker Mg-$C_{carbene}$ bond (relative to the Zn-$C_{carbene}$ bond) between the hard Mg^{II} ion and the soft $C_{carbene}$ centre may not be strong enough to make the synthesis of $Mg(L^D)_2$ favourable.

2.4 Synthesis and characterisation of M^{III} amide complexes

2.4.1 *mono*(ligand) M^{III} amide complexes

M^{III} amide complexes, $M(L^D)N''_2$ (M = Sc, Y, Ce and U), can all be synthesised in a straightforward protonolysis reaction of 1 equivalent of the appropriate MN''_3 and 1 equivalent of HL^D at room temperature in hexanes (M = Y, Ce or U) or 80 ºC in toluene (M = Sc). All of the reactions proceeded in reasonable yield (41 % – 76 %) (Equation 1).



Equation 1: Synthesis of $M(L^D)N''_2$ (M = Sc, Y, Ce, U)

The diamagnetic complexes $Sc(L^D)N''_2$ and $Y(L^D)N''_2$ both have very similar ^1H NMR spectra to that of $Zn(L^D)N''$ (with much more simplified resonances for bound L^D relative to the HL^D proligand). The $^{13}C\{^1H\}$ NMR spectrum is immediately diagnostic for $Y(L^D)N''_2$, the $C_{carbene}$ resonance at 216.3 ppm is a doublet due to the $^1J_{YC}$ coupling of 42 Hz. This resonance is at a considerably higher frequency than related unsaturated NHC complexes: δ = 186.3 ppm, $^1J_{YC}$ = 53 Hz for $Y(L)N''_2$ (L = $N^tBuCH_2CH_2$(1-C{NCHCHN^tBu})),[14] δ = 194.3 ppm, $^1J_{YC}$ = 48 Hz in Y(L)N''Cl (L = N[CH_2CH_2(1-C{NCHCHNMes})]$_2$,[15] and δ = 194.0 ppm in $Y(N\{SiHMe_2\}_2)_3$(1-C{NMeCH}$_2$).[16]

The paramagnetic $Ce(L^D)N''_2$ (Ce^{III}: [Xe]$4f^1$) and $U(L^D)N''_2$ (U^{III}: [Rn]$5f^3$) complexes have ^1H NMR spectra with resonances across spectral widths of 46.03 ppm – -9.11 ppm and 29.55 ppm – -19.30 ppm respectively. The ^1H NMR spectrum of $Ce(L^D)N''_2$ is shown for clarity (Figure 6). It is noted that the resonance for the *iso*-propyl $\underline{H}CMe_2$ is not labelled; it is likely to be too broad to be identified.

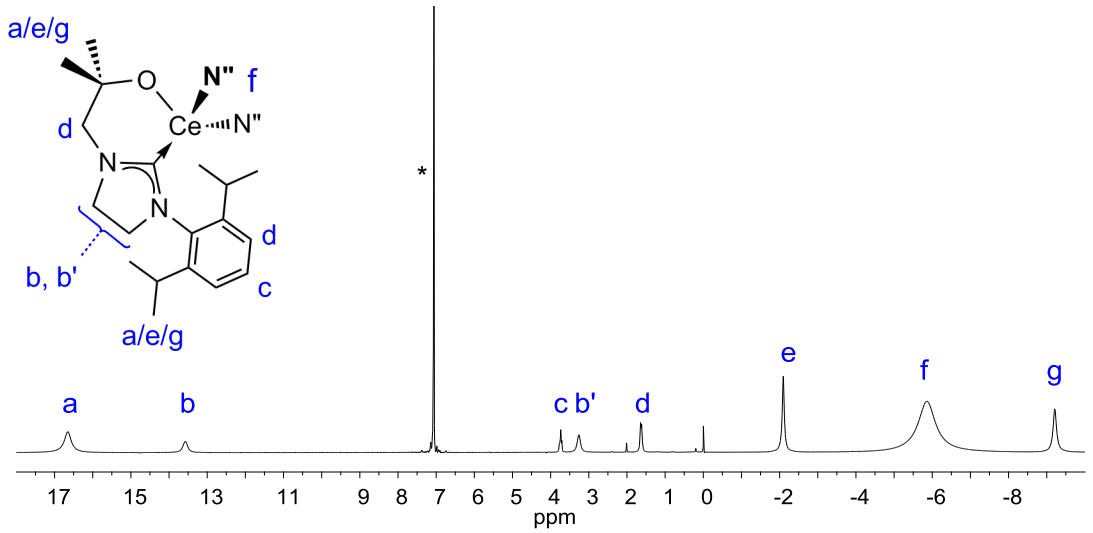
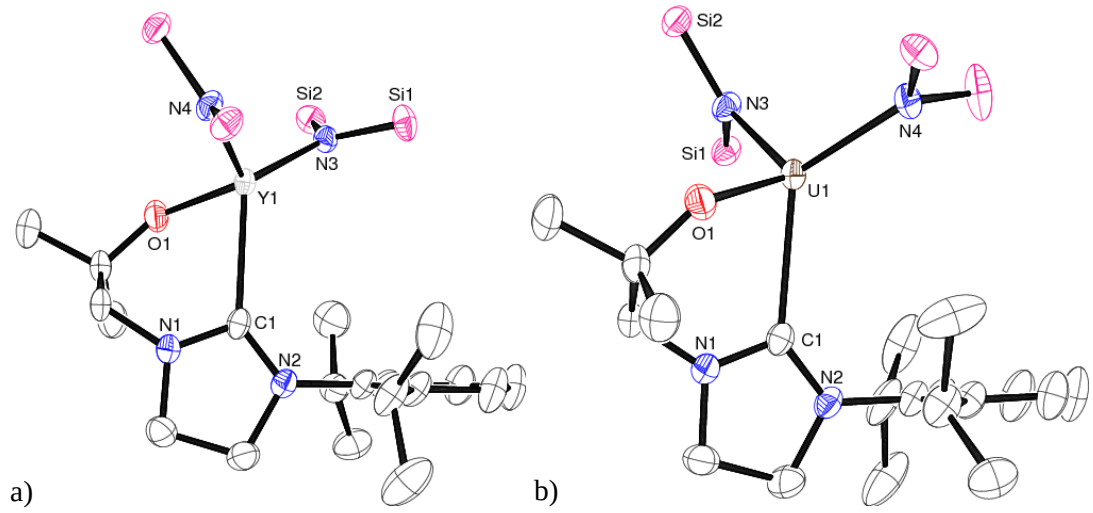


Figure 6: ^{1}H NMR spectrum (C_6D_6, 298 K, 360 MHz) of Ce(L^D)N"$_2$
'*' denotes residual protio solvent

Single crystals suitable for an X-ray diffraction study were grown for M(L^D)N"$_2$ from saturated toluene (M = Sc and Y) or hexanes solutions (M = U). The displacement ellipsoid plots for Y(L^D)N"$_2$ (Figure 7a)) and U(L^D)N"$_2$ (Figure 7b)) and selected bond lengths (Å) and angles (º) are provided for all M(L^D)N"$_2$ (Table 2).



a) b)

Figure 7: Displacement ellipsoid plots (50 %) of a) Y(L^D)N"$_2$ and b) U(L^D)N"$_2$
H atoms and silyl Me groups omitted for clarity.

In each case, the coordination about the metal centre is distorted tetrahedral with narrow ligand bite angles (Sc: 82.00(5) Å, Y: 77.90(7) Å, U: 74.53(10) Å) and widened angles between the silylamide substituents and N-heterocyclic ring (N4-M1-C1$_{average}$ = 123.07º) in order to accommodate the sterically demanding *N*-Dipp substituent. There is an increase in the bond lengths of ligating atoms to the metal centre from Sc to Y to U as is

expected from the increasing ionic radius of the metal ion ($rSc^{III,\ 6C.N.}$ = 0.745 Å, $rY^{III,\ 6C.N.}$ = 0.900 Å, $rU^{III,\ 6C.N.}$ = 1.025 Å; no four-coordinate radii are recorded within the Shannon lists)[13] and consequently, a decrease in the ligand bite angle is observed. The U-C, U-O and U-N bond lengths are slightly shorter than expected, taking into account its ionic radius, and this may imply some slightly enhanced contribution to covalent bonding for the 5f element.

With reference to $[H_2L^D]Cl$ (N1-C1-N2 = 113.7(2)°, C1-$N_{average}$ = 1.311 Å), the N1-C1-N2 bond angles are much smaller (N1-C1-$N2_{average}$ = 107°) which is consistent with a high degree of σ character with the M-$C_{carbene}$ bond.

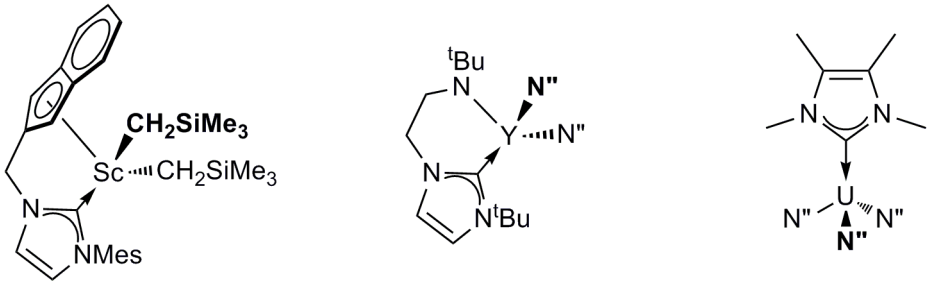
Table 2: Selected bond lengths (Å) and angles (º) of $M(L^D)N''_2$ (M = Sc, Y, and U)

	$Sc(L^D)N''_2$	$Y(L^D)N''_2$	$U(L^D)N''_2$
C1-M1	2.4301(17)	2.599(2)	2.693(4)
O1-M1	1.8870(12)	2.0313(16)	2.122(3)
N3-M1	2.1127(13)	2.2620(17)	2.369(3)
C1-N1	1.336(2)	1.331(3)	1.333(5)
C1-N2	1.361(2)	1.346(3)	1.347(5)
N2-C1-M1	141.49(11)	140.59(15)	137.9(3)
N1-C1-N2	106.83(14)	106.97(19)	107.2(3)
N4-M1-C1	124.20(5)	122.55(6)	122.47(10)
C1-M1-O1	82.00(5)	77.90(7)	74.53(10)

The Sc-$C_{carbene}$ (2.4301(17) Å) distance is long in comparison to other unsaturated NHC scandium complexes: 2.350(3) Å in **D**, $Sc(L)CH_2SiMe_3$ (L = $IndCH_2$(1-C{NCHCHNMes})) (Figure 8).[17] The effect of both less sterically demanding alkyl and *N*-Mes substituents is also apparent, with the $C_{carbene}$-Sc-C_{alkyl} angles (94.04(9)º and 105.67(10)º) being much smaller with respect to the $C_{carbene}$-Sc-N_{amide} angles (124.20(5)º and 108.16(5)º) in $Sc(L^D)N''_2$.

The Y-$C_{carbene}$ (2.599(2) Å) distance is also long compared with other unsaturated NHC yttrium complexes: 2.501(5) Å in **E**, $Y(L)N''_2$ (L = $N^tBuCH_2CH_2$(1-C{NCHCHN^{t}Bu})) (Figure 8),[14] 2.574(3) Å and 2.565(3) Å in Y(L)N''Cl (L = $N[CH_2CH_2(1\text{-}C\{NCHCHNMes\})]_2$,[15] and 2.55(1) Å in $Y(N\{SiHMe_2\}_2)_3$(1-C{NMeCH}$_2$).[16] The Y-$C_{carbene}$ bond length is comparable to longer Y-C_{alkyl} bonds; for example, in $[YCp^*(\mu\text{-}Me)_2]_3$ the Y-CH_3 distances are 2.539(3) Å and 2.550(3) Å.[18]

Though there are no functionalised NHC U^{III} complexes with which to compare metrical data, the U-$C_{carbene}$ distance is within reported literature values for low-coordinate U^{III} complexes: 2.672(4) Å in **F**, $UN"_3(1\text{-}C\{NMeCMe\}_2)$,[19] 2.789(14) Å in U(L)(1-$C\{NMeCMe\}_2$) (L = $(\{^{Ad}ArO\}_3tacn)$ where tacn = 1,4,7-triazacyclononane),[19] 2.768(5) Å in UCp*I(1-$C\{NMeCMe\}_2$) and 2.768(5) Å in U(1-^{t}Bu-C_5Me_4)(1-$C\{NMeCMe\}_2$) (Figure 8).[20]



D **E** **F**

Figure 8: Structurally characterised complexes comparable to $M(L^D)N"_2$

2.4.2 *bis* and *tris*(ligand) M^{III} amide complexes

The steric demands of the L^D ligand, with its large *N*-Dipp substituent, is highlighted when preparation of the *bis* and *tris*(ligand) M^{III} complexes was attempted. Treatment of $ScN"_3$ ($rSc^{III,\ 6C.N.}$ = 0.745 Å)[13] with 2 equivalents of the HL^D in C_6D_6 afforded only an equal mixture of $Sc(L^D)N"_2$ and HL^D, even on heating to 80 ºC for 2 days. Similarly, for Y^{III} ($rY^{III,\ 6C.N.}$ = 0.900 Å)[13], $Y(L^D)_2N"$ was not isolable. However, for Ce^{III} ($rCe^{III,\ 6C.N.}$ = 1.01 Å),[13] reaction of $CeN"_3$ with 2 equivalents of HL^D proceeded at room temperature to afford the yellow $Ce(L^D)_2N"$ in 81 % yield. The compound is poorly soluble and the ^{1}H NMR spectrum consists of broad overlapping resonances in the range 24.00 ppm - -10.00 ppm which is suggestive of a fluxional process occurring in solution.

$Ce(L^D)_2N"$ was also characterised by a single crystal X-ray diffraction study. The displacement ellipsoid plot (Figure 9) and selected bond lengths (Å) and angles (º) are provided (Table 3). The geometry around the cerium ion is square based pyramidal, minimising unfavourable interactions between the *N*-Dipp and silylmethyl groups, with an average ligand bite angle (C-Ce-$O_{average}$) of 71.4º.

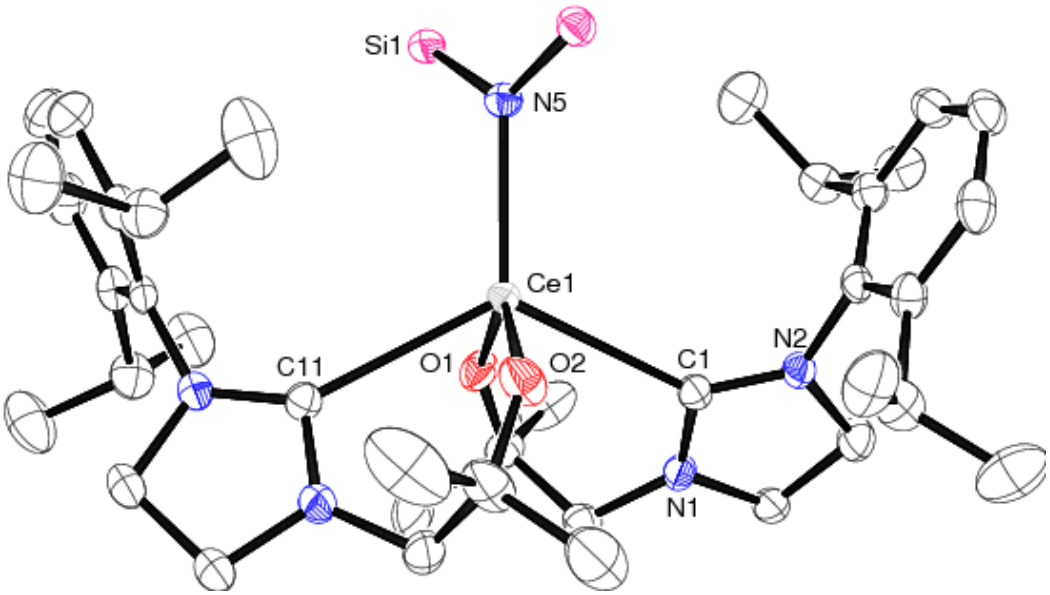
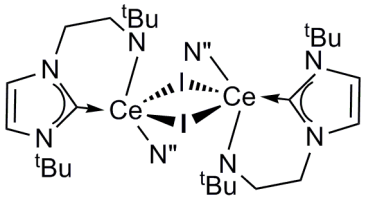


Figure 9: Displacement ellipsoid plot (50 %) of $Ce(L^D)_2N''$
Lattice solvent molecules, H atoms and silyl Me groups omitted for clarity

Table 3: Selected bond lengths (Å) and angles (º) of $Ce(L^D)_2N''$

Ce1-O1, Ce1-O2	2.1836(18), 2.201(2)
Ce1-C1, Ce1-C11	2.855(3), 2.813(3)
Ce1-N5	2.447(3)
C1-Ce1-C11	128.18(7)
O1-Ce1-O2	127.84(8)
C-Ce-$O_{average}$	71.4
N-C-$N_{average}$	106.2

The average Ce-$C_{carbene}$ (2.834 Å), Ce-$O_{alkoxide}$ (2.192 Å) and Ce-N_{amide} (2.447(3) Å) bond lengths are long; though there are no Ce^{III} saturated NHC complexes for direct comparison, the longest reported Ce-$C_{carbene}$ distance in the five-coordinate Ce^{III} NHC compound **G**, $(Ce\{L\}N''I\{\mu\text{-}I\})_2$ (L = $N^tBuCH_2CH_2(1\text{-}C\{NCHCHN^tBu\})$,[21] is 2.700(3) Å (Figure 10).



G

Figure 10: Molecular structure comparable to $Ce(L^D)_2N''$

In **G**, the geometry around cerium is distorted trigonal bipyramidal, a reflection of the lesser degree of steric congestion at the metal centre. The Ce-N_{amide} bond length in $Ce(L^D)_2N''$ (2.446(3) Å) is considerably longer with respect to the average Ce-N_{amide} bond length in **G** (2.279 Å).

Surprisingly, given the similar ionic radii of Ce^{III} ($rCe^{III,\ 6C.N.}$ = 1.01 Å) and U^{III} ($rU^{III,\ 6C.N.}$ = 1.025 Å), reactions to form $U(L^D)_2N''$ were not successful. Treatment of UN''_3 with 2 equivalents of HL^D in C_6D_6 resulted in the formation of equal amounts of $U(L^D)N''_2$ and HL^D. In a separate reaction, $U(L^D)N''_2$ and 1 equivalent of HL^D were combined to afford the same mixture with no further reaction. If left in solution for a period of 3 days, the solution became emerald green and the ^{1}H NMR spectrum indicated the presence of HL^D, HN'' and small resonances across the spectral width which could not be assigned to a single compound (Figure 11).

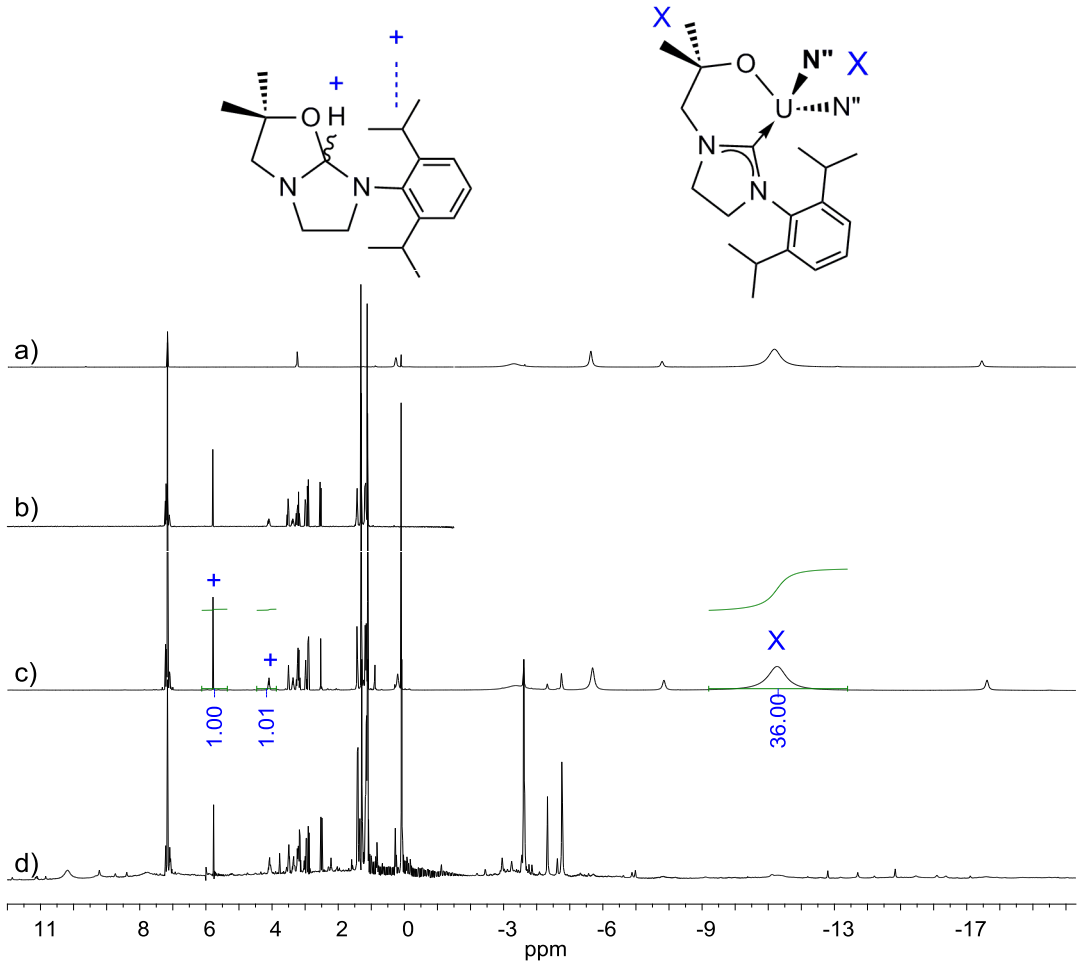


Figure 11: ^{1}H NMR spectra (C_6D_6, 298 K, 500 MHz) of a) Pure $U(L^D)N''_2$, b) HL^D, c) $U(L^D)N''_2$ with 1 equivalent of HL^D, d) Reaction mixtures left for 3 days.
'*' denotes residual protio solvent, 'X' a representative integrated resonance of $U(L^D)N''_2$ and '+' a representative integrated resonance of HL^D.

The large steric encumbrance of L^D does not preclude the formation of *bis*(ligand) uranium complexes. Indeed, $U(L^D)_2I_2$ can be readily prepared even though the metal ion now has a smaller ionic radius as a result of increased charge ($rU^{IV,\ 6C.N.}$ = 0.89 Å, $rU^{III,\ 6C.N.}$ = 1.025 Å) and is stable in solution and at high temperature (see section 3.3.1). This can be rationalised by examining the steric bulk of the $N(SiMe_3)_2^-$ and I^- ligands, which can be quantified by 'steric coordination number' (defined by the ratio of the solid angle which comprises the van der Waals spheres of the atoms in the ligand to the solid angle of a common ligand, such as Cl^-, when placed at a typical mean distance from the metal ion).[22] As a purely geometric parameter, this is useful for describing the bonding in lanthanide and actinide complexes which is principally ionic in nature. The steric coordination number for $N(SiMe_3)_2^-$ (2.17) is accordingly larger than that of I^- (1.00) (Figure 12).

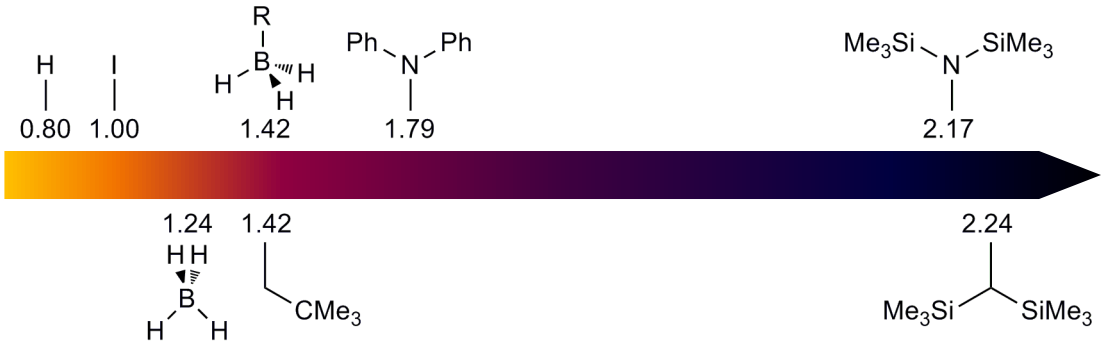


Figure 12: Steric coordination number of common halide and N,C and B ligands.

As expected, attempts to synthesise the *tris*(ligand) $U(L^D)_3$ compound were not successful. Combination of $UN"_3$ with 3 equivalents of HL^D resulted only in the formation of $U(L^D)N"_2$ which subsequently decomposed in solution as previously described.

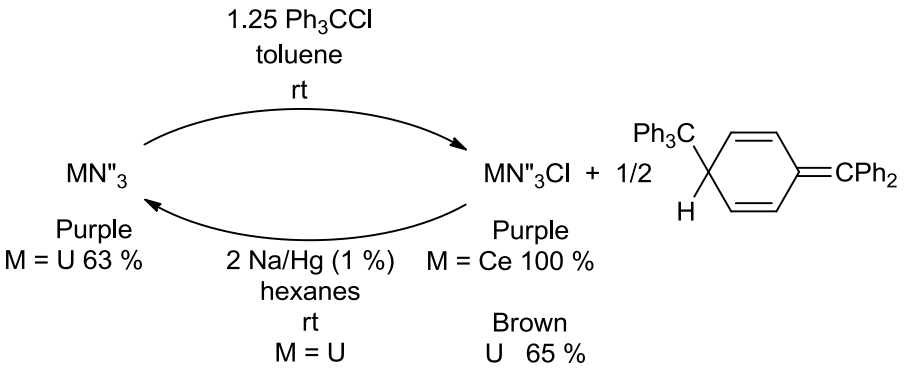
2.5 Synthesis and characterisation of M^{IV} amide complexes

2.5.1 M^{IV} amide complexes

There have only been a small number of Ce^{IV} amide complexes reported to date.[23-34] Dependence on the choice of reaction solvent, temperature and oxidant makes the synthesis of Ce^{IV} complexes challenging and preparations are often low-yielding. Trityl halide reagents have been previously used for the one electron oxidation of organometallic complexes, such as the treatment of UCp'_3 (Cp' = 1-$SiMe_3$-C_5Me_4) with Ph_3CF to afford UCp'_3F,[35] or the oxidation of $VCp(dmpe)(SiClPh_2)$ with Ph_3CCl to give $VCp(dmpe)(SiClPh_2)Cl$ (dmpe = 1, 2-*bis*(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$).[36] They can also act as abstraction agents for Me^-,[37,38] and in combination with Lewis acids, Ph_3CF was shown to form fluorometallate salts.[39]

In contrast to the original literature preparation of CeN''_3Cl which had a yield of 24 % using $TeCl_4$ as an oxidant,[23] we found that oxidation of CeN''_3 using 1.25 equivalents of Ph_3CCl proceeded to afford purple CeN''_3Cl in quantitative yield (as determined by integration of ^1H NMR spectra against an internal standard of 1,3,5-^{t}Bu-C_6H_3) before isolation. Similarly, oxidation of UN''_3 under the same conditions afforded brown UN''_3Cl in 65 % yield (though the existing preparation of UN''_3Cl proceeds in 70 % yield from the treatment of UCl_4 with 3 equivalents of NaN'') (Scheme 6).[40] Recrystallisation from a thf/hexanes mixture allowed separation from the reaction byproduct, 0.5 equivalents of Gomberg's dimer ($Ph_3C(H)C_2H_4CPh_2$),[41] to afford CeN''_3Cl and UN''_3Cl in 81 % and 50 % isolated yield respectively.

Reduction of UN''_3Cl back to UN''_3 was also achieved in a facile manner by treatment of UN''_3Cl with 2 equivalents of 1 % Na/Hg in hexanes. The ^1H NMR spectrum of an aliquot of the reaction mixture indicated UN''_3 as the only product with the isolated yield being 63 % (Scheme 6).



Scheme 6: Synthesis of MN''_3Cl starting materials from MN''_3

In an analogous way, the M^{IV} NHC complexes, $M(L^D)N''_2Cl$ (M = Ce and U), may be prepared by oxidation of the corresponding M^{III} NHC complex with 1 equivalent of Ph_3CCl in toluene. Attempts to oxidise $Ce(L^D)N''_2Cl$ with $TeCl_4$ (the oxidant originally used to oxidise CeN''_3 to CeN''_3Cl)[23,42] did not yield any tractable products. The complexes may also be prepared from the protonolysis reaction of MN''_3Cl with 1 equivalent of HL^D.

The ^1H NMR spectrum of $Ce(L^D)N''_2Cl$ (Ce^{IV}: $[Xe]4f^0$) confirms its diamagnetic nature (Figure 13). The $C_{carbene}$ resonance in the $^{13}C\{^1H\}$ NMR spectrum occurs at 237.4 ppm which is at a higher frequency with respect to the only other example of a Ce^{IV}-NHC complex, $Ce(L)_4$ (L = $OCMe_2CH_2$(1-C{NCHCHN^{i}Pr})), where the $C_{carbene}$ resonance is at 212 ppm.[43]

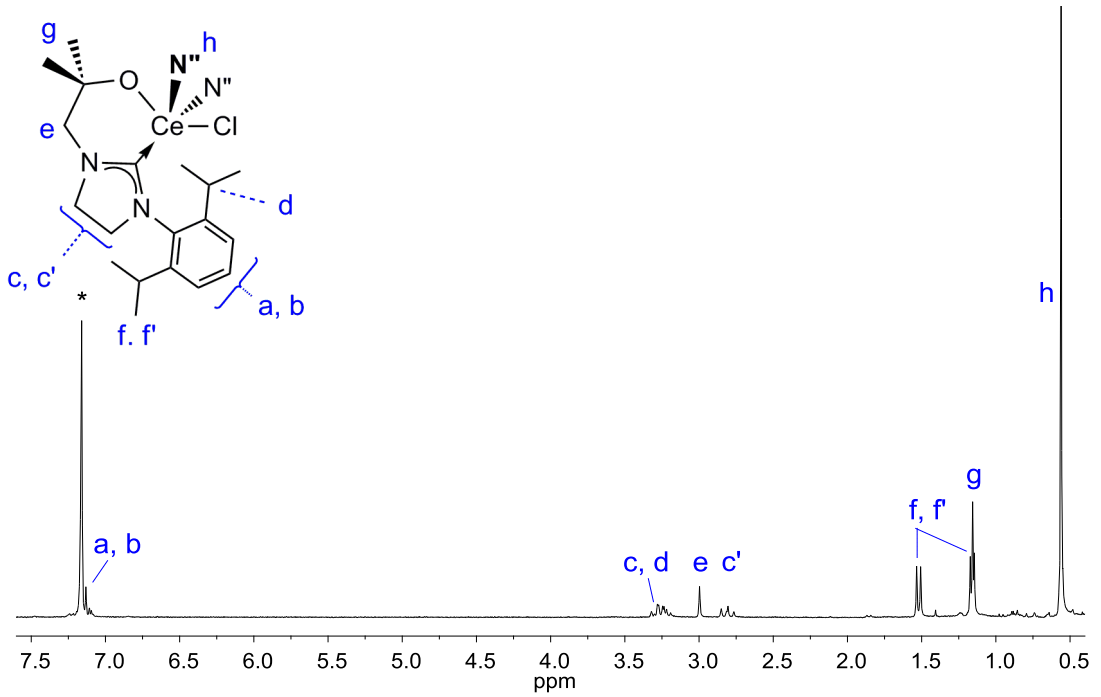
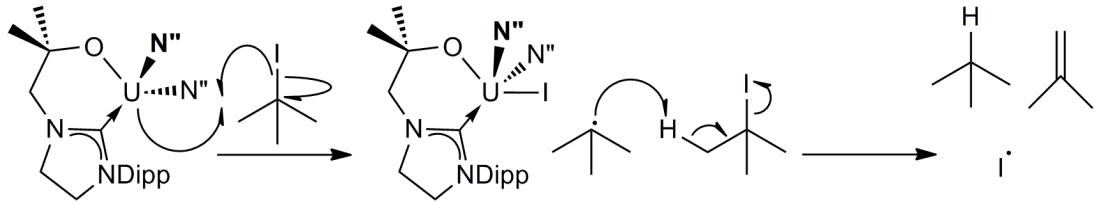


Figure 13: ^{1}H NMR spectrum (C_6D_6, 600 MHz, 298 K) of Ce(L^D)N"$_2$Cl
'*' denotes residual protio solvent

Preparation of other U(L^D)N"$_2$X was also shown to be possible. The pink iodide U(L^D)N"$_2$I can also be synthesised from U(L^D)N"$_2$ by one electron oxidation with ^{t}BuI in toluene. Though the reaction byproducts were not identified, a radical mechanism is likely and would result in the formation of *tert*-butane and 2-methyl-prop-1, 2-ene (Scheme 7). No reaction was observed between Ce(L^D)N"$_2$ and ^{t}BuI.

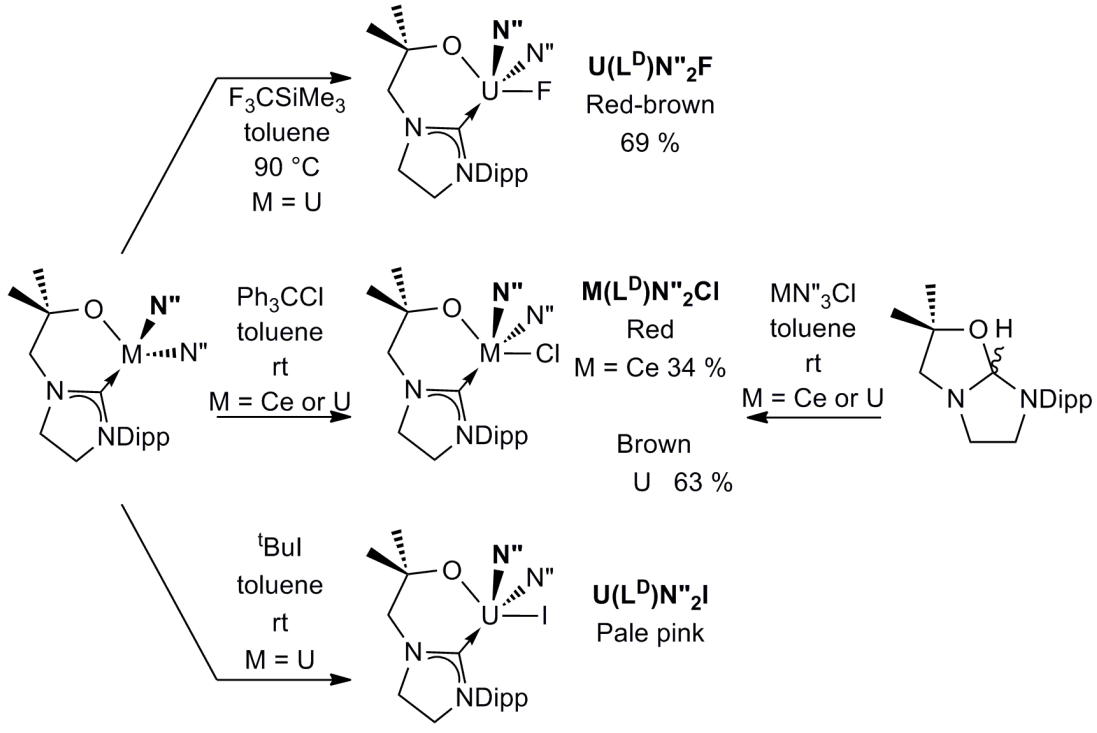


Scheme 7: Radical mechanism for the formation of U(L^D)N"$_2$I

Treatment of U(L^D)N"$_2$ with Ruppert's reagent, F_3CSiMe_3, afforded red-brown U(L^D)N"$_2$F in 69 % yield but the reaction byproducts could not be identified (see Scheme 8, where a summary of synthesis of all M(L^D)N"$_2$X is provided). In contrast to the transition and main group metals,[44,45] organometallic actinide fluoride complexes are rare and this is a result of the absence of general synthetic pathways.[46,47] In particular, only thirteen uranium fluoride complexes have been reported and all are stabilised by cyclopentadienyl-type

ligands. Organometallic fluorine chemistry is of ever-growing interest due to the unique reactivity of M-F bonds and their use in homogeneous catalysis.[44]

F_3CSiMe_3 is most commonly used as a reagent for the trifluoromethylation of organic substrates.[48] Its use in organometallic synthesis is more limited but it has been used to synthesise M-CF_3 complexes which can subsequently undergo α-fluoride abstraction to form difluorocarbene (M=CF_2) complexes.[49] Both examples use catalytic amounts of F^- in order to promote reaction. When the synthesis of U(L^D)N"$_2$F was monitored by ^{1}H NMR spectroscopy, the only observed paramagnetic species were the starting material U(L^D)N"$_2$ and the product U(L^D)N"$_2$F. This indicates that, if U(L^D)N"$_2$(CF_3) does form, it decomposes to the fluoride compound too quickly to be observed. It has been suggested that U-F bond formation can first result from U-CF_3 formation which undergoes α-fluoride abstraction.[50] However, no difluorocarbene (U=CF_2) formation was observed in this case and the reaction yield of the U-F compound was above 50 %. No reactivity was observed between Ce(L^D)N"$_2$ and F_3CSiMe_3, even on prolonged heating, which again demonstrates the difficulties in synthesis of Ce^{IV} amides.



Scheme 8: Synthetic routes to Ce(L^D)N"$_2$Cl and U(L^D)N"$_2$X (X = F, Cl, I)

X-ray diffraction studies of single crystals of Ce(L^D)N"$_2$Cl, U(L^D)N"$_2$Cl and U(L^D)N"$_2$F were undertaken. The displacement ellipsoid plots (Figure 14) and selected bond lengths (Å) and angles (°) are provided (Table 4).

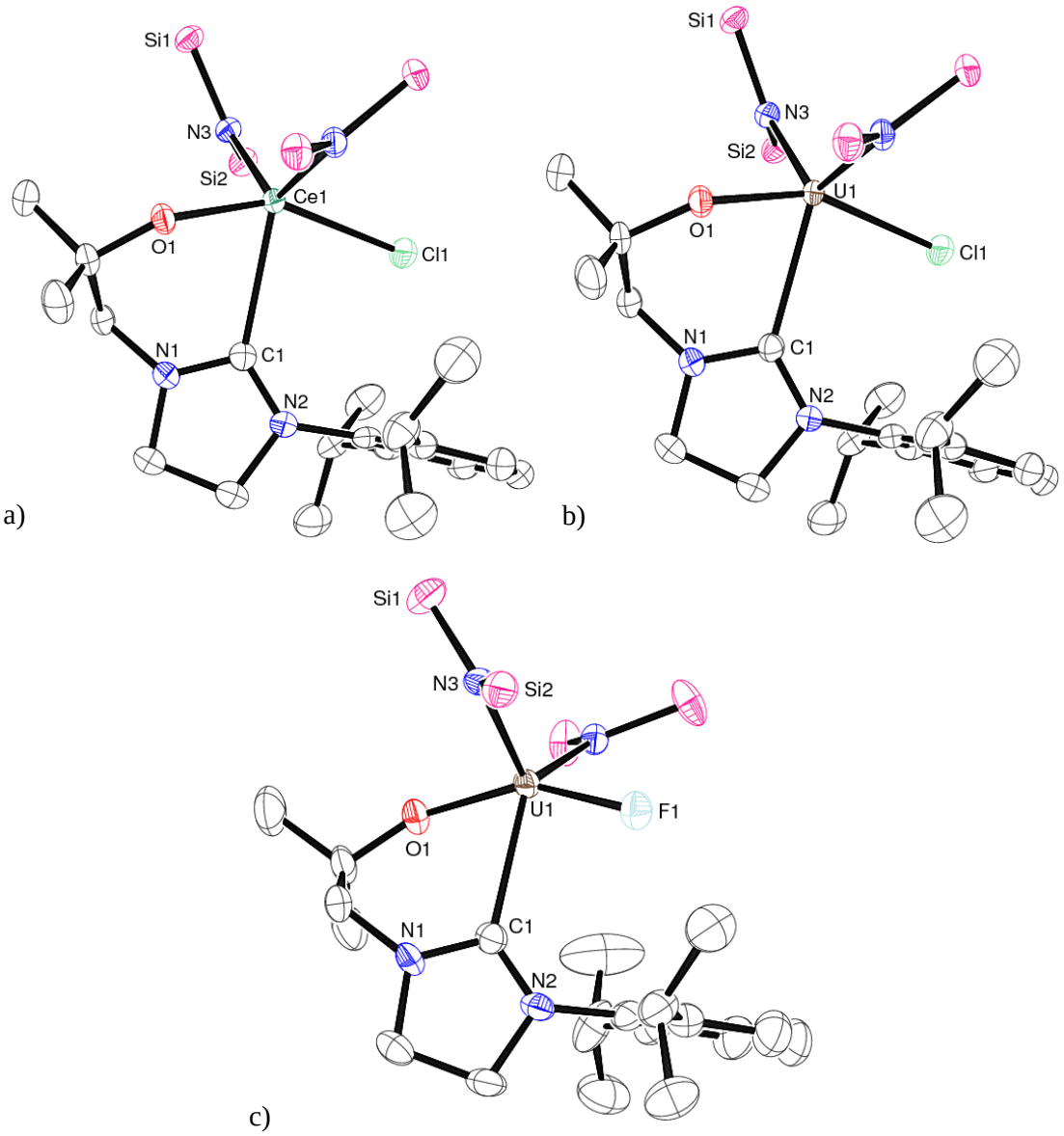


Figure 14: Displacement ellipsoid plots (50 %) of a) Ce(L^D)N"$_2$Cl, b) U(L^D)N"$_2$Cl and c) U(L^D)N"$_2$F

Lattice solvent molecules, H atoms and silyl Me groups omitted for clarity.

In each molecular structure, the metal centre is in a five-coordinate distorted trigonal bipyramidal geometry, the arrangement of the ligands being very similar in each case and so allowing for a detailed comparison. The ligand bite angle is small in each structure (72.18(8)º in Ce(L^D)N"$_2$Cl, 73.89(7)º in U(L^D)N"$_2$Cl and 71.59(17)º in U(L^D)N"$_2$F).

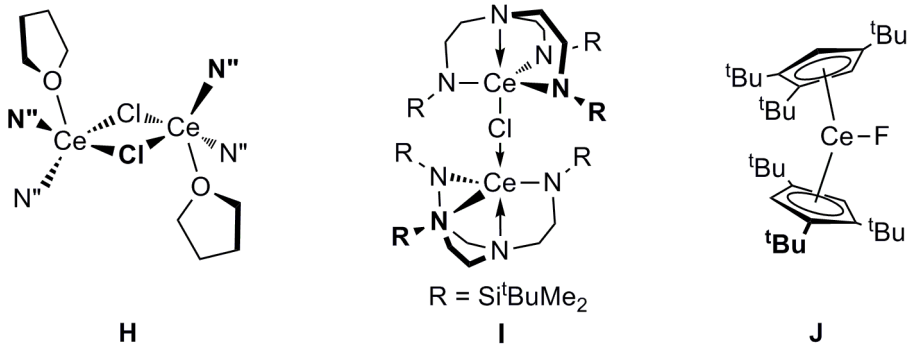
Examination of the bond lengths between the metal centres and soft ligands in M(L^D)N"$_2$X (M = Ce or U, X = Cl or F) should be able to provide an indication into the differences in covalency in these bonds. Taking into account the difference in ionic radii of the metal centres ($rCe^{IV,\ 6C.N.}$ = 0.87 Å, $rU^{IV,\ 6C.N.}$ = 0.89 Å; five-coordinate ionic radii are not

recorded in the Shannon lists),[13] the U-$C_{carbene}$ bond lengths of 2.668(2) Å (in U(L^D)N"$_2$Cl) and 2.654(6) Å (in U(L^D)N"$_2$F) are not significantly shorter than the Ce-$C_{carbene}$ bond length 2.692(3) Å (in Ce(L^D)N"$_2$Cl), within the 3σ criterion, implying only a small difference in covalency of the 4f and 5f element bonding. The U-Cl bond length (2.641(6) Å) is almost statistically equivalent with respect to the Ce-Cl bond length (2.643(7) Å).

Table 4: Selected bond lengths (Å) and bond angles (º) for Ce(L^D)N"$_2$Cl, Ce(L^D)N"$_2$F, U(L^D)N"$_2$Cl and U(L^D)N"$_2$F (Computational model values in [ ], see section 2.5.2)

	[Ce(L^D)N"$_2$F]	Ce(L^D)N"$_2$Cl	U(L^D)N"$_2$Cl	U(L^D)N"$_2$F
M1-C1	[2.696]	2.692(3) [2.614]	2.668(2) [2.631]	2.654(6) [2.694]
M1-O1	[2.121]	2.061(2) [2.103]	2.072(2) [2.093]	2.082(4) [2.093]
M1-N3	[2.308]	2.259(2) [2.282]	2.289(2) [2.279]	2.287(4) [2.308]
M1-N4		2.230(2)	2.2637(19)	2.322(4)
M1-X1	[2.102]	2.643(7) [2.641]	2.641(6) [2.636]	2.087(3) [2.113]
C1-X1		2.643	3.478	3.075
C1-M1-O1	[70.00]	72.18(8) [69.63]	72.89(7) [70.71]	71.59(17) [71.67]

There are no reported examples of structurally characterised organometallic Ce^{IV} chlorides with which to compare Ce(L^D)N"$_2$Cl and, with the exception of CeCp*$_2$Cl(thf) (for which no metrical parameters were reported)[51], all Ce^{III} examples contain bridging chlorides. The five-coordinate Ce^{IV} chlorides supported by amide ligands are **H**, [CeN"$_2$(μ-Cl)(thf)]$_2$[23] and **I**, (Ce{L})$_2$(μ-Cl) (L = N{$CH_2CH_2NSi^tBuMe_2$}$_3$).[25] Both contain bridging Cl^- ligands with Ce-Cl bond distances of 2.843(2)/2.859(2) Å and 3.0080(3) Å respectively and, as such, are considerably longer than in Ce(L^D)N"$_2$Cl (2.692(3) Å). For comparison, the Ce-Cl separation in CeN"$_3$Cl is 2.597(2) Å.[23] The sole example of an organometallic Ce^{III} complex with a Ce-F bond is the three-coordinate *bis*(cyclopentadienyl) complex **J**, Ce(1,3,4-^{t}Bu-C_5H_2)$_2$F which contains a Ce-F bond length of 2.165(2) Å (Figure 15).[52]



H **I** **J**

Figure 15: Structurally characterised Ce^{IV} chlorides (**H** and **I**) and the only fluoride (**J**)

The U-Cl bond length (2.668(2) Å) lies within the range (from 2.615(3) Å in **K**, $U(L)Cl_2$,[53] where L = 2,6-CH_2Cp-C_5H_3N, to 2.757(4) Å in **L**, $UCp^*_2Cl(OH)(HNSPh_2)$[54] of five-coordinate U^{IV} molecular structures which contain a terminal U-Cl bonds. The U-F bond length (2.087(3) Å) in $U(L^D)N''_2F$ is shorter than the U-Cl bond length in the analogous complex, as would be expected from the smaller ionic radius of F^- with respect with Cl^-.[13] It is within the range (from 2.073(5) Å in **M**, $[U(1,3\text{-}SiMe_3\text{-}C_5H_3)_2F(\mu\text{-}F)]_2$[55] to 2.43(2) Å in UCp^*_3F)[56] of previously reported molecular structures which contain a terminal U^{IV}-F bond in an organometallic complex. There are two examples of five-coordinate U^{IV} fluorides within the literature: **M** and $UCp^*_2F_2(py)$ (U-F = 2.146(5) Å) (Figure 16).[47]

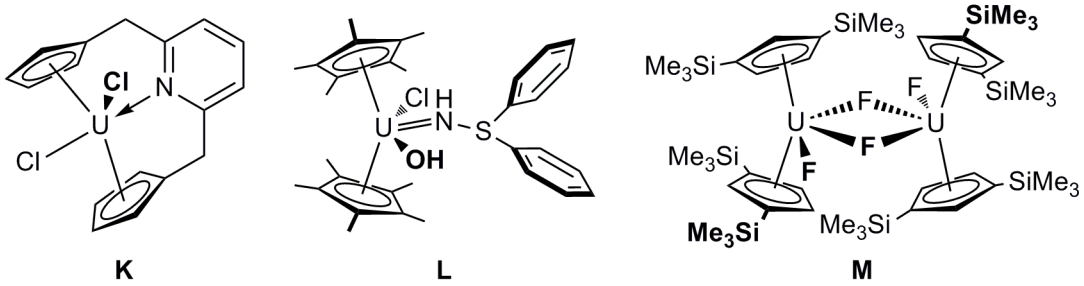


Figure 16: Examples of structurally characterised U^{IV} chlorides and fluorides

The $C_{carbene}$-halide distances are short ($Ce(L^D)N''_2Cl$: 2.643 Å, $U(L^D)N''_2Cl$: 3.478 Å, $U(L^D)N''_2F$: 3.075 Å) and are well within the sum of the van der Waals radii (3.75 Å, 3.61 Å and 3.47 Å respectively). There are two possibilities to explain this; electron donation from the *cis*-coordinated π-donor halide into the empty but high energy C 2p π orbital (**N**, Figure 17)[57] or simply minimising unfavourable steric repulsions between the halide and bulky silylamide groups (**O**, Figure 17)[58]. Transition metal examples which demonstrate short $C_{carbene}\cdots X$ interactions are usually of the more sterically crowded first row metal centres rather than their second and third row congeners and can be rationalised as purely steric effects; in terms of electronic effects, the Cl^- ligand is also likely to be stabilising the metal centre through π donation.[59] DFT analysis of the recently reported $U(1\text{-}C\{N^iPrCH\}_2)_2Cl_4$ also indicated that close $C_{carbene}\cdots Cl$ contacts were a result of steric repulsion.[60]

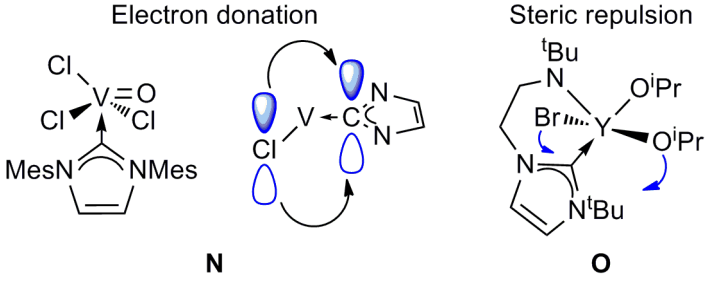


Figure 17: Examples of M-NHC complexes with short $C_{carbene}\cdots X$ contacts

Attempts to prepare the *bis*(ligand) compound, $Ce(L^D)_2N''Cl$, from 1 equivalent of CeN''_3Cl and 2 equivalents of HL^D afforded a new red-orange diamagnetic species. In the ^1H NMR spectrum, there is a single set of resonances accounting for L^D, which are shifted with respect to those of $Ce(L^D)N''_2Cl$. After 8 h at room temperature in solution, the solution became blue in colour and only HL^D was visible in the ^1H NMR spectrum indicating decomposition. A satisfactory $^{13}C\{^1H\}$ NMR spectrum was not obtained and so, the diagnostic high frequency $C_{carbene}$ resonance could not be identified. Considering the steric congestion of $Ce(L^D)_2N''$ and that the ionic radius of Ce^{IV} is smaller than Ce^{III} under the same coordination environment, it is likely that if $Ce(L^D)_2N''Cl$ could be formed then it would be unstable.

2.5.2 Computational analysis

A DFT computational analysis of $M(L^D)N''_2X$ (M = Ce or U, X = Cl or F) was undertaken by Prof N. Kaltsoyannis and Miss P. Pelekanaki. In this model, the $SiMe_3$ groups were replaced by SiH_3 and the Dipp groups by Me; the formula $M(L^D)N''_2X$ used in this section will imply these changes for computer modelling. The aim of this study was to probe the differences in covalent contributions to bonding between the Ce^{IV} and U^{IV} complexes (for which a DFT analysis is considered suitable).

Computational models reproduced the molecular structures determined by X-ray crystallography, and a Ce-F analogue, with little deviation from the experimental values within error (Table 4). The shortening of the M-$C_{carbene}$ bond in $U(L^D)N''_2Cl$ (2.631 Å) with respect to $Ce(L^D)N''_2Cl$ (2.694 Å) was slightly exaggerated computationally. A similar shortening of this bond is observed in the fluoride analogues (2.614 Å in $U(L^D)N''_2F$ and 2.696 Å in $Ce(L^D)N''_2F$).

To determine whether increased covalency in the 5f over the 4f M-X compound is indicated by the shortening of the bond between the metal centre to the soft $C_{carbene}$ atom, the electronic structures were first probed at optimised geometries using Mayer bond and natural analyses (Table 5). Mayer bond analysis provides Mayer bond orders (MBO) which contain all of the contributions to a bond, both bonding and antibonding, between two atoms.[61] It is useful because a single positive number reflects this (as in Wiberg bond orders)[62] and it can be used effectively in low symmetry complexes where the contributions to a bond may come from a large number of different orbitals. Mayer bond orders are basis set dependent and hence comparison between systems is only valid where the same, or analogous, basis sets have been used.

Table 5: Mayer bond orders, natural charges and populations for $M(L^D)N''_2X$ (M = Ce or U, X = F or Cl)

	$Ce(L^D)N''_2F$	$U(L^D)N''_2F$	$Ce(L^D)N''_2Cl$	$U(L^D)N''_2Cl$
$MBO_{M\text{-}Ccarbene}$	0.33	0.46	0.34	0.44
q_M	2.60	2.48	2.53	2.35
q_C	0.10	0.08	0.10	0.09
q_X	-0.65	-0.61	-0.65	-0.57
M s population	0.12	0.17	0.16	0.21
M d population	0.35	0.33	0.36	0.34
M f population	0.93	0.90	0.95	0.98

For the analysis of $M(L^D)N''_2X$, the $M\text{-}C_{carbene}$ MBOs are very similar for a given metal centre ($Ce(L^D)N''_2F$: 0.33, $Ce(L^D)N''_2Cl$: 0.34) and this is true for both cerium and uranium. However, comparing the $M\text{-}C_{carbene}$ MBOs for a given halide indicates significantly larger MBOs for the uranium complexes ($Ce(L^D)N''_2Cl$: 0.34, $U(L^D)N''_2Cl$: 0.44). This is consistent with the observation of shorter $M\text{-}C_{carbene}$ bonds in the 5f complexes resulting from greater covalency.

Natural analysis leads to natural population, the occupancy of a natural atomic orbital (NAO), and charge on a given atom.[63,64] NAOs are defined as orthonormal valence-shell atomic orbitals of maximal occupancy. They are an excellent way of describing the electron density around an atomic centre in a polyatomic molecule since they are largely localised. The value for the natural population is intrinsically positive (since the NAOs form an orthonormal set) and summing the NAO populations will give the total number of electrons on that atom.

The natural charges indicate that there is little change of the partial charge of the $C_{carbene}$ ($q_{C_{carbene}}$) across all four complexes ($Ce(L^D)N''_2Cl$: 0.10, $U(L^D)N''_2F$: 0.08). The charges on the halogens also vary little. The charges on the metals (q_M) show the greatest variation; the fluoride complexes have larger positive charges than the chloride complexes ($U(L^D)N''_2F$: 2.48, $U(L^D)N''_2Cl$: 2.35) and the cerium complexes have larger positive charges than the uranium complexes ($Ce(L^D)N''_2F$: 2.60, $U(L^D)N''_2F$: 2.48). These data indicate greater covalency in the chloride complexes with respect to fluoride but also support an overall larger ionic contribution to bonding in the cerium complexes with respect to the uranium.

The natural atomic populations are presented as number of electrons above the formal M^{IV} number (p populations were very close the formal value and are omitted) and indicate the participation of the orbitals in covalent bonding, where the value is greater than the formal value. Though the data shows mixed results, the overall M population (s + d + f) follows the order $U(L^D)N''_2Cl$ > $Ce(L^D)N''_2Cl$ > $U(L^D)N''_2F$ > $Ce(L^D)N''_2F$, and this also implies the order of covalency which agrees with the natural charge data.

Atoms-in-molecules (AIM) calculations were also completed, having been recently applied to other actinide systems.[65] AIM analyses the electron density topology rather than using an orbital-based approach. The analysis uses electron (ρ) and energy (H) density data to provide information on bonding and connectivity. AIM defines critical points such as the position of the atomic nucleus and for each bonded pair of atoms, there is one bond critical point. At this critical point, a significant covalent contribution to bonding is indicated for $H < 0$ and $\rho > 0.2$ In both cases, the larger the absolute value, the greater the covalent contribution. For all $M(L^D)N''_2X$, the electron (ρ) and energy (H) density data at the bond critical points indicate that M-$C_{carbene}$ and M-X bonding is mostly ionic (Table 6). However, the absolute values for the U-X complexes are larger than that of the Ce-X complexes, implying a greater covalency in the 5f M complexes over the 4f M complexes which is consistent with the data provided by the Mayer and natural analyses.

Table 6: Electron (ρ) and energy (H) density at the M-C and M-X bond critical points for $M(L^D)N''_2X$ (M = Ce or U, X = F of Cl)

	$Ce(L^D)N''_2F$	$U(L^D)N''_2F$	$Ce(L^D)N''_2Cl$	$U(L^D)N''_2Cl$
$\rho_{M\text{-}Ccarbene}$	0.045	0.055	0.045	0.053
$H_{M\text{-}X}$	-0.011	-0.013	-0.007	-0.009
$H_{M\text{-}Ccarbene}$	-0.003	-0.007	-0.004	-0.007
$\rho_{M\text{-}X}$	0.105	0.110	0.059	0.064

Overall, it can be summarised that the contribution to covalency is likely to be small across the four complexes (shown by the atoms-in-molecules analysis). However, the combined data from Mayer and natural analyses (orbital based) and AIM analysis (electron density based) support the idea that the covalency is greater in the 5f systems compared to the 4f systems.

2.6 Conclusions

In conclusion, new saturated backbone NHC proligands have been synthesised in the form of imidazolidinium salts and, after single deprotonation, the bicyclic compound, HL^D.

Proligand HL^D has been used successfully to synthesise a range of M^{II}, M^{III} and M^{IV} amide complexes.

Synthesis of the M^{II} complexes was straightforward, though surprisingly the *bis*(ligand) $Mg(L^D)_2$ compound could not be formed. This is most likely to be a combined result of the slightly smaller ionic radius of Mg^{II} and its weaker M-$C_{carbene}$ bond with respect to Zn^{II}.

The preparation of M^{III} complexes was used to show the effect of the steric encumbrance of the coordinated ligands which resulted in a differentiation between 4f and 5f metal reactivity; the *bis*(ligand) complexes $Ce(L^D)_2N''$ and $U(L^D)_2I_2$ being easily isolated but the analogous $U(L^D)_2N''$ not isolable in our hands.

In preparing the M^{IV} complexes, trityl chloride was identified as a useful oxidant for the preparation of the Ce^{IV} amide CeN''_3Cl in high yield. An X-ray diffraction and a DFT study of the M^{IV} complexes indicated that, though the bonding in Ce^{IV} and U^{IV} systems is largely ionic, there is a greater covalent contribution to bonding in the case of the 5f metal.

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Reactivity of metal amide complexes

3.1 Introduction

Transition metal N-heterocyclic carbene complexes have been applied successfully as homogeneous catalysts for numerous processes; for example, lactide polymerisation, cross-coupling reactions and hydroelementation.[1-3] Trivalent Ce^{III} and U^{III} cations have very similar ionic radii ($rCe^{III,\ 6C.N.}$ = 1.01 Å, $rU^{III,\ 6C.N.}$ = 1.025 Å).[4] This facilitates the comparison of the bonding (in particular, the understanding of the role of the f-electrons) and reactivity 4f and 5f metal complexes,[5-10] which has important implications for nuclear waste management.[11,12]

This chapter describes the reactivity studies completed on the M^{II}, M^{III} and M^{IV} amide complexes supported by the alkoxy-functionalised saturated NHC ligand, L^D. The addition-elimination chemistry discussed for the M^{III} amide complexes will be extended to M^{III} alkyl complexes in Chapter Four.

3.2 Reactivity of M^{II} amide complexes

3.2.1 Study of $M(L^D)N''$ and $M(L^D)_2$ as initiators for lactide polymerisation

Poly(lactide) (PLA) is an important biocompatible, biodegradable polymer which is produced from inexpensive, renewable resources.[13-15] The main synthetic route is the ring opening polymerisation (ROP) of the lactide monomer.[16] Owing to a range of desirable properties, PLA has found uses in packaging, biomedical applications and microelectronics.[17,18] The physical properties of the polymer are largely dependent on tacticity, molecular weight and polydispersity and well-defined homogeneous metal-based catalysts have been used successfully to achieve controlled polymerisation of PLA.[16,19]

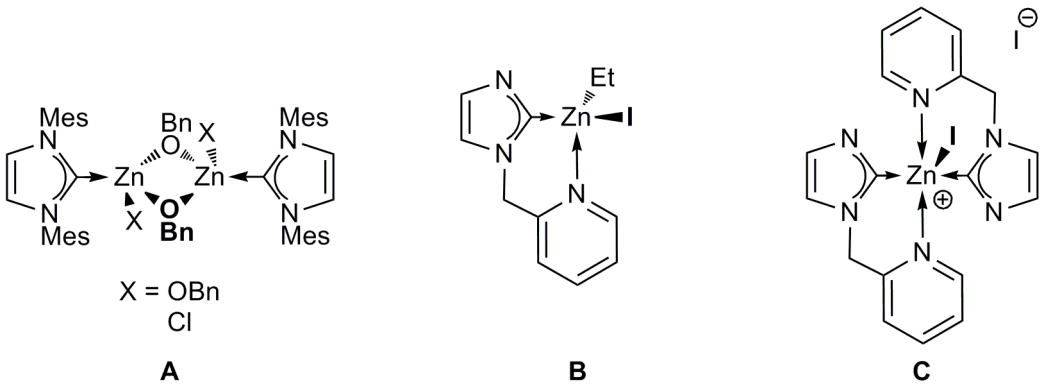


Figure 1: Zn NHC complexes that have been used for the ROP of lactide

Magnesium and zinc complexes are especially suitable for the ROP of lactide as they are non-toxic, colourless and have a low cost. As such, there are many examples of their use,[20] but none using NHC-supported magnesium complexes and only four using NHC supported zinc complexes, **A** – **C**, which showed excellent activity (Figure 1).[21,22] The homobimetallic complexes **A** showed good control over polymer molecular weight, produced polymer with relatively narrow PDIs (Polydispersity Index). Data were consistent with one growing polymer chain per alkoxide group. The *mono* and *bis*(pyridyl-NHC) complexes **B** and **C** rapidly polymerised lactide (For example, [LA]/[**B**] = 100, 5 minutes, 140 ºC, 96 % yield) in a melt reaction to afford *poly*(lactide) with broad PDIs (**B**: 2.04 – 2.35, **C**: 1.78 – 2.51). We chose to investigate lactide polymerisation with M(L^D)N" (M = Mg or Zn) and M(L^D)$_2$ (M = Zn). All lactide polymerisation runs were undertaken by Dr. I. J. Casely and the results of each polymerisation are collated below (Table 1).[23]

Table 1: Polymerisation of *rac*-lactide using M(L^D)N" (M = Mg or Zn) and M(L^D)$_2$ (M = Zn)*

Entry	Catalyst	t (h)	Conv.[a] (%)	$M_{n\,theo}$[b] ($gmol^{-1}$)	$M_{n\,exp}$[c] ($gmol^{-1}$)	PDI[d]	P_r[e]
1	Mg(L^D)N"	0.75	27	13 564	18 000	1.32	0.50
2	Mg(L^P)N"	0.75	98	36 327	26 000	1.57	0.58
3	Zn(L^D)N"	17	92	48 928	16 000	1.32	0.68
4	Zn(L^D)$_2$	17	92	62 085	35 500	1.40	0.55
5	MgN"$_2$(thf)$_2$	16	95	46 788	24 500	1.79	0.54

*Catalyst:Monomer:Solvent = 1:100:1000 where solvent = thf, T(ºC) = 25, L^P = $OCMe_2CH_2$(1-C{$NCH_2CH_2N^iPr$}),
[a] Conversion of lactide (LA) monomer (($[LA]_0$-[LA])/$[LA]_0$), [b] Theoretical molecular weight = Conversion x [LA]/[cat.] x M_{LA},
[c] Measured by GPC, values based on polystyrene standards and weight corrected by multiplication by 0.58 (Mark-Houwink equation), [d] Polydispersity Index (M_w/M_n) measured by GPC, [e] Probability of forming the next *isi* or *sis* tetrad, measured by integration of the methine proton region in the decoupled ^{1}H NMR spectra

Each polymerisation run was carried out at room temperature; a thf solution of the catalyst (3.00 mg) was added to a thf solution of *rac*-lactide monomer (300 mg), with vigorous stirring, to afford a total volume of 3 mL. The reaction was quenched by addition of wet THF and exposure to ambient atmosphere, followed by removal of the volatiles under

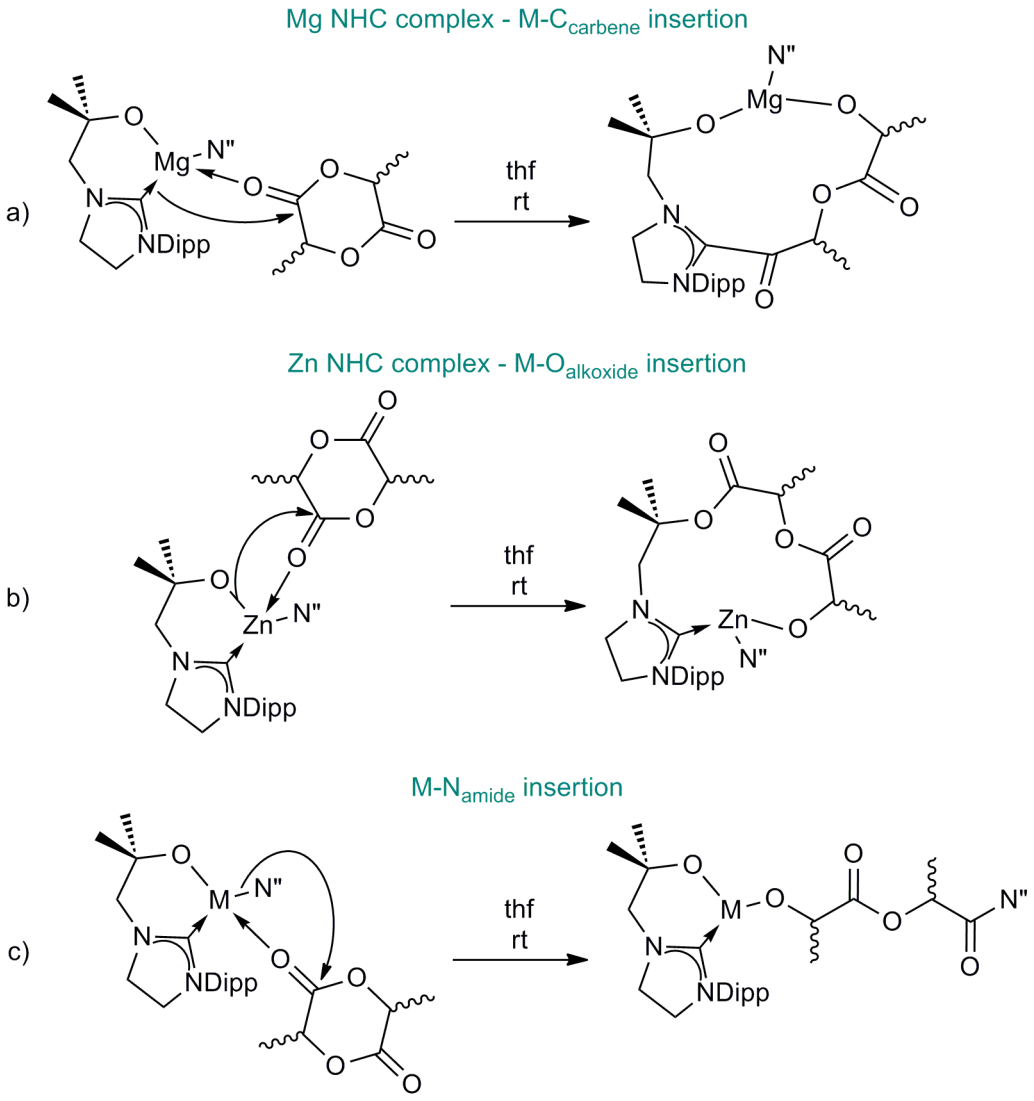
reduced pressure. The polymers were characterised by ^{1}H, $^{13}C\{^{1}H\}$, $^{1}H\{^{1}H\}$ NMR spectroscopy ($CDCl_3$ solutions) and by Gel Permeation Chromatography (GPC).

The PDIs are relatively low, vary little and compare well with polymerisation data obtained for complex **A** (benzyl: 1.25, benzyl chloride: 1.18 – 1.68) and are better than that obtained for **B** (2.04 – 2.45) and **C** (1.78 – 2.51). Apart from Mg(L^D)N", which produces completely atactic (random stereocentres) polymer (P_r = 0.50), the other catalysts produce polymer with some level of heterotacticity (polymer microstructure consists of doubly alternating stereocentres, *RRSSRRSSRR*).[19] Only the polymer produced by Zn(L^D)N" displays a significant heterotactic enrichment (P_r = 0.68), indicating that there is some stereocontrol over polymerisation in this case. Complexes **A**, **B** and **C** produce polymer with the same level of heterotacticity (P_r = 0.60).

Both metal alkoxides and metal carbene complexes have been shown to be able to polymerise *rac*-lactide and metal alkoxide groups are known to be faster initiating groups than metal amido groups.[3] Hence, there are three possible mechanisms for the initiation process; monomer insertion into the M-$O_{alkoxide}$ bond, M-N_{amide} bond or the M-$C_{carbene}$ bond (Equation 1a-c)).

Mg(L^P)N" (L^P = $OCMe_2CH_2$(1-C{$NCH_2CH_2N^iPr$}) achieves 98 % conversion after 0.75 h, while Mg(L^D)N" achieves only 27 % conversion after the same time. This indicates that increasing the steric profile of the ligand has a dramatic effect on the rate of polymerisation for the Mg NHC complexes. Hence, for the hard Mg^{II} ion, initiation is expected to occur into the weaker Mg-$C_{carbene}$, which is close to the bulky *N*-Dipp substituent, bond rather than the stronger Mg-$O_{alkoxide}$ bond (Equation 1a)). As such, increasing the steric encumbrance of the ligand makes insertion into this bond more unfavourable. Zn(L^D)N" and Zn(L^D)$_2$ reach the same conversion (92 %) after 17 h. This suggests that initiation is independent of the Zn-N" amide group and that the steric profile of the ligand does not have the same effect as in the magnesium complexes. Hence, for the soft Zn^{II} ion, initiation is expected to occur into the weaker Zn-$O_{alkoxide}$ bond rather than the stronger Zn-$C_{carbene}$ bond. The Zn-$O_{alkoxide}$ bond is further from the bulky *N*-Dipp group and so its effect on the rate of polymerisation is small (Equation 1b)).

It was not possible to identify the identity of the polymer end group by ^{1}H NMR spectroscopy. This may be due to further reactions occurring during quenching of the polymerisation runs.

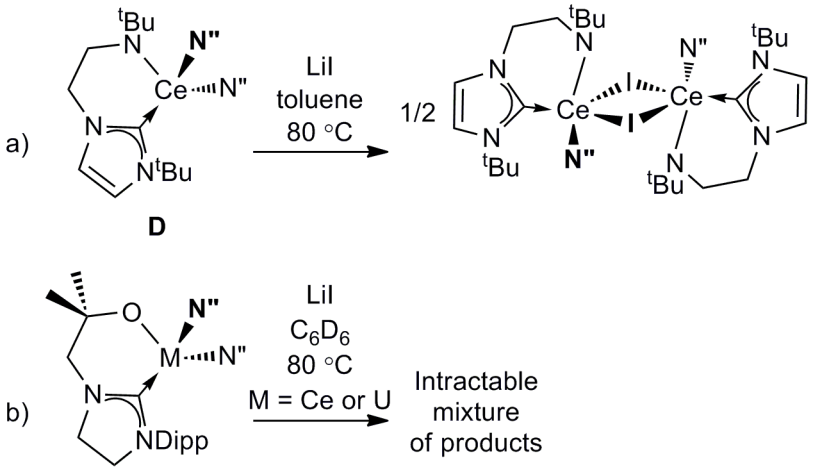


Equation 1: Potential initiation mechanisms for the ROP of *rac*-lactide by M(L^{D})N"
a) NHC initiation, b) alkoxide initiation and c) amide initiation

3.3 Reactivity of M^{III} amide complexes

3.3.1 Addition-elimination reactions across the metal-NHC bond

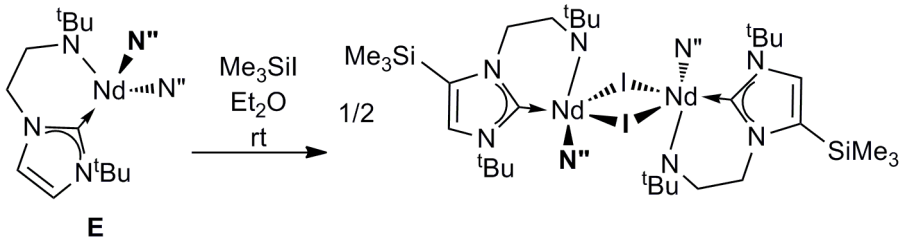
For the unsaturated NHC complex **D**, Ce(L)N"$_2$ (L = ^{t}BuNCH$_2$CH$_2$(1-C{NCHCHN^{t}Bu})), amide-iodide exchange could be effected with the use of LiI in toluene at 80 ºC. LiN" was eliminated during the reaction (Equation 2a)).[24] Ce(L^{D})N"$_2$ was also treated with 1 equivalent of LiI in order to form Ce(L^{D})N"I. This iodide complex would provide a useful starting material for further salt metathesis reactions (Equation 2b)).[25]



Equation 2: Reactions of a) unsaturated (**D**) and b) saturated NHC complexes with LiI

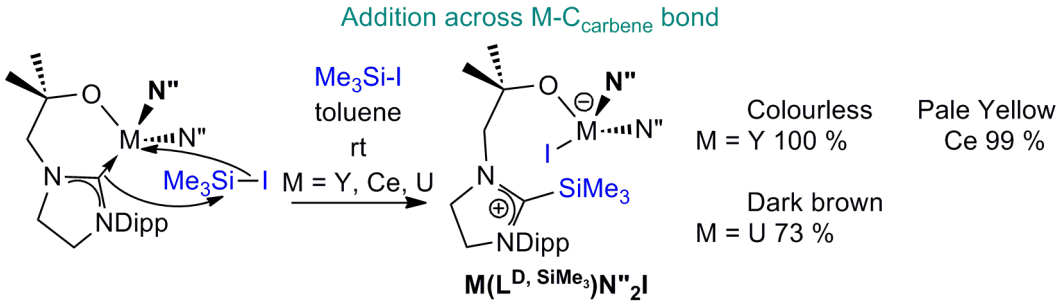
No reaction occurred at room temperature but when the reaction mixture was heated to 80 ºC, all of the Ce(L^D)N"$_2$ starting material was fully consumed and no LiI remained in solution. However, though the ^{1}H NMR spectrum contained a resonance for anticipated by-product LiN", the remaining resonances were overlapping in the range of 9.80 ppm – -8.52 ppm and could not be assigned to a single product. Similar reactivity was observed with U(L^D)N"$_2$ and, in both cases, repeated recrystallisations failed to yield a single pure product (Equation 2b)). The reaction was not repeated with Y(L^D)N"$_2$ since the higher Lewis acidity of the yttrium cation means that it can compete much better with the lithium cation for the amide ligand and is therefore unlikely to undergo amide-iodide exchange.

For the unsaturated NHC complex **E**, Nd(L)N"$_2$ (L = ^{t}BuNCH$_2$CH$_2$(1-C{NCHCHN^{t}Bu})), amide-iodide exchange could also be achieved with Me_3SiI but the acidic nature of the ligand backbone protons resulted in the regiospecific silylation of the C4 position (Equation 3).[26] Reaction with Me_3SiI was therefore attempted for the saturated NHC complexes M(L^D)N"$_2$ (M = Y, Ce or U); ligand backbone silylation here is unlikely as the backbone protons are much less acidic and so, a clean amide-iodide exchange was initially targeted.



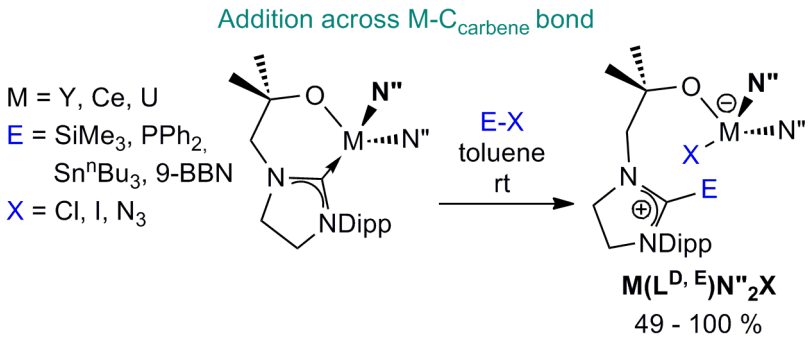
Equation 3: Regiospecific silylation of the C4 position of an NHC using Me_3SiI

Treatment of $M(L^{D})N''_2$ (M = Y, Ce or U) with 1 equivalent of Me_3SiI in benzene or toluene immediately resulted in colourless (M = Y), pale yellow (M = Ce) or dark brown (M = U) solutions. In each case, $M(L^{D, SiMe_3})N''_2I$ was isolated in good yield (73 % – 100 %) (Equation 4).



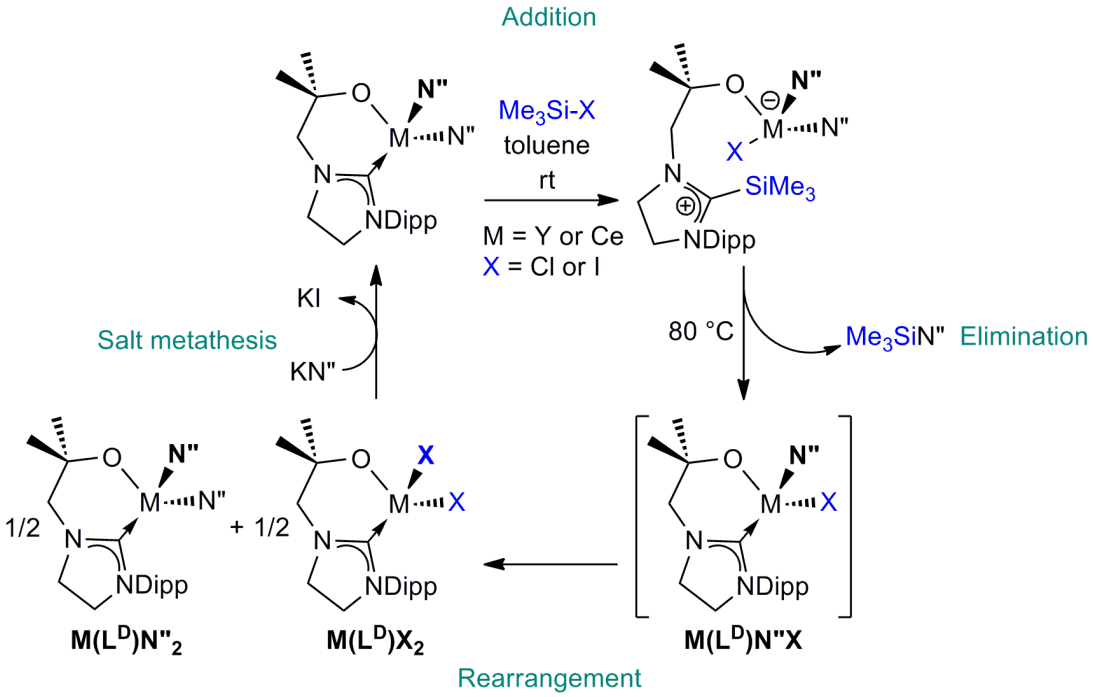
Equation 4: Reaction of Me_3SiI with $M(L^{D})N''_2$ (M = Y, Ce or U)

The complex $M(L^{D, SiMe_3})N''_2I$ is the product of addition of Me_3SiI across the M-$C_{carbene}$ bond. Each $M(L^{D, SiMe_3})N''_2I$ is zwitterionic with, formally, a positive charge on the N-heterocyclic ring and a negative charge on the metal centre. The reaction has been generalised to include a number of E-X reagents (E = phosphine, borane, stannane, X = halide or *pseudo*halide) and the resulting product is denoted as $M(L^{D, E})N''_2X$ (Equation 5).



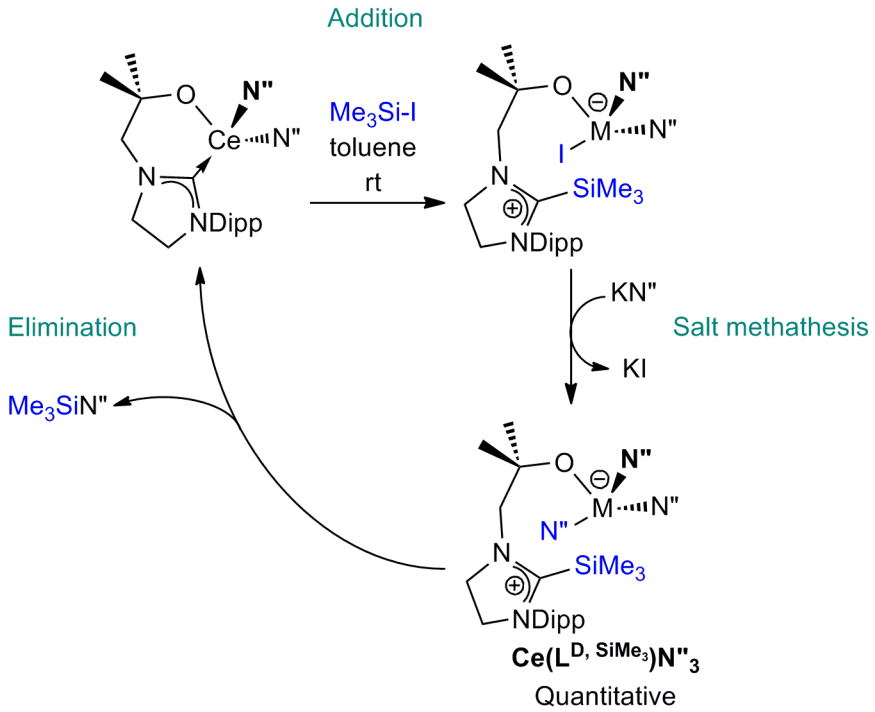
Equation 5: Addition of E-X to $M(L^{D})N''_2$

Heating a solution of $M(L^{D, SiMe_3})N''_2X$ (M = Y or Ce, X = Cl or I) in C_6D_6 resulted in the reformation of the M-$C_{carbene}$ bond to yield $M(L^{D})XN''$ and the resulting elimination of *tris*(trimethylsilyl)amine, N'''. $M(L^{D})XN''$ was not directly observed,[26] but rearranged into a 50:50 mixture of $M(L^{D})N''_2$ and $M(L^{D})X_2$, which could be converted back to the starting material by a salt elimination reaction with KN'' (Scheme 1).



Scheme 1: Addition-elimination of E-X (E = $SiMe_3$, X = Cl or I) with $M(L^D)N''_2$ (M = Y or Ce)

Treatment of $Ce(L^{D,\ SiMe_3})N''_2I$ with 1 equivalent of KN" resulted in salt metathesis to form $Ce(L^{D,\ SiMe_3})N''_3$ in quantitative yield (by analysis of the ^1H NMR spectrum). The complex also underwent elimination of N''' and $Ce(L^D)N''_2$ was reformed (Scheme 2).



Scheme 2: Alternative addition-elimination reactivity cycle for $Ce(L^D)N''_2$ with Me_3Si-I

Single crystals of M($L^{D, E}$)N"$_2$X (M = Y, Ce and U, E = $SiMe_3$, X = I and M = Ce, E = $SiMe_3$, X = N_3) were grown from saturated toluene or benzene solutions. The displacement ellipsoid plots of M($L^{D, E}$)N"$_2$X (M = Ce, E = $SiMe_3$, X =I or N_3) (Figure 2) and selected bond lengths (Å) and angles (º) (Table 2) are provided for all M($L^{D, E}$)N"$_2$X.

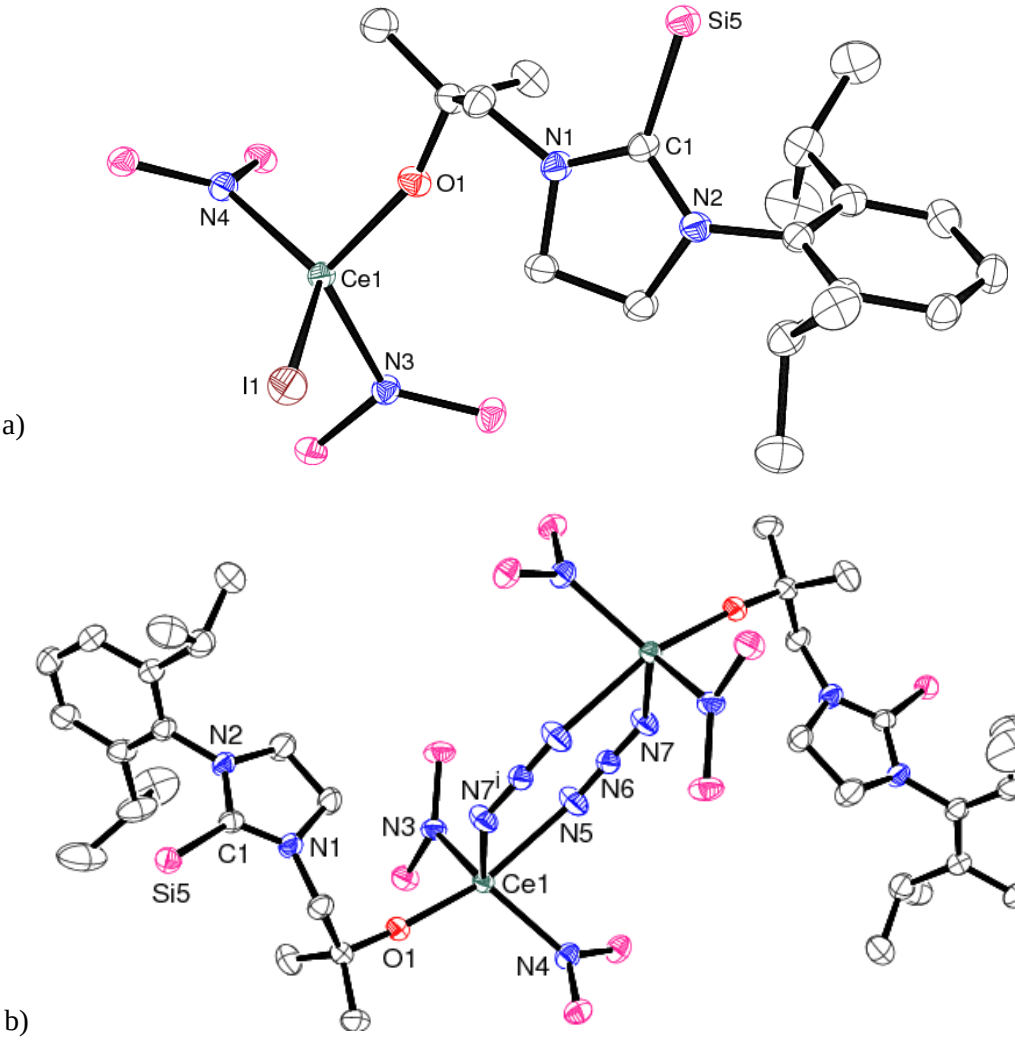


Figure 2: Displacement ellipsoid plots (50 %) of a) Ce($L^{D, SiMe_3}$)N"$_2$I and b) Ce($L^{D, SiMe_3}$)N"$_2$$N_3$
Lattice solvent molecules, H atoms and silyl Me groups are omitted for clarity

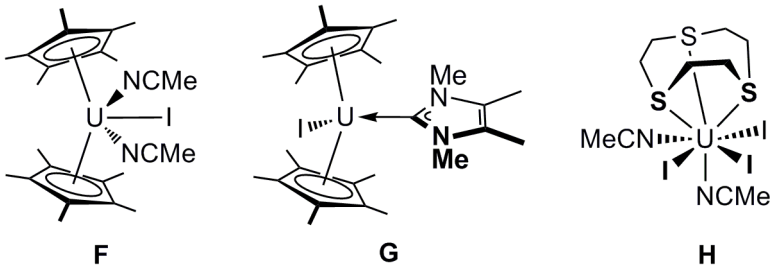
The molecular structures of all M($L^{D, SiMe_3}$)N"$_2$I (M = Y, Ce or U) are monomeric and the metal centre is in a distorted tetrahedral environment. The metrical data of the N-heterocyclic ring supports the formulation of the complexes as zwitterions, with a positive charge on the ring; the N-C-$N_{average}$ angle (110.24º) has increased with respect to the M(L^D)N"$_2$ starting materials (107.0º) but remains smaller than that of the imidazolidinium complex [H_2L^D]Cl (113.7º), likely as a result of the bound electropositive $SiMe_3$ group. The bonds to the metal centres increase in length from Y to Ce according to the increase in ionic

radius ($rY^{III, 6C.N.}$ = 0.900 Å, $rCe^{III, 6C.N.}$ = 1.01 Å)[4] but all of the bonds to the uranium metal centre are shorter than expected ($rU^{III, 6C.N.}$ = 1.025 Å) which may imply some enhanced covalent contributions to bonding in this case. This is most noticeable in the bonds to the softest element, iodine (U1-I1 = 3.1155(4) Å, Ce1-I1 = 3.1506(2) Å). The bonds to the metal centres in $M(L^{D, SiMe_3})N''_2I$ (M = Y or U) are also not significantly different compared to the molecular structures of $M(L^{D})N''_2$ (M = Y or U) (see section 2.4.1). Longer bonds should be expected due to the formal negative charge ascribed to the metal centre in $M(L^{D, SiMe_3})N''_2I$. However, though the coordination numbers are the same, the coordination environment is significantly different and so direct comparison cannot be made.

Table 2: Selected bond lengths (Å) and angles (º) for $M(L^{D, E})N''_2X$ (M = Y, Ce or U, E = $SiMe_3$, X = I or N_3)

	$Y(L^{D, SiMe_3})N''_2I$	$Ce(L^{D, SiMe_3})N''_2I$	$U(L^{D, SiMe_3})N''_2I$	$Ce(L^{D, SiMe_3})N''_2N_3$
M1-X	3.0030(3)	3.1506(2)	3.1155(4)	2.538(2)/2.585(3)
M1-O1	2.0420(13)	2.1451(17)	2.142(3)	2.1955(19)
$M1\text{-}N_{average}$	2.2603	2.3805	2.368	2.4005
N1-C1-N2	109.96(15)	110.0(2)	110.7(4)	110.3(2)
N1-C1-Si5	123.87(13)	125.43(18)	123.6(3)	123.81(19)
N5-N6-N7	-	-	-	177.8(3)

The U-I bond length (3.1155(4) Å) is within the range of values reported for existing U^{III} iodides: For example, 3.2076(7) Å in **F**, $UCp^*_2I(MeCN)_2$,[27] 3.1266(4) Å in **G**, $U(L)Cp^*_2I$ (L = 1-C(NMeCMe)$_2$,[8] 3.0872(3) Å to 3.1543(3) Å in **H**, U(1,4,7-trithiacyclononane)$I_3(MeCN)_2$[28] and 3.103(2) Å to 3.167(2) Å in $UI_3(thf)_4$ (Figure 3).[29]



F **G** **H**

Figure 3: Examples of structurally characterised U^{III} iodide complexes

The azide complex, $Ce(L^{D, SiMe_3})N''_2N_3$, is dimeric in the solid state with a [Ce(μ-1,3-N_3)]$_2$ core centred over a crystallographic inversion centre. This core is skewed with Ce1-N5 and Ce1-$N7^i$ bond distances of 2.538(2) Å and 2.585(3) Å respectively. These distances are significantly shorter than that of Ce1-I1 in $Ce(L^{D, SiMe_3})N''_2I$ (3.1506(2) Å) which is

anticipated from the decreased ionic radius of the azide terminal N atom with respect to the iodide. The values are consistent with the values reported in the complex Nd(L)N"N_3 (L= ^{t}BuNCH$_2$CH$_2$[1-C{NC(SiMe$_3$)CHN^{t}Bu}] (Ce1-N5 = 2.513(3) Å, Ce1-N7 = 2.521(3) Å).[26] With the exception of **I**, LaCp*$_2$(η^2-N,N'-Cp*NN'N"Ad)(AdN_3),[30] the structurally characterised rare earth azide complexes are all symmetric and often contain the azide group as a bridging ligand to form oligomeric and polymeric structures. For example, the trimeric lanthanum *bis*(cyclopentadienyl) complex **J**, [LaCp*$_2$(CNN{SiMe$_3$}$_2$)(μ-N_3)]$_3$ (Figure 4).

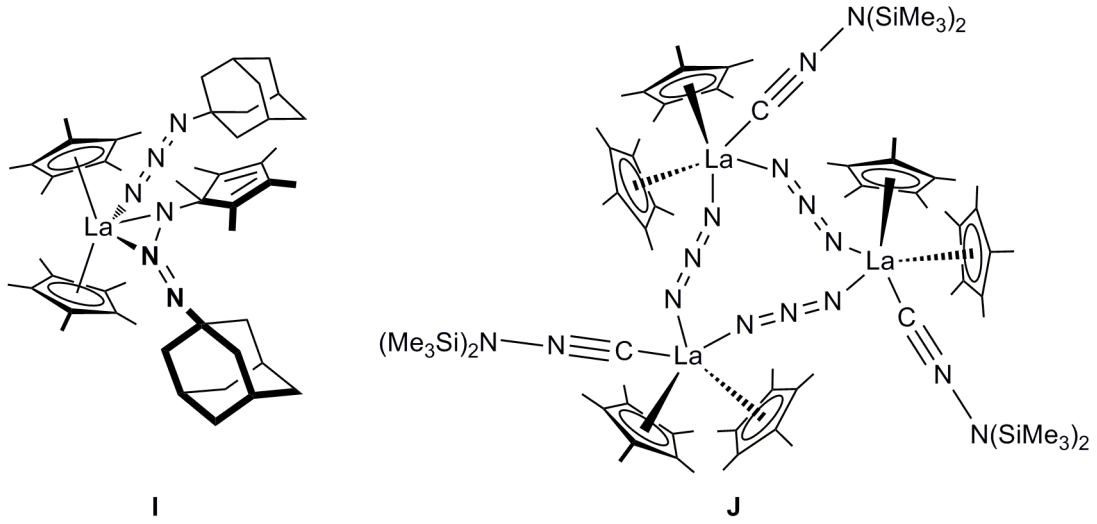
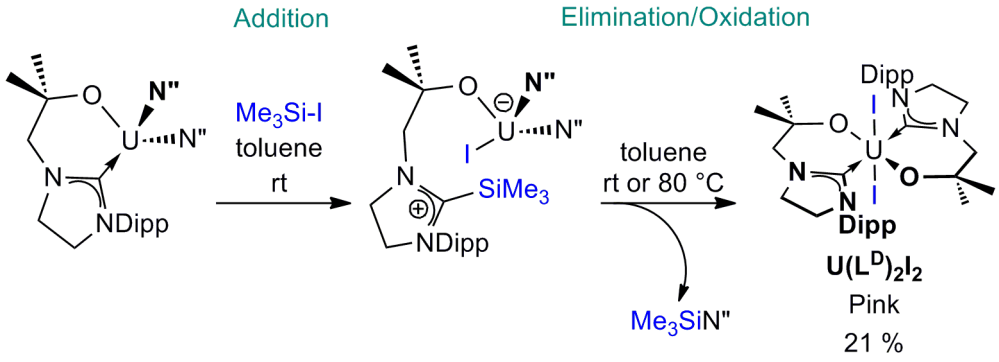


Figure 4: Structurally characterised rare earth azide complexes

When the uranium complex U(L$^{D, SiMe_3}$)N"$_2$ is treated with Me_3SiI, the M-$C_{carbene}$ bond is also reformed with elimination of N"' but then undergoes ligand redistribution and oxidation at room temperature in a toluene solution to form the thermodynamically stable, pink U(L^D)$_2$I$_2$ in 21 % yield (Scheme 3).



Scheme 3: Formation of U(L^D)$_2$I$_2$ from U(L$^{D, SiMe_3}$)N"$_2$

Oxidation from U^{III} to U^{IV} and the formation of a second strong U-O bond are likely to be the driving forces of the rearrangement. Further reaction was attempted with the

addition of 2 equivalents of NaN_3 in order to form the azide complex $U(L^D)_2(N_3)_2$. However, no reaction occurred at room temperature and heating resulted in deposition of a grey solid; the ^1H NMR spectrum of the solution indicated only overlapping resonances over a diamagnetic sweepwidth which could not be identified.

Crystals of $U(L^D)_2I_2$ suitable for a diffraction study were grown at room temperature from a toluene solution but were also observed to form on heating the solution to 80 ºC. The displacement ellipsoid plot (Figure 5) and selected bond lengths (Å) and angles (º) are provided (Table 3).

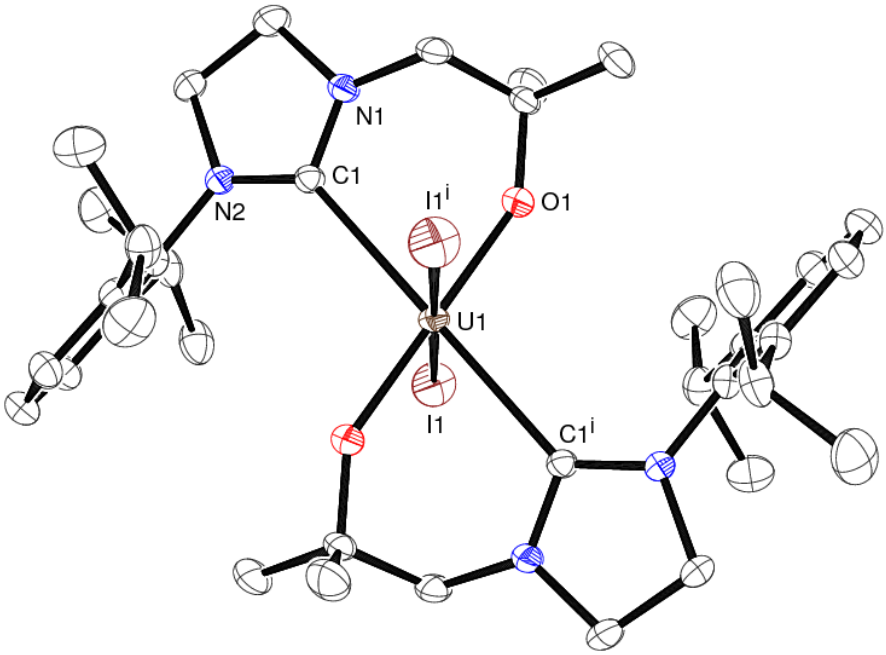


Figure 5: Displacement ellipsoid plot (50 %) of $U(L^D)_2I_2$
H atoms omitted for clarity

Table 3: Selected bond lengths (Å) and angles (º) for $U(L^D)_2I_2$

U1-C1	2.647(3)
U1-O1	2.053(3)
U1-I1	3.0727(3)
O1-U1-C1	75.12(10)
O1-U1-C1^i	104.88(10)
O1-U1-I1	91.40(8)
I1-U1-I1^i	180.00(10)

The U^{IV} ion lies on a crystallographic inversion centre and is in a *pseudo*octahedral environment (I1-U1-I1^i = 180.00(10)º, O1-U1-C1 = 75.12(10)º, O1-U1-C1^i = 104.88(10)º)

with both the iodide and carbene ligands mutually *trans*. The ligands are twisted out of the equatorial plane by 19.9º in order to accommodate the steric bulk of the *N*-Dipp groups. The U1-$C_{carbene}$ distance is comparable to that in other six-coordinate U^{IV} molecular structures with unsaturated NHC ligands which have a range of 2.573(5) Å – 2.687(7) Å.[31] For example; 2.573(5) Å and 2.587(5) Å in **K**, $U(L)Cl_4$ (L = 2,6-(1-C{NCHCHNDipp}$_2$)C_5H_3N,[32] 2.633(7) Å in **L**, $U(L)_2O_2$ (L = $^tBuNCH_2CH_2$(1-C{NCHCHNMes})[33] and 2.675(7) Å and 2.687(7) Å in **M**, U(1-C{N^{i}PrCH}$_2$)$_2Cl_4$ (Figure 6).[31]

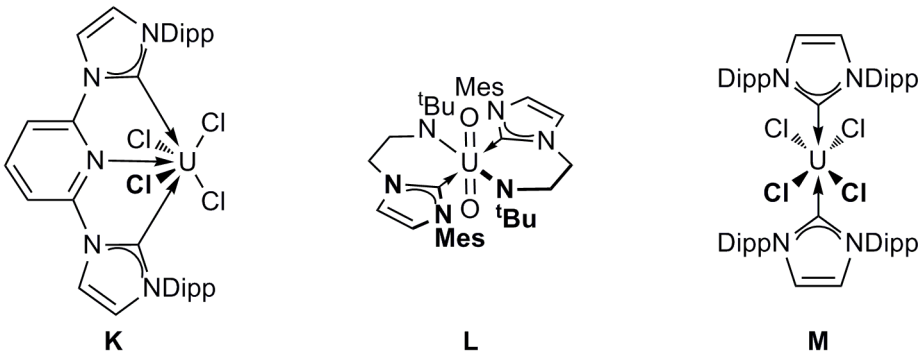
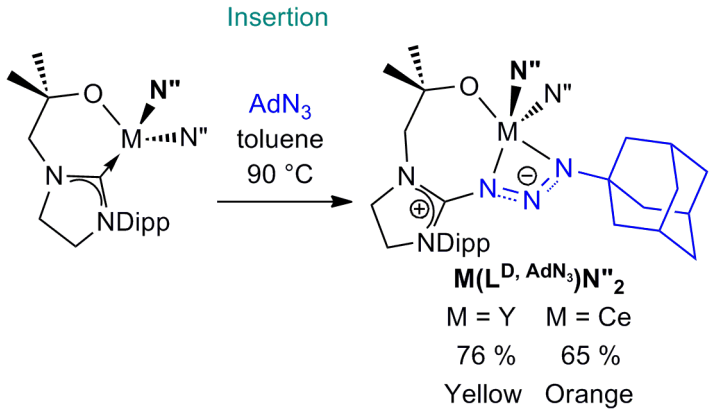


Figure 6: Molecular structures comparable with $U(L^D)_2I_2$

3.3.2 Further attempted addition-elimination reactivity: organic azides

Attempts to complete the addition reaction of an organic azide, AdN_3, with $M(L^D)N''_2$ (M = Y, Ce) resulted in no reaction at room temperature. Heating to 80 ºC in toluene for 16 h led to an insertion of the azide into the M-$C_{carbene}$ bond to form $M(L^{D, AdN_3})N''_2$ as yellow (M = Y) and orange (M = Ce) solids in 76 % and 65 % yield respectively (Equation 6). No loss of N_2 was observed on heating a solution of $Ce(L^{D, AdN_3})N''_2$ to 80 ºC under a partial static vacuum.



Equation 6: Insertion of AdN_3 in the M-$C_{carbene}$ bond of $M(L^D)N''_2$ (M = Y or Ce)

Diffraction-quality crystals were grown for both $M(L^{D,\ AdN_3})N''_2$ (M = Y or Ce) from a toluene solution at -20 ºC. The data confirmed the connectivity of the molecular structures but were not of sufficient quality for a detailed discussion of the metrical parameters. The displacement ellipsoid plot is shown for $Ce(L^{D,\ AdN_3})N''_2$ (Figure 7). The inserted triazenido group is $\kappa^2N^{1,3}$ bound to the cerium metal centre, forming a covalent bond to the $C_{carbene}$ atom. The complex is zwitterionic, with a positive charge on the N-heterocyclic ring and a negative charge on the N_3 group to achieve charge balance. As a result, the N_3 group is clearly bent with respect to the linear arrangement in the AdN_3 starting material.

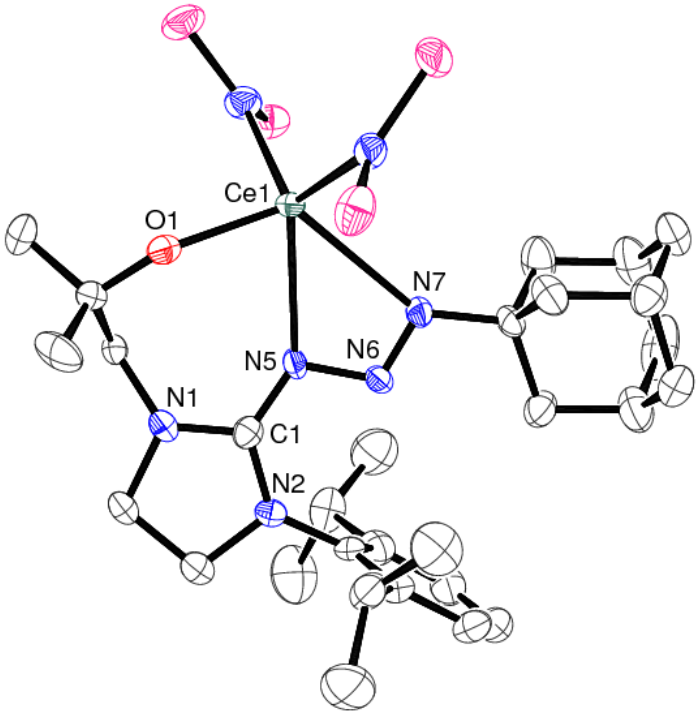
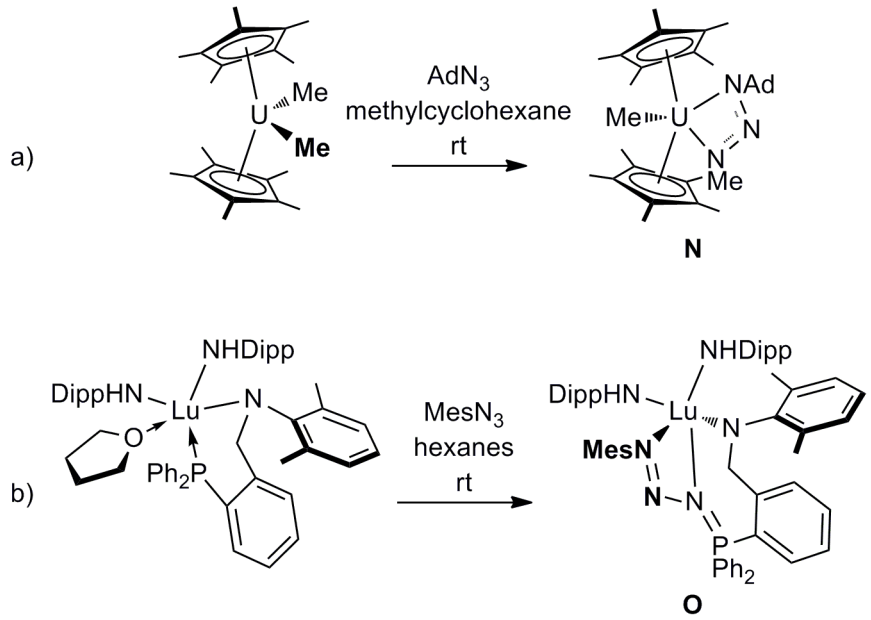


Figure 7: Displacement ellipsoid plot (50 %) of $Ce(L^{D,AdN_3})N''_2$

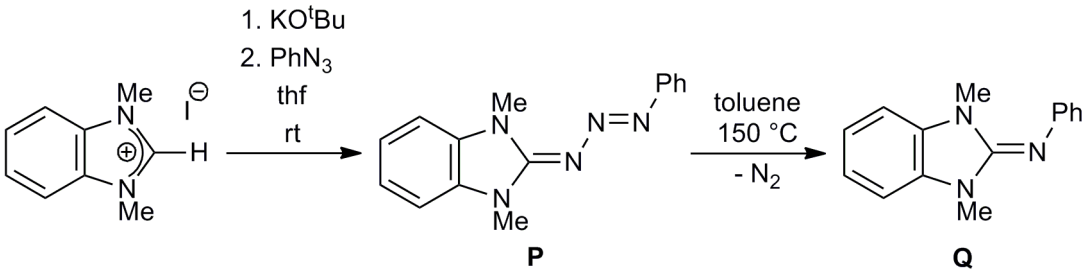
Lattice solvent molecules and silyl Me groups omitted for clarity

This binding mode has been previously reported whereby AdN_3 inserts into the U-Me bond of Cp^*UMe_2 to form **N**, $Cp^*UMe(Me\text{-}\kappa^2N^{1,3}\text{-}N_3Ad)$ (Equation 7a)).[34] $MesN_3$ reacts with the lutetium *bis*(amido) complex $Lu(L)(NH\text{-}2,6\text{-}^iPr\text{-}C_6H_3)_2(thf)$ (L = $(2,6\text{-}Me\text{-}C_6H_3)NCH_2C_6H_4PPh_2$) by insertion into the Lu-P bond rather than the Lu-N amide bonds to afford **O**, $Lu(L\text{-}P\text{-}N_3Mes)(NH\text{-}2,6\text{-}^iPr\text{-}C_6H_3)_2$ (Equation 7b)).[35] However, there are no examples of insertion into a metal-ligand dative bond. Organic azides have been shown to typically react with transition metal complex *via* insertion reactions and cycloadditions.[36]



Equation 7: An example of the insertion chemistry of AdN_3 with Cp^*UMe_2 (**N**) and $MesN_3$ with $Lu(L)(NH\text{-}2,6\text{-}^{i}Pr\text{-}C_6H_3)_2(thf)$ (**O)**

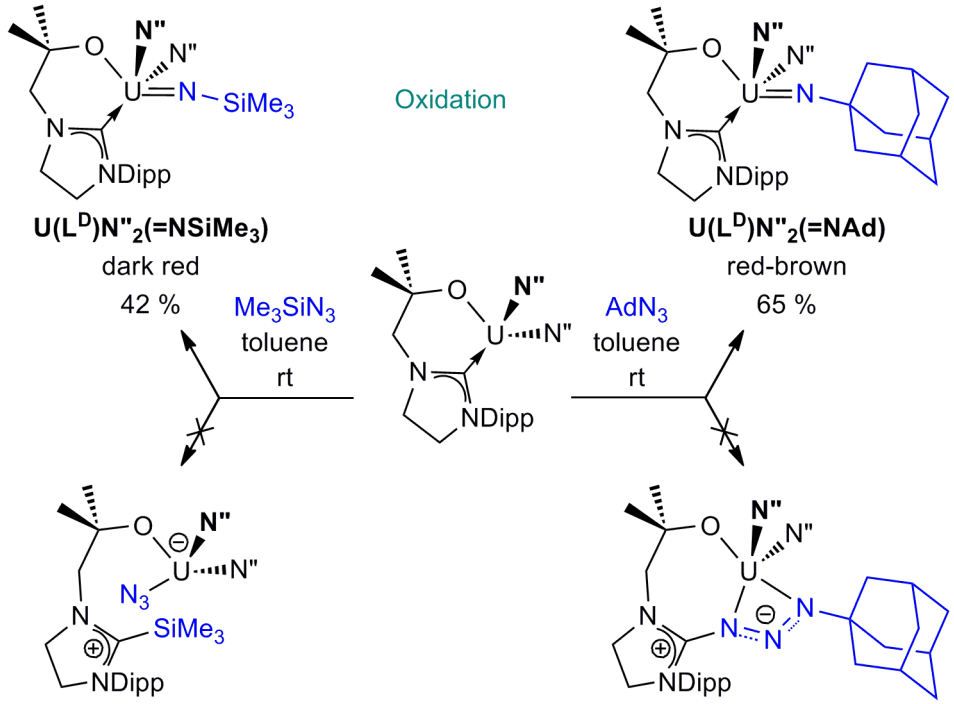
Imidazolin-2-ylidenes (free or generated *in situ*) have been demonstrated to react with alkyl or aryl azides to form stable triazenes (for example, **P**, Scheme 4). These triazenes can be forced to extrude N_2 at high temperature (> 120 ºC) to form 2-iminoimidazolines (for example, **Q**, Scheme 4).[37,38] Mechanistic studies using ^{15}N-labelled triazenes are consistent with the overall process following the mechanism of the Staudinger reaction.[39] Combining *bis*(NHC)s and *bis*(azides)s has been reported to form polytriazenes which were thermally stable and showed good optical and electronic properties.[40]



Scheme 4: Reaction of imidazolin-2-ylidenes with alkyl and aryl azides to form triazenes (**P**) and 2-iminoimidazolines (**Q**)

Whereas the reactions of $M(L^D)N''_2$ (M = Y or Ce) with Me_3SiN_3 and AdN_3 resulted in addition across the $M\text{-}C_{carbene}$ bond and insertion into the $M\text{-}C_{carbene}$ bond respectively, their reaction with $U(L^D)N''_2$ resulted in the formation of the U^V imido complexes,

$U(L^D)N''_2(=NSiMe_3)$ and $U(L^D)N''_2(=NAd)$ (Scheme 5). AdN_3 and Me_3SiN_3 have both been previously reported as oxidising agents that form U^V imido complexes.[41-44]



Scheme 5: Reactivity summary of $U(L^D)N''_2$ with the azides, Me_3SiN_3 and AdN_3

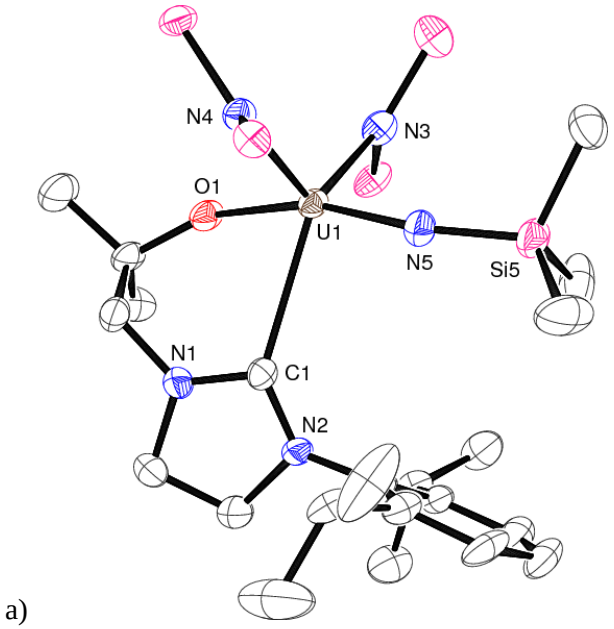
Diffraction-quality crystals of both $U(L^D)N''_2(=NSiMe_3)$ and $U(L^D)N''_2(=NAd)$ were grown from toluene solutions at -20 ºC. The displacement ellipsoid plots (Figure 8) and selected bond lengths (Å) and angles (º) are provided (Table 4).

Table 4: Selected bond lengths (Å) and angles (º) of $U(L^D)N''_2(=NSiMe_3)$ and $U(L^D)N''_2(=NAd)$

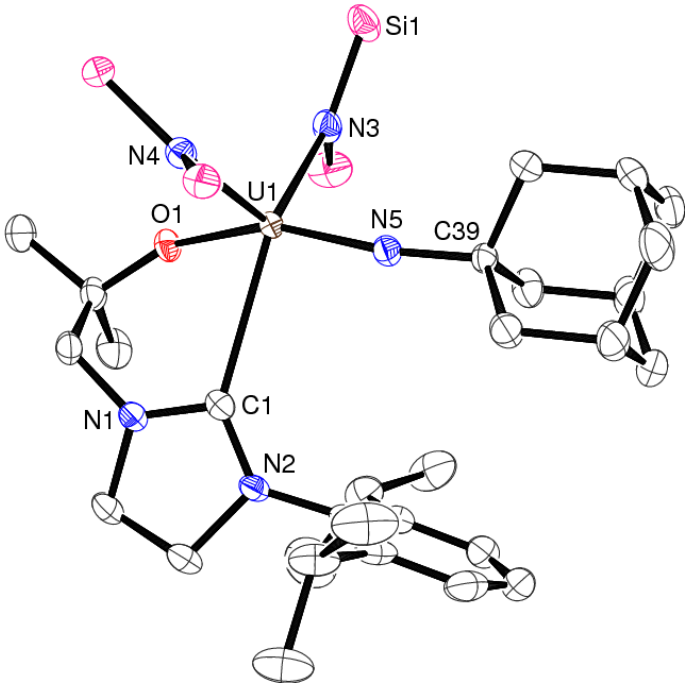
	$U(L^D)N''_2(=NSiMe_3)$	$U(L^D)N''_2(=NAd)$
U1-C1	2.772(5)	2.828(2)
U1-N5	1.924(4)	1.9296(18)
U1-N3	2.313(4)	2.3179(19)
U1-N5-C39	-	165.70(15)
U1-N5-Si5	159.6(2)	-

In both molecular structures, the coordination geometry of the metal centre is distorted trigonal bipyramidal with the equatorial plane defined by the two amide ligands and the carbene. In accordance with previously reported imido complexes, the U1-N5 bond lengths of $U(L^D)N''_2(=NSiMe_3)$ and $U(L^D)N''_2(=NAd)$ are short (1.924(4) Å and 1.9296(18) Å respectively) and significantly shorter than the U-N_{amide} bond lengths (U1-N3 =

2.313(4) Å and 2.3179(19) Å). The reason for the longer U1-N5 bond length in U(L^D)N"$_2$(=NAd) is likely to be a steric effect.



a)



b)

Figure 8: Displacement ellipsoid plots (50 %) of
a) U(L^D)N"$_2$(=NSiMe$_3$) and b) U(L^D)N"$_2$(=NAd)
H atoms and selected silyl Me groups omitted for clarity

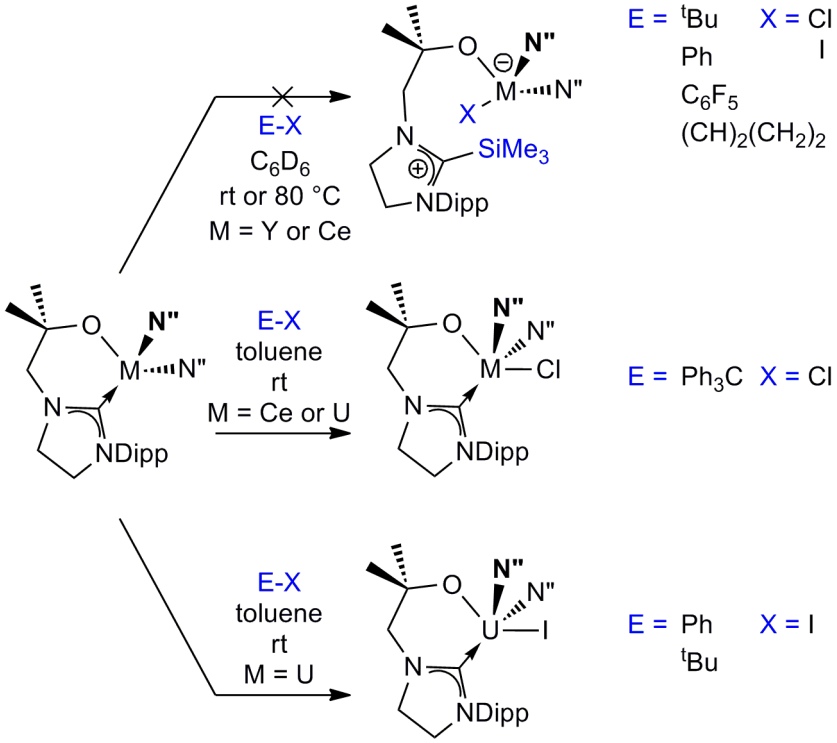
Though there are a number of examples of uranium imido complexes, none are supported by an N-heterocyclic carbene. In the only other two uranium imido complexes where the metal centre is five-coordinate, the trigonal bipyramidal U^{VI} complexes **R**,

$UN''_3F(=NSiMe_3)$ and **S**, $UN''_3F(=NPh)$,[45] the $U\text{-}N_{imido}$ bond lengths are 1.854(23) Å and 1.979(8) Å respectively. In $U(L^D)N''_2(=NSiMe_3)$ and $U(L^D)N''_2(=NAd)$, the U1-N5-Si5 and U1-N5-C39 angles are approaching linearity (159.6(2)º and 165.70(15)º) as are the $U\text{-}N_{imido}$-C bond angles in **R** and **S** (178.3(11)º and 173.5(7)º respectively) (Figure 9).

Figure 9: Five-coordinate uranium imido complexes

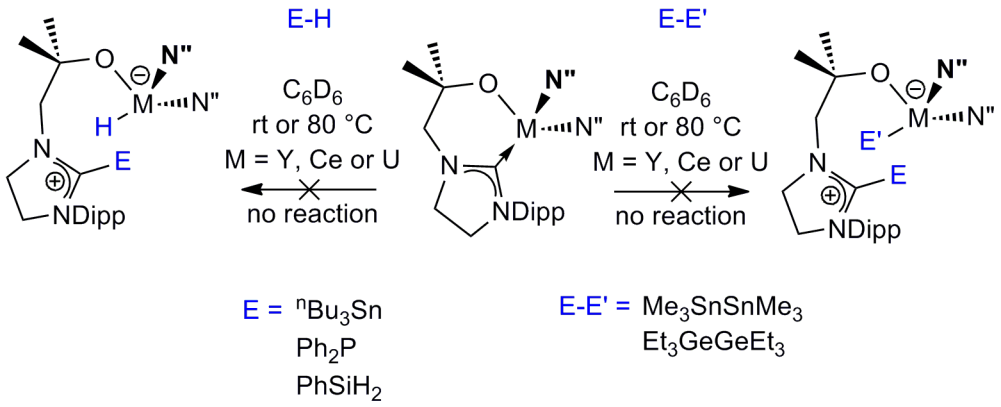
3.3.3 Further attempted addition-elimination reactivity: new E-X, E-H and E-E' reagents

$M(L^D)N''_2$ (M = Y, Ce or U) were also reacted with a number of other E-X reagents (E = alkyl or aryl group) in order to extend the addition-elimination reaction to the formation of C-N bonds. However, for $M(L^D)N''_2$ (M = Y, Ce or U), no reactivity was observed (the only reactions observed were the one electron oxidations of $M(L^D)N''_2$ (M = Ce of U) to $M(L^D)N''_2X$ (X = Cl or I) previously discussed in section 2.5.1. This suggests that the nature of the electrophile transferred to the N-heterocyclic ring is an important factor (Scheme 6).



Scheme 6: Reactivity of $M(L^D)N''_2$ (M = Y, Ce or U) with E-X (E = aryl or alkyl, X = halide)

In a similar way, E-E' and E-H reagents (where E and E' are main group elements) were also tested and no reactivity was observed (Scheme 7).



Scheme 7: Summary of reactions of $M(L^{D})N''_2$ (M = Y, Ce or U) with E-H and E-E'

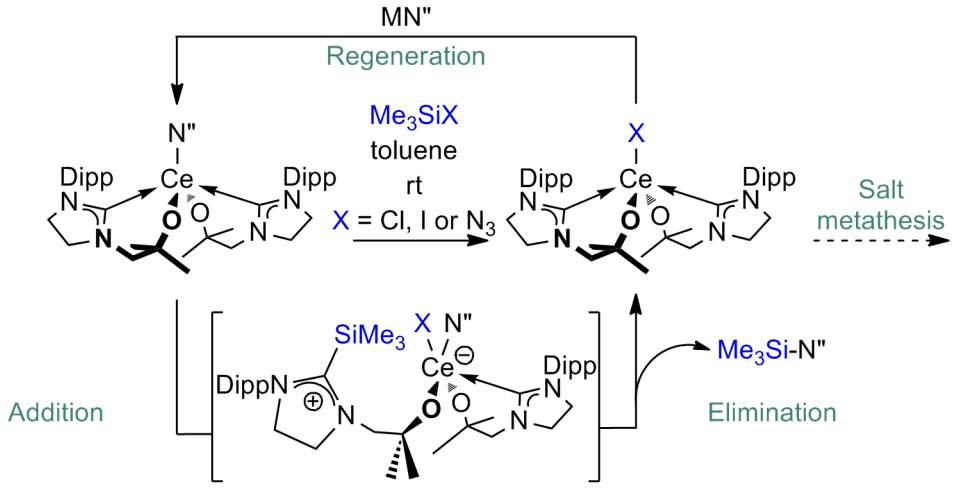
Whereas Ph_2PCl and $^{n}Bu_3SnCl$ led to addition-elimination reactivity, Ph_2PH and $^{n}Bu_3SnH$ resulted in no reaction. The dissociation energies of E-Cl bonds (for the diatomic species) are generally higher (Sn-Cl = 350 ± 8 kJmol^{-1}, P-Cl ≤ 376 kJmol^{-1}) than those of E-H bonds (Sn-H = 264 ± 17 kJmol^{-1}, P-H = 297 ± 2.1 kJmol^{-1}) and E-E' bonds (Sn-Sn = 187.01 ± 0.3 kJmol^{-1}, P-P = 489.1 kJmol^{-1}) (Table 5).[46,47] Overall, this suggests that the formation of a strong Ce-Cl bond (457.0 kJmol^{-1} for the diatomic species) and use of a polar reagent facilitate the reaction where addition across the M-$C_{carbene}$ bond occurs.

Table 5: A selection of E-X, E-H and E-E' bond dissociation energies (BDE, kJmol^{-1}) and summary of addition-elimination reactivity

Compound	BDE (kJmol^{-1})	Addition-elimination?
CeCl	457.0	-
SnCl	350 ± 8	Y
Me_3SnCl	425 ± 17	Y
PCl	≤ 376	Y
SnH	264 ± 17	N
$^{n}Bu_3SnH$	308.4 ± 8.4	N
PH	297 ± 2.1	N
SnSn	187.01 ± 0.3	N
$Me_3SnSnMe_3$	257.7	N
PP	489.1	N
H_2PPH_2	256.1	N

3.3.4 Further attempted addition-elimination reactivity: $Ce(L^D)_2N''$

Following the success of the addition-elimination cycles identified for the *mono*(ligand) amide complexes, $M(L^D)N''_2$ (M = Y or Ce), the reactions with Me_3SiX (X = Cl, I or N_3) were run with the *bis*(ligand) amide complex, $Ce(L^D)_2N''$ (Scheme 8).



Scheme 8: Anticipated reactivity of $Ce(L^D)N''_2$ with Me_3SiX (X = Cl, I or N_3)

If the analogous reactivity seen in section 3.3.1 occurred, then addition across the M-$C_{carbene}$ bond followed by N-Si bond formation and elimination of N''' would generate $Ce(L^D)_2X$ as the final inorganic product. This could then be converted back to the starting material, $Ce(L^D)_2N''$ (using MN''), or converted (through salt metathesis reactions) to new *bis*(ligand) complexes (Scheme 8).

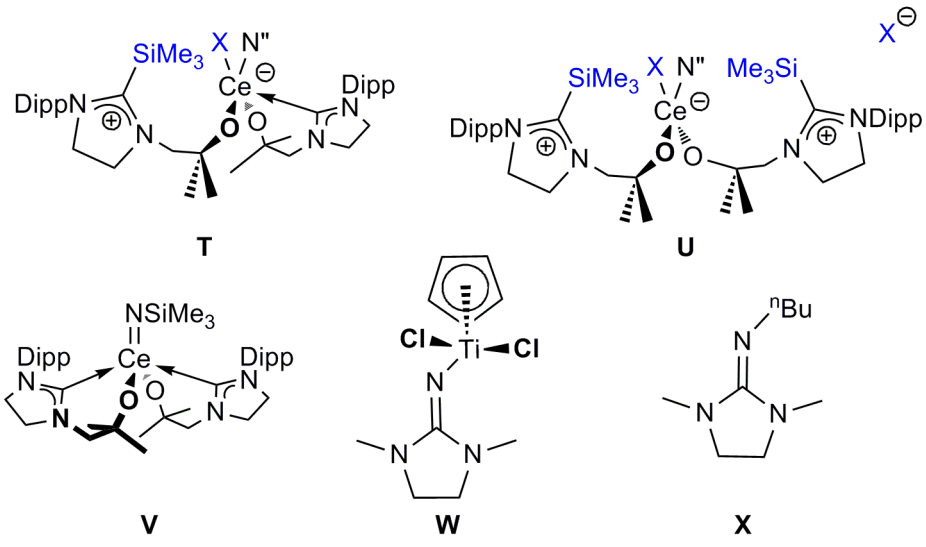


Figure 10: Potential products (**T** – **V**) from reaction of $Ce(L^D)_2N''$ with Me_3SiX (X = Cl, I or N_3)

In all three cases, after work up, the same ^{1}H NMR spectrum was obtained and indicated that the major product formed was diamagnetic and contained only one set of ligand resonances. The $^{13}C\{^{1}H\}$ NMR spectrum also contained one set of ligand resonances which included a high frequency resonance at 243.5 ppm. The organic reaction byproducts could not be identified.

The diamagnetic NMR spectra imply the one electron oxidation of Ce^{III} ($[Xe]4f^{1}$) to Ce^{IV} ($[Xe]4f^{0}$) and the high frequency resonance at 243.5 ppm is indicative of a $C_{carbene}$ bound to an electropositive Ce^{IV} centre (it compares well with the $C_{carbene}$ resonance in the Ce^{IV} complex, $Ce(L^{D})N''_{2}Cl$, section 2.5.1). The single ligand environment indicates that both ligands are either bound to the metal centre or that they are both attached at only one point, most likely through the alkoxide group as the $M\text{-}O_{alkoxide}$ bond is stronger than the $M\text{-}C_{carbene}$ bond. Though the ^{1}H NMR spectrum obtained for $Zn(L^{D})_{2}$ (section 2.3.1) was asymmetric, it is feasible that this would not be the case for a $Ce(L^{D})_{2}$ fragment, owing to the larger ionic radius of Ce^{IV} with respect to Zn^{II} under the same coordination environment ($rZn^{II,\ 6C.N.}$ = 0.74 Å, $rCe^{IV,\ 6C.N.}$ = 0.87 Å).[4] These results indicate that single or double addition of Me_3SiX across a $M\text{-}C_{carbene}$ bond, to form **T** or **U** respectively, has not occurred (Figure 10); in this case, there would be no oxidation of the metal centre and the resonance accounting for the C_{NCN} of the N-heterocyclic ring would appear at the much lower frequency expected of an imidazolidinium species. The reaction also appears to be independent of the nature of the X group in Me_3SiX (X = Cl, I or N_3).

Potential *bis*(ligand) Ce^{IV} complexes include a Ce^{IV} imido species, **V** (Figure 10), for which the NMR spectral data would be consistent. Theoretical calculations have suggested that the existence of a terminal Ln=N imido bond is possible,[48] and very recently, the first scandium imido complex was isolated.[49] The formation of 2-iminoimidazolidines, **W** and **X**,[50,51] (Figure 10) can also be ruled out as the frequency of the NCN carbon in the $^{13}C\{^{1}H\}$ NMR spectrum is significantly lower than would be observed in these cases.

3.3.5 Small molecule activation: Ph_2CN_2

Diazoalkanes have often been used in organometallic synthesis owing to their reactive nature,[52] which can broadly be split into two groups: reactivity involving either the loss or retention of N_2. Diazoalkanes can be drawn as several resonance forms and multiple binding modes to metal centres have been documented,[53] on which subsequent reactivity is often dependent (Figure 11).

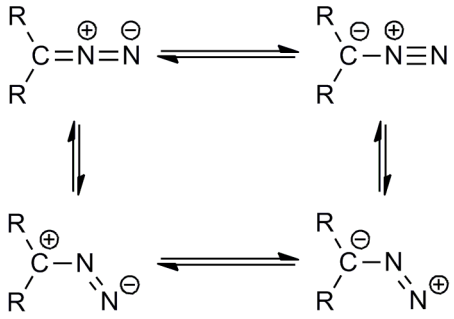
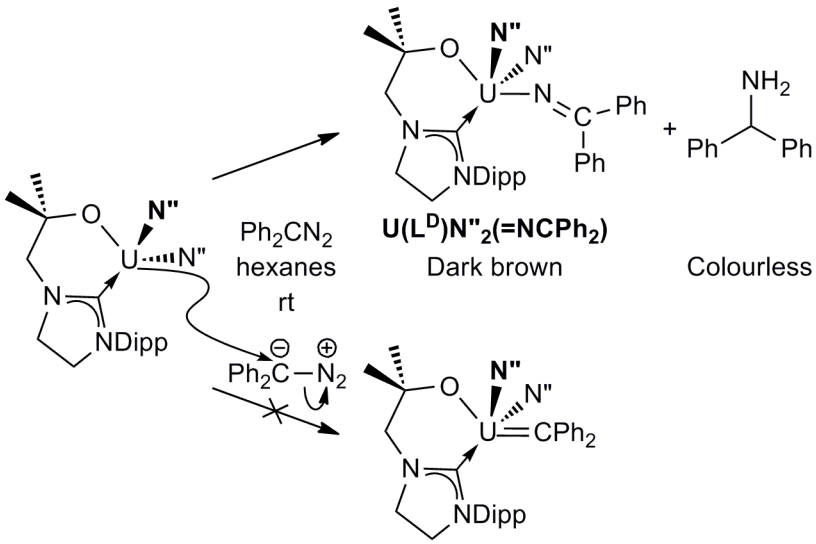


Figure 11: Diazoalkane resonances forms

The use of diazoalkanes as reagents of f-element organometallic chemistry is much more limited but they have been used in the synthesis of imido complexes and hydrazonato complexes,[54,55] as well as reactive coordination complexes.[56] The 'diazo route' as a method for the synthesis of transition metal carbene complexes has been well documented and mechanistic studies show that it likely proceeds through the formation of an η^1-C diazo complex which subsequently undergoes loss of N_2 to form a metal carbene complex.[57-59] It is dependent on steric factors and requires the metal centre to have a vacant coordination site. While there are a few examples of characterised UC-ylid type multiple bonds, terminal uranium alkylidenes are yet to be isolated and could hopefully provide more information about the roles of the f-orbitals in the stabilisation of such reactive species.[60]

Treatment of $U(L^D)N''_2$ with 1 equivalent of Ph_2CN_2 at room temperature afforded a dark brown solution. From this, dark brown and colourless single crystals of the ketimido complex $U(L^D)N''_2(N{=}CPh_2)$ and amine H_2NCHPh_2, respectively, were grown (Scheme 9). They could not be separated by sequential recrystallisations.



Scheme 9: Reactivity of $U(L^D)N''_2$ with the diazo compound Ph_2CN_2

A small number of uranium ketimido complexes have previously been prepared.[61-66] The ligand is of interest because it has the ability to act as both σ- and π-donor and so, it can help to probe f-element ligand bonding further (already evidenced by molecular spectroscopy and DFT studies).[67,68] While ketimido complexes are traditionally synthesised by the salt metathesis reactions of a metal halide with a ketimido salt or protonolysis reactions with ketimines, a number of other routes have been reported.[69] The mechanism of formation of $U(L^D)N''_2(N{=}CPh_2)$ is not through any of these reported routes and has not yet been able to be identified.

$U(L^D)N''_2(N{=}CPh_2)$ was characterised by a single crystal X-ray crystallographic study. The displacement ellipsoid plot (Figure 12) and selected bond lengths (Å) and angles (º) (Table 6) are given.

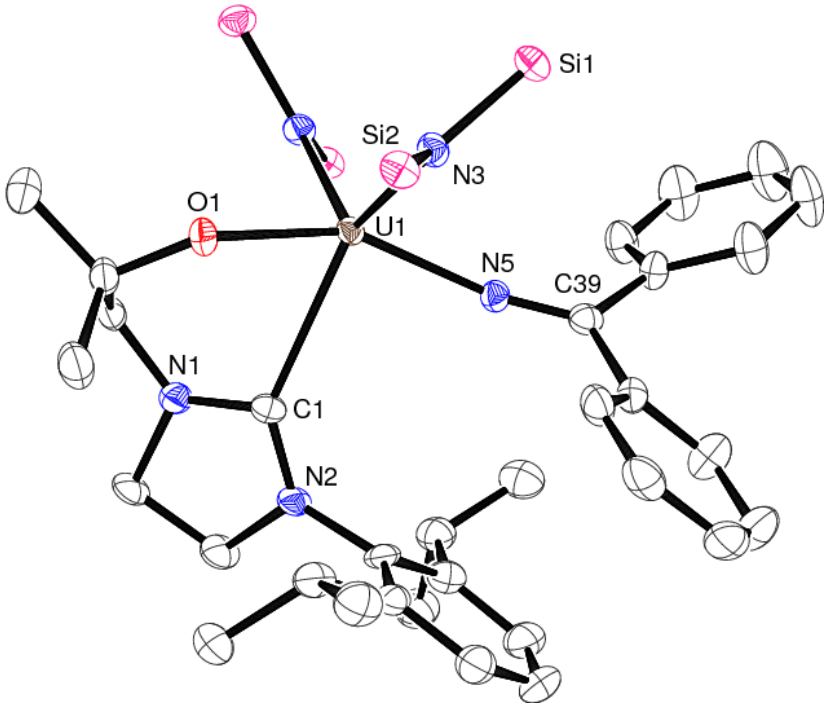


Figure 12: Displacement ellipsoid plot (50 %) of $U(L^D)N''_2(NC{=}Ph_2)$
H atoms and selected silyl Me groups omitted for clarity

Table 6: Selected bond lengths (Å) and angles (º) of $U(L^D)N''_2(NC{=}Ph_2)$

U1-C1	2.719(5)
U1-N5	2.226(4)
U1-N3	2.298(4)
U1-N5-C39	159.6(3)

The coordination geometry of the metal centre is distorted trigonal bipyramidal, with the two amide groups and the carbene defining the equatorial plane. The U1-N5 distance (2.226(4) Å) is the longest yet reported (U-$N_{ketimido}$ range = 2.179(6) Å – 2.220(3) Å),[66] significantly longer than the U-N_{imido} bond lengths of U(L^D)N"$_2$(=NAd) (1.9296(18) Å) and U(L^D)N"$_2$(=$NSiMe_3$) (1.924(4) Å) previously discussed and very close to the U1-N3 amide bond length (2.298(4) Å). This implies a bond order closer to 1 and hence little π-donation from the N 2p lone pairs to the uranium centre. The U1-N5-C39 angle (159.6(3)º) is also small compared to reported examples, which further supports that the U-$N_{ketimido}$ bond is single. The phenyl rings of the ketimido ligand are splayed by 58.67º and there is π-π stacking between one ring and the *N*-Dipp aromatic ring, with the distance between the ring centroids being 3.814 Å.[70]

There are two U^{IV} complexes with the $NCPh_2^-$ ketimido ligand: **Y**, Cp*U($NCPh_2$)$_2$[61] and **Z**, Cp*$_2$U(2,6-*N*-Dipp-C_6H_3)($NCPh_2$) (Figure 13).[66] Both have almost linear U-$N_{ketimido}$-C bond angles (**Y**: 173.4(6)º and 176.5(5)º) and **Z**: 178.2(5)º) and shorter U-$N_{ketimido}$ bond lengths with respect to U(L^D)N"$_2$(NC=Ph_2) (**Y**: 2.179(6) Å and 2.185(5) Å and **Z**: 2.199(4) Å). Multiple bond character to the U-$N_{ketimido}$ bond has been suggested for both **Y** and **Z**.

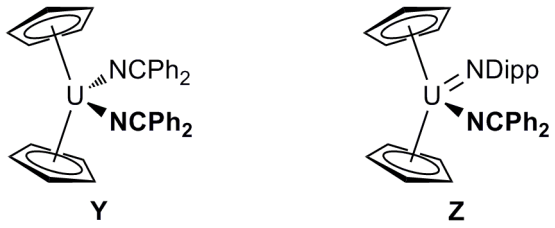
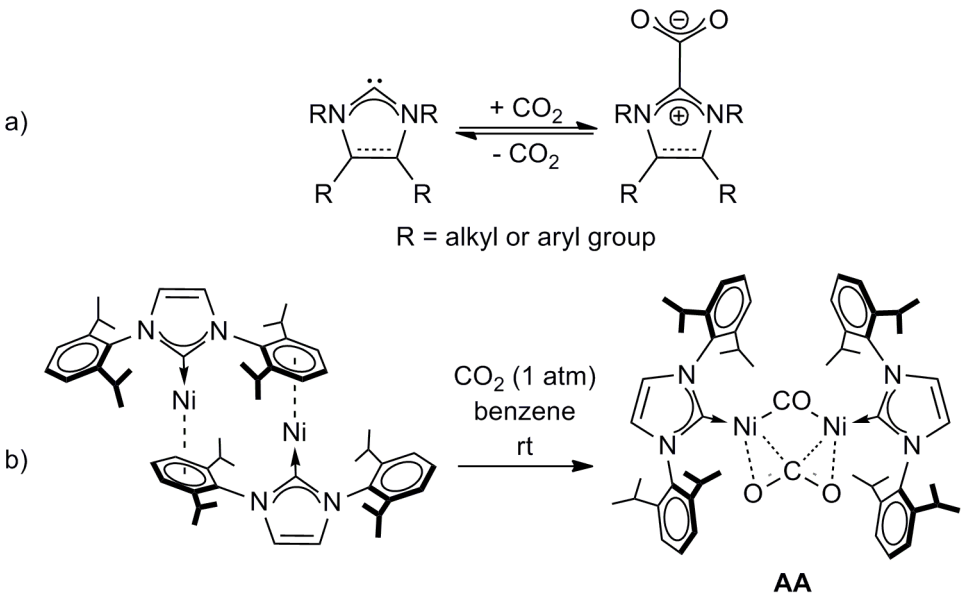


Figure 13: Uranium ketimido complexes with the $NCPh_2^-$ ligand

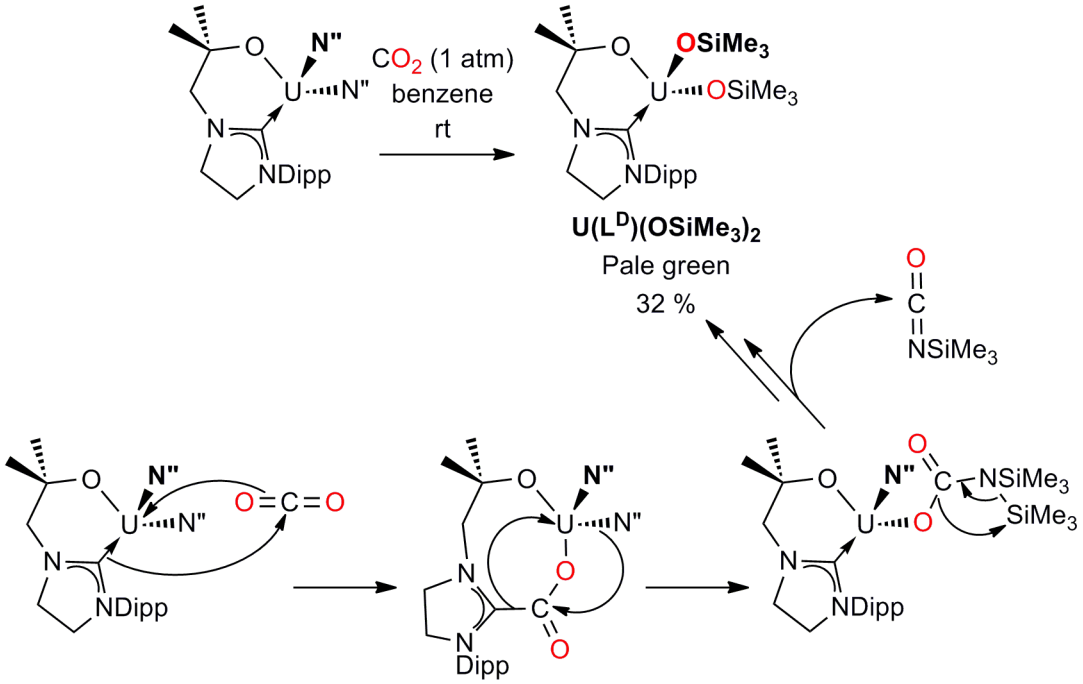
3.3.6 Small molecule activation: CO_2

CO_2 is an abundant, inexpensive natural resource and its utilisation is important given its negative environmental impact. It offers a C_1 building block to make more valuable carbon-containing molecules.[71-74] Transition metals have already been used in CO_2 activation (Equation 8b)),[75-78] but the f-elements offer the potential of previously unknown transformations.[79-85] Saturated and unsaturated backbone N-heterocyclic carbenes reversibly react with CO_2 to form imidazolium and imidazolidinium carboxylates respectively (Equation 8a)).[86,87] These carboxylates have been used as ligand transfer reagents for the formation of transition metal complexes,[88] CO_2 transfer to organic substrates such as ketones, aldehydes and alcohols and in halogen-free ionic liquids.[89,90] They have been shown to be catalysts for the co-polymerisation of CO_2/epoxide,[91] cyclotrimerisation of isocyanates,[92] carbonate synthesis,[93] and reduction of CO_2 to methanol.[94]



Equation 8: a) Reaction of free NHCs with CO_2 to form carboxylates and b) Reaction of a Ni NHC complex to form a dinuclear complex (**AA**) with bound CO_2.

The dimeric $[Ni(L)]_2$ (L = 1-C(NDippCH)$_2$) mediates the disproportionation of CO_2 to CO and CO_3^{2-}.[95] This results in the formation of **AA**, $[Ni(L)]_2(\mu\text{-CO})(\mu\text{-}\eta^2,\eta^2\text{-}CO_2)$ and a Ni^{II} carbonate complex (which could not be isolated cleanly) (Equation 8b)). A single crystal X-ray diffraction study of **AA** shows that the C-O bond lengths in the bound CO_2 group (1.2552(19) Å and 1.257(2) Å,) are lengthened with respect to free CO_2 (1.16 Å).



Scheme 10: Reaction of $U(L^D)N''_2$ with CO_2

Treatment of $M(L^D)N''_2$ (M = Y or Ce) with CO_2 immediately resulted in the precipitation of a colourless (M = Y) or pale yellow solid (M = Ce). In both cases, NMR spectral analysis of the solution showed broad resonances in the diamagnetic spectral region (10 ppm – 0 ppm) including resonances for HL^D. After isolation, NMR spectral analysis of the precipitate (which was soluble solely in C_5D_5N) only contained resonances for HL^D and so the reaction was not pursued further. Reaction of $U(L^D)N''_2$ with CO_2 instantly afforded a pale green-brown solution and a fine green precipitate, which is proposed to be $U(L^D)(OSiMe_3)_2$ in 32 % yield (Scheme 10).

The isolated product was poorly soluble in common deuterated solvents which did not allow for satisfactory ^1H NMR spectra analysis. IR analysis (nujol mull) indicated an absorption band at 2183 cm^{-1}.

The insertion of CO_2 into metal-silylamide bonds has been previously reported, with accompanying release of trimethylsilyl isocyanate and/or 1,3-*bis*(trimethylsilyl)carbodiimide [96,97] Insertion was shown to occur into all metal-silylamide bonds present. Though further analysis is required, we propose that the carbene first nucleophilically attacks a molecule of CO_2 to afford a metallacyclic intermediate. Rearrangement reforms the U-$C_{carbene}$ bond and results in the elimination of 1 equivalent of isocyanate (ν = 2183 cm^{-1}) and the formation of $U(L^D)N''(OSiMe_3)$, which reacts further to yield $U(L^D)(OSiMe_3)_2$ (Scheme 10). The likely driving forces of the reaction are the release of this volatile isocyanate, which is entropically favourable, and the formation of a strong U-O bond and O-Si bonds.

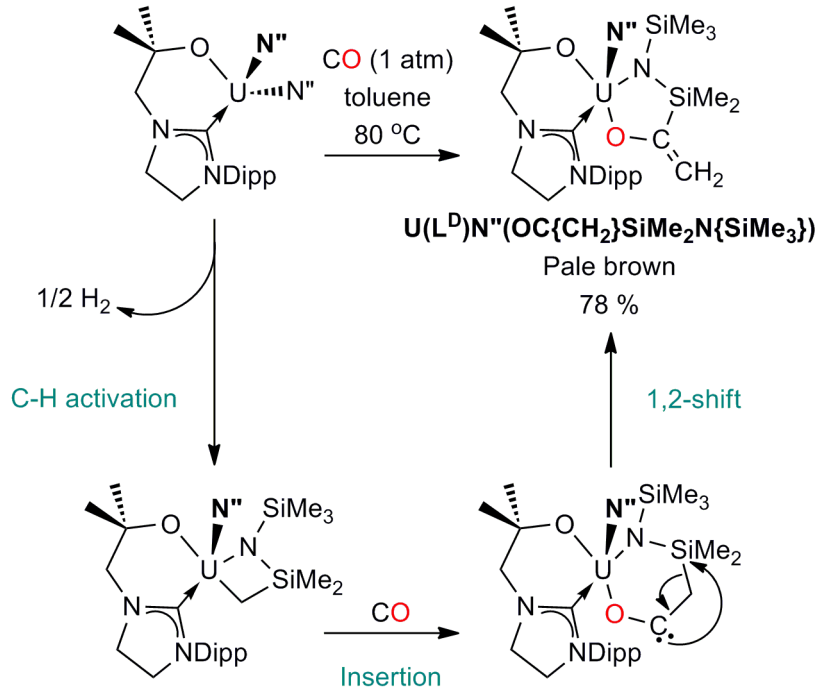
The reaction of UN''_3 with CO_2 was examined in order to clarify the above reaction Treatment of a toluene solution of UN''_3 with CO_2 at ambient temperature and pressure immediately afforded a pale green solution. The elemental analysis was consistent with the formation of $U(OSiMe_3)_3$, the product of three insertions of CO_2 into the M-N_{amide} bond.

3.3.7 Small molecule activation: CO

Despite the ubiquitous nature of transition metal carbonyl complexes,[98,99] simple carbonyl coordination complexes of the lanthanides are not known and remain rare for the actinides. Stabilisation of metal carbonyl complexes comes from synergic bonding; electron donation from the filled σ orbital on carbon into an empty metal orbital of the same symmetry and similar energy and back π-donation from filled metal π orbitals into the empty π^* antibonding orbital of the CO ligand. Such carbonyl complexes are stabilised by low oxidation state metals which have electrons available for back donation.

The rarity of uranium carbonyl complexes is therefore surprising,[84,100-103] as uranium can exist in a range of oxidation states (U^{III} – U^{VI}) and has both 6d and 5f orbitals available for bonding. Early actinide carbonyl complexes are stabilised, with respect to lanthanide carbonyl complexes, by the superior overlap of their valence orbitals (which are both more polarisable and a better energy match for CO) with those of the carbonyl ligand. Therefore, we decided to investigate at the reactivity of M(L^D)N"$_2$ (M = Y, Ce and U) with CO.

No reaction was observed with M(L^D)N"$_2$ (M = Y or Ce) with CO at room temperature or on heating at 80 ºC. This is not unexpected, given the reasoning above. Though addition of CO at ambient pressure and temperature to U(L^D)N"$_2$ resulted in no reaction, heating at 80 ºC for 7 days afforded the pale brown CO insertion product, U(L^D)N"(OC{CH_2}SiMe_2N{$SiMe_3$}), which was isolated in 78 % yield (Scheme 11). It has been characterised by ^{1}H NMR spectroscopy, elemental analysis and X-ray crystallography.



Scheme 11: Proposed mechanism for the formation of U(L^D)N"(OC{CH_2}SiMe_2N{$SiMe_3$})

The reactivity of uranium complexes with CO has commonly been limited to CO insertion into uranium-hydrocarbyl and -amide bonds and this form of reactivity was observed with U(L^D)N"$_2$ also.[104-110] The mechanism suggested first involves the intramolecular C-H activation of a silylmethyl group to form the four-membered metallacycle with the concomitant loss of 1/2 H_2. This four-membered ring is strained and reactive as a result; CO inserts into the U-C bond which is thermodynamically more favourable than insertion into the U-N bond. The resulting carbenoid complex then

undergoes a classical 1,2-shift reaction to afford U(L^D)N"(OC{CH_2}$SiMe_2$N{$SiMe_3$}) (Scheme 11). This mechanism has been proposed previously in a small number of reactions involving early transition metals and actinide metals but has not been proven.[104,111-114]

When the reaction to form U(L^D)N"(OC{CH_2}$SiMe_2$N{$SiMe_3$}) was monitored by ^{1}H NMR spectroscopy, only starting material and the insertion product were visible in the NMR spectra during the reaction. This is consistent with the metallation being the rate-limiting step. The reaction is affected by the steric profile of the *N*-R groups; a long reaction time and forcing conditions are required for U(L^D)N"$_2$ but, in the analogous complex U(L^M)N"$_2$ (M = mesityl = 2,4,6-Me-C_6H_2), where the less sterically demanding *N*-Mes groups are utilised, the reaction occurs over the course of only a few hours at room temperature.[23] In an attempt to isolate the proposed metallacyclic reaction intermediate, U(L^D)N"$_2$ was heated to 80 ºC for 7 days under a partial static vacuum in an N_2 atmosphere. Over this time, a small amount of decomposition was observed in the ^{1}H NMR spectrum but no resonances to indicate the presence of H_2 or the metallacyclic intermediate.

Single crystals were grown from a toluene solution at -20 ºC. The displacement ellipsoid plot (Figure 14) and selected bond lengths (Å) and angles (º) are provided (Table 7).

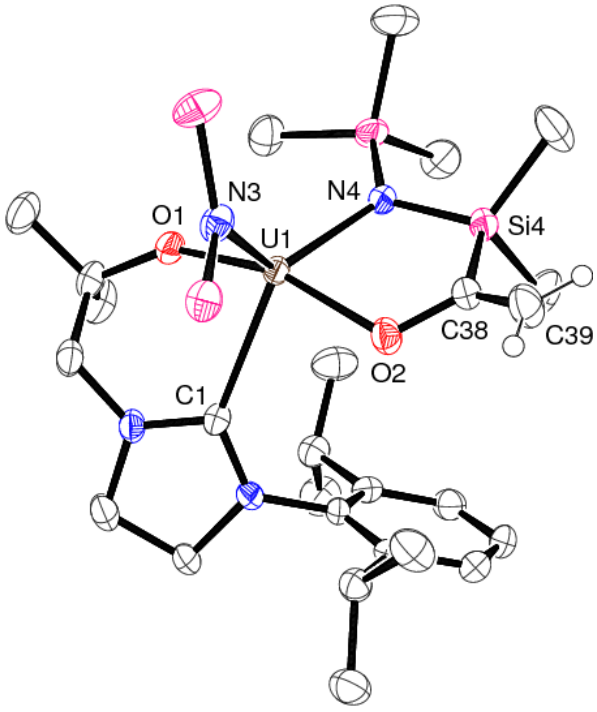


Figure 14: Displacement ellipsoid plot (50 %) of U(L^D)N"(OC{CH_2}$SiMe_2$N{$SiMe_3$}) H atoms (except for those bound to C39) and silyl Me groups omitted for clarity

Table 7: Selected bond lengths (Å) and angles (º) of U(L^D)N"(OC{CH_2}$SiMe_2$N{$SiMe_3$})

C1-U1	2.630(6)
O1-U1	2.084(5)
O2-U1	2.151(5)
C38-C39	1.330(10)
O1-U1-O2	161.87(19)
N3-U1-N4	123.9(2)

The U^{IV} centre is in a distorted trigonal bipyramidal geometry, with the amide and carbene ligands defining the equatorial plane. CO is incorporated into a five-membered metallacyclic ring. The C38-C39 bond distance (1.330(10) Å) is consistent with a double bond. The metrical parameters of the five-membered metallacycle are in good agreement with the only other molecular structures that contain this M(OC{CH_2}$SiMe_2$N{$SiMe_3$}) ring motif: **AB**, [TiN"$_2$(OC{CH_2}$SiMe_2$N{$SiMe_3$})][Na(12-crown-4)$_2$][111] and **AC**, [VN"(OC{CH_2}$SiMe_2$N{$SiMe_3$})]$_2$ (Figure 15).[112]

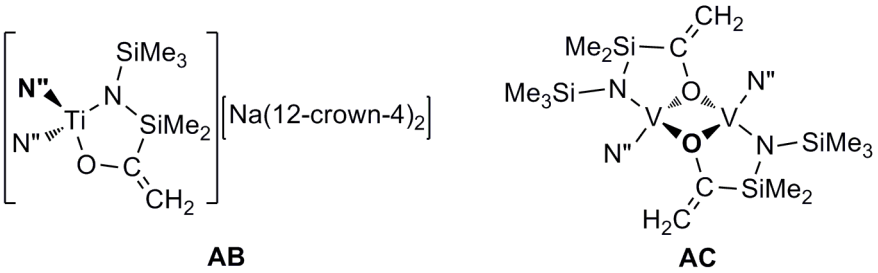
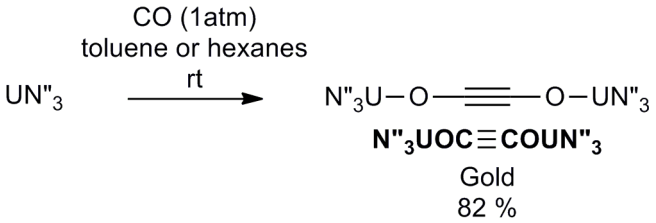


Figure 15: Structurally characterised examples of complexes with the M(OC{CH_2}$SiMe_2$N{$SiMe_3$}) motif

Following this interesting example of reactivity, we decided to complete the control reaction of UN"$_3$ with CO, though it has been previously reported as inert towards CO.[115] Addition of CO to a purple solution of UN"$_3$ at ambient pressure and temperature resulted in a gradual colour change to amber and the formation of golden crystals of N"$_3$UOC≡COUN"$_3$ in 82 % yield (Equation 9).

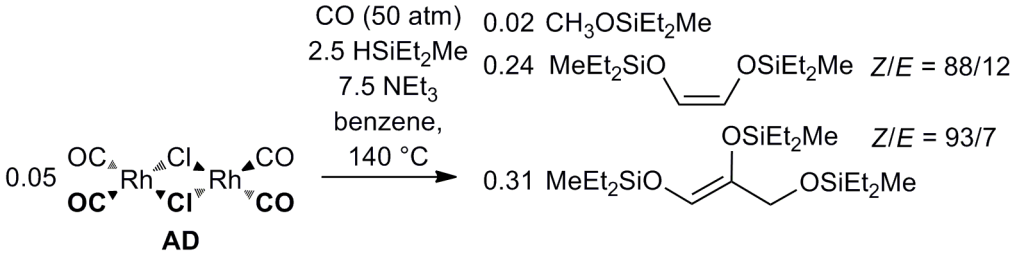


Equation 9: Reductive coupling of CO by UN"$_3$

This is the product of reductive coupling of CO between two uranium centres to form the ynediolate core ,$^{-}$OC≡CO^{-}, with resulting oxidation of U^{III} to U^{IV}. The reaction proceeds in both toluene and hexanes but not in the donor solvents, thf and pyridine, which suggests that their competing coordination to the U^{III} centre inhibits the reaction. The original report of the inertness of UN"$_3$ towards CO is noted not to have included the details of the solvent in which the reaction was attempted.[115]

There is increasing demand placed on non-renewable resources and uncertainty of remaining supplies or crude-oil.[116] CO, principally derived from coal and biomass, has an important role in meeting future energy demands through synthesis gas (CO + nH_2) in the Fischer-Tropsch process for the catalytic production of hydrocarbons and oxygenated complexes.[117-119] It is also used world-wide as a C_1 building block in bulk chemical synthesis, such as the Cativa or Monsanto processes for the production of acetic acid from methanol,[120] and hydroformylation for the synthesis of aldehydes.[121]

The CO bond is the strongest in the periodic table and the process of direct CO coupling to form O=C=C=O is thermodynamically unfavourable (ΔG^{o} = + 306.7 kJmol^{-1}).[122] There are a number of examples of systems which can achieve reductive coupling of CO containing transition metals[123-128] lanthanides,[129,130] and actinides,[131-135] though only one other organometallic example of the formation of an ynediolate ($C_2O_2^{2-}$ = $^{-}$OC≡CO^{-}) complex.[133] Many of these systems require elevated pressure or temperature, the formation of $C_nO_n^{2-}$ (n > 2) is rare and none are catalytic at lower pressures and temperatures;[136] for example, the homobimetallic rhodium complex **AD**, $[RhCl(CO)_2]_2$ was reported to catalytically oligomerise CO under high pressures (50 atm) at 140 ºC over a period of 2 – 5 days in the presence of a hydrosilane (Equation 10).[137] GC-MS analysis suggested that C_1 – C_5 products were formed and isolated alkenyl products showed a high *E*/*Z* selectivity. The reaction intermediates were not isolated but the mechanism was proposed to proceed through metal carbyne and metal dioxyacetylene complexes. As such, the reductive homologation of CO by a well-defined catalytic homogeneous system under ambient conditions is an important goal.



Equation 10: Catalytic oligomerisation of CO using a rhodium catalyst (**AD**)

The reductive coupling using $UN"_3$ is driven by the one electron oxidation of U^{III} to U^{IV} and formation of two strong U-O bonds. The process is simple (the $UN"_3$ starting material can be made relatively cheaply on a big scale; the precursor silylamide salt currently costs under 100 € mol^{-1}), selective (only the ynediolate complex is isolated in high yield regardless of the stoichiometry) and occurs under ambient conditions.

$N"_3UOC{\equiv}COUN"_3$ has been fully characterised by NMR spectroscopy, elemental analysis and X-ray crystallography. The ^1H NMR spectrum of $N"_3UOC{\equiv}COUN"_3$ contains a single, broad resonance at -8.55 ppm for the SiMe protons. Completing the reaction using ^{13}CO afforded $N"_3UO^{13}C{\equiv}^{13}COUN"_3$. A single resonance was observed in the $^{13}C\{^1H\}$ NMR spectrum at 171.0 ppm for the $^{13}C{\equiv}^{13}C$ carbons. No C≡C stretch was observed in the IR spectrum, which is expected for a symmetrical molecule with no change in dipole moment. An X-ray diffraction study was completed; the ellipsoid displacement plot (Figure 16) and selected bond lengths (Å) and angles (º) are provided (Table 8).

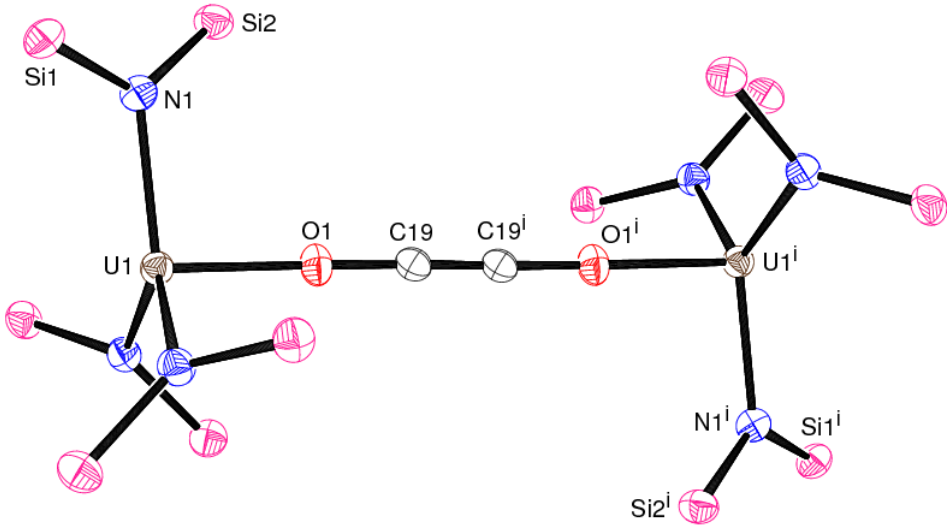
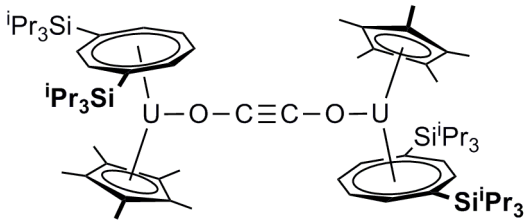


Figure 16: Displacement ellipsoid plot (50 %) of $N"_3UOC{\equiv}COUN"_3$
Lattice solvent molecules, H atoms and silyl Me groups omitted for clarity

Table 8: Selected bond lengths (Å) and angles (º) for $N"_3UOC{\equiv}COUN"_3$

U1-O1	2.101(2)
U1-N1	2.251(3)
O1-C19	1.304(4)
C19-C19^i	1.180(7)
U1-O1-C19	177.5(2)
O1-U1-N1	95.13(10)

The molecular structure of $N"_3UOC{\equiv}COUN"_3$ has D_{3d} symmetry, with the silylamide groups in an antiperiplanar conformation. The C19-C19^{i} bond distance (1.180(7) Å) is comparable to the only other molecular structure with the MOC≡COM motif, **AE**, $(C_8H_6\{1,4\text{-}Si^iPr_3\}_2)Cp^*_2UOC{\equiv}COUCp^*(C_8H_6\{1,4\text{-}Si^iPr_3\}_2)$[133] (1.177(12) Å) (Figure 17) and the UOC≡COU unit is essentially linear (U1-O1-C19 = 177.5(2)º, O1-C19-C19^{i} = 178.6(5)º).

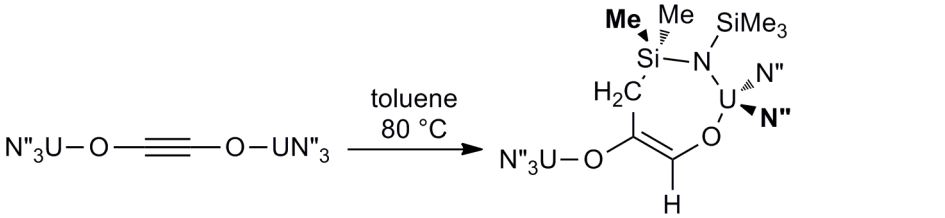


AE

Figure 17: Comparable molecular structure with ynediolate core bound between U^{IV} centres

The pyramidal geometry at the metal centre, seen in $UN"_3$, has been flattened out; the U centre now lies only 0.15 Å above the plane defined by the three N atoms compared to 0.46 Å in $UN"_3$.[115] The U-$N_{average}$ bond distance (2.253 Å) has also decreased with respect to $UN"_3$ (2.320 Å) which agrees with one electron oxidation of the U^{III} metal centre.

Heating a sample of $N"_3UOC{\equiv}COUN"_3$ in toluene at 80 ºC led to the formation of $N"_3UOC{=}C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N"_2$ as a golden solid in 67 % yield. This is the result of the activation and intramolecular addition of a silylmethyl C-H group across the ynediolate to afford an alkene contained within a seven-membered metallacyclic ring (Equation 11).



$N"_3UOC{=}C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N"_2$
Gold
67 %

Equation 11: Functionalisation of $N"_3UOC{\equiv}COUN"_3$ by intramolecular C-H activation

Functionalisation, either inter- or intramolecular, of the ynediolate core has no precedent. In the example of **^{13}C-AE**, $[UCp^*_2(C_8H_6\{1,4\text{-}Si^iPr_3\}_2)](^{13}CO)_2$, the complex was found to undergo no further reaction and this result was supported by a DFT study.[133]

Formation of $C_3O_3^{2-}$ (deltate) and $C_4O_4^{2-}$ (squarate) complexes was found only to be possible through a "zig-zag" transition state before the ynediolate was formed. For $N"_3UOC{\equiv}COUN"_3$, the steric bulk of the silylamide ligands precludes an intermolecular reaction but does allow intramolecular reaction to form a further C-C bond and a C-H bond.

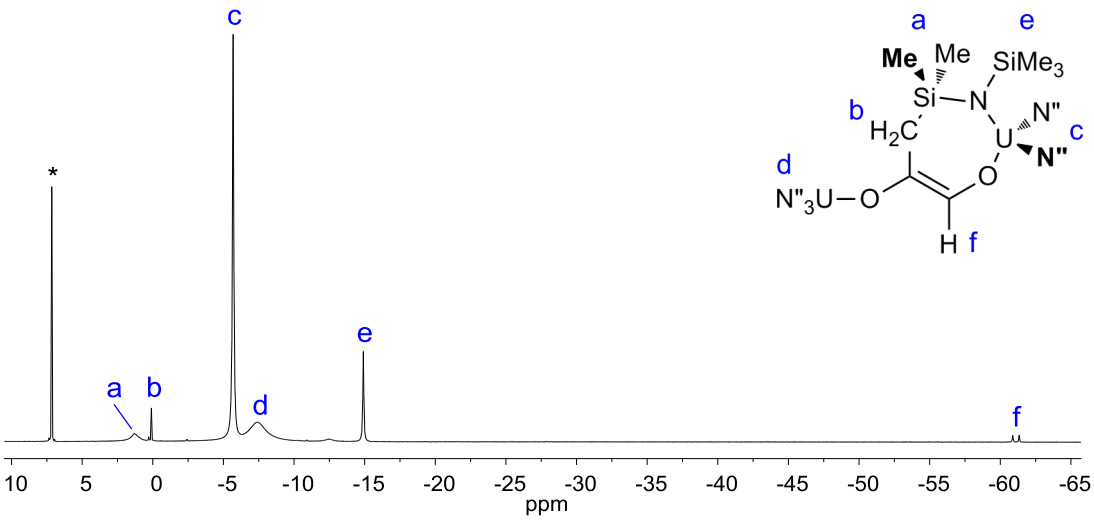


Figure 18: ^{1}H NMR spectrum (C_6D_6, 298 K, 400 MHz) of $N"_3UOC{=}C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N"_2$. '*' indicates residual protio solvent

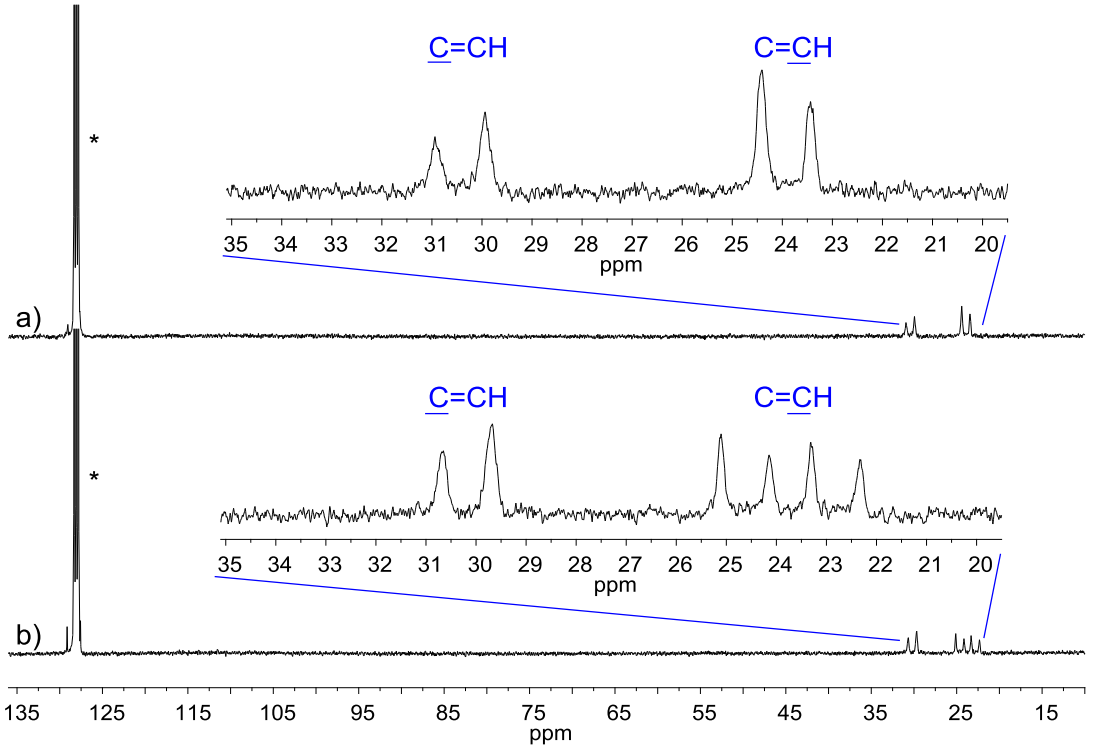


Figure 19: a) $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K, 400 MHz) and b) ^{13}C NMR spectrum of $N"_3UO^{13}C{=}^{13}C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N"_2$. '*' indicates solvent

By completing the reaction using the labelled $N''_3UO^{13}C{\equiv}^{13}COUN''_3$ starting material, $N''_3UO^{13}C{=}^{13}C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N''_2$ was formed. The ^1H NMR spectrum contains six resonances over the range 1.32 ppm – -60.70 ppm. When the ^1H NMR spectrum includes ^1H-^{13}C coupling, the resonance at -60.70 ppm splits into a doublet ($^1J_{CH}$ = 182 Hz) as a result of coupling of the $^{13}C{=}^{13}CH$ proton to the labelled carbon one bond away (Figure 18). The $^{13}C\{^1H\}$ NMR spectrum contains two doublets, as a result of coupling between the two $^{13}C{=}^{13}C$ carbon nuclei, at 30.4 ppm and 23.9 ppm (both $^1J_{CC}$ = 98 Hz) (Figure 19a)). The ^{13}C NMR spectrum contains one doublet for the $^{13}\underline{C}{=}^{13}CH$ carbon at 30.4 ppm ($^1J_{CC}$ = 98 Hz) which couples only to the other labelled carbon and a doublet of doublets at 23.7 ppm for the $^{13}C{=}^{13}\underline{C}H$ carbon ($^1J_{CH}$ = 182 Hz, $^1J_{CC}$ = 98 Hz) which couples to both the neighbouring labelled carbon and the directly attached proton (Figure 19b)). No other resonances are observed in the spectrum.

An X-ray diffraction study was completed and the displacement ellipsoid plot (Figure 20) and selected bond lengths (Å) and angles (º) are provided (Table 9).

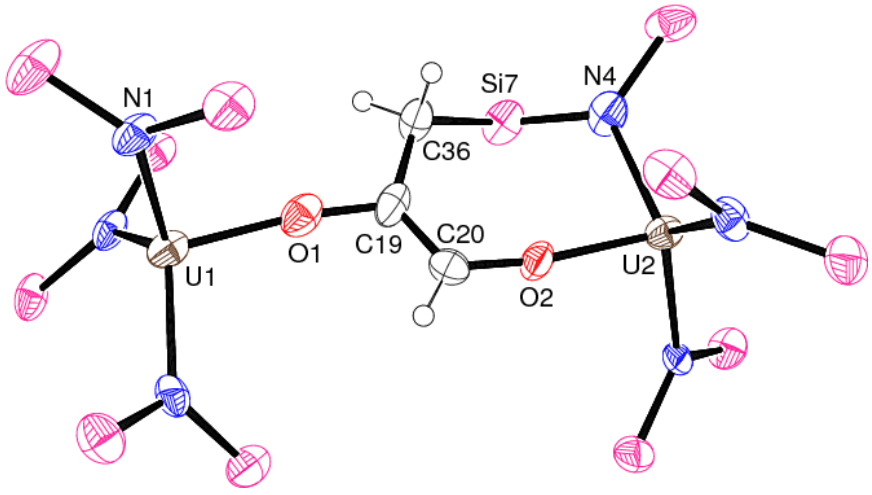


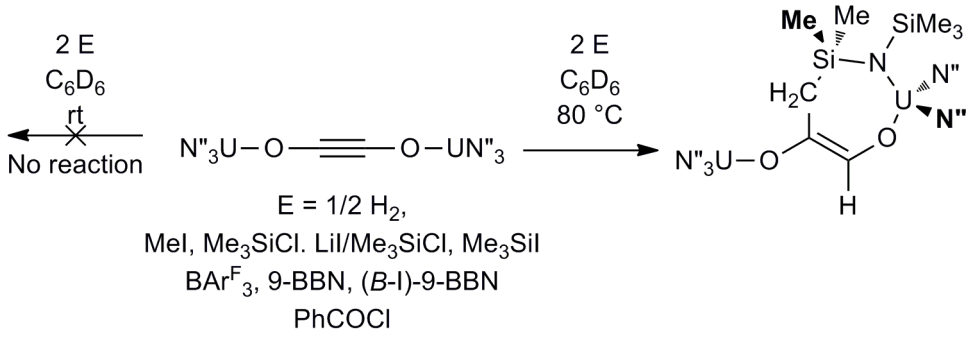
Figure 20: Displacement ellipsoid plot (50 %) of $N''_3UOC{=}C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N''_2$ H atoms (except for those bound to C20 and C36) and silyl Me groups omitted from clarity

The U1 centre is in a pyramidal environment, moving to 0.445 Å from the plane defined by the N atoms. This is in stark contrast to the U2 centre which only now only lies 0.104 Å above this plane, with the sum of the angles around U2 being 359.4º. The C19-C20 bond distance (1.310(13) Å) is consistent with a double bond. This *trans* double bond is part of a seven membered metallacyclic ring, defined by C19=C20-O2-U2-N4-Si7-C36, which is in an envelope type conformation. As in $N''_3UOC{\equiv}COUN''_3$, the UOC=COU unit is near linear.

Table 9: Selected bond lengths (Å) and angles (º) for $N"_3UOC=C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N"_2$

U1-O1	2.093(7)
O1-C19	1.402(11)
C19-C20	1.310(13)
U1-N1	2.242(7)
U1-O1-C19	171.6(6)
U2-O2-C20	170.9(6)
O1-U1-N1	98.9(3)
C36-C19-C20	125.8(9)

In an attempt to isolate the ynediolate core from the uranium ions, a C_6D_6 solution of $N"_3UOC{\equiv}COUN"_3$ was treated with a number of reagents (for example, Me_3SiCl, Me_3SiI and MeI). However, it was found to be unreactive in almost every case at room temperature and heating to 80 ºC led to the formation of the metallacyclic product $N"_3UOC=C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N"_2$, which did not subsequently react further (Scheme 12).



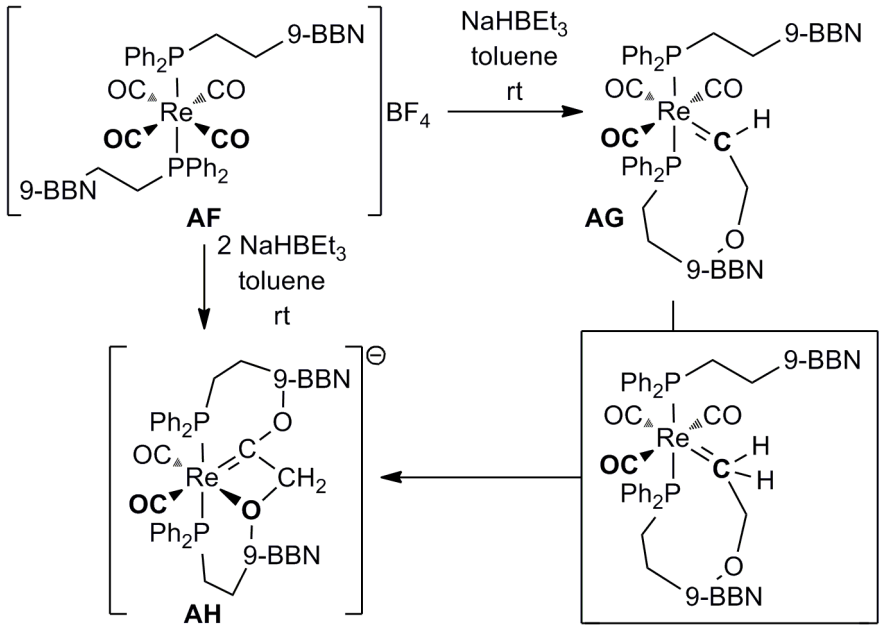
Scheme 12: Attempts to trap the ynediolate core

Examination of general reactivity of $N"_3UOC{\equiv}COUN"_3$ was carried out treating a C_6D_6 solution with, for example, hydrocarbons (CH_4), multiple bonds (PhCCH) and donor solvents (Et_2O) but no reaction was observed at room temperature. Heating the reaction mixture to 80 ºC for 16 h resulted in the formation of $N"_3UOC=C(H)OU(N\{SiMe_2CH_2\}\{SiMe_3\})N"_2$ which did not subsequently react further.

Uranium complexes have already been employed as catalysts, as a result of their unique properties; a range of stable oxidation states, availability of 5f orbitals for bonding and large ionic radius.[138-142] In order to achieve a catalytic cycle, three key processes must occur; the reductive coupling of CO, the isolation of the organic product (HOC≡COH) and

the regeneration of the active catalyst form. A simple system would be the direct reaction of $UN"_3$ with a H_2/CO mixture, where the ynediol would be released and H_2 would also regenerate $UN"_3$. However, reaction with H_2/CO (1/2) led only to the slow formation of $N"_3UOC{\equiv}COUN"_3$. A second alternative explored was the combination of $UN"_3$, a chlorosilane and CO over a bed of Na/Hg amalgam; after CO coupling the silylated $R_3SiOC{\equiv}COSiR_3$ would be generated alongside $UN"_3Cl$ which would be reduced back to $UN"_3$ with Na/Hg. It was first identified that $UN"_3$ did not react with R_3SiCl (R = Me or Ph) under an N_2 atmosphere over a period of 14 days and that $UN"_3Cl$ did not react with CO. The reduction of $UN"_3Cl$ to $UN"_3$ has already been demonstrated (see 2.5.1). However, formation of $N"_3UOC{\equiv}COUN"_3$ occurred on exposure of $UN"_3$ to CO (before any other reaction).

The reduction of C-C coupled species and C-H bond formation is a major challenge in CO coupling chemistry. This was addressed by the phosphinoborane complex **AF**, *trans*-$[Re(Ph_2P\{CH_2\}_2\{9\text{-}BBN\})_2(CO)_4][BF_4]$ which incorporates a pendant Lewis acidic borane group which makes **AF** a better hydride acceptor.[127] Consequently, addition of 1 equivalent of $NaHBEt_3$ results in the reduction of a bound carbonyl group to form **AG**, a seven-membered metallacycle with a Re-CH-O-B linkage. **AG** undergoes further reaction to afford the rhenium carbene complex **AH**, which contains a new C-C bond. It is proposed that this transformation occurs through alkyl migration to CO in an unobserved intermediate which contains a Re-CH_2-O-B link. **AH** can also be formed directly by addition of 2 equivalents of $NaHBEt_3$ to **AF** (Scheme 13). The number and nature of the Lewis acids in this rhenium system have been shown to be have important effects for CO coupling.[143]

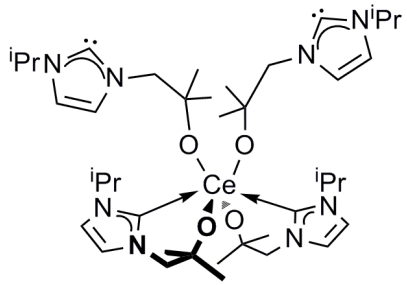


Scheme 13: C-H/C-C bond formation at bound CO groups in a phosphinoborane complex

3.4 Reactivity of M^{IV} amide complexes

3.4.1 Towards Ce^{IV} alkyl species

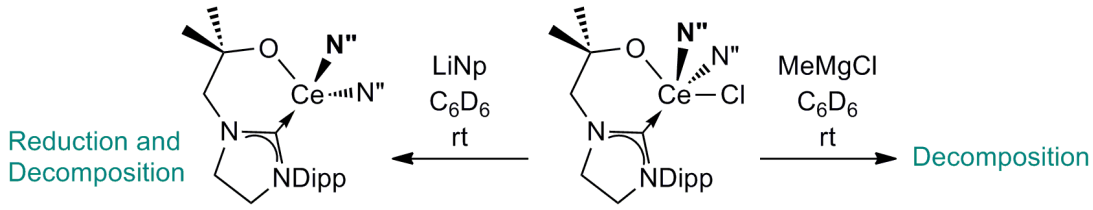
The reactivity of $Ce(L^D)N''_2Cl$ was first investigated with metal alkyl complexes with the aim of salt metathesis and the formation of a Ce^{IV} alkyl complex with a simple two electron σ bond. The synthesis of $Ce(cot)_2$ (cot = cyclooctatetraene)[144] and related complexes,[145-147] combine the highly oxidising Ce^{IV} cation with a reducing ligand and have led to intensive debate over the assignment of the Ce^{IV} oxidation state. Aside from $Ce(L^D)N''_2Cl$, there is only one previous example of a complex with a Ce^{IV}-C σ bond, **AI**, CeL_4 (L = $OCMe_2CH_2(1\text{-}C\{NCH_2CH_2N^iPr\})$,[148] and both involve a dative bond from the NHC $C_{carbene}$ to the metal centre (Figure 21).



AI

Figure 21: The first example of complex containing a Ce^{IV}-C dative bond

$Ce(L^D)N''_2Cl$ was treated with 1 equivalent of LiNp in C_6D_6. ^1H NMR spectroscopic analysis showed that there were a new set of overlapping resonances in a diamagnetic spectral region and resonances for $Ce(L^D)N''_2$ which indicated the reduction of Ce^{IV} to Ce^{III} had occurred. Therefore, the less reducing Grignard reagent MeMgCl was then used. In this case, the ^1H NMR spectrum only showed resonances over a diamagnetic sweepwidth but they were broad and overlapping and could not be assigned to a single product (Scheme 14).



Scheme 14: Reaction of $Ce(L^D)N''_2Cl$ with metal alkyl reagents

3.4.2 Towards Ce^{IV} cationic species

There are no examples of cationic Ce^{IV} complexes in the literature and the combination of a very Lewis acidic metal ion with an overall positive charge could result in new reactivity and the potential to activate, for example, inert small molecules.

$Ce(L^D)N''_2Cl$ was treated with 1 equivalent of BAr^F_3 in C_6D_6 at room temperature to afford a red solution. The ^1H NMR spectrum showed 0.33 equivalents $Ce(L^D)N''_2$, which was not present in the starting material, and a single set of ligand resonances over a diamagnetic sweepwidth of 7.25 ppm – 0.25 ppm (Figure 22). The presence of $Ce(L^D)N''_2$ within the ^1H NMR spectrum cannot be explained but the resonances within the diamagnetic region of the spectrum can be assigned to two potential products, the Ce^{IV} cationic species $[Ce(L^D)N''_2][BAr^F_3Cl]$ or the Ce^{IV} carbene borane adduct $Ce(L^{D,\ BArF_3})N''_2Cl$ (Figure 22).

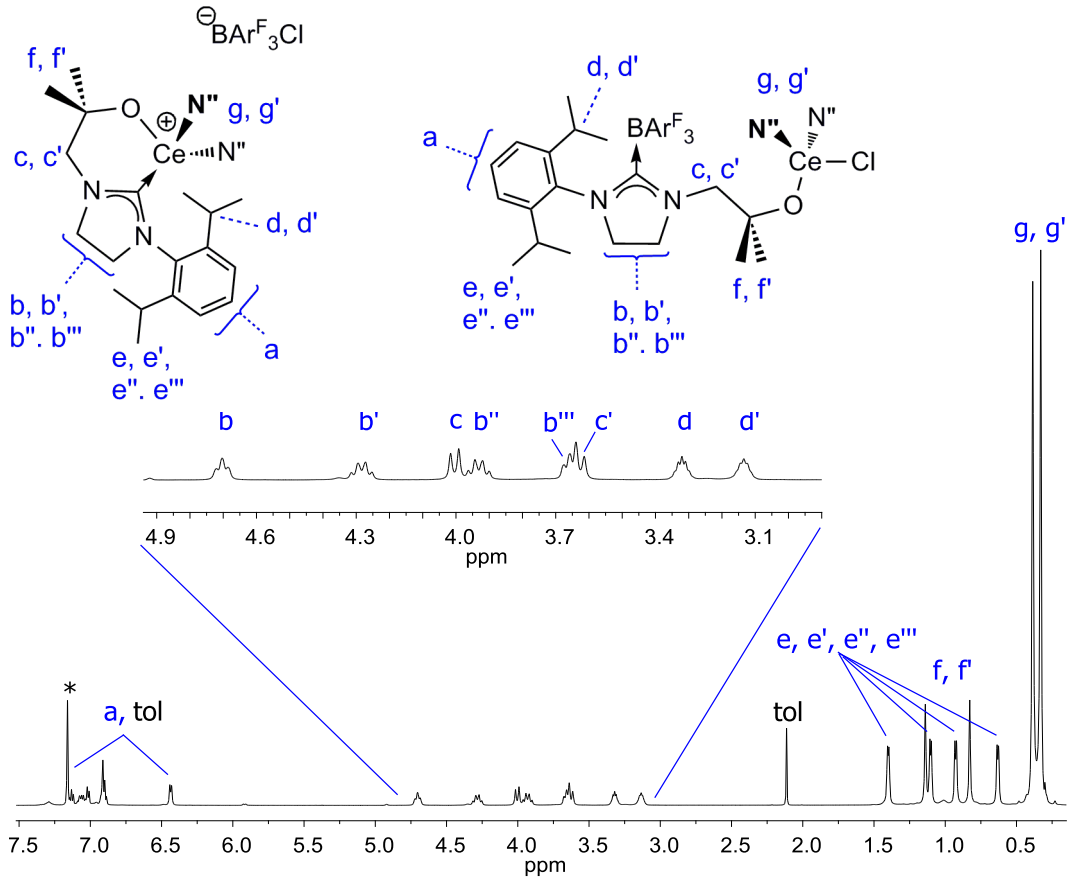
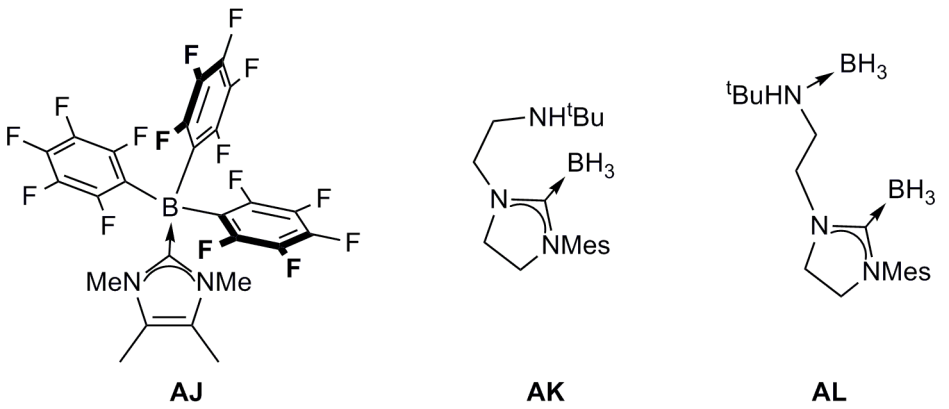


Figure 22: ^1H NMR spectrum (C_6D_6, 298 K, 600 MHz) of the reaction between $Ce(L^D)N''_2Cl$ and BAr^F_3. Only the range 7.52 ppm – 0.15 ppm is shown for clarity.
'*' denotes residual protio solvent and 'tol' denotes toluene

The ^1H NMR spectrum contains a set of magnetically inequivalent proton resonances, implying a rigid and asymmetric final product. Though in $Ce(L^{D,\ BArF_3})N''_2Cl$, the

steric bulk of the *N*-Dipp substituents and the coordinated BAr^F_3 may lead to a rigid part of the structure, it is difficult to see how this would result in the SiMe protons, for example, being magnetically equivalent. In $[Ce(L^D)N''_2][BAr^F_3Cl]$, both the formal cationic charge of the Ce^{IV} fragment and potential interaction of the $BAr^F_3Cl^-$ with the metal centre would result in increased steric crowding which, in turn, could lead to the magnetic inequivalence of both the ligand and the SiMe protons.

The ^{11}B NMR spectrum contains one resonance at -16.4 ppm, which is consistent with the single boron environment. Reported δ values for the $BAr^F_3Cl^-$ anion have been reported to vary over a relatively large range (for example, -0.16 ppm in $[TaCp^*(=NP^tBu_3)Cl_2][BAr^F_3Cl]$[149] to -7.34 ppm in 1-C(N^nBuCHCHNMe)[150]) and so cannot be used reliably to rule out the presence of $BAr^F_3Cl^-$. NHC borane adducts are not numerous but well-defined examples have been characterised.[151-155] An NHC adduct of BAr^F_3 has been reported, **AJ**, 1-C$(NMeCMe)_2$ but only characterised in the solid state (Figure 23).[156] A more sterically demanding NHC (1-C$(N^tBuCH)_2$) did not afford a simple adduct but rather a "frustrated Lewis pair" capable of heterolytically cleaving dihydrogen.[157] Rearrangement to an abnormally bound NHC borane adduct was observed in toluene solution over a 2 h period. The first functionalised NHC adducts of a borane, **AK** and **AL** (Figure 23), were recently reported.[152] In **AK** and **AL** the resonance in the ^{11}B NMR spectrum associated with the carbene-bound boron was at a very similar frequency, -37.1 and -37.4 ppm respectively. However, in the monodentate NHC borane adduct, (L)(anthracene) (L = 1-C(NDippCH$_2$, anthracene = $C_{14}H_{10}$), the ^{11}B NMR spectrum contained a single resonance at 27 ppm. [153]



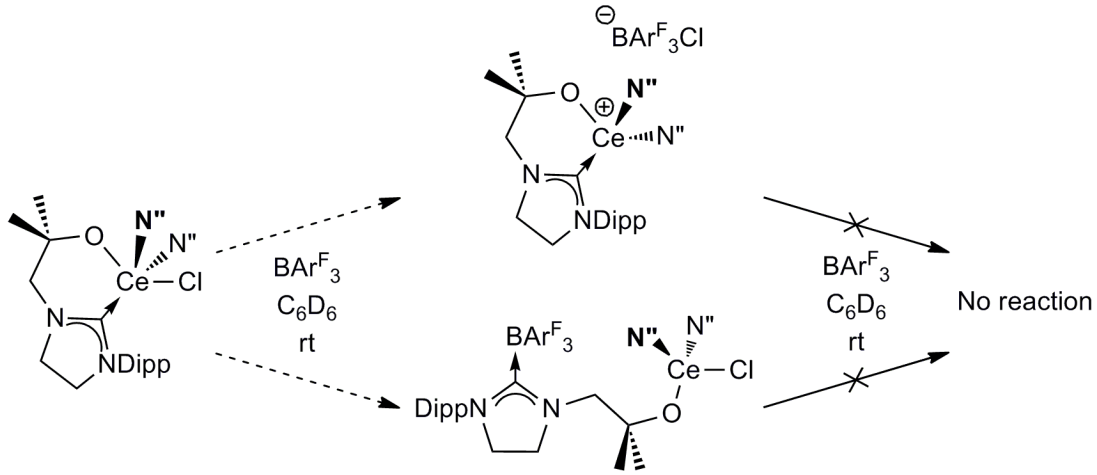
AJ **AK** **AL**

Figure 23: N-Heterocyclic carbene borane adducts

In the $^{13}C\{^1H\}$ NMR spectrum, the asymmetry of the product is also evident. No high frequency $C_{carbene}$ resonance could be detected which would be diagnostic of the Ce^{IV} cationic species and so, though its formation cannot be ruled out with further supporting data, it is likely to be an indication that the $C_{carbene}$ atom is coupling to the quadrupolar B

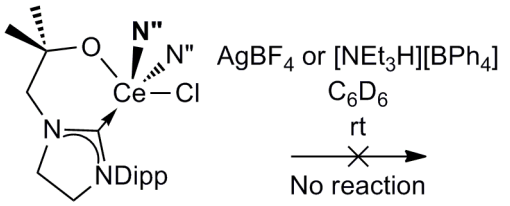
atom in BAr^F_3, broadening the signal in the $^{13}C\{^1H\}$ spectrum. The $C_{carbene}$ resonance was also not reported for **AK** or **AL**.

Addition of a second equivalent of BAr^F_3 did not result in further reaction at room temperature (Scheme 15). Similar NMR spectra were obtained when $Ce(L^D)N''_2Cl$ was treated with $AlMe_3$, also with the aim of producing a cationic Ce^{IV} species. As ^{27}Al is also quadrupolar (I_{Al} = 5/2), $Ce(L^{D,\ AlMe_3})N''_2Cl$ is also suggested as the likely product in this case. NHC allane complexes have also been described;[158,159] with broad $C_{carbene}$ resonances accounting for the $C_{carbene}$ carbon in the $^{13}C\{^1H\}$ NMR spectra reported in the range 175 ppm – 180 ppm.



Scheme 15: Possible products from the reaction of $Ce(L^D)N''_2Cl$ with $B(Ar^F)_3$

Finally, attempts to produce cationic species by reacting $Ce(L^D)N''_2Cl$ with $AgBF_4$ or $[NEt_3H][BPh_4]$ resulted in no reaction (Equation 12).



Equation 12: Reaction of $Ce(L^D)N''_2Cl$ with $AgBF_4$ or $[NEt_3H][BPh_4]$

3.5 Conclusions

Preliminary lactide polymerisation studies were completed with the M^{II} complexes, $M(L^D)N''$ (M = Mg or Zn) and $Zn(L^D)_2$, and all were shown to act as catalysts producing poly(lactide) with reasonable molecular weights and polydispersities.

The M^{III} complexes, $M(L^D)N''_2$ (M = Y or Ce) were used to demonstrate a new form of NHC reactivity, where a range of polar substrates, E-X (E = silyl, boryl, stannyl, phosphoryl and X = halide or *pseudo*halide) were added across the $M\text{-}C_{carbene}$ bond and a new organic product was subsequently eliminated, resulting in N-Si, N-P, N-B or N-Sn formation. The reaction also highlighted the difference in 4f/5f metal reactivity; $U(L^D)N''_2$ reacted with $Me_3Si\text{-}I$ to afford the same addition product across the $M\text{-}C_{carbene}$ bond but underwent rearrangement and oxidation to U^{IV} on elimination of the organic product N'''. Further investigation was completed with a range of substrates, which confirmed that the formation of the strong M-X bond was the driving force for the addition reaction.

Reaction of $M(L^D)N''_2$ (Y, Ce or U) with organic azides did not result in addition-elimination chemistry. Instead, for the complexes where the metal centre oxidation is not favourable (M = Y or Ce), insertion of the azide into the $M\text{-}C_{carbene}$ bond was observed resulting in an unusual $\kappa^2N^{1,3}$ coordination of the triazenido group to the metal centre. Where oxidation is more favourable (M = U), formation of U^V imido complexes occurred in good yield.

While $M(L^D)N''_2$ (M = Y or Ce) did not react with CO, CO was found to insert into a silylamide ligand of $U(L^D)N''_2$ and the mechanism was suggested by examination of similar reactivity within the literature. The formation of a strong U-O bond and the oxidation from U^{III} to U^{IV} drives the reaction. Surprisingly, the simple *tris*(amide) starting material, UN''_3, was found to reductively couple two molecules of CO between two uranium centres at ambient temperature and pressure to yield a ynediolate core. The first example of functionalisation of the ynediolate core then resulted from the intramolecular reaction of a silylamide group to form an enediolate core. Further reactivity studies, with a view towards a catalytic cycle, are ongoing.

The M^{IV} complex, $Ce(L^D)N''_2Cl$ was explored in efforts to create previously unknown Ce^{IV}-C covalent bonds (which are not dative) and Ce^{IV} cationic species. Reactivity with BAr^F_3 and $AlMe_3$ were most promising with respect to the latter, though further work is required to isolate and fully characterise the resulting products.

3.6 References

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Synthesis and reactivity of metal alkyl complexes

4.1 Introduction

Lanthanide and actinide alkyl complexes often display interesting, new transformations as well as being useful homogeneous catalysts for both olefin[1] and polar monomer polymerisation,[2-4] and hydroelementation reactions.[5,6] Their chemistry is dominated by four centre σ-bond metathesis pathways rather than oxidative addition/reductive elimination. There are also very few reported examples of NHC-supported rare earth alkyl complexes.[4,7]

This chapter describes the synthesis and reactivity of well-defined metal alkyl complexes supported by the ligand L^D. These complexes will be used to examine the preparation of metal hydrides and cationic species and to develop the addition-elimination reactivity of polar substrates to metal N-heterocyclic carbene complexes, which was first discussed in Chapter Three, with a view to new C-E (E = Si, Sn, P, B and C) bond formation.

4.2 Synthesis of M^{III} alkyl complexes

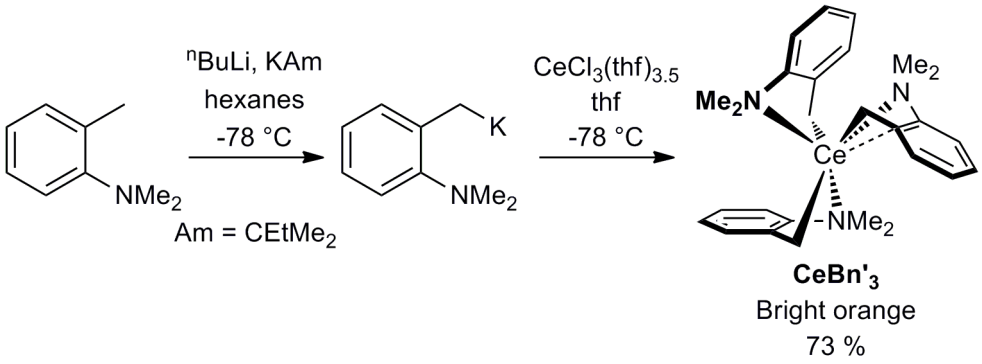
4.2.1 Synthesis of M^{III} benzyl complexes

Rare earth metal *tris*(alkyl) precursors are extremely useful for the synthesis of alkyl complexes by protonolysis reactions. Some of the most commonly used alkyl starting materials are the neosilyl derivatives $M(CH_2SiMe_3)_3(thf)_x$ (M = Y, Sc, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu, x = 2 or M = Sm, x =3) but such complexes can only be prepared for the smaller lanthanides; the alkyl ligand does not provide enough steric protection to stabilise the complexes of larger metal ions, which are highly Lewis acidic and have larger coordination spheres.

The synthesis of the *tris*(*o*-benzylamino) metal complexes MBn'_3 (M = Y (**A**), Sc, La (**B**), Sm, Dy, Ho and Nd, Bn' = 1-CH_2-2-NMe_2-C_6H_4) has been previously described.[8,9] These are attractive starting materials as they are thermally stable, require no donor solvents for stabilisation (the *o*-NMe_2 group can coordinate to the metal centre), can be used for a range of metals with different ionic radii ($rLa^{III,\ 6C.N.}$ = 1.032 Å, $rSc^{III,\ 6C.N.}$ = 0.745 Å)[10] and remain highly reactive due to the basic nature of the coordinated benzylic group. Their use as supporting ligands has been reported in the use of complexes for the polymerisation of

styrene and the copolymerisation of hex-1-ene and dicyclopentadiene.[11,12] Therefore, the synthesis of CeBn'$_3$ was initially investigated as a new route into Ce^{III} alkyl chemistry.

$CeCl_3(thf)_{3.5}$ was treated with KBn' in thf at -78 ºC, in a salt elimination reaction to form CeBn'$_3$, which was isolated as large, bright orange crystals in 73 % yield (Equation 1).



Equation 1: Synthesis of CeBn'$_3$

Single crystals of CeBn'$_3$ were grown from a toluene solution at -30 ºC. The displacement ellipsoid plot (Figure 1) and selected bond lengths (Å) and angles (º) are provided (Table 1).

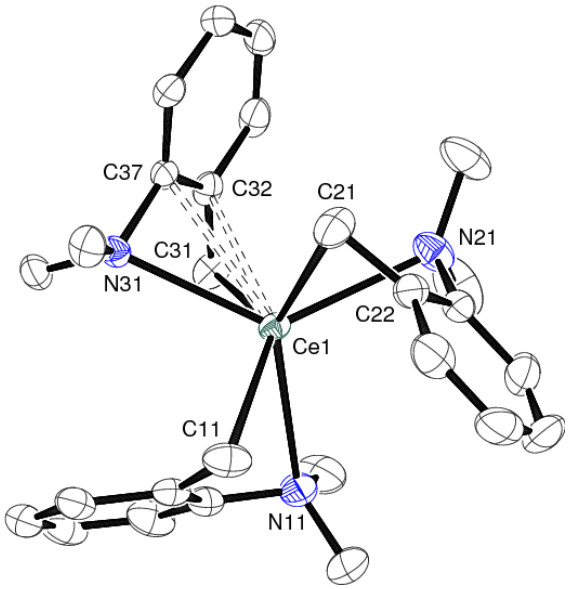


Figure 1: Displacement ellipsoid plot (50 %) of CeBn'$_3$
Solvent molecules and H atoms omitted for clarity. Two representative Ce-C_{ipso} and Ce-C_{ortho} interactions (observed for each ligand) are indicated by dashed bonds.

A number of MBn'$_3$ (M = Y (**A**), La (**B**), Sm, Dy, Ho and Nd) analogues have been previously structurally characterised.[8,9] All MBn'$_3$ are chiral, adopting a six-coordinate trigonal prismatic coordination, whereby the molecular C_3 symmetry is broken by the

rotation of one benzyl ligand by 180º with respect to the other two. This is likely to be a result of steric hindrance between *o*-NMe_2 substituents.

Table 1: Selected bond lengths (Å) and angles (º) for $CeBn'_3$

Ce1-$C_{benzyl,\ average}$	2.617
Ce1-C12	2.9549(18)
Ce1-C22	2.7946(18)
Ce1-C32	2.8464(17)
Ce1-N11	2.6916(17)
Ce1-N21	2.6976(17)
Ce1-N31	2.6379(14)
Ce1-C11-C12	87.50(12)
Ce1-C21-C22	82.86(12)
Ce1-C31-C32	84.22(11)

The configuration about the metal centres can be described as Λ/Δ –meridional (Figure 2) and both enantiomers are present within the unit cell.

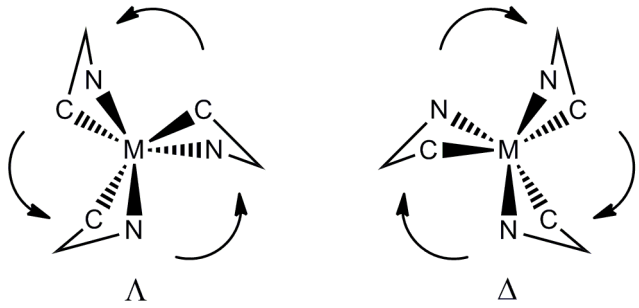
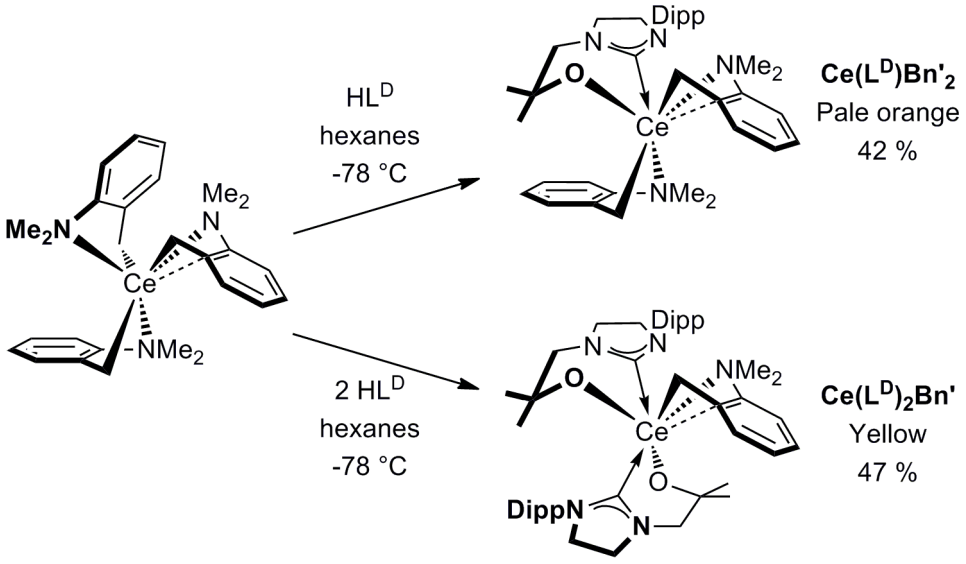


Figure 2: Chirality in MBn'_3 - Λ/Δ –meridional configurations

A and **B** will be compared with $CeBn'_3$. The average M-C_{benzyl}, M-C_{ipso} and M-N bond lengths increase from **A** to $CeBn'_3$ to **B**. This is the trend expected from the ionic radii ($rY^{III,\ 6C.N.}$ = 0.90 Å, $rCe^{III,\ 6C.N.}$ = 1.01 Å and $rLa^{III,\ 6C.N.}$ = 1.032 Å)[10] and consequently, the average ligand bite angle decreases (Y: 68.8°, Ce: 66.3° and La: 64.7°). Additional stabilising interactions between the metal centre and C_{ipso} and C_{ortho} atoms are observed in all three structures; the lanthanum and cerium analogues displaying this multi-hapto bonding in all three ligands. Evidence for this is provided by the M-C_{ipso} bond lengths (which increase less than that expected solely from increasing ionic radius) and the M-C_{benzyl}-C_{ipso} bond angles (which are small as a result of this stabilising interaction). For example, the Ce-$C_{benzyl,\ average}$ bond length (2.617 Å) increases by 0.145 Å relative to Y-$C_{benzyl,\ average}$ bond

length (2.472 Å) which is larger than expected considering the difference in ionic radii (0.11 Å). However, the Ce-$C_{ipso,\ average}$ bond length (2.865 Å) is only 0.064 Å larger than the Y-$C_{ipso,\ average}$ bond length (2.801 Å); this is much less than the difference in ionic radii and so increased multi-hapto bonding in $CeBn'_3$ is implied in order to stabilise the larger coordination sphere of Ce^{III}. For **B**, the La-$C_{benzyl,\ average}$ bond lengths (2.645 Å) are also slightly longer than expected relative to $CeBn'_3$ but the La-$C_{ipso,\ average}$ bond length (2.884 Å) is only 0.019 Å longer than the Ce-$C_{ipso,\ average}$ bond length. This is in line with the increase in ionic radius and so similar metal-ligand bonding is expected.

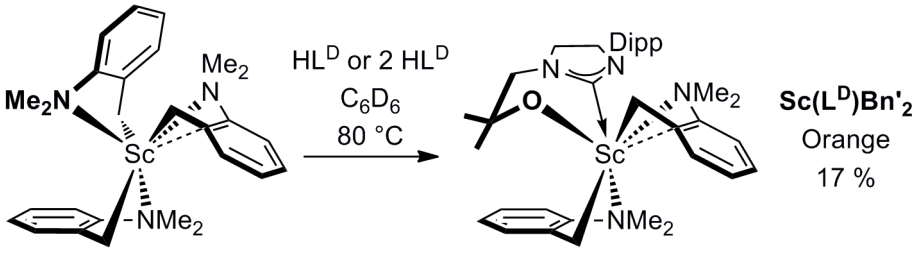
Treatment of $CeBn'_3$ with 1 equivalent of HL^D at -78 ºC in hexanes afforded $Ce(L^D)Bn'_2$ as a pale orange solid in 42 % yield after work-up. Similarly, addition of 2 equivalents of HL^D under the same reaction conditions afforded $Ce(L^D)_2Bn'$ as a yellow solid in 47 % yield (Scheme 1).



Scheme 1: Synthesis of $Ce(L^D)Bn'_2$ and $Ce(L^D)_2Bn'$

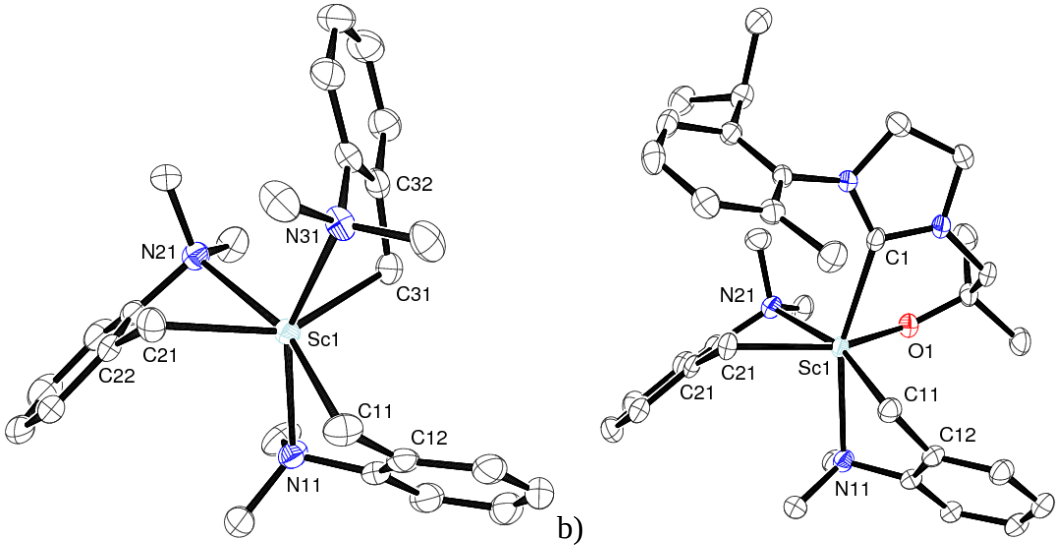
Following the success of the synthesis of $CeBn'_3$ and its subsequent protonolysis reactions with HL^D, the reactivity of $ScBn'_3$ with HL^D was investigated as a useful diamagnetic comparison. Hence, $ScBn'_3$ was treated with 1 equivalent of HL^D in C_6D_6 and heated to 80 ºC for 16 h to afford $Sc(L^D)Bn'_2$ as an orange solid in 17 % yield (Equation 2). When the reaction mixture was heated for less than 16 h, completion was not achieved and $ScBn'_3$ crystallised from the reaction mixture on cooling. The reaction of the yttrium analogue YBn'_3 did not yield an isolable product under the same conditions; the ^1H NMR spectrum showing only broad resonances in the diamagnetic spectral region.

Attempts to form $Sc(L^D)_2Bn'$ by reaction of $ScBn'_3$ with 2 equivalents of HL^D at 80 ºC for 16 h resulted only in the formation of $Sc(L^D)Bn'_2$ alongside unreacted HL^D (Equation 2). Combination of the small ionic radius of Sc^{III} ($Sc^{III,\ 6C.N.}$ = 0.745 Å) and the steric bulk of both benzyl group and NHC ligand precludes the formation of *bis*(ligand) Sc^{III} complexes.



Equation 2: Synthesis of $Sc(L^D)Bn'_2$ and attempted synthesis of $Sc(L^D)_2Bn'$

Single crystals suitable for an X-ray diffraction study were grown of both $ScBn'_3$ and $Sc(L^D)Bn'_2$ from toluene solutions. The displacement ellipsoid plots (Figure 3) and selected bond lengths (Å) and angles (º) are provided (Table 2) for both.



a) b)

Figure 3: Displacement ellipsoid plots (50%) of a) $ScBn'_3$ and b) $Sc(L^D)Bn'_2$
H atoms and selected Me groups are omitted for clarity

As for $CeBn'_3$, the molecular structure of $ScBn'_3$ is six-coordinate trigonal prismatic. In comparison to **A**, YBn'_3; while the Sc1-$C_{benzyl,\ average}$ bond length (2.295 Å) is shorter than expected (2.317 Å), based on the contracted ionic radius of Sc^{III} with respect to Y^{III}, both the Sc1-$N_{average}$ and Sc1-$C_{ipso,\ average}$ bond lengths (2.489 Å and 2.942 Å respectively) are longer than expected (2.411 Å and 2.801 Å respectively). Overall, this results in the molecular structure of $ScBn'_3$ displaying a splayed set of benzylamino ligands. The average

Sc1-C_{benzyl}-C_{ipso} bond angle (100.5º) is much smaller that than of **A** (87.18º), which implies no interactions between the metal centre and the C_{ipso} or C_{ortho} atoms.

Table 2: Selected bond lengths (Å) and angles (º) for $ScBn'_3$ and $Sc(L^D)Bn'_2$

	$ScBn'_3$	$Sc(L^D)Bn'_2$
Sc1-C1	-	2.4442(19)
Sc1-C1-O1	-	81.82(6)
Sc1-C_{benzyl}-$C_{ipso,average}$	100.50	105.58
Sc1-$N_{average}$	2.489	2.507
Sc1-$C_{benzyl,\ average}$	2.295	2.321
Sc1-$C_{ipso,average}$	2.942	3.057

For $Sc(L^D)Bn'_2$, the coordination geometry at the metal centre is six-coordinate prismatic and the L^D ligand has displaced the inverted ligand of $ScBn'_3$. The Sc1-$C_{carbene}$ and Sc1-O1 bond lengths (2.4442(19) Å and 1.9544(14) Å respectively) are comparable to those in the amide complex, $Sc(L^D)N''_2$ (2.4301(17) Å and 1.8870(12) Å) (see 2.4.1).

There are a small number of structurally characterised complexes with *bis*(*o*-benzylamino) coordination to a metal centre and a third mono anionic ligand: **C**, $Sc(L)Bn'_2$ (L = (1-P{1,4-^{t}Bu-2,3-Me-C_4})),[11] **D** (L = (1-N{1,4-^{t}Bu-C_4H_2}))[12] and **E** (L = (1-$SiMe_3$-C_4Me_4))[12] (Figure 4). In each, the metal centre is in a distorted square-based pyramidal geometry, where the benzylamino ligands form the four corners of the base and are coordinated such that the NMe_2 groups are *trans* to each other. The Sc1-C_{benzyl} and Sc1-N bond lengths in $Sc(L^D)Bn'_2$ are slightly longer than those in **C**– **E** but not significantly so, which indicates that the steric bulk of L^D does not have a large effect on bonding in this case. The Sc1-$C_{ipso,average}$ (3.057 Å) and Sc1-$C_{otho,average}$ (3.158 Å) bond lengths are comparable to those in **C** (3.017 Å and 3.108 Å respectively), where it was considered that there were no additional interactions between these atoms. Furthermore, the average Sc1-C_{benzyl}-C_{ipso} angle is large at 105.08º in $Sc(L^D)Bn'_2$, which compares well to 104.37º in **C** (Figure 4).

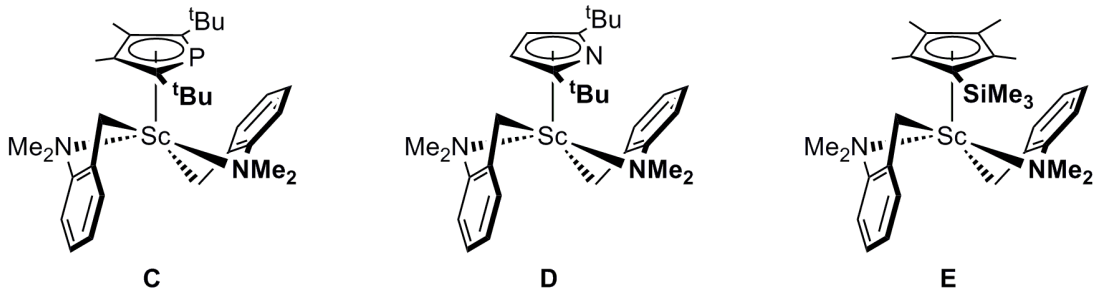
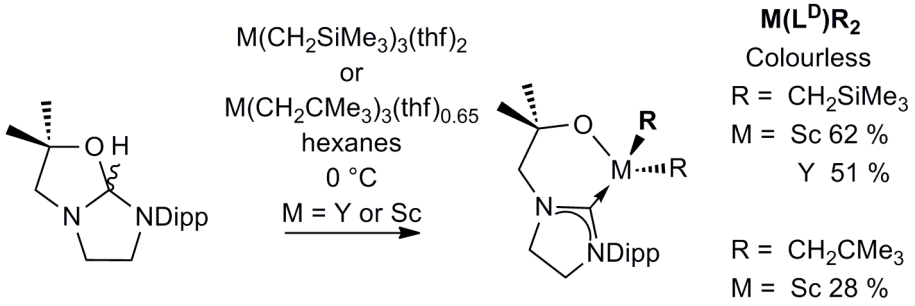


Figure 4: $Sc(L^D)Bn'_2$ (L = mono-anionic ligand) molecular structures

4.2.2 Synthesis of M^{III} silylalkyl and neopentyl complexes

The use of the 1-CH_2-2-NMe_2-C_6H_4,$^-$ ligand in the synthesis of both Ce^{III} and Sc^{III} complexes supported by L^D demonstrated its versatility. However, its bulk meant that only a *mono*(ligand) complex could be prepared for a small metal centre. As it is particularly desirable in subsequent reactivity studies to only have one reactive M-C_{alkyl} bond, the traditional neosilyl $CH_2SiMe_3^-$ and neopentyl $CH_2CMe_3^-$ ligands were used in order to synthesise both *mono* and *bis*(ligand) complexes of the smaller Y^{III} and Sc^{III} cations.

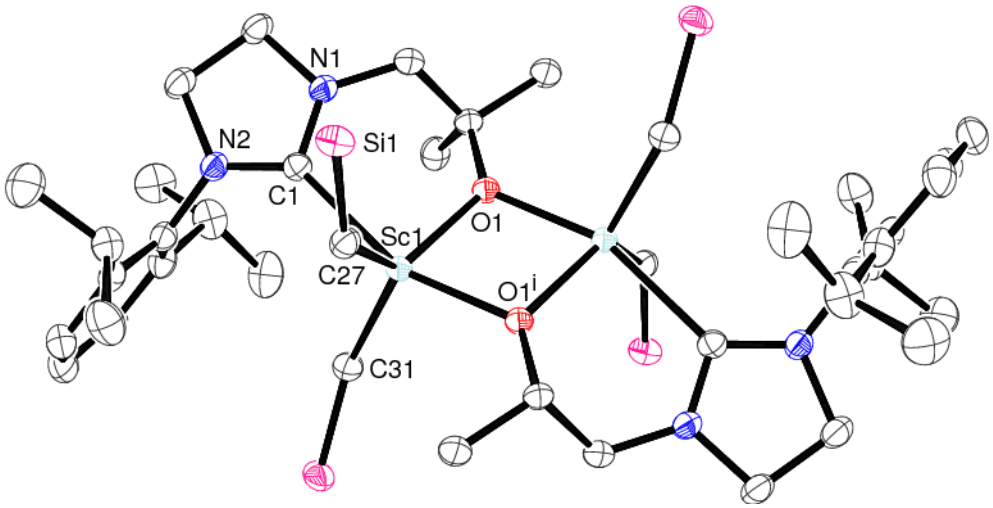
$M(L^D)(CH_2SiMe_3)_2$ (M = Sc or Y) and $M(L^D)(CH_2CMe_3)_2$ (M = Sc) were prepared by the dropwise addition of HL^D to a cold solution (0 ºC) of $M(CH_2SiMe_3)_3(thf)_2$ or $M(CH_2SiMe_3)_3(thf)_{0.65}$ (M = Sc or Y) respectively. After being stirred for 1 – 3 h, $M(L^D)(CH_2SiMe_3)_2$ precipitated from the reaction mixture as an analytically pure, colourless solid in reasonable yield (Sc: 62 % and Y: 51 %). $M(L^D)(CH_2CMe_3)_2$ (M = Sc) was crudely obtained by the same procedure in 28 % yield (Equation 3).



Equation 3: Synthesis of $M(L^D)(CH_2SiMe_3)_2$ (M = Sc or Y) and $M(L^D)(CH_2CMe_3)_2$ (M = Sc)

Single crystals of $M(L^D)(CH_2SiMe_3)_2$ (M = Sc or Y) were grown from toluene solutions at -20 ºC. The displacement ellipsoid plots (Figure 5) and selected bond lengths (Å) and angles (º) are provided (Table 3). In each case, the molecular structure of $M(L^D)(CH_2SiMe_3)_2$ (M = Sc or Y) is dimeric in the solid state with the alkoxy groups bridging the metal centres to form an M_2O_2 core which is centred over a crystallographic inversion centre. Each metal centre is five-coordinate, in a distorted trigonal bipyramidal geometry where the silylalkyl groups and one alkoxy bridging group define the equatorial plane. The L^D ligand is not parallel with the C_2O_2 plane but pitched away from the plane defined by the C_2O_2 core by approximately 28º (Y: 28.59º and Sc: 27.89º).

a)



b)

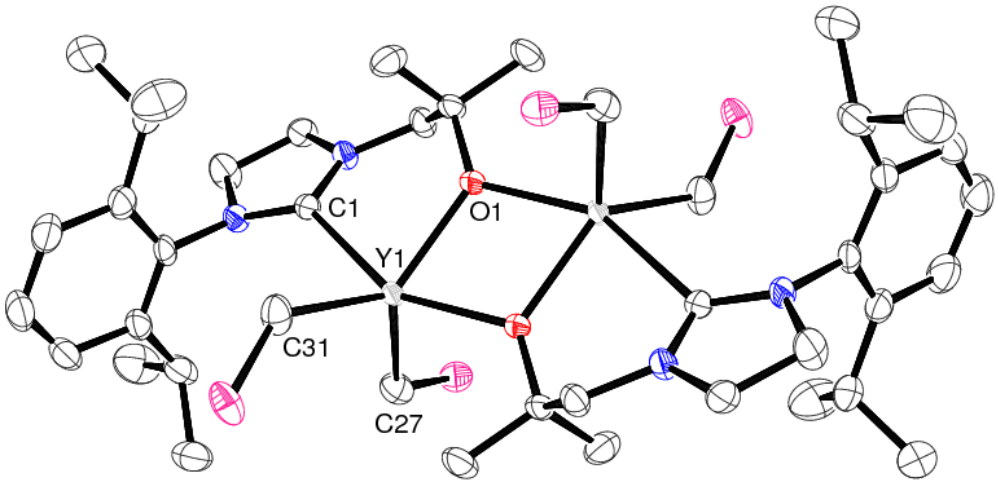


Figure 5: Displacement ellipsoid plots (50 %) of
a) $Sc(L^D)(CH_2SiMe_3)_2$ and b) $Y(L^D)(CH_2SiMe_3)_2$
Solvent molecules, H atoms and silyl Me groups are omitted for clarity

Table 3: Selected bond lengths (Å) and angles (º) for $M(L^D)(CH_2SiMe_3)_2$ (M = Sc or Y)

	$Sc(L^D)(CH_2SiMe_3)_2$	$Y(L^D)(CH_2SiMe_3)_2$
M1-C1	2.4572(16)	2.625(5)
$M1\text{-}C_{alkyl,\ average}$	2.247	2.401
M1-O1	2.0821(11)	2.254(3)
$C1\text{-}M1\text{-}O1^i$	159.17(5)	150.86(13)
C1-M1-C27	87.13(6)	85.84(17)
O1-M1-C27	121.40(5)	118.00(15)

In $Sc(L^D)(CH_2SiMe_3)_2$ the $Sc\text{-}C_{carbene}$ (2.4572(16) Å) and $Sc\text{-}C_{alkyl,\ average}$ (2.247 Å) bond lengths are comparable to those previously reported complexes: $Sc\text{-}C_{carbene}$ =

2.350(3) Å and Sc-$C_{alkyl,\ average}$ = 2.209 Å in **F**, Sc(L)$(CH_2SiMe_3)_2$ (L = IndCH_2CH_2(1-C{NCHCHNMes}),[7] Sc-$C_{carbene}$ = 2.343(4) Å and Sc-$C_{alkyl,\ average}$ = 2.201 Å in **G**, Sc(L)$(CH_2SiMe_3)_2$ (L = FluCH_2CH_2(1-C{NCHCHNMes}))[3] (Figure 6).

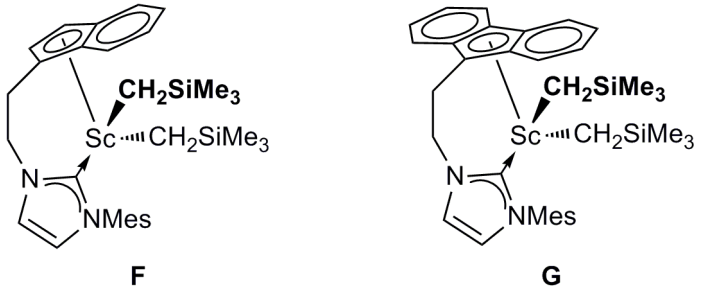


Figure 6: N-heterocyclic carbene scandium alkyl complexes

In Y(L^D)$(CH_2SiMe_3)_2$, the Y-$C_{carbene}$ (2.457(2) Å) and Y-$C_{alkyl,\ average}$ (2.401 Å) bond lengths are comparable to those of previously reported complexes: Y-$C_{carbene}$ = 2.555(2) Å and Y-$C_{alkyl,\ average}$ = 2.354 Å in **H**, Y(IPr)$(CH_2SiMe_3)_3$,[13] Y-$C_{carbene}$ = 2.501(3) Å and Y-$C_{alkyl,\ average}$ = 2.370 Å in **I**, Y(L)$(CH_2SiMe_3)_2$ (L = IndCH_2CH_2(1-C{NCHCHNMes}))[7] and Y-$C_{carbene}$ = 2.547(5) Å and Y-C_{alkyl} = 2.372(5) Å in **J**, [Y(L)(CH_2SiMe_3)Br]$_2$ (L = 4-7-Me_2-IndCH_2CH_2(1-C{NCHCHNDipp}))[14] (Figure 7).

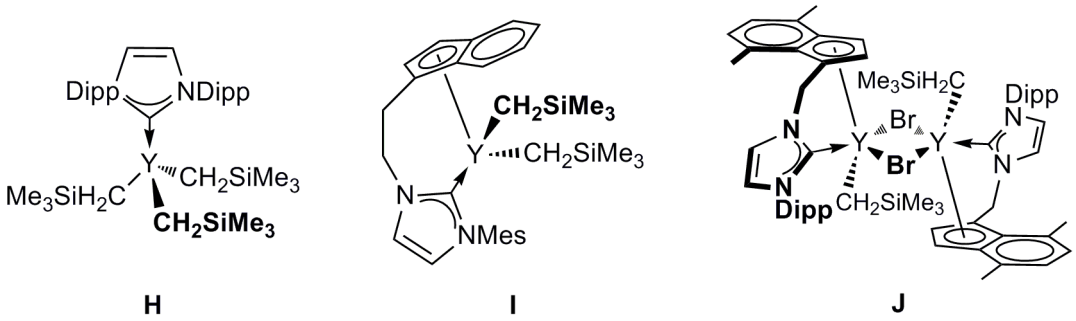
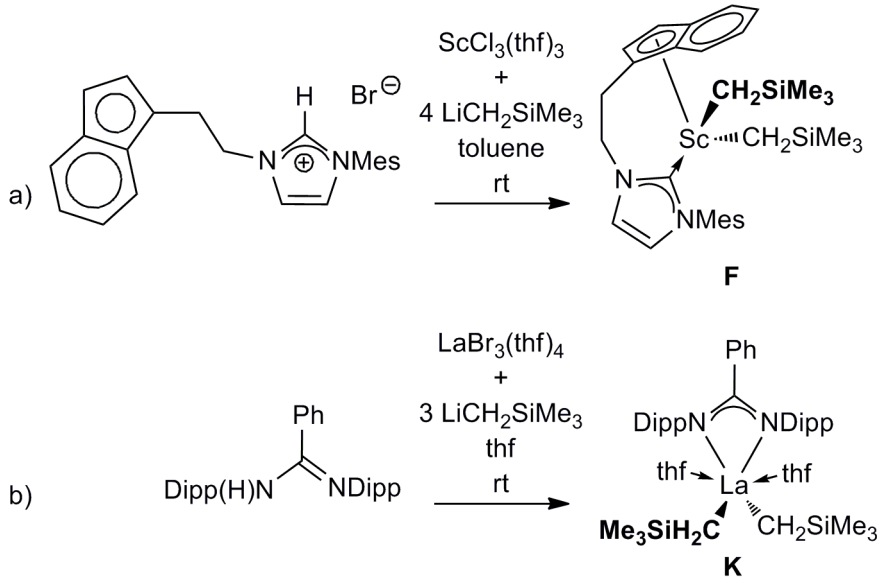


Figure 7: N-heterocyclic carbene yttrium alkyl complexes

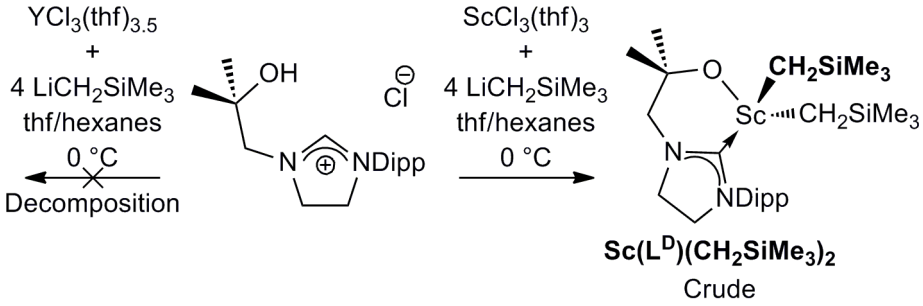
Protonolysis reactions of homoleptic *tris*(alkyl) starting materials remain the most common method in the preparation of alkyl complexes, since salt metathesis reactions often suffer from salt incorporation, 'ate' complex formation and ligand redistribution. Attempted *in situ* preparations of M(L^D)$(CH_2SiMe_3)_2$ (M = Sc or Y) were investigated in order to avoid the isolation of the temperature sensitive *tris*(alkyl) starting materials, M$(CH_2SiMe_3)_3(thf)_2$.[7,15] *In situ* alkylation reactions have been demonstrated successfully in the preparation of *bis*(alkyl) complexes of a larger rare earth metal, lanthanum, though their success has been found to be dependent on the nature of the supporting ligand set. For example, the imidazolium bromide salt [H_2L]Br (L = IndCH_2CH_2(1-C{NCHCHNMes}))

was treated with $[Sc(CH_2SiMe_3)_4][Li(thf)_4]$, generated *in situ*, in order to prepare **F**, $Sc(L)(CH_2SiMe_3)_2$ in 65 % yield (Equation 4a)).[7] Furthermore, when a mixture of $LaBr_3(thf)_4$ and $LiCH_2SiMe_3$ was reacted with HL (L = PhC(NAr)(NHDipp)), **K**, $La(L)(CH_2SiMe_3)_2(thf)_2$ was isolated in 33 % yield (Equation 4b)).[15]



Equation 4: *in situ* preparation of a) $Sc(L)(CH_2SiMe_3)_2$ (L = $IndCH_2CH_2(1\text{-}C\{NCHCHNMes\})$) (**F**) and b) $La(L)(CH_2SiMe_3)_2(thf)_2$ (L = PhC(NAr)(NHDipp) (**K**)

In the first instance, $ScCl_3(thf)_3$ was reacted with 4 equivalents of $LiCH_2SiMe_3$ at -78 ºC and then allowed to warm to 0 ºC in order to form $[Sc(CH_2SiMe_3)_4][Li(thf)_4]$. To this reaction mixture was added 1 equivalent of $[H_2L^D]Cl$ and the elimination of LiCl, the driving force of this reaction, was observed (Scheme 2).

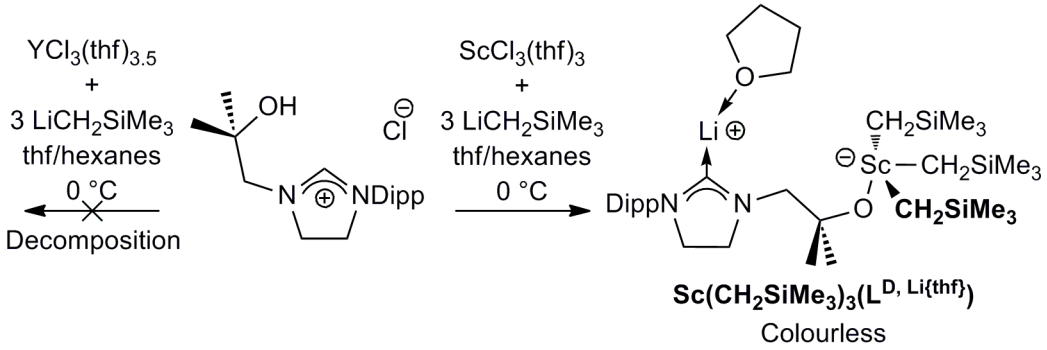


Scheme 2: Attempted *in situ* preparation of $M(L^D)(CH_2SiMe_3)_2$ (M = Y or Sc) from $MCl_3(thf)_x$, (x = 3.5 or 3 respectively), $LiCH_2SiMe_3$ and $[H_2L^D]Cl$

After work-up, the colourless solid obtained was analysed by ^1H NMR spectroscopy and shown to contain $Sc(L^D)(CH_2SiMe_3)_2$ as the major product alongside impurities. The analogous reaction with $YCl_3(thf)_{3.5}$ was not successful. Since this route required the

additional step of recrystallisation for purification and only worked in the case of scandium, it was not pursued further.

In a similar reaction, $ScCl_3(thf)_3$ was reacted with 3 equivalents of $LiCH_2SiMe_3$ at -78 ºC and then allowed to warm to 0 ºC. To this reaction mixture was added 1 equivalent of HL^D. However, instead of $M(L^D)(CH_2SiMe_3)_2$, the 'ate' complex, $M(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (M = Sc) was isolated as a colourless solid in low yield. The analogous yttrium complex could not be prepared (Scheme 3).



Scheme 3: Attempted *in situ* preparation of $M(L^D)(CH_2SiMe_3)_2$ (M = Sc or Y)

Rare earth metal 'ate' complexes are common and often unwanted reaction products where an alkali-metal ion is retained, commonly as a solvated ion or by bridging halides, in order to increase the coordination number of the rare earth metal. They have been observed in a number of metal amide,[16-18] alkoxide[19,20] and alkyl species.[21-23] However, these heterometallic complexes can be useful synthetic precursors and have also been applied successfully and purposefully to homogeneous catalysis.[24,25] For example, $[Li(thf)_4][M(CH_2SiMe_3)_4]$ (M = Sc or Y) [7] (**L**, Figure 8) has been used in the preparation of the first rare earth *bis*(alkyl) NHC complexes and magnesium borohydridolanthanidocenes (**M**, Figure 8) were found to be catalytically active for the polymerisation of isoprene. Though not as active as the parent lanthanidocene complexes, they were selective for *trans*-1,4-isoprene.[24]

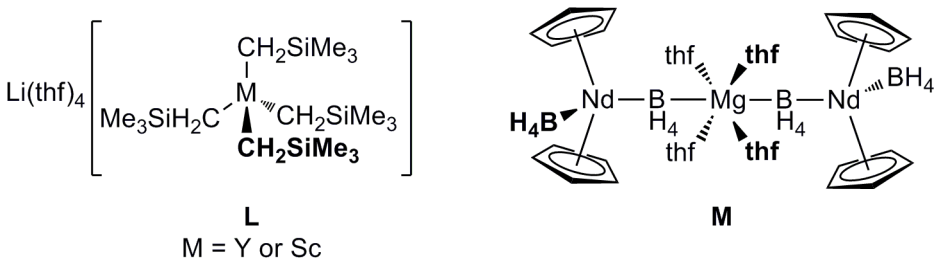
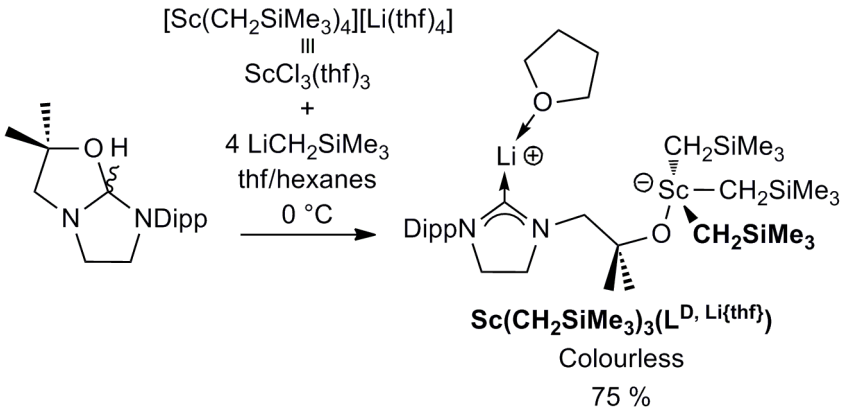


Figure 8: Rare earth metal 'ate' complexes

HL^{D} has reacted with $[Li(thf)_4][Sc(CH_2SiMe_3)_4]$ present within the reaction mixture rather than $Sc(CH_2SiMe_3)_3(thf)_2$. Hence, a rational synthesis of $Sc(CH_2SiMe_3)_3(L^{D, Li\{thf\}})$ was completed under the same reaction conditions but with 4 equivalents of $LiCH_2SiMe_3$ and this improved the reaction yield to 75 % (Equation 5).



Equation 5: Preparation of $Sc(CH_2SiMe_3)_3(L^{D, Li\{thf\}})$

Crystals of $Sc(CH_2SiMe_3)_3(L^{D, Li\{thf\}})$ were grown from a toluene solution at -20 ºC. The displacement ellipsoid plot (50 %) (Figure 9) and selected bond lengths (Å) and angles (º) are provided (Table 4).

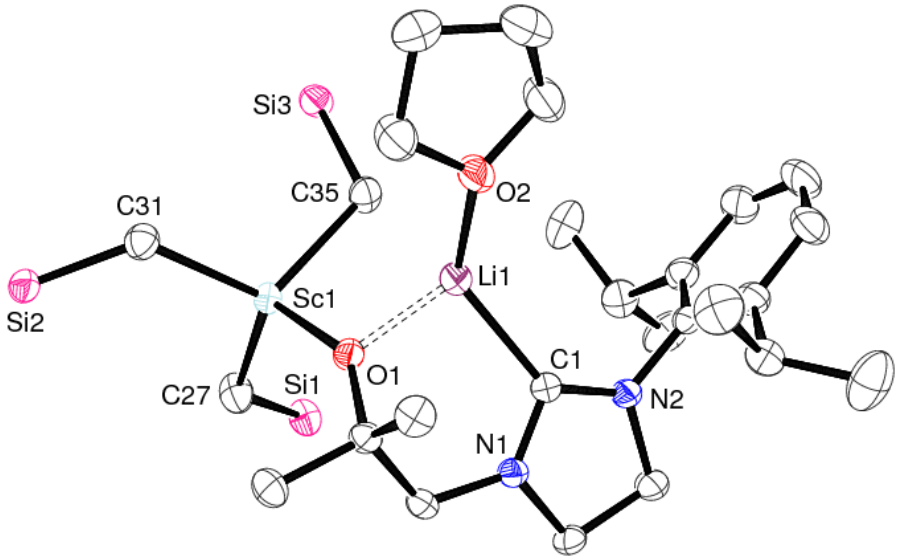


Figure 9: Displacement ellipsoid plot (50 %) of $Sc(CH_2SiMe_3)_3(L^{D, Li\{thf\}})$
H atoms and silyl Me groups omitted for clarity

Lithium NHC complexes remain rare,[26] with those reported ranging from simple monomeric complexes to dimers and higher oligomers. There are also only a small number of crystallographically characterised examples where both scandium and lithium ions are present within the same structure and bridged by one atom.

Table 4: Selected bond lengths (Å) and angles (º) for $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$

Li1-C1	2.114(5)
Li1-O1	1.904(5)
Li1-O2	1.921(5)
Sc1-O1	1.9524(19)
$Sc1\text{-}C_{alkyl,\ average}$	2.245

The molecular structure of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ contains the shortest reported $Li\text{-}C_{carbene}$ distance (2.114(5) Å) in the literature. Existing examples range from 2.124(4) Å in **N**, $[Li(L)]_2$ (L = ^{t}BuNCH$_2$CH$_2$(1-C{NCHCHN^{t}Bu})),[27] to 2.237(3) Å in **O**, $[Li(L)(C{\equiv}C^tBu)]_4$ (L = (1-C{NMeCMe}$_2$))[28] (Figure 10). The $Li\text{-}C_{carbene}\text{-centroid}_{NHC}$ angle is approaching linearity (166.5º) and so there is not the severe distortion shown for **N** (147.9º).

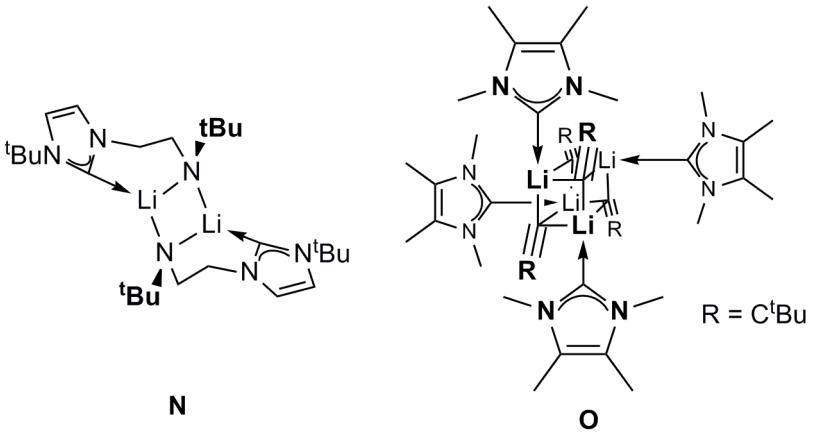


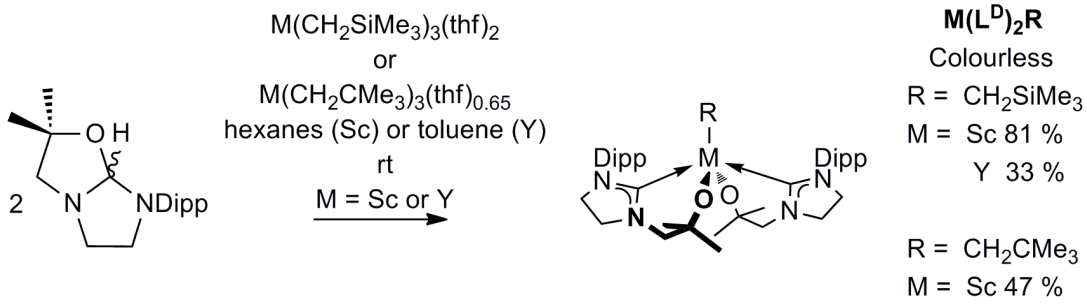
Figure 10: Li-NHC molecular structures

The $Li\text{-}C_{carbene}$ distance is far shorter than the $Sc\text{-}C_{carbene}$ distance in $Sc(L^D)(CH_2SiMe_3)_2$ (2.4572(16) Å) and much shorter than expected based on the differences in ionic radii ($Li^{I,\ 6C.N.}$ = 0.76 Å, $Sc^{III,\ 6C.N.}$ = 0.745 Å).[10] This implies a higher bond order and consequently, stronger bonding between the Li^I ion and the $C_{carbene}$ atom with respect to the Sc^{III} ion. This also indicates why $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ was formed preferentially to $Sc(L^D)(CH_2SiMe_3)_2$ when $[Sc(CH_2SiMe_3)_4][Li(thf)_4]$ is present in the reaction mixture alongside $Sc(CH_2SiMe_3)_3(thf)_2$; both the $Li\text{-}O_{alkoxide}$ and $Li\text{-}C_{carbene}$ bonds, based on the metrical data, have higher bond orders than the $Sc\text{-}O_{alkoxide}$ bond or the $Sc\text{-}C_{carbene}$ bonds in $Sc(L^D)(CH_2SiMe_3)_2$.

The coordination geometry at the scandium centre is distorted tetrahedral, with the $Sc\text{-}C_{alkyl,\ average}$ bond length (2.245 Å) very similar to that in $Sc(L^D)(CH_2SiMe_3)_2$ (2.247 Å). The Li^I ion forms part of a six-membered metallacyclic ring where five of the atoms (O1-

Li1-C1-N1-C8) are, unusually, virtually co-planar and Li1 is in a distorted trigonal coordination environment, sitting 0.471 Å above the plane defined by O1-O2-C1.

$M(L^D)_2CH_2SiMe_3$ (M = Sc or Y) and $M(L^D)_2CH_2CMe_3$ (M = Sc) were synthesised by treatment of $M(CH_2SiMe_3)_3(thf)_2$ or $M(CH_2SiMe_3)_3(thf)_{0.65}$ (M = Sc or Y) with 2 equivalents of HL^D in hexanes (Sc) or toluene (Y) at room temperature. Removal of the volatiles from the reaction mixture yielded the final products in 33 % ($Y(L^D)_2CH_2SiMe_3$), 81 % ($Sc(L^D)_2CH_2SiMe_3$) and 47 % ($Sc(L^D)_2CH_2CMe_3$) yield (Equation 6).



Equation 6: Synthesis of $M(L^D)_2CH_2SiMe_3$ (M = Sc or Y) and $M(L^D)_2CH_2CMe_3$ (M = Sc)

The ^1H NMR spectra of all of the *bis*(ligand) alkyl complexes are indicative of a rigid molecular structure in solution at room temperature. The spectrum of $Sc(L^D)_2CH_2SiMe_3$ is shown for clarity (Figure 11).

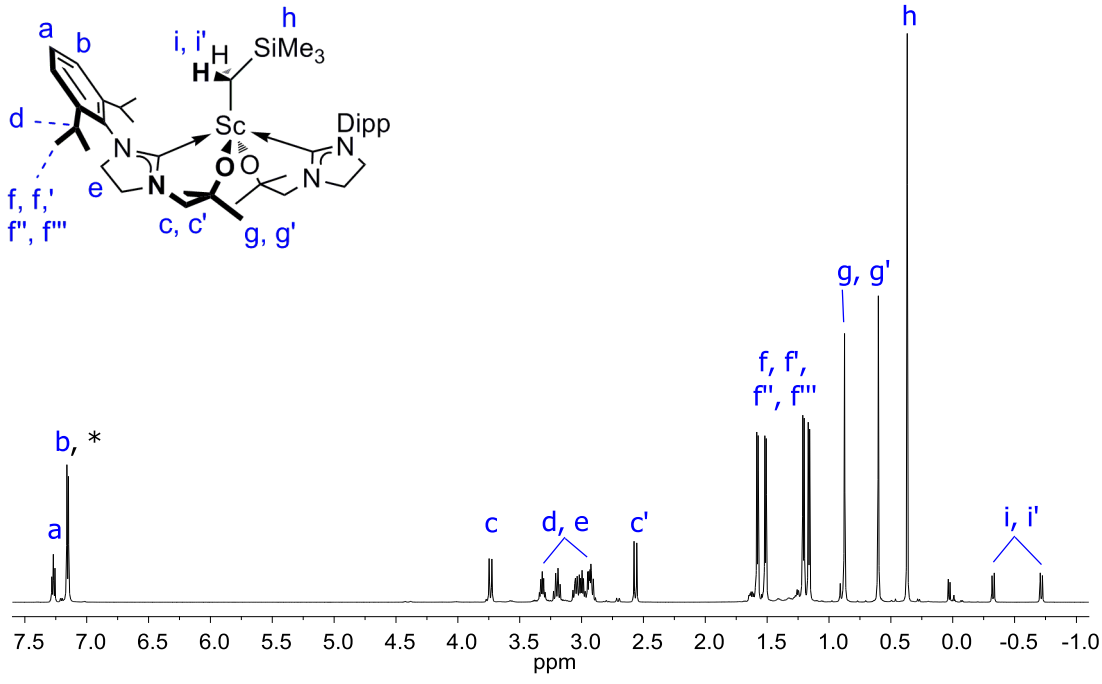


Figure 11: ^1H NMR spectrum (C_6D_6, 500 MHz, 298 K) of $Sc(L^D)_2(CH_2SiMe_3)$
'*' denotes residual protio solvent

The resonances for one ligand of $Sc(L^D)_2CH_2SiMe_3$ are split out, a consequence of the rigid structure making the protons magnetically inequivalent. Notably, the resonances for the $C\underline{H}_2SiMe_3$ alkyl group are geminally coupled (^2J = 11 Hz) and appear as two doublets. This implies the restricted rotation of the **Sc-C**H_2SiMe_3 bond. In the analogous $Y(L^D)_2CH_2SiMe_3$, there is coupling to yttrium (I = 1/2) in addition to the geminal coupling of the protons ($^2J_{HH}$ = 11 Hz, $^1J_{YH}$ = 3 Hz). The geminal coupling of these alkyl protons has been previously observed in $M(L)(CH_2SiMe_3)_2$ (M = Sc (**F**) and Y (**I**), L = $IndCH_2CH_2$(1-C{NCHCHNMes})),[7] and $M(L)(CH_2SiMe_3)_2$ (M = Sc (**G**), L = $FluCH_2CH_2$(1-C{NCHCHNMes})).[3] (Figures 6 and 7). The coupling constants reported match also those recorded for $M(L^D)_2CH_2SiMe_3$.

The preparative scale synthesis of the yttrium complex $Y(L^D)_2CH_2SiMe_3$ was low yielding (33 %) and proved to be capricious in nature despite promising initial NMR scale reactions. Attempts of recrystallisation invariably led to decomposition; the ^{1}H NMR spectra displaying broad resonances over a diamagnetic sweepwidth. On one occasion, attempted recrystallisation of the crude product from hexanes afforded a colourless solid. There was only one set of ligand resonances in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra, split out as for $Y(L^D)_2CH_2SiMe_3$ with the resonances for the CH_2SiMe_3 alkyl protons no longer present (Figure 12).

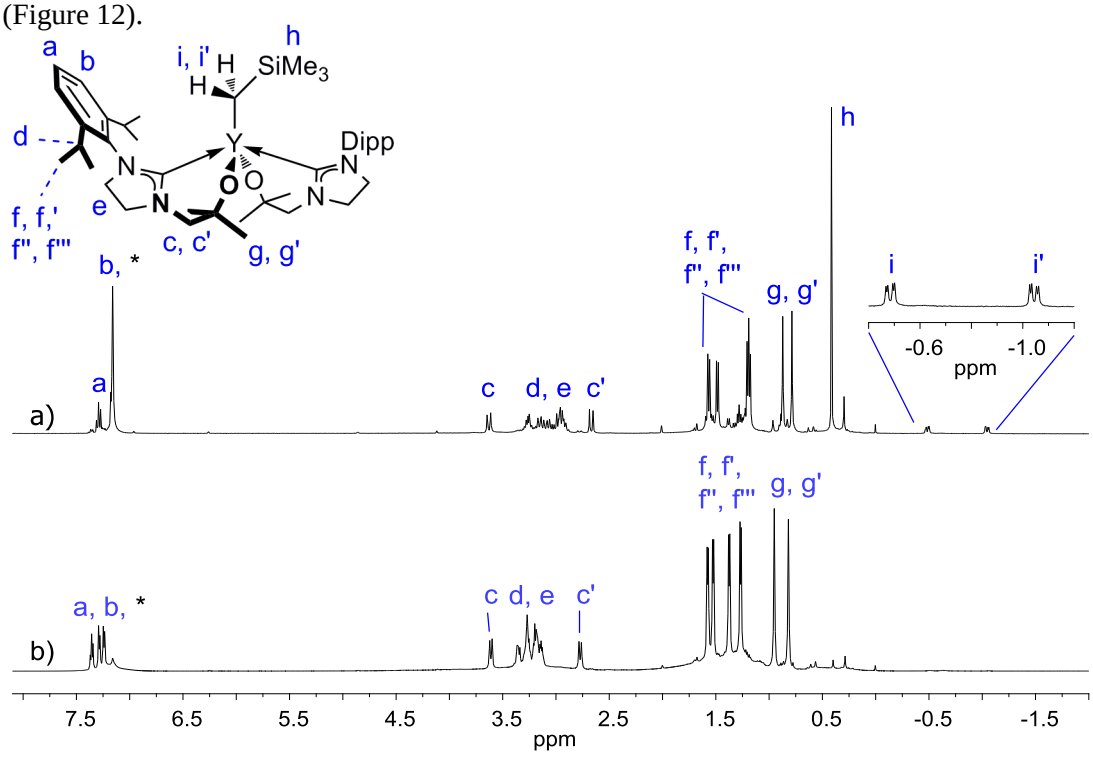


Figure 12: ^{1}H NMR spectra (C_6D_6, 400 MHz, 298 K) of a) $Y(L^D)_2CH_2SiMe_3$ and b) the product after washing $Y(L^D)_2CH_2SiMe_3$ with hexanes, '*' denotes residual protio solvent

This reaction could not be repeated but it is proposed a hydroxide or oxo species are possible products, as a consequence of solvent activation or hydrolysis (Figure 13). Such yttrium complexes would give no additional resonance in the $^{13}C\{^1H\}$ NMR spectrum and, for the protic examples, the additional proton resonances could be easily mistaken in the ^1H NMR spectrum if overlapping with another.

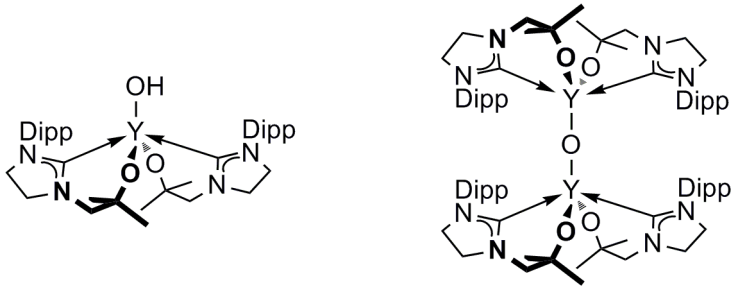


Figure 13: Possible products in the attempted isolation of $Y(L^D)_2CH_2SiMe_3$

4.2.3 Synthesis of M^{III} *bis*(trimethylsilyl)methyl complexes

The $CH(SiMe_3)_2^-$ ligand, bulkier than its neosilyl derivative, has been used in the synthesis of alkyl complexes of the larger lanthanides and actinides, as its larger steric profile offers greater stability for reactive, coordinatively unsaturated metal ions. For example, the first homoleptic U^{III} alkyl complex **P**, $U(CH\{SiMe_3\}_2)_3$.[29] However, since this report, there have only been two examples of U^{III} alkyl complexes using the same ligand, **Q** and **R**, and both are supported by $C_5Me_5^-$ ligands and contain one alkyl group per metal (Figure 14). The $CH(SiMe_3)_2^-$ ligand is a suitable choice for investigation into U^{III} alkyl chemistry, since it has a similar steric profile to $N(SiMe_3)_2^-$,[30] which we have shown allows the formation of U^{III} amide complexes which are thermally stable and require no additional donor ligands.

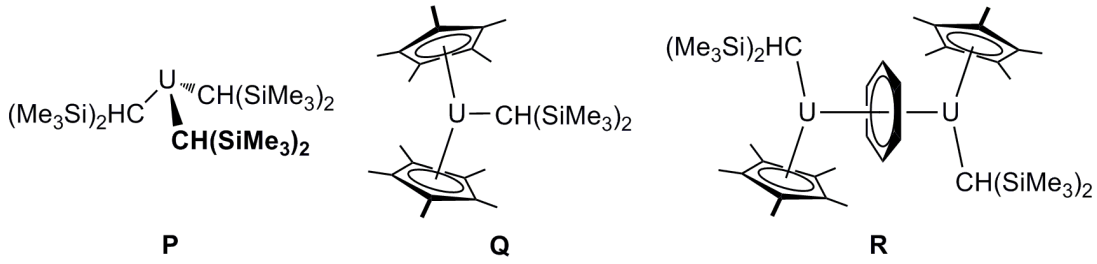
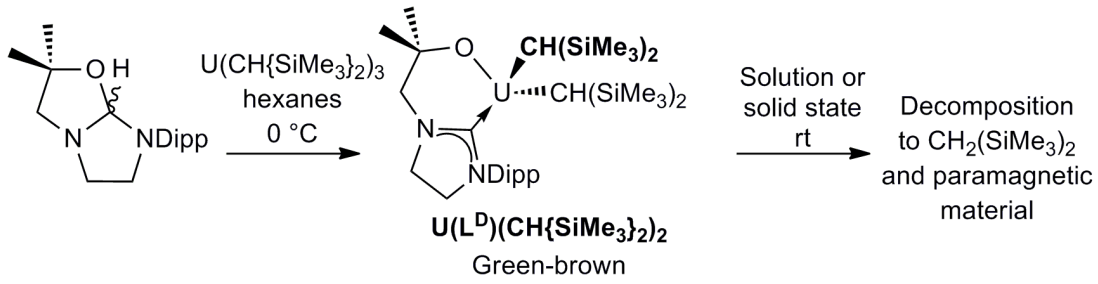


Figure 14: U^{III} alkyl complexes

$U(CH\{SiMe_3\}_2)_3$ was treated with 1 equivalent of HL^D at 0 ºC in hexanes to afford a dark-green brown solution. The ^1H NMR spectrum was consistent with the formation of $U(L^D)(CH\{SiMe_3\}_2)_2$ but storage in either hydrocarbon solutions or in the solid state at room

temperature led to full decomposition over the course of 1 h to $CH_2(SiMe_3)_2$ and small unidentified paramagnetic resonances over a range of 37.2 ppm – -38.1 ppm. All subsequent attempts to recrystallise $U(L^D)(CH\{SiMe_3\}_2)_2$ were not successful (Scheme 4).



Scheme 4: Synthesis and resulting decomposition of $U(L^D)(CH\{SiMe_3\}_2)_2$

The thermal instability of the *mono*(alkyl) complex implies that the L^D ligand cannot sterically protect against its decomposition. The ^1H NMR spectrum of the initial reaction mixture (Figure 15a)) shows clearly the formation of one major complex (assigned as $U(L^D)(CH\{SiMe_3\}_2)_2$), the full consumption of the starting materials, HL^D and $U(CH\{SiMe_3\}_2)_3$, and the production of 1 equivalent of $CH_2(SiMe_3)_2$. After 1 h, the ^1H NMR spectrum now shows an array of unassignable resonances over a paramagnetic sweepwidth and the production of an additional 2 equivalents of $CH_2(SiMe_3)_2$, consistent with the full decomposition of $U(L^D)(CH\{SiMe_3\}_2)_2$ (Figure 15b)).

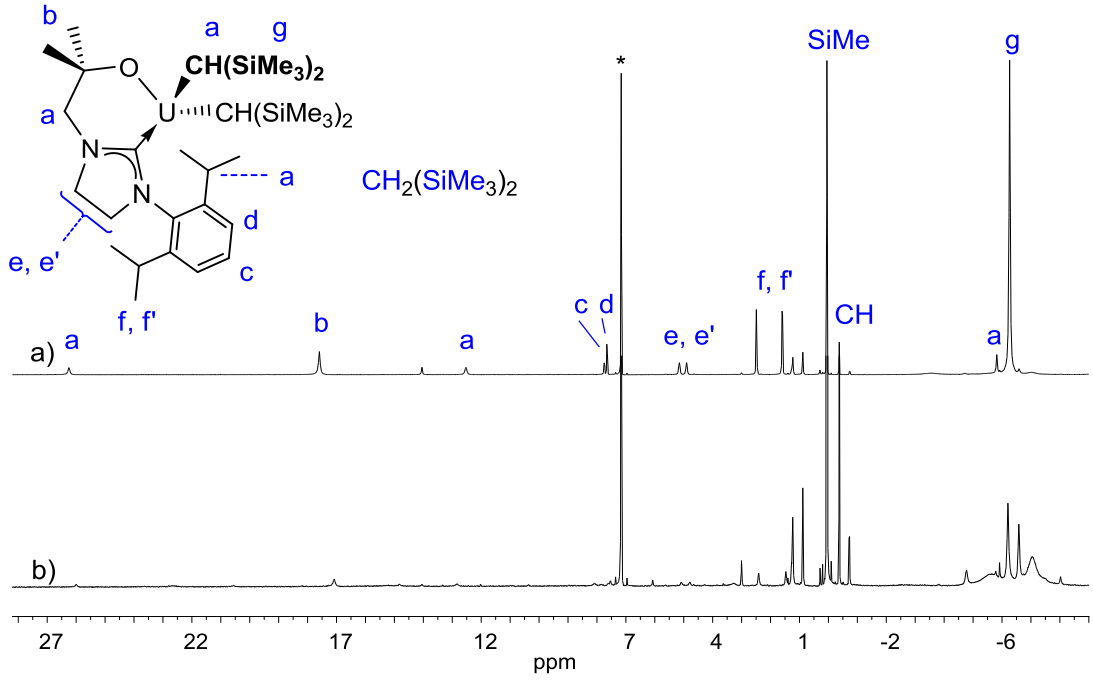


Figure 15: ^1H NMR spectra (C_6D_6, 298 K, 400 MHz) of a) $U(L^D)(CH\{SiMe_3\}_2)_2$ with 1 equivalent of $CH_2(SiMe_3)_2$ byproduct b) the same reaction mixture after 1 h at room temperature in solution, '*' denotes residual protio solvent

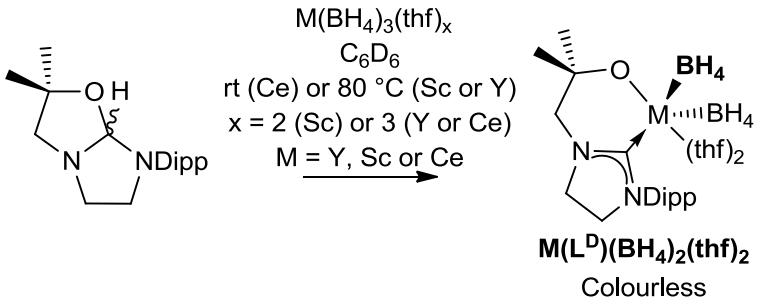
Therefore, we looked to prepare the *bis*(ligand) complex $U(L^D)_2CH(SiMe_3)_2$ to increase the steric bulk of the complex in order to make an isolable species. However, as for the amide system (see 2.4.2), attempts to form $U(L^D)_2CH(SiMe_3)_2$ initially resulted in the formation of 1 equivalent of $U(L^D)(CH\{SiMe_3\}_2)_2$ and 1 equivalent of unreacted HL^D. Over the course of 1 h, the solution did not visibly change appearance but the ^1H NMR spectrum showed the unassigned resonances over the same paramagnetic sweepwidth seen in the decomposition of $U(L^D)(CH\{SiMe_3\}_2)_2$ and 1 equivalent of unreacted HL^D. Given that the steric profile of $N(SiMe_3)_2^-$ and $CH(SiMe_3)_2^-$ are similar, this decomposition is now understandable. It also tells us that both *mono* and *bis*(ligand) cerium analogues should be viable targets; for the amide complexes, only cerium allowed the synthesis of both.

4.3 Synthesis of M^{III} borohydride complexes

4.3.1 Synthesis of M^{III} borohydride complexes

Following some success in synthesis of $M(L^D)R_2$ and $M(L^D)_2R$ (M = Ce, Sc or Y, R = 1-CH_2-2-$NMe_2C_6H_4$, CH_2SiMe_3, $CHCMe_3$), the synthesis of related *mono* and *bis*(ligand) borohydride complexes was also attempted. The *tris*(borohydride) $M(BH_4)_3(thf)_x$ (x = 3 for M = Y or Ce, X = 2 for M = Sc) starting materials are easily prepared in high yield and have the benefit of being thermally stable.[31] Most commonly, they are used in salt metathesis reactions, acting as *pseudo*halides[32-34] (synthesis of alkyl complexes from borohydride complexes has been previously described)[35,36] but it has been demonstrated that metal borohydrides can be used in protonolysis reactions, acting as hydrides.[33,37-39] This duality means that they have the potential to be versatile in synthesis. No borohydride metal complexes supported by N-heterocyclic carbenes have been reported in the literature.

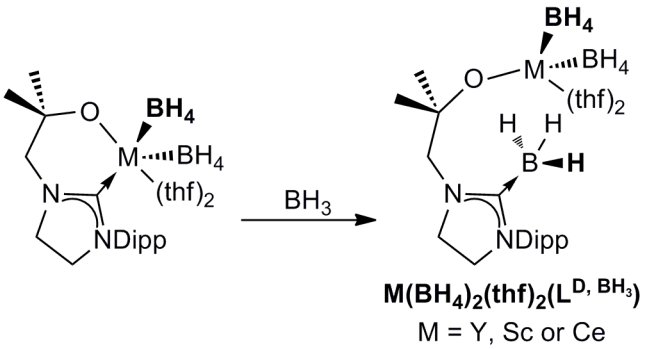
Treatment of $M(BH_4)_3(thf)_x$ (x = 3 for M = Y or Ce, x = 2 for M = Sc) with 1 equivalent of HL^D in C_6D_6 at room temperature (Ce) or 80 ºC (Y or Sc) afforded gluey, colourless solids, initially proposed to be the borohydride complexes $M(L^D)(BH_4)_2(thf)_2$ (Equation 7).



Equation 7: Attempted synthesis of *mono*(ligand) borohydride complexes

The ^{1}H NMR spectra of M(L^{D})(BH_4)$_2$(thf)$_2$ (M = Y or Sc) were analogous to those of the related amide complexes M(L^{D})N"$_2$ (see 2.4.1), with resonances consistent for a single L^{D} ligand environment, two bound borohydride groups and two coordinating thf ligands. The borohydride resonances were broad and overlapped with others.

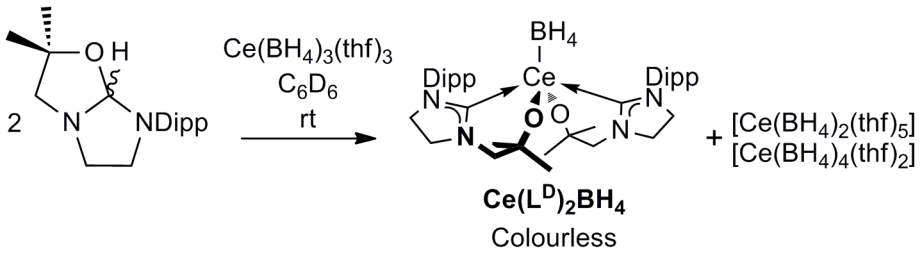
However, in the ^{13}C{^{1}H} NMR spectrum, as was anticipated for a scandium carbene complex (I_{Sc} = 7/2), the high frequency resonance diagnostic of the metal bound $C_{carbene}$ was not observed as a result of signal broadening. This was, however, also the case for the yttrium analogue; no doublet for the $C_{carbene}$ atom coupled to Y was observed. This could be explained by coordination of the NHC to a boron atom; for example, M(L^{D})(BH_4)$_2$(thf)$_2$ could react with BH_3 liberated in the protonolysis reaction for form a carbene borane adduct (Equation 8).



Equation 8: Insertion of BH_3 into the M-$C_{carbene}$ bond to form a carbene borane

Unfortunately, all attempts to purify the complexes by recrystallisation were not successful and they were found to decompose in hexanes.

Reaction of the smaller *tris*(borohydride) starting materials, M(BH_4)$_3$(thf)$_x$ (M = Y or Sc), with 2 equivalents of HL^{D} afforded only "M(L^{D})(BH_4)$_2$(thf)$_2$" and 1 equivalent of unreacted of HL^{D}. However, treatment of the larger Ce(BH_4)$_3$(thf)$_3$ with 2 equivalents of HL^{D} resulted in immediate reaction at room temperature and visible evolution of gas. In the ^{1}H NMR spectrum, the broad resonance for the BH_4 protons shifted to a higher frequency with respect to the borohydride starting material. As seen for the *bis*(ligand) amide Ce(L^{D})$_2$N" (see 2.4.2), the resonances associated with L^{D} were broad and overlapping, suggestive of a fluxional process occurring in solution. However, all attempts to isolate the anticipated product Ce(L^{D})$_2$(BH_4) through recrystallisation only yielded single crystals of the ion pair [Ce(BH_4)$_2$(thf)$_5$][Ce(BH_4)$_4$(thf)$_2$] (Equation 9, Figure 16).



Equation 9: Attempted synthesis of a cerium *bis*(ligand) borohydride complex

Single crystals suitable for an X-ray diffraction study were grown from a thf solution at -20 ºC. The displacement ellipsoid plot (Figure 16) and selected bond lengths (Å) and angles (º) are shown for clarity (Table 5).

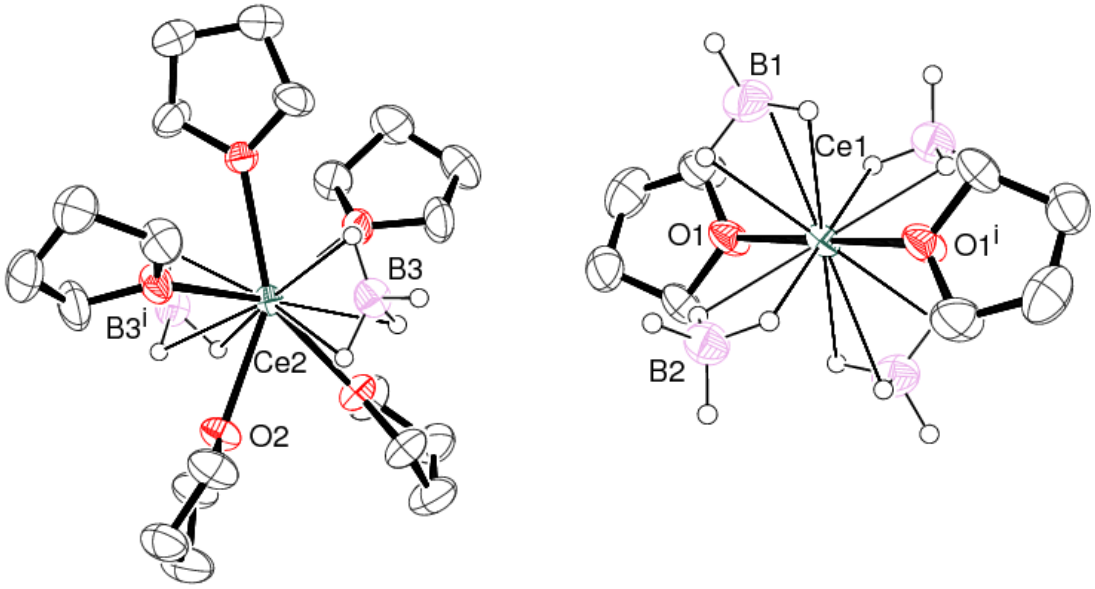


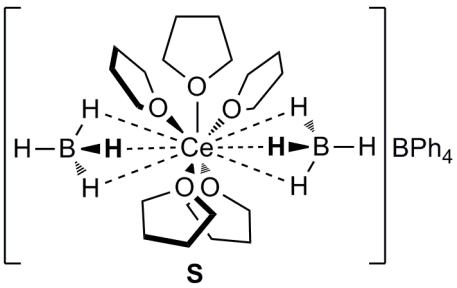
Figure 16: Displacement ellipsoid plot (50 %) of $[Ce(BH_4)_2(thf)_5][Ce(BH_4)_4(thf)_2]$
All H atoms except those of the borohydride ligands omitted for clarity

Table 5: Selected bond lengths (Å) and bond angles of $[Ce(BH_4)_2(thf)_5][Ce(BH_4)_4(thf)_2]$

Ce1···B1	2.694(2)
Ce1···B2	2.900(3)
Ce1-O1	2.518(2)
Ce2···B3	2.682(3)
Ce2-O2	2.528(2)
O1-Ce1-O1^{i}	180.000(1)
B1···Ce1···B2	89.83(5)
B3···Ce2···B3^{i}	178.07(11)
O2-Ce2-B3	72.28(6)

In the $[Ce(BH_4)_4(thf)_2]^-$ anion, Ce1 lies in an octahedral coordination environment (O1-Ce1-O1^i = 180.000(1)^o, B1-Ce1-B2 = 89.83(5)^o) with the borohydride ligands defining the equatorial plane. The Ce1···B bond lengths, 2.694(2) Å and 2.900(3) Å, are consistent with the two sets of mutually *trans* tridentate and bidentate borohydride ligands respectively. In the $[Ce(BH_4)_2(thf)_5]^+$ cation, Ce2 lies in a pentagonal bipyramidal coordination environment (O2-Ce2-B3 = 72.28(6)^o, B3-Ce2-B3^i = 178.07(11)^o) with the thf ligands defining the equatorial plane. The cerium ion and a single thf ligand are bisected by a C_2 axis. The borohydride ligands are tridentate and the Ce2···B3 distance (2.682(3) Å) is similar to the distance for the tridentate ligand in the cation.

The $M(BH_4)_3(thf)_3$ starting materials (M = Y or La) have previously been shown to disproportionate into such ion pairs and have been crystallised in the solid state, $[M(BH_4)_2(thf)_x][M(BH_4)_4(thf)_y]$ (M = Y, x = 4, y = 0 or M = La, x = 5, y = 2).[40,41] The molecular structure of $[Ce(BH_4)_2(thf)_5][Ce(BH_4)_4(thf)_2]$ is isostructural with the lanthanum complex. Ion pair molecular structures containing rare earth metals are well known; for example, $YCl_3(thf)_{3.5}$ crystallises as $[YCl_2(thf)_5][YCl_4(thf)_2]$ in the solid state.[42] The $[M(BH_4)_5(thf)_2]^+$ (M = lanthanide or actinide) cation has also been characterised in the solid state in several compounds. For example, **S**, $[Ce(BH_4)_2(thf)_5][BPh_4]$ was prepared by the reaction of $Ce(BH_4)_3(thf)_3$ with $[NEt_3H][BPh_4]$ (Figure 17).[43] The geometry is also pentagonal bipyramidal, as expected for an ionic complex where the geometry is defined by electrostatic repulsion. All of the bond lengths to the Ce^{III} cation are slightly contracted with respect to $[Ce(BH_4)_2(thf)_5][Ce(BH_4)_4(thf)_2]$. For example, Ce1···B1 = 2.694(2) Å (2.678(6) Å in **S**) and Ce1···B2 = 2.900(3) Å (2.704(7) Å in **S**).



S

Figure 17: Structurally characterised example of the $[Ce(BH_4)_2(thf)_5]$ cation

4.4 Reactivity of M^{III} benzyl complexes

4.4.1 M^{III} benzyl cationic complexes

Cationic group 4 alkyl complexes have been widely studied due to their role as the 14 electron active catalysts in homogenous olefin polymerisation.[44-46] Cationic rare earth

alkyl complexes are a developing area due to their highly electrophilic nature which offers potential use in homogeneous catalysis; in olefin polymerisation (**T**, $Sc(L)(CH_2SiMe_3)_3$ (L = 1,4,7-Me-triazacyclononane) on activation by $BAr^F{}_3$)[1] and in hydroamination (**U**, $[Sc(L)Me][MeB(Ar^F)_3]$ (L = DippNC(Me)CHC(Me)NDipp)[47] (Figure 18).

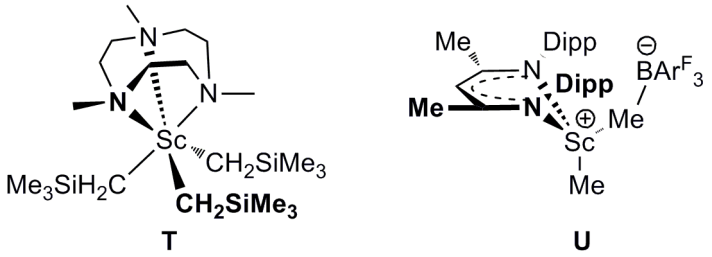


Figure 18: Rare earth alkyl complexes for homogeneous catalysis

The synthesis and subsequent reactivity of such organometallic species are dependent on the use of a weakly coordinating anion to allow charge separation and ion formation.[48]

A number of routes to cationic rare earth complexes have been employed in the literature,[49,50] with the majority of the cationic species stabilised using cyclopentadienyl-type ligands. Recently, use of the *o*-aminobenzyl ligand has also been reported in this role; for example, **V**, $[Sc(L)Bn'][BAr^F{}_4]$ (L = (1-N{1,4-^{t}Bu-C_4H_2})) and **W**, $[Sc(L)Bn'][BAr^F{}_4]$ (L = 1-$SiMe_3$-C_4Me_4) (Figure 19).[12] This bidentate ligand facilitates the synthesis of Lewis base-free complexes, which are particularly desirable for catalytic uses and reactivity studies; there is no competition between the Lewis base and the substrate at the metal centre.

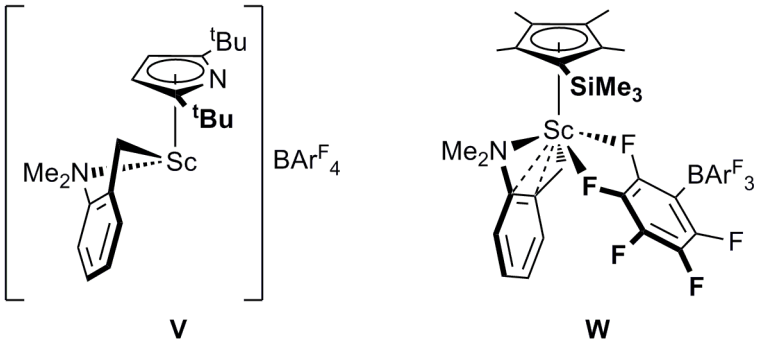
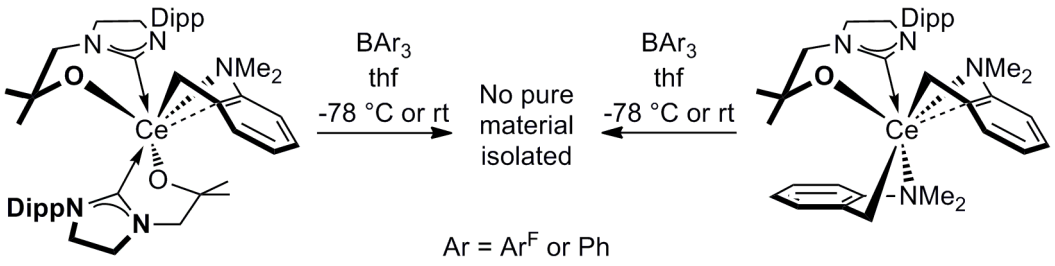


Figure 19: Cationic Sc^{III} species supported by the *o*-benzylamino ligand

Given that the neutral M^{III} alkyl complexes $M(L^D)R_2$ and $M(L^D)_2R$ (M = Y, Sc or Ce and R = 1-CH_2-2-NMe_2-C_6H_4, CH_2SiMe_3 or CH_2CMe_3) have already been isolated, we chose to focus here (and in 4.5.8) only on alkyl abstraction by Lewis acids or the $[Ph_3C]^+$ cation and protonolysis reactions. Reaction of 1 equivalent of $Ce(L^D)Bn'_2$ or $Ce(L^D)_2Bn'$ with 1

equivalent of BAr_3 (Ar = Ar^F or C_6H_5) in thf over 16 h afforded an orange and yellow solid respectively after work-up. In both cases, the products obtained were poorly soluble in C_6D_6 and so satisfactory NMR spectral analysis could not be obtained, though the ^1H NMR spectrum did indicate the full consumption of the starting alkyl complexes. Unfortunately, no pure material was obtained by successive recrystallisations (Scheme 5).

As previously discussed (see 3.4.2), reaction of the amide complex $Ce(L^D)N''_2Cl$ with BAr^F_3 resulted in a product most likely to be the carbene borane adduct $Ce(L^{D,\ BArF_3})N''_2Cl$. The analogous product may be forming in the alkyl system too. As shown for complex **W** (Figure 19), there may be the presence of stabilising Sc···Ar interactions.



Scheme 5: Attempted synthesis of M^{III} benzyl complexes using BAr_3 (Ar = Ph or Ar^F)

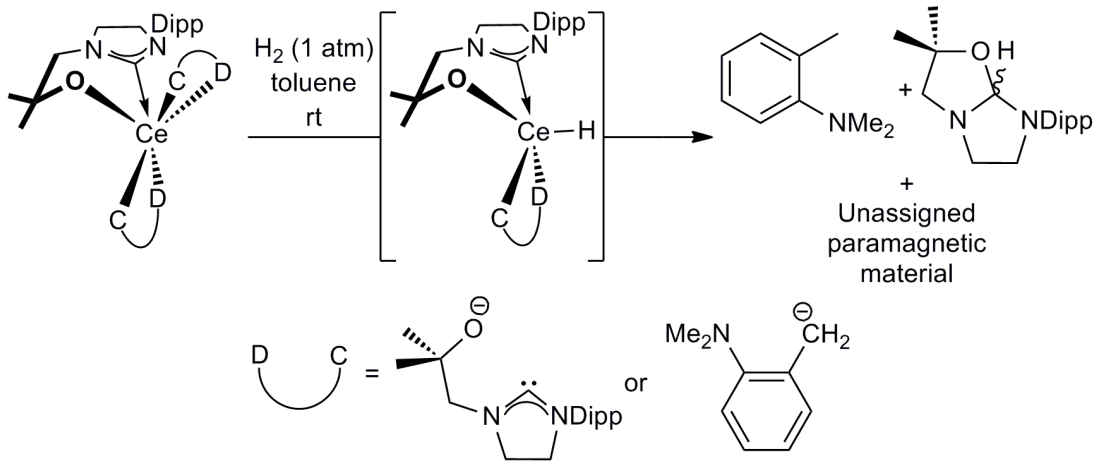
4.4.2 M^{III} benzyl hydrides

Transition metal hydrides are numerous and also hold an important role in homogeneous catalysis with M-H bonds playing a key role in most industrial petrochemical processes (for example, hydroformylation and hydrogenation).[51] In contrast, the chemistry of rare earth hydrides is underdeveloped but they have been shown to undergo both interesting stoichiometric (such as σ bond metathesis and addition reactions) and catalytic reactivity (such as H/D exchange, alkene isomerisation, alkene and alkyne hydrogenation, alkene hydrosilylation, intramolecular hydroamination and organic halide dehalogenation), the latter often with greater activity than their transition metal counterparts.[32,52-54]

A number of synthetic routes to rare earth hydrides have been reported but hydrogenolysis is the most common. The majority of rare earth hydrides synthesised utilise cyclopentadienyl-based support ligands and none supported by N-heterocyclic carbenes have been reported. Therefore, we sought to prepare the first NHC supported rare earth hydrides and examine fundamental σ bond metathesis reactivity.

Exposure of freeze-pump-thaw degassed solutions of $Ce(L^D)Bn'_2$ or $Ce(L^D)_2Bn'$ to H_2 (1 atm) in toluene over a period of 2 h led to a darkening in colour of the solutions. Unfortunately, ^1H NMR spectral analysis of the solids obtained after work up indicated the

presence of HL^D as well as HBn', the expected byproduct. It was concluded that any hydride species formed during the reaction was not sufficiently stable to be isolated and decomposed (Scheme 6). Therefore, alternative routes to hydride species were not pursued.

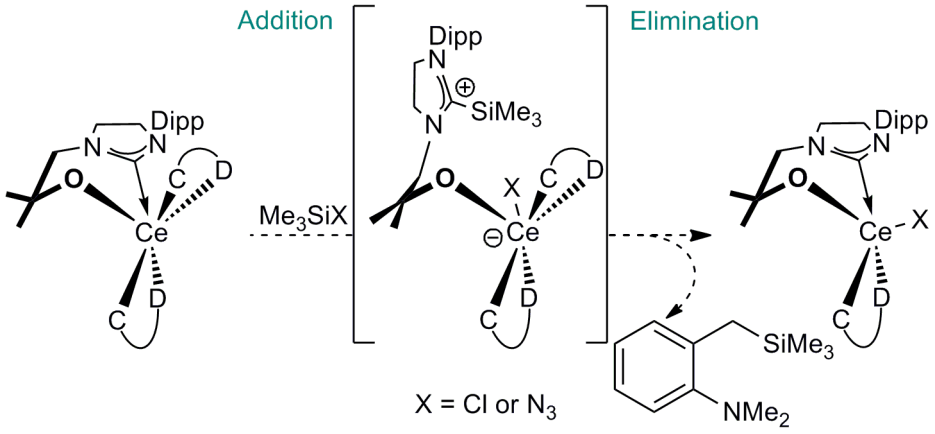


Scheme 6: Attempted synthesis of M^{III} benzyl hydrides using H_2

4.4.3 Addition-elimination reactivity of M^{III} benzyl complexes

Following the observed addition-elimination reactivity of polar reagents across the M-$C_{carbene}$ bond for the metal amide complexes and subsequent N-E (E = Si, P, Sn and B) bond formation described in Chapter Three (3.3.1), the metal alkyl complexes were also investigated for their use in the formation of C-E bonds.

$Ce(L^D)Bn'_2$ was treated with Me_3SiX (X = Cl or N_3) in C_6D_6 at room temperature for a period of 2 h. In each case (X = Cl or N_3), the ^1H NMR spectrum of the reaction mixture only contained resonances in the diamagnetic spectral region. For Me_3SiCl, a single set of diamagnetic ligand resonances (split out at in the case of HL^D or $Zn(L^D)_2$) was observed and 1 equivalent of an unidentified *o*-benzylamino-containing compound (which was not the free amine HBn' or complex $Ce(L^D)_2Bn'$). If the addition-elimination process was occurring, the product of C-Si coupling, 1-CH_2SiMe_3-2-NMe_2-C_6H_4, is expected alongside the inorganic species $Ce(L^D)(Bn')Cl$. The latter could not be identified as there are no paramagnetically shifted resonances in the NMR spectrum. Similarly, for the analogous reaction with Me_3SiN_3, the same *o*-benzylamino product was observed but no ligand resonances (Scheme 7). Related reactivity was observed when the *bis*(ligand) complex $Ce(L^D)_2Bn'$ was treated with Me_3SiX (X = Cl or N_3) in C_6D_6 at room temperature for 2 h and the reaction monitored by ^1H NMR spectroscopy (Scheme 7).



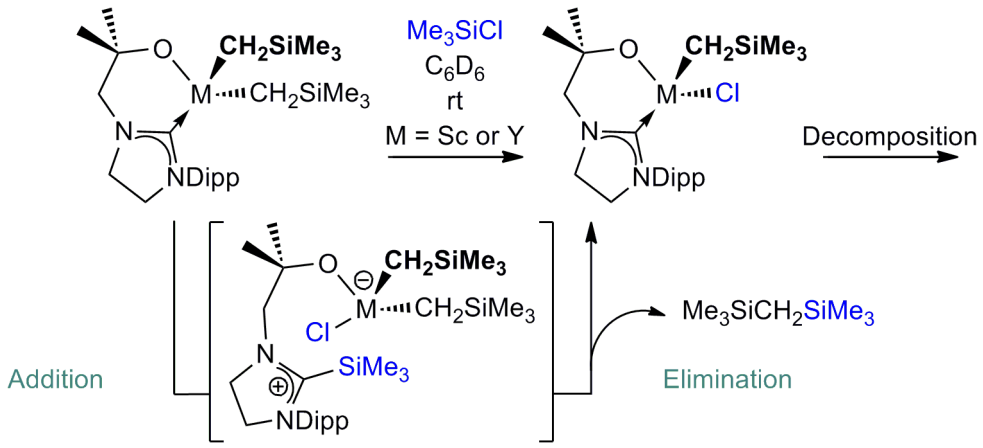
Scheme 7: Reaction of *mono* and *bis*(ligand) benzyl complexes with Me_3SiX (X = Cl or N_3)

Due to the difficulties in identifying and isolating the reaction products using the benzyl complexes, subsequent reactivity studies were completed on the neosilyl and neopentyl complexes.

4.5 Reactivity of M^{III} neosilyl and neopentyl complexes

4.5.1 Carbon-silicon bond formation

The reaction of the *mono*(ligand) neosilyl complexes, $M(L^D)(CH_2SiMe_3)_2$ (M = Y or Sc) with 1 equivalent of Me_3SiCl in C_6D_6 immediately gave rise to C-Si bond formation and the product $Me_3SiCH_2SiMe_3$ was identified by ^1H NMR spectroscopy (Scheme 8). These complexes display the same reactivity observed for the amide system (see 3.3.1) whereby Me_3SiCl is added across the M-$C_{carbene}$ bond to functionalise the N-heterocyclic ring. The resulting zwitterionic intermediate decomposes at room temperature (compared to 80 ºC for the $M(L^D)N''_2$ complexes, where M = Y, Sc or Ce) to eliminate $Me_2SiCH_2SiMe_3$.

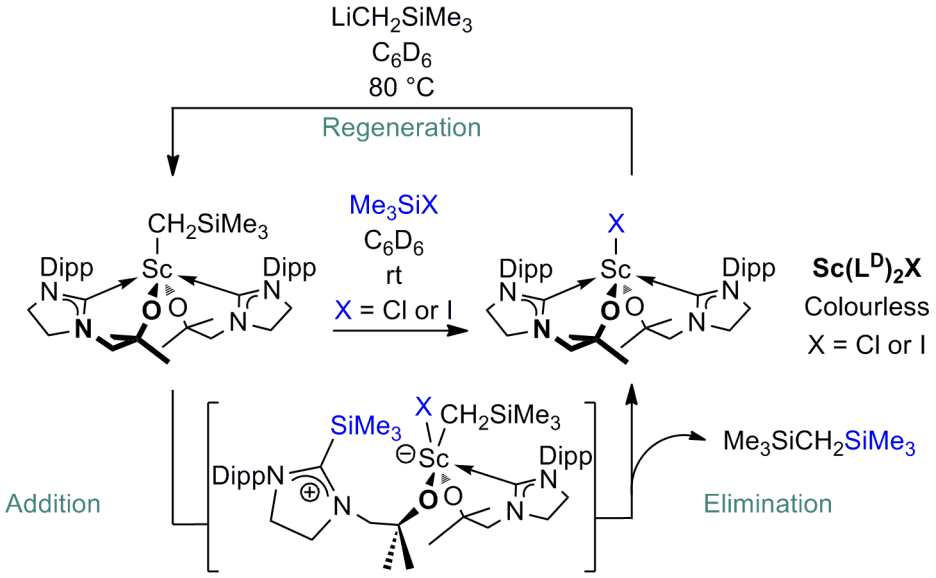


Scheme 8: C-Si bond formation by addition elimination reactions of Me_3SiCl to $M(L^D)(CH_2SiMe_3)_2$ (M = Y or Sc)

The intermediate zwitterion, unlike in the related metal amide chemistry, is not sufficiently stable to be observed and this highlights the increased reactivity of the alkyl *versus* the amide system. The inorganic product, based on the expected mechanism should be $M(L^D)(CH_2SiMe_3)Cl$. However, the ^1H NMR spectrum did not contain resonances that could be assigned to this complex, only broad resonances in the diamagnetic spectral region. Ligand redistribution in the *mono*(ligand) amide species was previously observed (see 3.3.1) and, in this case, the inorganic product is not sufficiently stable to be isolated.

The improved thermal stability of the *bis*(ligand) with respect to the *mono*(ligand) complexes (4.2.2) prompted the C-Si, and the following C-E, bond formation reactions to be largely based on them. This should improve the stability of the inorganic reaction products, which gives them the potential to be recycled back to the starting material or reacted on further.

Treatment of the *bis*(ligand) neosilyl or neopentyl complex $Sc(L^D)_2R$ (R = CH_2SiMe_3 or CH_2CMe_3) with Me_3SiX (X = Cl or I) in a C_6D_6 solution slowly resulted in the formation of $Sc(L^D)_2X$ and the product of C-Si bond formation, $Me_3SiCH_2SiMe_3$ or $Me_3SiCH_2CMe_3$ respectively (5 days for $Sc(L^D)_2CH_2SiMe_3$, 10 days for $Sc(L^D)_2CH_2CMe_3$) (Scheme 9).



Scheme 9: C-Si bond formation by addition elimination reactions of Me_3SiX (X = Cl or I) to $Sc(L^D)_2CH_2SiMe_3$

The resulting zwitterionic intermediate decomposes at room temperature to eliminate $Me_2SiCH_2SiMe_3$ and form the metal halide $Sc(L^D)_2X$ (X = Cl or I). Though the intermediate is not observed, it is proposed that only one NHC group is functionalised; no inorganic

products other than $Sc(L^D)_2Cl$ are isolated and functionalisation of two NHC groups would place a large negative charge on the Sc centre which would be unlikely to be stable. Compared to the *mono*(ligand) example, the resulting inorganic product is stable and readily isolated. This parallels the increased thermal stability of $Sc(L^D)_2CH_2SiMe_3$ with respect to $Sc(L^D)(CH_2SiMe_3)_2$.

$Sc(L^D)_2Cl$ was isolated as single crystals suitable for an X-ray diffraction and was also fully characterised by elemental analysis and NMR spectroscopy. The ^1H NMR contains similar features to that of $Sc(L^D)_2CH_2SiMe_3$, with the protons on one ligand being magnetically inequivalent as a consequence of a rigid structure (Figure 20). The splitting pattern is also supported by the molecular structure in the solid state which possesses a C_2 axis that runs through the **Sc-Cl** bond.

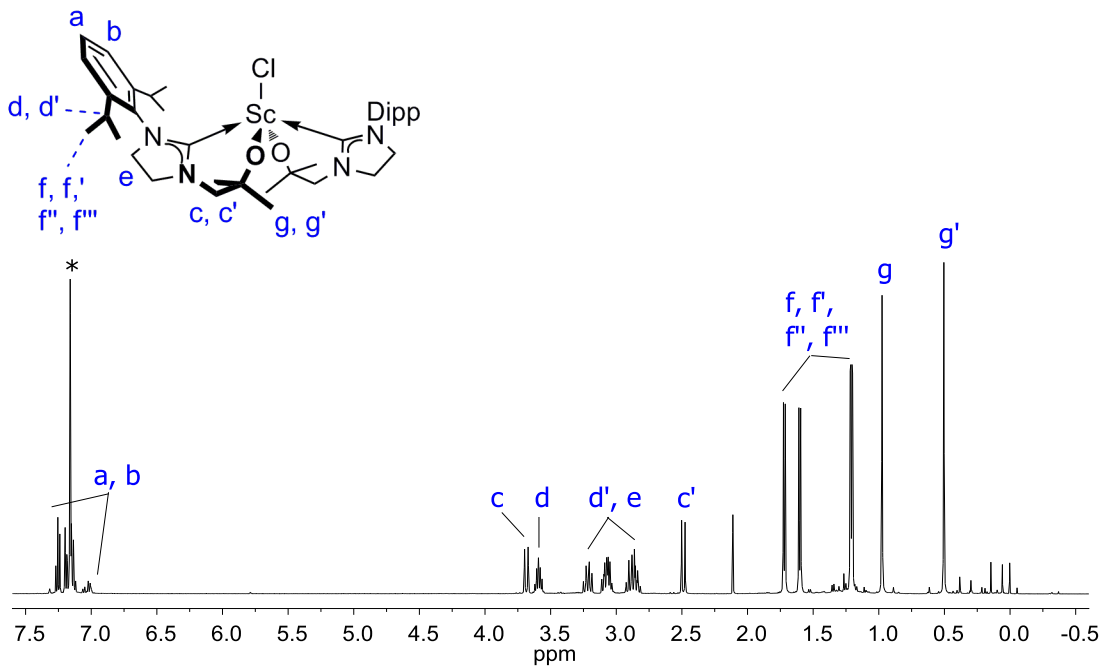
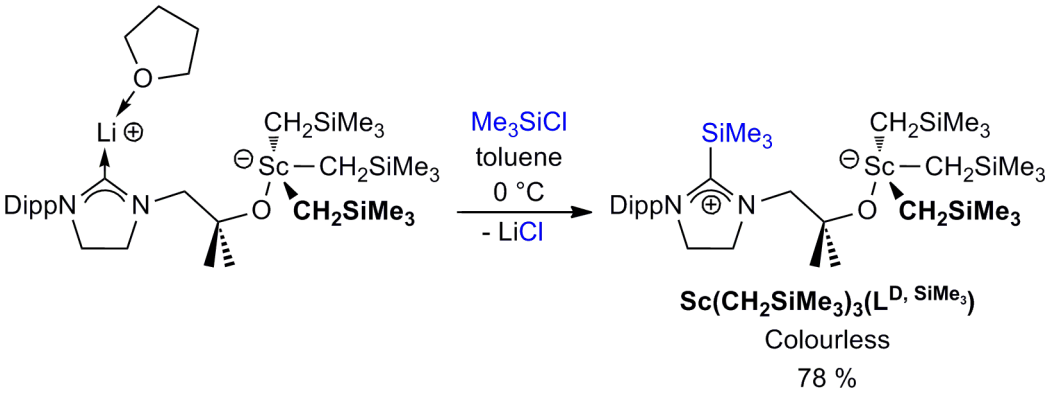


Figure 20: ^1H NMR spectrum (C_6D_6, 500 MHz, 298 K) of $Sc(L^D)_2Cl$
'*' denotes residual protio solvent

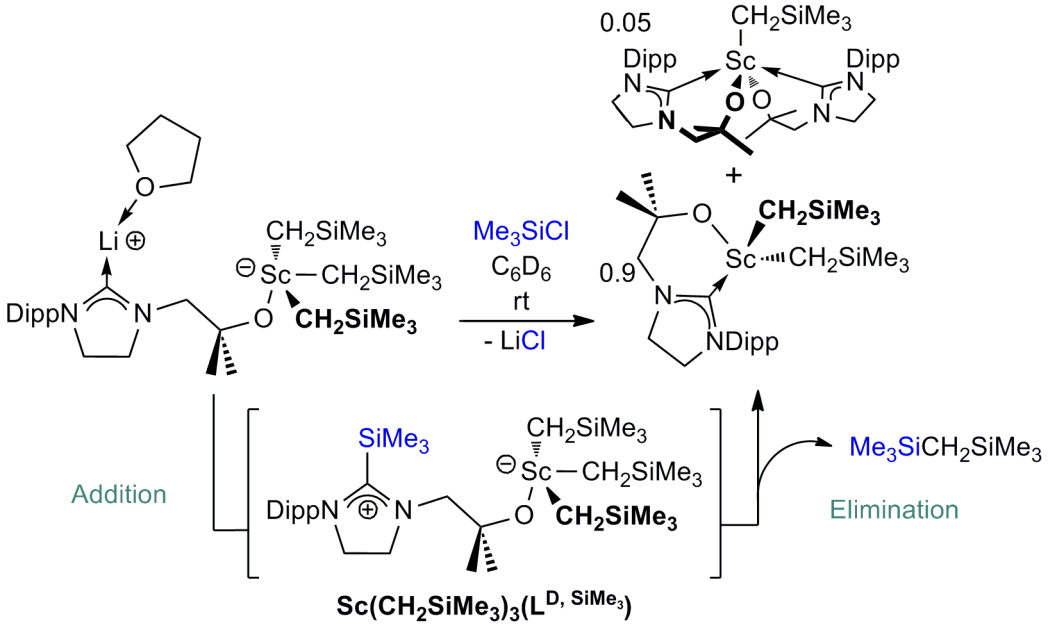
The heterobimetallic complex $Sc(CH_2SiMe_3)_3(L^{D,\,Li\{thf\}})$ was reacted with 1 equivalent of Me_3SiCl, in toluene at 0 ºC for 1 h, in a salt elimination reaction to afford the colourless, silylated product $Sc(CH_2SiMe_3)_3(L^{D,\,SiMe_3})$ in 78 % yield (Equation 10). This reaction effectively generates the intermediate in the addition-elimination reactivity scheme which could not be isolated when the *mono*(ligand) alkyl complexes were treated with Me_3SiCl (Scheme 8). The increased stability may arise from the greater steric protection of

the scandium centre by the presence of three $CH_2SiMe_3^-$ ligands rather than two and a Cl^- ligand, which has a lesser steric demand.[30]



Equation 10: Synthesis of $Sc(CH_2SiMe_3)_3(L^{D,\ SiMe_3})$

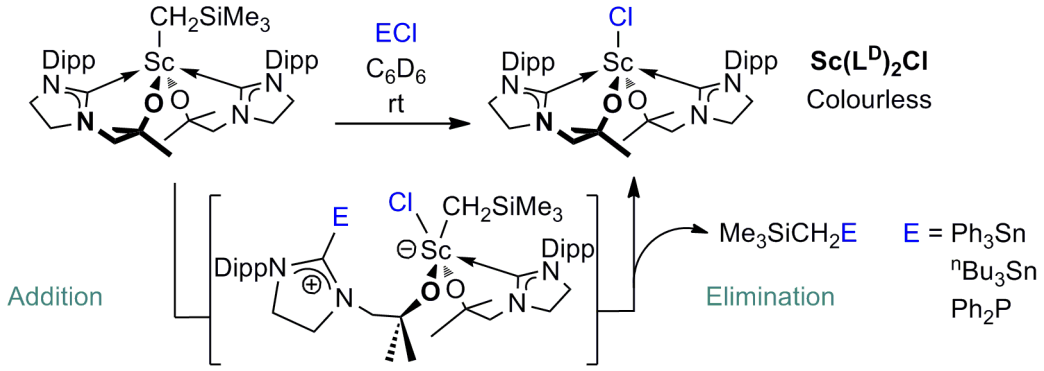
On storage at room temperature in either the solid state or in solution, $Sc(CH_2SiMe_3)_3(L^{D,\ SiMe_3})$ was found to decompose. In solution, this occurred *via* C-Si bond formation and the elimination of $Me_3SiCH_3SiMe_3$. By integration of the ^1H NMR spectrum, approximately 0.9 equivalents of the anticipated $Sc(L^D)(CH_2SiMe_3)_2$ was formed. However, a small amount of $Sc(L^D)_2CH_2SiMe_3$ (~ 0.05 equivalents) was also observed, presumably as a result of ligand redistribution to this more stable product (Scheme 10).



Scheme 10: C-Si bond formation from $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$

4.5.2 Carbon-phosphorus and -tin bond formation

Reaction of $Sc(L^D)(CH_2SiMe_3)_2$ at room temperature in C_6D_6 with 1 equivalent of R_3SnCl (R = ^{t}Bu of Ph) or Ph_2PCl resulted in C-Sn and C-P bond formation to yield $R_3SnCH_2SiMe_3$ and $Ph_2PCH_2SiMe_3$ respectively and the generation of $Sc(L^D)_2Cl$ (Scheme 11).



Scheme 11: C-Sn and C-P bond formation by addition-elimination reactions of tin and phosphorus chlorides with $Sc(L^D)_2CH_2SiMe_3$

Despite the C-P bond forming reaction taking 5 days to reach completion, the intermediate zwitterionic imidazolinium species (which were isolated in the case of the amide complexes, 3.3.1) was not observed. This suggests that the addition step across the M-$C_{carbene}$ bond is rate limiting. Similarly, C-Sn bond formation utilising Ph_3SnCl takes 5 days to reach completion. However, when $^nBu_3SnCl$ is used, the reaction occurs quantitatively over a period of only 17 h and so steric factors may account for the difference in rates of reaction for the tin reagents. The Sn-Cl bond strength is high (for example, 425 ± 17 kJmol^{-1} in Me_3SnCl, 439 kJ.mol^{-1} in $^nBu_3SnCl$ and 350 ± 8 kJmol^{-1} for the diatomic Sn-Cl)[55] but the polarity of the bond and the formation of a strong Sc-Cl bond (464 kJmol^{-1} in $ScCl_3$ and 331 kJmol^{-1} for the diatomic Sc-Cl)[55,56] is presumed to facilitate the reaction.

The $^nBu_3SnCH_2SiMe_3$ product was identified by both EI-MS (*m/z* = 363.1 [M-Me]$^+$ (5 %), 321.1 [M-^{n}Bu]$^+$ (100 %), 264.0 [M-2^{n}Bu]$^+$ (18 %), 207.0 [M-3^{n}Bu]$^+$ (66 %)) and ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance for the methylene ^{n}Bu carbons of $^nBu_3SnCH_2SiMe_3$ occurs at 10.7 ppm and coupling to the NMR active ^{119}Sn and ^{117}Sn isotopes was visible as tin satellites ($^2J_{^{119}SnC}$ = 162 Hz, $^2J_{^{117}SnC}$ = 155 Hz). The ^{1}H NMR spectra of both $Sc(L^D)_2Cl$ (Figure 21a)) and the reaction mixture after 17 h (Figure 21b)) are shown for clarity.

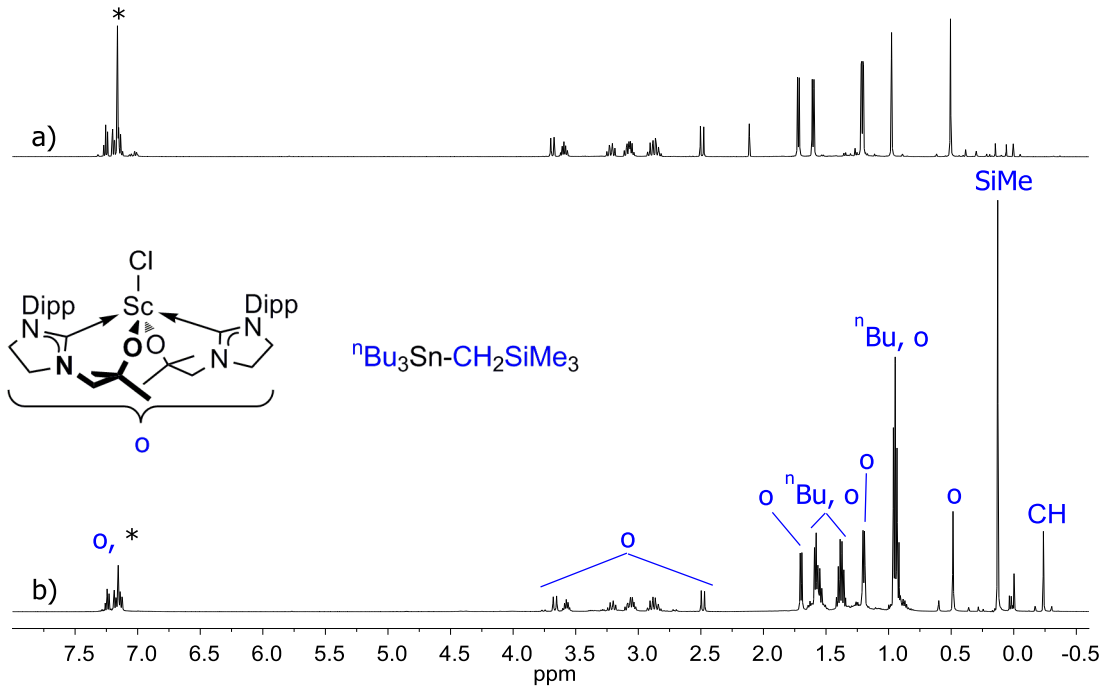


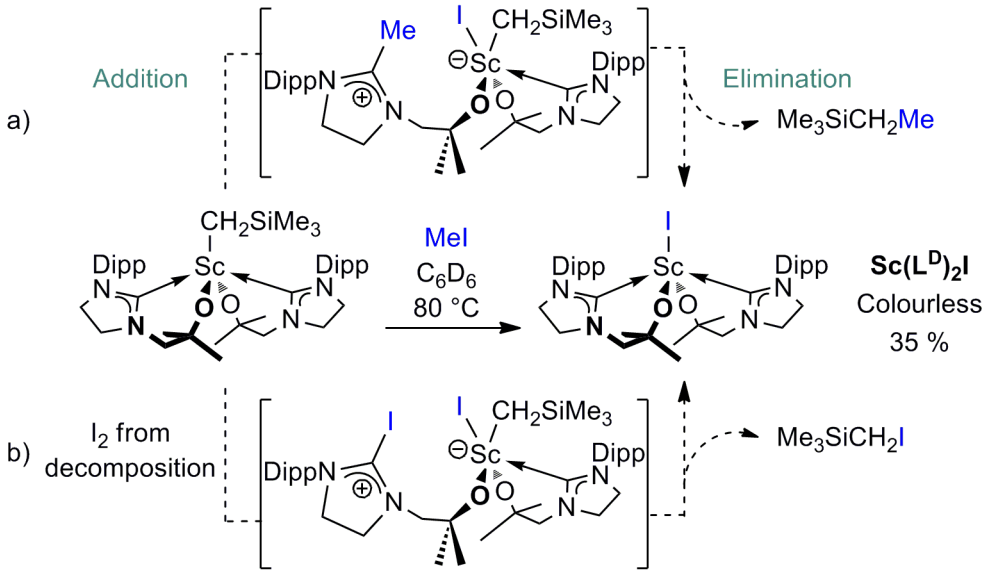
Figure 21: ^{1}H NMR spectrum (C_6D_6, 500 MHz, 298 K) of a) $Sc(L^D)_2Cl$ and b) the reaction mixture of $Sc(L^D)_2CH_2SiMe_3$ and $^{n}Bu_3SnCl$ after 17 h

'*' denotes residual protio solvent

4.5.3 Carbon-carbon bond formation

In an effort to extend C-Si bond formation to C-C bond formation, we completed the reactions of $M(L^D)_2CH_2SiMe_3$ (M = Sc or Y) with a number of alkyl halides (MeI, ^{i}PrCl, ^{i}PrI, ^{t}BuI, Ph_3CCl, CH_2CHCH_2Cl, BnBr, Me3SiCH$_2$Cl) and aryl halides (PhCl, PhI, Ar^FI). In a typical reaction, an equimolar quantity of each reagent was combined in a J-Young Teflon valve NMR tube in C_6D_6 (0.5 mL) and the ^{1}H NMR spectrum was recorded immediately, and then after the reaction mixture had been heated to 80 ºC for 16 h. In all but the treatment of $Sc(L^D)_2CH_2SiMe_3$ with MeI (Scheme 12) and Ar^FI (4.5.5), no reaction occurred.

The reaction with Ar^FI afforded products formally arising from the reverse addition across M-$C_{carbene}$ bond and subsequent C-I bond formation, *i.e.* $Sc(L^D)_2Ar^F$ and Me_3SiCH_2I (see 4.5.5 for full discussion). In the case of MeI; $Sc(L^D)_2CH_2SiMe_3$ was treated with 1 equivalent of MeI in C_6D_6 at 80 ºC for 2 h to afford $Sc(L^D)_2I$ which was isolated in 35 % yield after work-up (Scheme 12a)).



Scheme 12: Reaction of MeI with $Sc(L^D)_2CH_2SiMe_3$

The previous reactivity studies would imply that reaction may proceed through the addition of MeI across the M-$C_{carbene}$ bond with following elimination of Me_2SiCH_2Me. However, the organic byproducts could not be identified. The same outcome was observed in the absence of light and in daylight, where MeI is known to liberate free I_2. When the reaction was completed with an excess of MeI, the solution became red-brown in colour due to the formation of I_2. If the reaction is being effected by trace amounts of I_2 present within the reaction mixture (Scheme 12b)), the expected byproduct would be Me_3SiCH_2I; this is also not observed. The decomposition temperature of MeI is 270 ºC and the reductive elimination of MeI from Pt^{IV} complexes at 80 ºC has been previously reported.[57]

Crystals of $Sc(L^D)_2I$ suitable for an X-ray diffraction study were grown by slow evaporation of a toluene solution at room temperature. The displacement ellipsoid plot (Figure 22) and selected bond lengths (Å) and angles (º) are provided (Table 6).

Table 6: Selected bond lengths (Å) and angles (º) of $Sc(L^D)_2I$

Sc1-C1	2.4306(17)
Sc1-I1	2.8480(5)
C1-Sc1-$C1^i$	173.98(8)
C1-Sc1-I1	93.01(4)
N1-C1-Sc1	115.64(12)
N2-C1-Sc1	136.69(12)

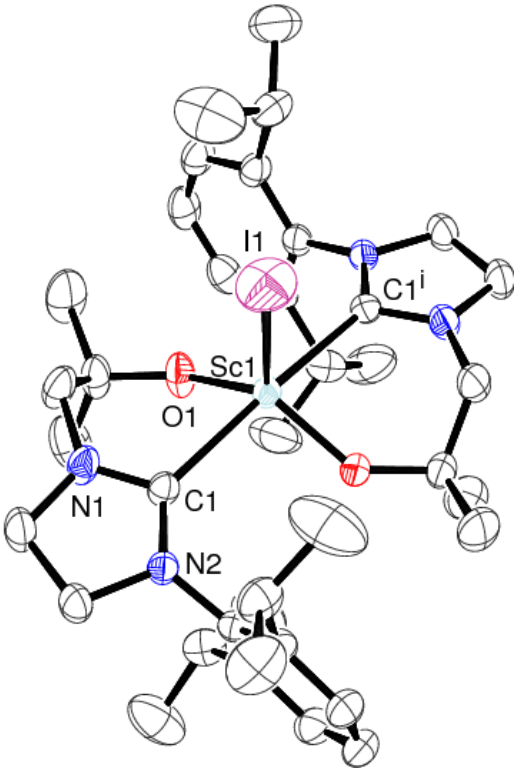


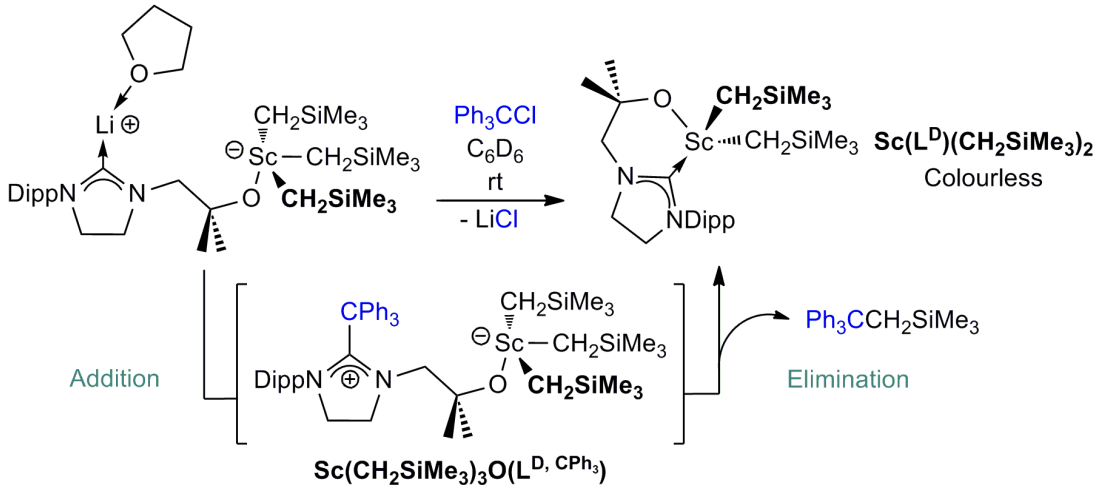
Figure 22: Displacement ellipsoid plot (50 %) of $Sc(L^D)_2I$
H atoms are omitted for clarity

The scandium centre is in a distorted trigonal bipyramidal coordination environment (C1-Sc1-$C1^i$ = 173.98(8)º, C1-Sc1-I1 = 93.01(4)º) with the alkoxide and iodide groups defining the equatorial plane. In comparison to the molecular structure of $Ce(L^D)_2N''$ (see 2.4.2), which was square based pyramidal, the coordination geometry in $Sc(L^D)_2I$ reflects the lesser steric demand of the I^- ligand with respect to $N(SiMe_3)_2^-$ (steric coordination number 1.00 and 2.17 respectively).[30] The Sc-$C_{carbene}$ bond distance (2.4306(17) Å) is almost identical to that of the *mono*(ligand) complex $Sc(L^D)N''_2$ (2.4301(17) Å) (see 2.4.1) and so remains long with respect to reported scandium NHC complexes in the literature.[3] As for $Sc(L^D)N''_2$ (N1-C1-Sc1 = 111.62(11)º, N2-C1-Sc1 = 141.49(11)º), there is a significant asymmetry to the coordination of the N-heterocyclic ring to the metal ion (N1-C1-Sc1 = 115.64(12)º, N2-C1-Sc1 = 136.69(12)º), with the *N*-Dipp groups being forced backwards in order to minimise unfavourable interactions. There are only four examples of crystallographically characterised Sc-I bonds in the literature; $[ScCp^*(bipy)(\mu\text{-}I)]_2$,[58] $[ScCp^*((\mu\text{-}I)_2]_4$ and the scandium cluster complexes, $Sc_6I_{11}C_2$ and $Sc_4I_6C_2$.[59] They all involve bridging iodides with Sc-I bond lengths ranging from 2.765(9) Å to 3.577(3) Å.

As previously demonstrated with Me_3SiCl (see 4.5.1), functionalisation of the carbene in the heterobimetallic complex $Sc(CH_2SiMe_3)_3(L^{D,\,Li\{thf\}})$ can be achieved *via* a

straightforward salt elimination reaction to afford $Sc(CH_2SiMe_3)_3(L^{D,\ SiMe_3})$ in good yield (78 %). Therefore, the addition of haloalkanes RX to $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ was investigated in order to form the analogous $Sc(CH_2SiMe_3)_3(L^{D,\ R})$ which on elimination would form C-C bonds.

Treatment of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ in C_6D_6 at room temperature with Ph_3CCl afforded an orange solution and a colourless precipitate of LiCl over a period of 1 h. NMR spectroscopic analysis of the reaction mixture showed the reformation of $Sc(L^D)(CH_2SiMe_3)_2$ (Scheme 13). The compound $Ph_3CCH_2SiMe_3$ was also characterised by EI-MS (*m/z*: 330.2 $[M]^+$ (25 %), 315.2 $[M\text{-}Me]^+$ (6 %), 243.1 $[M\text{-}CH_2SiMe_3]^+$ (100 %)). From this reaction mixture, crystals of $Sc(L^D)(CH_2SiMe_3)_2$ suitable for an X-ray diffraction study were grown from a toluene solution at -20 °C (see 4.2.2)



Scheme 13: C-C bond formation from $Sc(CH_2SiMe_3)_3(L^{D,\ CPh_3})$

The C-Cl bond strength in Ph_3CCl is weak (estimated at 280 $kJmol^{-1}$)[60], making it an ideal example with which to test this type of reaction. Disappointingly, attempts to generalise the reaction to various simple alkyl halides (^{i}PrCl, ^{i}PrI, ^{t}BuI and BnBr) and aryl halides (PhCl and PhI) did not result in any reaction.

The addition-elimination reaction of Me_3SiCl with the *mono* and *bis*(alkyl) complexes has been demonstrated to be facile. The Si-Cl bond dissociation energy in Me_3SiCl is 472 ± 8 $kJmol^{-1}$,[161] considerably higher than the bond dissociation energies of any of the C-Cl bonds in the chloroalkanes tested. Similarly, though MeI and Ar^FI have been shown to react with the *bis*(ligand) complex $Sc(L^D)_2CH_2SiMe_3$ and have lower C-X bond strengths than in Ph_3CCl (Me-I = 238.9 ± 9 $kJmol^{-1}$, Ar^FI = 273.6 ± 8.3 $kJmol^{-1}$), the remaining haloalkanes used show no reactivity even when the C-X bond strength is lower.

This suggests that the reactivity is not dependent on the C-X bond dissociation energy alone. The bond dissociation data are summarised for clarity (Table 7).

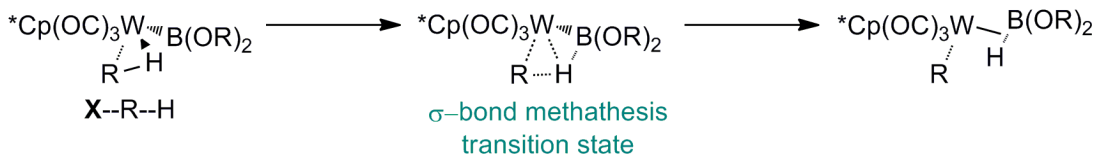
Table 7: C-X bond dissociation energies (BDE, $kJmol^{-1}$) of haloalkanes and silanes and summary of reactivity with *mono* and *bis*(alkyl) complexes

Compound	E-X BDE ($kJ\ mol^{-1}$)	Reactivity		
		mono	*bis*	'ate'
Me_3SiCl	472 ± 8	Y	Y	Y
Ph_3CCl	280	Dec.	N	Y
$^{i}PrCl$	354.0 ± 6.3	Dec.	N	N
PhCl	399.6 ± 6.3	Dec.	N	N
BnBr	225.1 ± 6.3	Dec.	N	N
^{i}PrI	236.8 ± 4.2	Dec.	N	N
^{t}BuI	227.2 ± 6.3	Dec.	N	N
MeI	273.6 ± 8.4	Dec.	Y	N
PhI	272.0 ± 4.2	Dec.	N	N
$Ar^{F}I$	273.6 ± 8.3	Y	Y	-

4.5.4 Carbon-boron bond formation

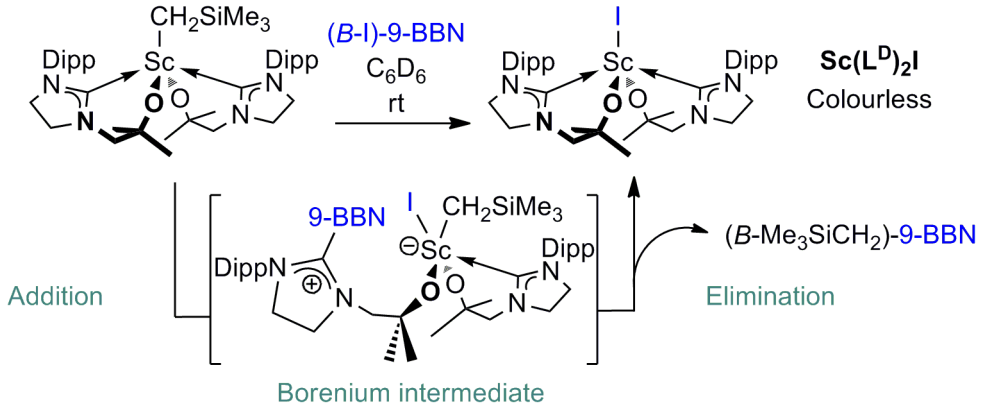
The metal-catalysed functionalisation of C-H bonds by C-B bond formation is a rapidly growing area of research. Borylation is an attractive method of alkane functionalisation since the process is thermodynamically favourable, can be completed under mild conditions and can also be selective. The method is currently reliant on a small number of boron sources: B_2cat_2, B_2pin_2, HBpin and HBdan (cat = catecholate = 1,2-O-C_6H_4, pin = pinocolate = $(OCMe_2)_2$, dan = 1,8-*N*-napthalene) but remains successful for a large range of substrates.[62] Borylation is often combined with the Suzuki-Miyaura cross coupling to form new C-C bonds.[63,64]

In the photochemical reaction of the tungsten boryl complex, **X**, W(L)Cp*$(CO)_3$ (L = $B(OR)_2$ where OR =1,2-O-3,5-Me-C_6H_2) with branched, linear or cyclic alkanes, alkane borylation was observed with a bias towards 1º C-H bond activation.[65] Experimental and computational mechanistic studies on this system have investigated both σ bond metathesis and oxidative addition/reductive elimination pathways, with the former calculated to be the lower energy route (Scheme 14).



Scheme 14: Proposed σ-bond metathesis route to C-H borylation with W(L)Cp*(CO)$_3$

Following on from the N-B bond forming reaction achieved for the *mono*(ligand) amide complex, Y(L^D)N"$_2$ (see 3.3.1), we also sought to investigate the potential of C-B bond formation with the alkyl complexes. As for the other p-block halides, (*B*-I)-9-BBN also added and eliminated across the M-C$_{carbene}$, at room temperature in C_6D_6 over 16 h, to generate a zwitterionic intermediate whereby the carbene has been functionalised by the borane reagent and a strong Sc-I bond has formed. C-B bond formation occurred through the elimination of (*B*-CH_2SiMe_3)-9-BBN from this intermediate (Scheme 15).



Scheme 15: C-B bond formation by the addition-elimination reaction of (*B*-I)-9-BBN with Sc(L^D)$_2$CH$_2$SiMe$_3$

The boron chemistry of NHCs previously reported includes neutral carbene diborenes,[66] borane adducts,[67] boranthracene adducts and, recently, both a stabilised borrole anion[68] and a borenium cation, [B(L)Mes$_2$]OTf (L = 1-C(NMeCH)$_2$).[69]

The intermediate in this addition-elimination reaction formally contains a borenium cation.[70,71] In a borenium cation B(L)R$_2$ (L = neutral donor, R = σ-donor), the sp^2 boron centre is three-coordinate with two σ-bound groups and one dative interaction (Figure 23). Though more stable than the related two coordinate BR$_2^+$ borinium ions, they remain very reactive, electrophilic and are accordingly rare. They can be stabilised electronically by π-donation to the empty B 2p orbitals as well as sterically by bulky groups.[72] Though limited by rarity, their practical use has been demonstrated, for example, as chiral catalysts for enantioselective Diels Alder reactions.[73]

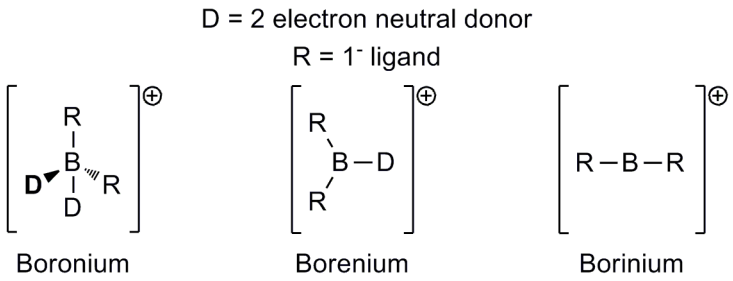
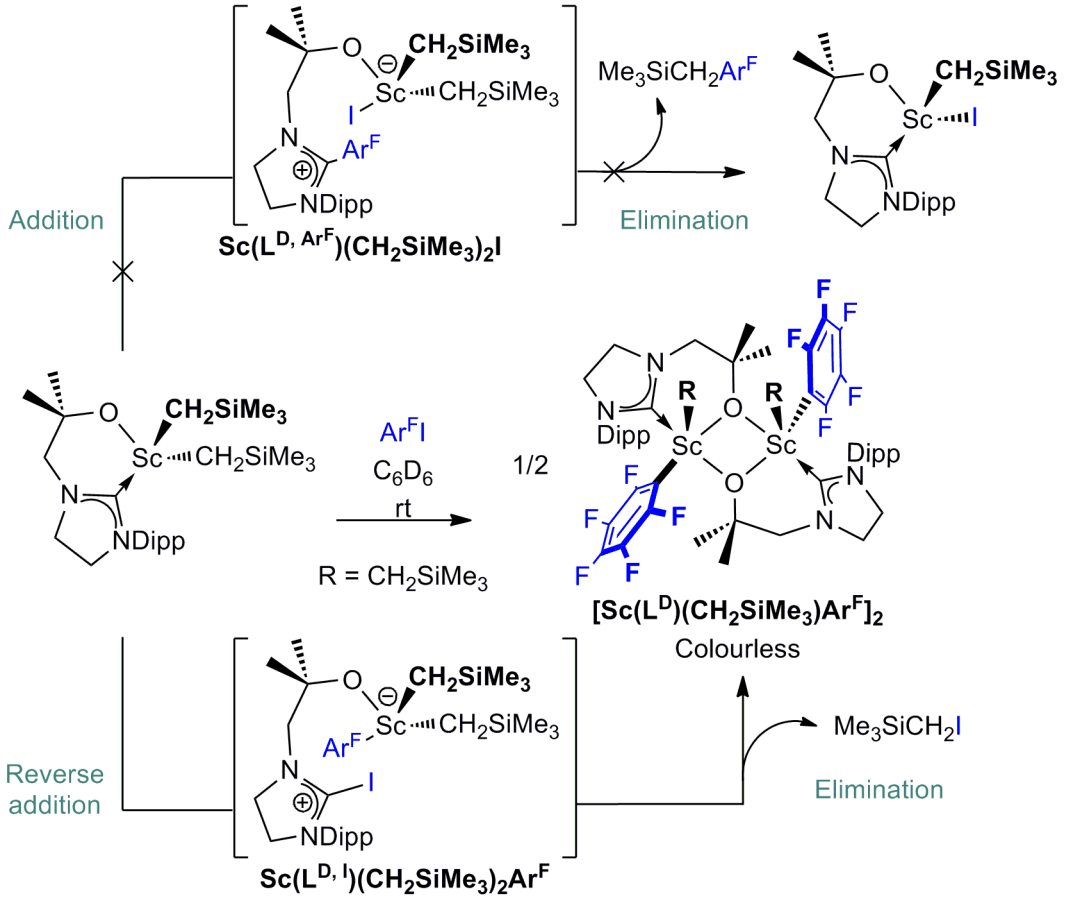


Figure 23: Boron cationic species

4.5.5 Carbon-iodine bond formation

Reaction of $Sc(L^D)(CH_2SiMe_3)_2$ with 1 equivalent of Ar^FI at room temperature in C_6D_6 immediately afforded the mixed aryl-neosilyl complex $[Sc(L^D)(CH_2SiMe_3)Ar^F]_2$ (Scheme 16).



Scheme 16: C-I bond formation by the reverse addition of C_6F_5I to $[Sc(L^D)(CH_2SiMe_3)Ar^F]_2$

Contrasting the addition-elimination reactions of the p-block halides (see 4.5.1 – 4.5.4), $[Sc(L^D)(CH_2SiMe_3)(Ar^F)]_2$ is the product from the 'reverse addition' across the M-$C_{carbene}$ bond whereby, in the intermediate, the carbene forms an iodoimidazolinium species

and an M-C_{aryl} bond forms. The resulting elimination reaction yields $[Sc(L^D)(CH_2SiMe_3)(Ar^F)]_2$.

Precedent for the reverse addition of Ar^FI to form the iodoimidazolidinium intermediate (which is not directly observed) has been previously set. The free carbene 1-$C(NAdCH)_2$ reacts with Ar^FI to form **Y**, 1-$CAr^FI(NAdCH)_2$ (Figure 24).[74] This adduct is best described as a halonium methylene ylid, a zwitterion where a positive charge is formally centred on the N-heterocyclic ring and a negative charge is on the iodine atom. The adduct underwent some decomposition in solution at room temperature over several hours, suggesting that C-I bond cleavage may occur. The iodoimidazolium salt, $[1\text{-}CI(NAdCH)_2]I$ was prepared by treatment of the corresponding free carbene with elemental iodine and salt **Z**, $[1\text{-}CI(NEtCH)_2]I$ was reported by the reaction of molybdenum and chromium carbonyl complexes $[M(1\text{-}C(NEtCH)_2)(CO)_5]$ (M = Mo or Cr) in chloroform with iodine (Figure 24).[75]

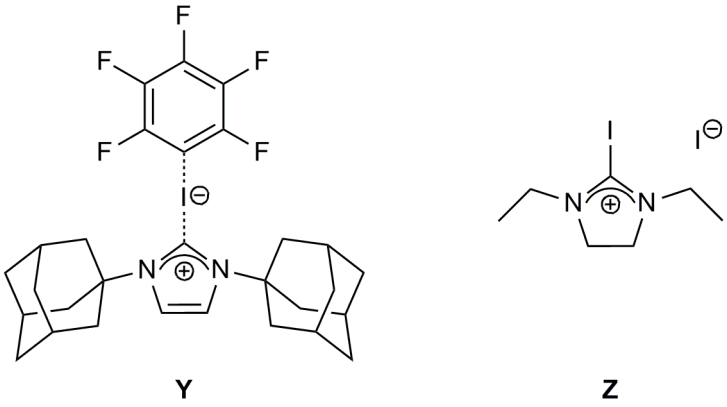


Figure 24: Related complexes to the iodoimidazolidinium intermediate

The syntheses of lanthanide complexes with a M-Ar^F bond have been previously reported from: transmetallation reactions of elemental ytterbium and europium or $SmCp^*_2$ with $HgPhAr^F$ [76] or $HgAr^F_2$ [77-80] (**AA**, Figure 25), Si-C bond cleavage reaction of a lanthanide hydride (for example, $[SmCp^*(\mu\text{-}H)]_2$ with Ar^FSiH_3) and phenyl group transfer between $[SmCp^*(\mu\text{-}Ph)]_2$ and Ar^FSiH_3 (**AB**, Figure 25),[78,81] decomposition of the cationic species ($[Sc(L)][MeBAr^F_3]$ to **AC**, $[Sc(L)Ar^F][Me_2BAr^F]$ (L = DippNC(Me)CHC(Me)NDipp),[82] the protonolysis reaction of the chiral metallacycle $Ce(\{1,2,4\text{-}^tBu\}_3C_5H_2)(\{1,2\text{-}^tBu\text{-}4\text{-}CMe_2CH_2\}C_5H_2)$ with Ar^FH to form $Ce(\{1,2,4\text{-}^tBu\}_3C_5H_2)_2C_6F_5$ (**AD**, Figure 25) and from C-H or C-F bond activations of Ar^FX (X = H or F) by the cerium hydride $Ce(\{1,2,4\text{-}^tBu\}_3C_5H_2)_2H$.[83]

There are also a limited number of metal NHC complexes with a M-Ar^F bond, being formed by oxidative addition of Ar^FX (X = F, CF_3, Ar^F),[52,84] as in the case of **AE**, *trans*-$[Ni(L)_2(F)Ar^F]$ (L = 1-C(^{i}PrNCH)$_2$)[84] or by simple substitution reactions, as for **AF**, $Au(L)Ar^F$ (L = 1-C(MeNCH)$_2$) (Figure 25).[85]

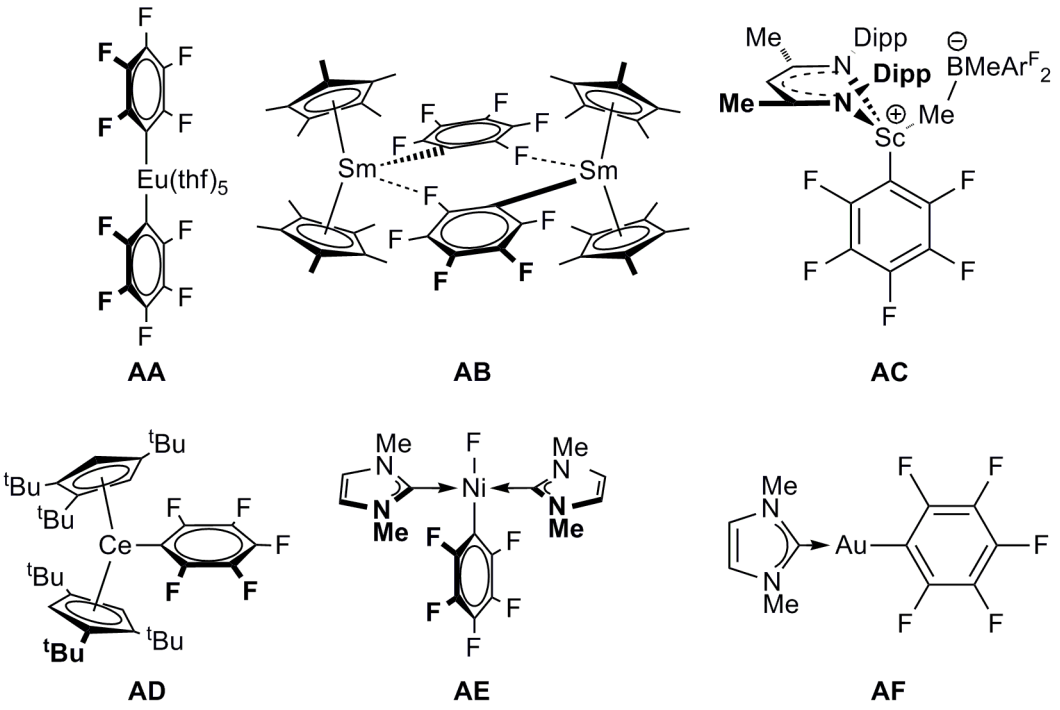


Figure 25: Other examples of metal pentafluorobenzene complexes

Crystals of $[Sc(L^D)(CH_2SiMe_3)Ar^F]_2$ suitable for an X-ray diffraction study were grown from a toluene solution at -20 ºC. The displacement ellipsoid plot is provided (Figure 26). The data confirms the connectivity of the molecular structure but were not of sufficient quality for a detailed discussion of the metrical parameters.

$[Sc(L^D)(CH_2SiMe_3)Ar^F]_2$ is an asymmetric dimer in solid state. The ^{1}H NMR spectrum of $[Sc(L^D)(CH_2SiMe_3)(Ar^F)]_2$ is also consistent with the dimer existing in solution since it contains two sets of sharp resonances for two distinct ligand environments. In the solid state molecular structure, Sc1 is in a distorted trigonal bipyramidal coordination environment and Sc2 is in a distorted square based pyramidal geometry. There is also an apparent π-π stacking interaction between both *N*-Dipp and Ar^F rings.

There is a significant asymmetry in the coordination of the Ar^F group to both scandium centres (for example, C48-C47-Sc2 = *ca*. 110º and C52-C47-Sc2 = *ca*. 140º). Combined with one short Sc···F distance (for example, Sc2···F6 = *ca*. 3.0 Å, Sc2···F10 = *ca*. 3.7 Å), which is well within the combined van der Waals' radii of 3.47 Å, this suggests

the presence of stabilising Sc···F interactions such as those observed in **AB**, [SmCp*(μ-Ar^F)]$_2$ (Sc···F = 2.531(8) Å and 2.539(7) Å), **AD**, Ce({1,2,4-^{t}Bu}$_3$C$_5$H$_2$)$_2$Ar^F (Sc···F = 2.682(2) Å) and YbCp*Ar^F(thf)$_3$ (Sc···F = 3.162(4) Å).[86]

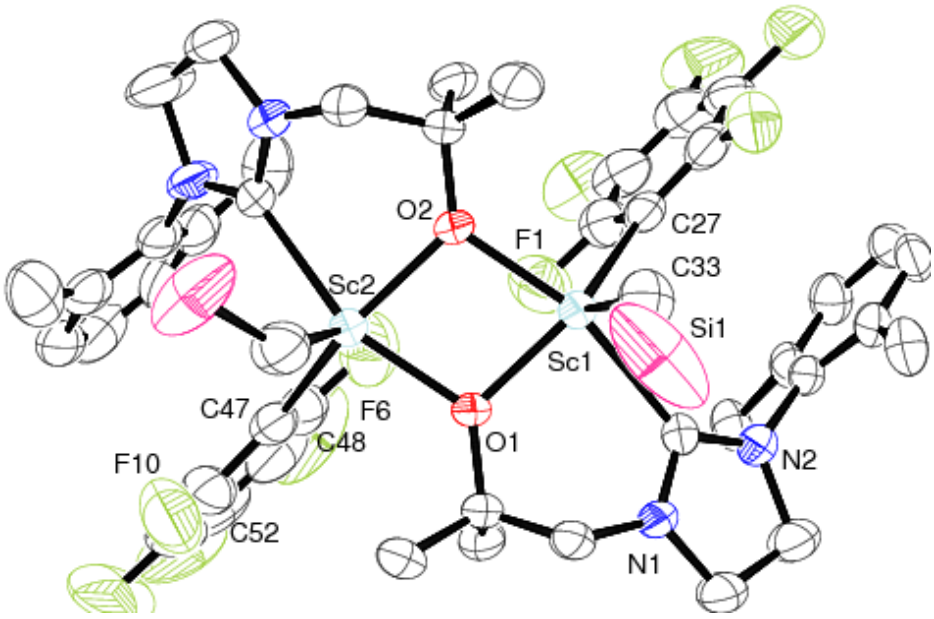
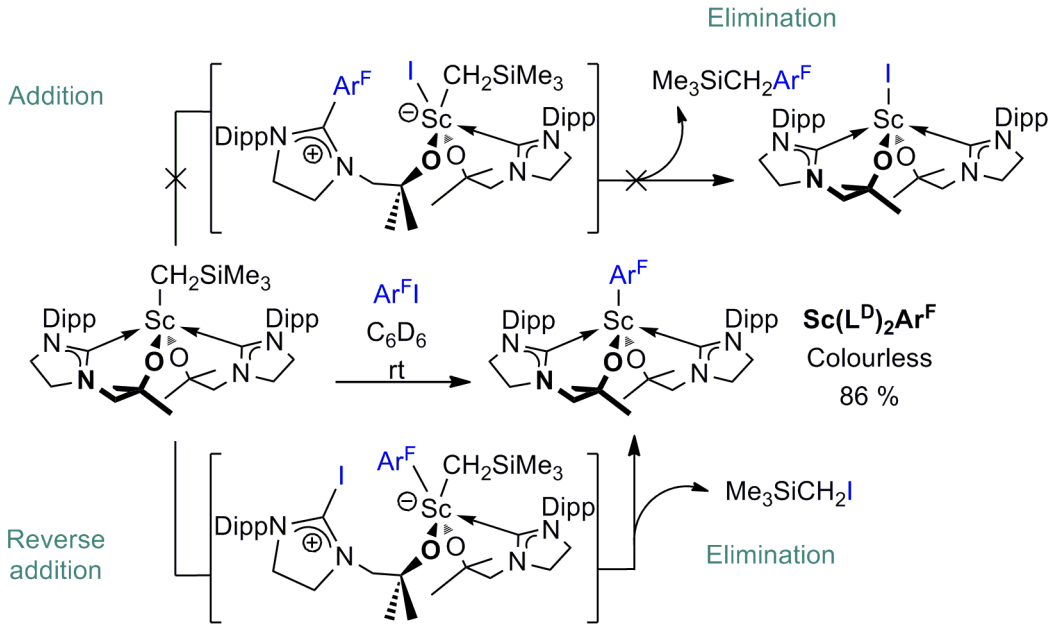


Figure 26: Displacement ellipsoid plot (50 %) of [Sc(L^D)(CH$_2$SiMe$_3$)(C$_6$F$_5$)]$_2$
H atoms, solvent molecules, Dipp Me and silyl Me groups omitted for clarity

Similarly, treatment of *bis*(ligand) Sc(L^D)$_2$(CH$_2$SiMe$_3$) with 1 equivalent of Ar^{F}I at room temperature in C$_6$D$_6$ immediately afforded the aryl complex Sc(L^D)$_2$Ar^F in 86 % yield (Scheme 17).



Scheme 17: C-I bond formation by the reverse addition of Ar^{F}I to Sc(L^D)$_2$CH$_2$SiMe$_3$

Crystals of $Sc(L^D)_2Ar^F$ suitable for an X-ray diffraction study were grown from a saturated toluene solution at -20 ºC. The displacement ellipsoid plot (Figure 27) and selected bond lengths (Å) and angles (º) are provided (Table 8).

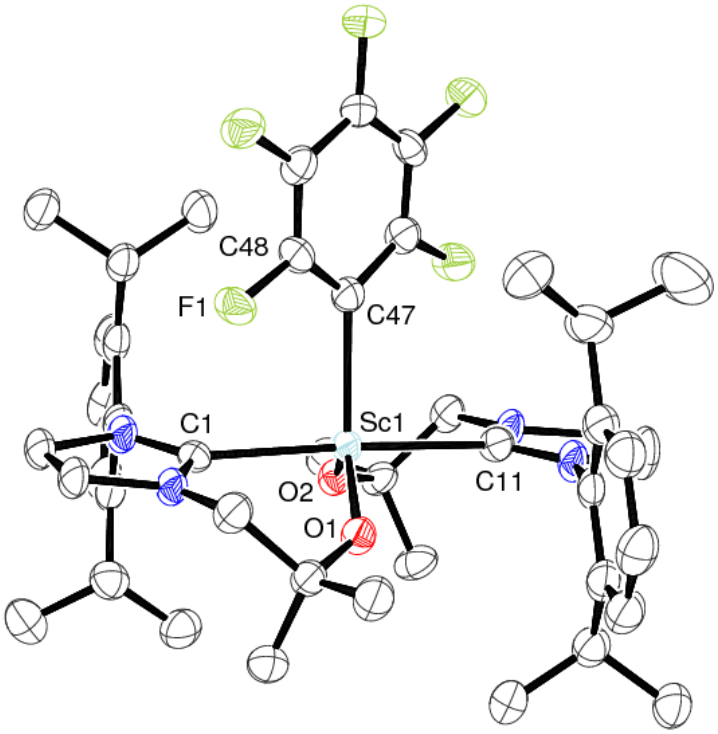


Figure 27: Displacement ellipsoid plot (50 %) of $Sc(L^D)_2Ar^F$
H atoms omitted and only one of two molecules in the asymmetric unit is shown for clarity

Table 8: Selected bond lengths (Å) and angles (º) of $Sc(L^D)_2Ar^F$

Sc1-C1	2.412(5)
Sc1-O1	1.918(4)
Sc1-C47	2.417(6)
C1-Sc1-C11	177.2(2)
O1-Sc1-O2	120.96(19)
C48-C47-Sc1	125.0(4)
C48-C47-Sc1-O1	47.8(6)

$Sc(L^D)_2Ar^F$ crystallised with two molecules in each asymmetric unit of the unit cell and, since both have very similar metrical parameters, only one is discussed here for clarity. The metal ion has a trigonal bipyramidal coordination geometry with the carbene donors as axial groups (O1-Sc1-O2 = 120.96(19)º and C1-Sc-C11 = 177.8(2)º), the N-heterocyclic rings being near co-planar (interplane angle defined by N1-C1-N2 and N3-C11-N4 = 8.73 Å) and the bulky *N*-Dipp groups opposite to each other in order to minimise unfavourable

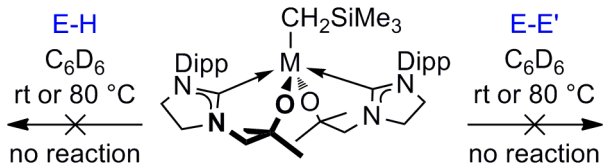
interactions. The Sc-$C_{carbene}$ bond length (2.412(5) Å) is comparable to that in $Sc(L^D)_2I$ (2.431(2) Å).

The Sc-C_{aryl} bond length in $Sc(L^D)_2Ar^F$ (2.412(5) Å) is long. Comparison with $Y(L)Ar^F_2(thf)$ (L = 1-NPh-2-CHNPh-C_6H_4) (2.492(3) Å) confirms this even when taking into account with 0.155 Å difference in ionic radii of Sc^{III} and Y^{III}.[10] The Sc···$F_{average}$ bond distance of 3.53 Å is also long (outwith the combined van der Waals' radii of 3.47 Å) and there is no significant asymmetry in the coordination of the Ar^F group to the scandium centre (C48-C47-Sc1 = 125.0(4) Å and C52-C47-Sc1 = 123.89(4) Å) to indicate the presence of any stabilising Sc···F interactions.

4.5.6 Further attempted addition-elimination reactivity: E-E' and E-H

Although no reactivity was observed for the *mono*(ligand) amide system, $M(L^D)N''_2$ (M = Y, Sc, Ce or U) with E-E' and E-H reagents (where E and E' = main group elements), these reactions were attempted for the *mono* and *bis*(ligand) alkyl systems, $M(L^D)_2CH_2SiMe_3$ and $M(L^D)(CH_2SiMe_3)_2$ (M = Y or Sc), because of their higher intrinsic reactivity.

Unfortunately, treatment of $M(L^D)_2CH_2SiMe_3$ (M = Y or Sc) with the E-H (E-H = CH_4, Ph_3CH, Ar^FH, PhCCH, $^nBu_3SnH$ or Ph_2SiH_2) and E-E' (E-E' = B_2pin_2, $Et_3GeGeEt_3$, $Me_3SnSnMe_3$, $Me_2PhSiB(OCMe_2CMe_2O)$ or 1,1-Me_2-Si-$(CH_2)_3$) resulted in no reaction in C_6D_6 even after heating to 80 ºC for 16 h (Scheme 18). Similarly, the *mono*(ligand) complexes displayed no reactivity with E- E' ($Me_3SnSnMe_3$) or E-H (1,1-Me-Si-$(CH_2)_3$ or $^nBu_3SnH$) at room temperature and were found to decompose on heating to 80 ºC for 16 h.



E = CH_3, PhCC, Ph_3C, $^nBu_3Sn$, Ar^F, Ph_2SiH

M = Y or Sc

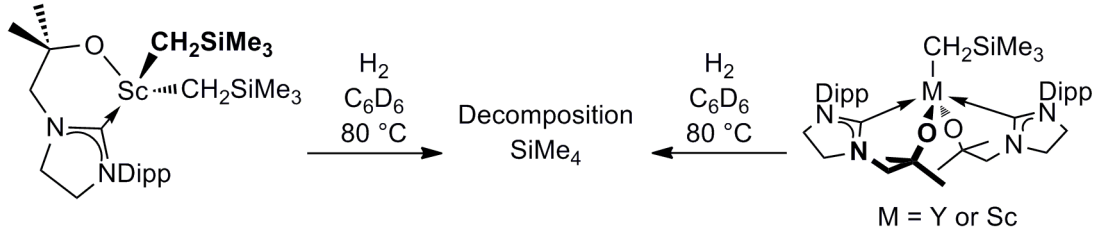
E-E' = $Me_3SnSnMe_3$, $Et_3GeGeEt_3$, $Me_2PhSiB(OCMe_2CMe_2O)$, 1,1-Me-Si-$(CH_2)_3$

Scheme 18: Reactivity with E-E' and E-H reagents

As previously discussed (see 3.3.3), the addition reaction appears to be driven by the formation of a strong M-X bond (Sc-Cl: 464 $kJmol^{-1}$ in $ScCl_3$ and 331 $kJmol^{-1}$ for the diatomic ScCl, Y-Cl: 523 ± 84 $kJmol^{-1}$ for diatomic YCl) and the use of a polar substrate.

4.5.7 Attempted preparation of M^{III} carbene hydrides

Reaction of $M(L^D)_2CH_2SiMe_3$ (M = Y or Sc) with H_2 (1 atm) in C_6D_6 at 80 ºC for 72 h resulted in no reaction apart from the generation of a small amount of $SiMe_4$, which is also observed on heating the *bis*(ligand) alkyl complexes in the absence of H_2. Similarly, reaction of *mono*(ligand) $Sc(L^D)(CH_2SiMe_3)_2$ resulted in some decomposition to $SiMe_4$ at room temperature and the expected thermal decomposition when the reaction mixture was heated to 80 ºC for 2 h (Scheme 19). No resonances associated with the desired metal hydride products were observed.



Scheme 19: Reaction of *mono* and *bis*(ligand) silylalkyl complexes with H_2

Treatment of $M(L^D)_2CH_2SiMe_3$ (M = Sc or Y) with 1 equivalent of $PhSiH_3$ in C_6D_6 at room temperature afforded a clear, pale yellow solution immediately. ^{1}H NMR spectral analysis indicated full consumption of $PhSiH_3$, resonances for $M(L^D)_2CH_2SiMe_3$, some small broad resonances between 3.50 ppm – 2.50 ppm and 1.75 ppm – 1.00 ppm, a singlet at 0.02 ppm which integrates to 9 protons and two addition triplets at 4.58 ppm and -0.08 ppm (2 H, t, J_{XH} = 5 Hz) (Figure 28). Addition of a second equivalent of $PhSiH_3$ resulted only in decomposition (M = Y) or no further reaction, even on heating to 80 ºC for 16 h (M = Sc). The ^{1}H NMR spectrum of the reaction (M = Sc) is shown for clarity (Figure 28).

If a hydride complex had been formed, then $SiMe_4$ would be eliminated and a singlet at 0 ppm integrating to 12 protons would be expected in the ^{1}H NMR spectrum. The new hydride group would most likely be present as a bridging group in a dimer rather than as a terminal hydride; if symmetric, a singlet would be anticipated for the hydride and if the dimer was asymmetric a doublet would be expected from mutual coupling in the NMR spectrum. When the metal centre is yttrium, additional coupling would be expected. The NMR spectrum (Figure 28c)) does show a sharp singlet at 0.02 ppm integrating to 9 protons. However, the resonances associated with CH_2SiMe_3 protons are also clearly visible, they have not shifted in frequency or changed in integration with respect the $Sc(L^D)_2CH_2SiMe_3$ starting material Indeed, the resonances associated with the $Sc(L^D)_2CH_2SiMe_3$ complex appear unchanged. The appearance of two triplets at 4.58 ppm and -0.08 ppm that show only mutual coupling in a ^{1}H-^{1}H COSY spectrum is curious and cannot be explained. Overall,

based on the spectral data, the synthesis of a hydride complex can be ruled out but the reaction that does occur with $PhSiH_3$ is not known from this data.

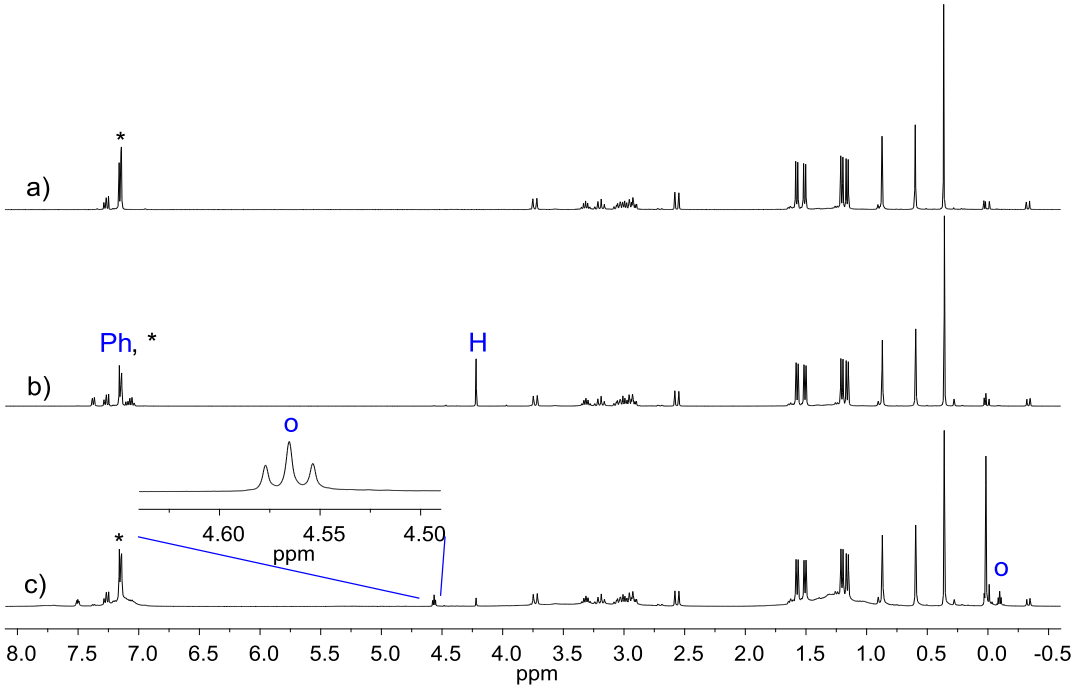
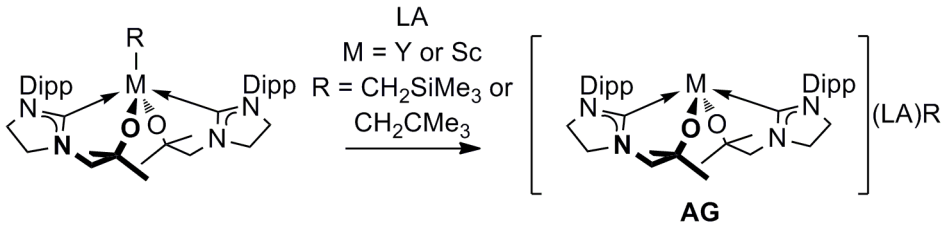


Figure 28: ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of a) $Sc(L^D)_2CH_2SiMe_3$ and $PhSiH_3$ b) $Sc(L^D)_2CH_2SiMe_3$ and $PhSiH_3$ after 10 minutes and c) after 16 h
'*' denotes residual protio solvent, 'o' the new triplets and 'Ph,H' the phenylsilane resonances

Treatment of $Sc(L^D)(CH_2SiMe_3)_2$ with 1 equivalent of $PhSiH_3$ led to no reaction at room temperature and decomposition, as previously observed, on heating $Sc(L^D)(CH_2SiMe_3)_2$ to 80 ºC for 16 h. No reaction was observed when the analogous silyl amide complexes $M(L^D)N''_2$ (M = Y or Sc) were treated with $PhSiH_3$ at room temperature on heating to 80 ºC for 16 h.

4.5.8 Attempted preparation of M^{III} neosilyl cationic complexes

The preparation of cationic species was first attempted with Lewis acids (LAs) to abstract a single alkyl group and generate the cation $[MR_2][(LA)R]$ (**AG**, Equation 11).

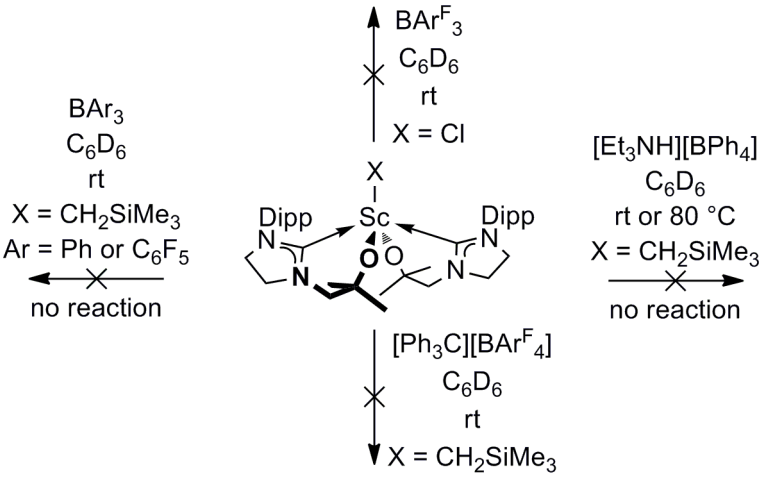


Equation 11: Preparation of an alkyl cation using a Lewis acid (LA)

Hence $Sc(L^D)_2CH_2SiMe_3$ was reacted with 1 equivalent of BPh_3 or $BAr^F{}_3$ at room temperature in C_6D_6. In both cases the ^1H NMR spectra indicated that over a period of days most started material remained unreacted but some resonances indicative of decomposition (HL^D and $SiMe_4$ in the case of $BAr^F{}_3$) were also observed. Alternatively, protonolysis with 1 equivalent of $[NEt_3H][BPh_4]$ in C_6D_6 was attempted but no reaction was observed at room temperature or on heating to 80 ºC for 16 h (Scheme 20).

The reaction of $Sc(L^D)_2CH_2SiMe_3$ with $[Ph_3C][BAr^F{}_4]$ in C_6D_6 was anticipated to result in alkyl abstraction. However, after storage of the reaction mixture for 16 h at room temperature, the ^1H NMR spectrum indicated that the starting material $Sc(L^D)_2CH_2SiMe_3$ was still present. Small resonances that had appeared over the 16 h period were indicative of decomposition rather than any cationic species (Scheme 20).

Finally, chloride abstraction from $Sc(L^D)_2Cl$ was attempted with $BAr^F{}_3$. The ^1H NMR spectrum indicated immediate consumption of the $Sc(L^D)_2Cl$ starting material and contained very broad resonances which could not be assigned to a single new product (Scheme 20).



Scheme 20: Attempted M^{III} neosilyl cation formation summary

4.6 Conclusions

The synthesis of *o*-aminobenzyl (Bn') complexes was first investigated, with the new *tris*(alkyl) precursor $CeBn'_3$ being prepared and then used in the synthesis of *mono* and *bis*(ligand) complexes, $Ce(L^D)Bn'_2$ and $Ce(L^D)_2Bn'$. Analogous reactions of $ScBn'_3$ indicated that the Sc^{III} ion was too small to support two L^D ligands in this system (previously observed for the amide system, 3.3.1).

In order to gain a larger family of complexes, specifically those which used two supporting L^D ligands and hence had only one reactive M-$C_{carbene}$ bond, the classical neosilyl and neopentyl alkyl complexes $M(L^D)(CH_2SiMe_3)_2$, $M(L^D)_2CH_2SiMe_3$ and $M(L^D)(CH_2CMe_3)_2$ and $M(L^D)_2CH_2CMe_3$ (M = Y or Sc) were prepared successfully from alkane elimination reactions. Attempted *in situ* syntheses which avoided the isolation of the thermally unstable *tris*(alkyl) starting materials were not possible in the case of yttrium or, for scandium, either led to less clean products or an undesired 'ate' complex, $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$.

The bulkier $CH(SiMe_3)_2^-$ ligand was used to examine the synthesis of U^{III} alkyl complexes. The *mono*(ligand) complex $U(L^D)(CH\{SiMe_3\}_2)_2$ was not stable at room temperature for more than 1 h and purification proved difficult. As in the case of the amide complexes, the *bis*(ligand) $U(L^D)_2CH(SiMe_3)_2$ could not be prepared and this is not surprising considering the similar steric profile of the $CH(SiMe_3)_2^-$ and $NH(SiMe_3)_2^-$ ligands.

Finally, the preparation of borohydride complexes was attempted in order to provide versatile starting materials, capable of acting as both hydrides and halides, which could also allow the synthesis of new alkyl complexes. However, despite the initial promising reactions to synthesise both $M(L^D)(BH_4)_2$ (M = Y, Sc or Ce) and $M(L^D)_2(BH_4)$ (M = Ce), isolation of pure products was not possible. In attempts to purify $M(L^D)_2(BH_4)$ (M = Ce), the ion pair $[Ce(BH_4)_2(thf)_5][Ce(BH_4)_4(thf)_2]$ was consistently isolated.

In reactivity, the addition of polar substrates across the M-$C_{carbene}$ bond (first discussed in Chapter Three for the amide systems) has been extended to C-Si, C-P, C-Sn and C-B bond forming reactions. The addition of Ar^FI occurred in a reverse sense, with the pentafluorophenyl group delivered to the metal centre and the formation of an intermediate iodoimidazolidinium species. Elimination afforded C-I bond formation and a metal aryl complex. However, this was not a general reaction of all alkyl and aryl halides; the addition of MeI resulted in the formation a *bis*(ligand) scandium iodide but the organic byproducts could not be identified.

For the zwitterionic complex $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$, functionalisation of the N-heterocyclic ring was achieved through salt metathesis reactions with Me_3SiCl or Ph_3CCl. The elimination reactions of these functionalised complexes afforded the products of C-Si and C-C bond formation respectively. Unfortunately, this process could not be extended to a range of metal halides.

The synthesis of metal hydrides and cationic species was explored, though no successful routes to these complexes were identified from preliminary studies.

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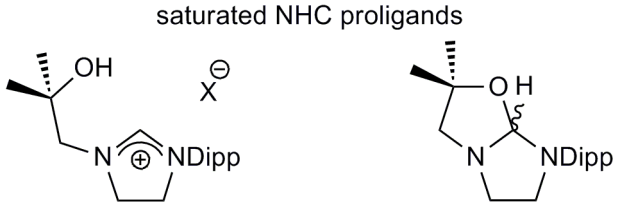
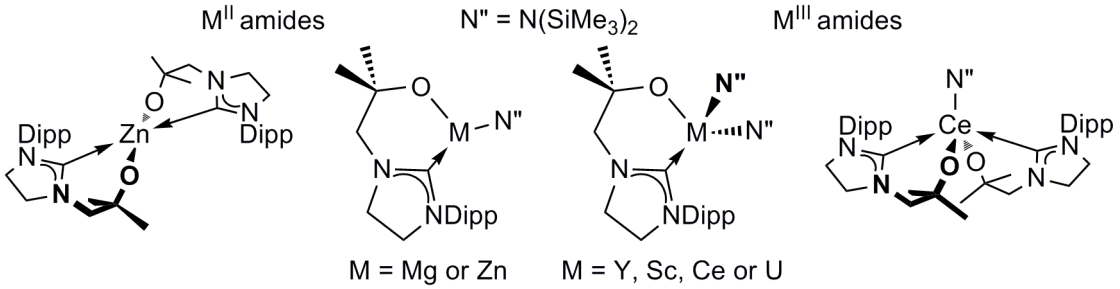
Conclusions

New saturated backbone NHC proligands were first prepared as imidazolidinium salts and could be singly deprotonated to form a bicyclic compound. The modular synthesis of these proligands was shown to be high yielding. They incorporate a sterically demanding *N*-Dipp substituent and are functionalised with an alkoxy-tether, which facilitates binding to electropositive metal centres.



mono and *bis*(ligand) M^{II} and M^{III} silylamide complexes were prepared by straightforward protonolysis reactions of the appropriate metal silylamide. The balance of the steric demands of the central metal ion with those of the ligands, and the strength of the M-O and M-C bonds formed determined whether the *bis*(ligand) complexes were isolable.



Preliminary lactide polymerisation studies were completed with the M^{II} silylamide complexes and all were shown to act as catalysts producing *poly*(lactide) with reasonable molecular weights and polydispersities, although no significant level of stereocontrol was observed.

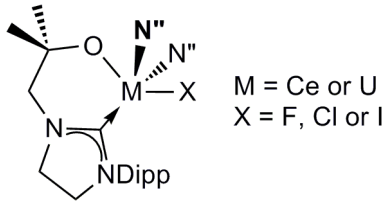
The M^{III} amide complexes (M = Y or Ce) were used to demonstrate a new form of NHC reactivity, where a range of polar substrates were added across the M-$C_{carbene}$ bond to functionalise the N-heterocyclic ring. The resulting zwitterionic intermediate decomposed at elevated temperature (80 ºC) to eliminate E-N" (E = silyl, boryl, stannyl or phosphoryl).

The differences in reactivity of the 4f/5f metal complexes were also highlighted in a number of examples with the M^{III} amide complexes. Alongside the addition-elimination reaction, the U^{III} complex also underwent oxidation to U^{IV} on reaction with Me_3SiI. While organic azides were found to insert into the M-$C_{carbene}$ bond of the Ce^{III} NHC amide complex, they reacted with the U^{III} analogue to form U^{V} imido complexes. CO was found to insert into the silylamide ligand of the U^{III} complex to yield a U^{IV} metallacycle whereas no reaction was observed for the Y^{III} or Ce^{III} analogues.

Surprisingly, the simple *tris*(amide) starting material, $UN"_3$, was found to reductively homologate two molecules of CO between two U^{III} centres to yield a ynediolate core, $^-OC{\equiv}CO^-$ The reaction proceeded at ambient temperature and pressure, with accompanying oxidation of U^{III} to U^{IV}. The first example of functionalisation of the ynediolate core then resulted from the intramolecular reaction of a silylamide group to form an enediolate core.

mono(ligand) M^{IV} (M = Ce or U) silylamide complexes could be prepared from the M^{III} complex *via* oxidation or the protonolysis reaction of the bicyclic proligand with $MN"_3Cl$. In preparing the M^{IV} complexes, a new and convenient entry to Ce^{IV} amide chemistry was also identified. Though the bonding in Ce^{IV} and U^{IV} systems is largely ionic, a DFT study suggested there is a greater covalent contribution to bonding in the case of the more polarisable 5f metal ion.

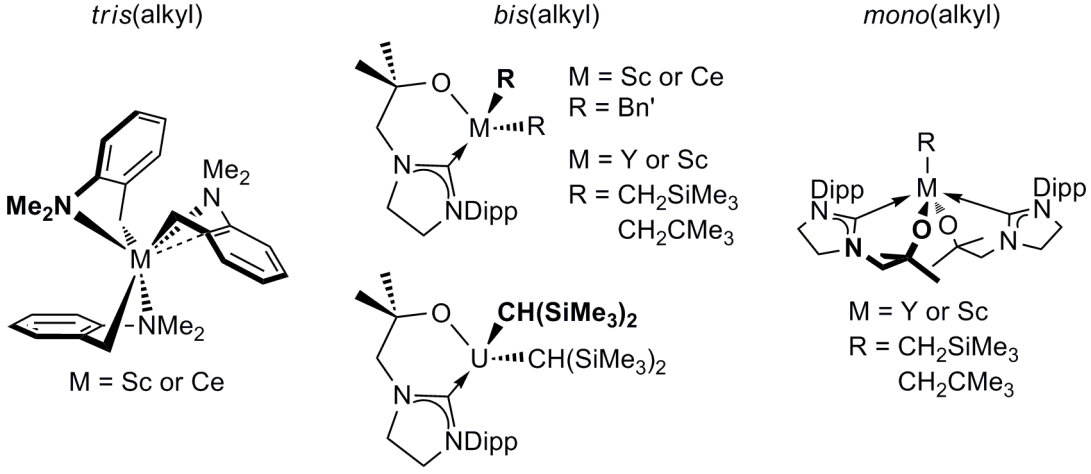
M^{IV} amides



The reactivity of the Ce^{IV} chloride complex was explored in order to create unknown Ce^{IV}-C covalent bonds and Ce^{IV} cationic species. Attempts to prepare Ce^{IV} cations using Lewis acids to abstract the chloride ion suggested that the NHC group may coordinate to the Lewis acid.

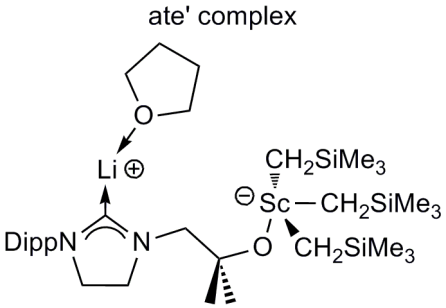
mono(ligand) and/or *bis*(ligand) M^{III} alkyl complexes were prepared by alkane elimination reactions with the appropriate *tris*(alkyl) starting materials. Attempted *in situ* syntheses were not successful and were found to generate undesired 'ate' complexes. The bulky $CH(SiMe_3)_2^-$ ligand was used to examine the synthesis of U^{III} alkyl complexes. The *mono*(ligand) complex $U(L^D)(CH\{SiMe_3\}_2)_2$ was not stable at room temperature. As in the case of the amide complexes, the *bis*(ligand) U^{III} alkyl complex could not be prepared and this is not surprising considering the similar steric profile of the $CH(SiMe_3)_2^-$ and $N(SiMe_3)_2^-$ ligands.

tris(alkyl) *bis*(alkyl) *mono*(alkyl)



The addition-elimination reactivity of polar substrates across the M-$C_{carbene}$ bond was extended to the alkyl complexes, resulting in C-E (E = Si, P, Sn B) bond forming reactions. The reactions were found to occur immediately at room temperature and the intermediate zwitterions could not be isolated. C-I bond formation followed the addition of Ar^FI across the M-$C_{carbene}$ bond, which occurred in a reverse sense.

Functionalisation of the N-heterocyclic ring in the scandium 'ate' complex was achieved through salt metathesis reactions with Me_3SiCl or Ph_3CCl. The elimination reactions at room temperature afforded the products of C-Si and C-C bond formation respectively.



In summary, this thesis has described the synthesis of new saturated backbone N-heterocyclic carbene (NHC) proligands. The preparation and characterisation of well-defined electropositive metal amide and metal alkyl complexes has shown the NHC to be a robust supporting ligand. A range of reactivity has been examined; in particular, N- and C-E bond forming reactions have been demonstrated at the redox-inactive M^{III} centres. The NHC ligand is labilised in these reactions and used to deliver functional groups to the metal centre. This offers an interesting alternative to traditional four-centre σ bond metathesis reactivity, showing that the NHC is not always a spectator ligand. Reactivity of the softer, more polarisable 5f U^{III} amide complexes clearly demonstrated that oxidation was more favourable with respect to the 4f Ce^{III} complexes.

The NHC complexes synthesised during this work demonstrate that this is an excellent platform for the examination of organometallic electropositive metal complexes. The width of reactivity observed shows that these complexes are capable of a range of small molecule activation and that much remains to be explored.

Experimental details and characterising data

6.1 General methods and instrumentation

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of dinitrogen. Protio solvents were degassed by sparging with dinitrogen, dried by passing through a column of activated sieves and stored over potassium mirrors (hexanes, toluene, benzene) or activated 4 Å molecular sieves (thf). Deuterated solvents were dried over potassium (C_6D_6, C_5D_5N, C_4D_8O), distilled under reduced pressure, freeze-pump-thaw degassed three times prior to use.

^{1}H NMR spectra were recorded at 298 K, unless otherwise stated, on Bruker DPX 360, AVA 400, DMX 500, AVA 500 or AVA 600 spectrometers and ^{13}C{^{1}H} or ^{13}C spectra on the same spectrometers at operating frequencies of 90, 100, 125, 125 and 150 MHz respectively. Two dimensional ^{1}H-^{1}H and ^{13}C-^{1}H correlation experiments were used, when necessary, to confirm ^{1}H and ^{13}C assignments. All NMR spectra were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz.

Mass spectra were recorded by the mass spectrometry service of Edinburgh University's Department of Chemistry. Elemental analyses were carried out at London Metropolitan University. Gas chromatographic data were collected using an Agilent Technologies 7890A GC system.

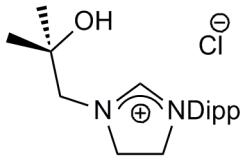
X-ray crystallographic data were collected at 150 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), 170 K on an Oxford Diffraction Excalibur diffractometer using graphite monochromated Mo-Kα radiation or 100 K on an Oxford Diffraction Supernova diffractometer using mirror monochromated Cu-Kα radiation (λ = 1.5418 Å). Using the WinGX suite of programs, all structures were solved using direct methods and refined using a full-matrix least square refinement on $|F|^2$ using SHELXL-97. Unless otherwise stated, all non-hydrogen atoms refined with anisotropic displacement parameters and hydrogen atoms were placed using a riding model.

N-(2,6-di-*iso*-propylphenyl)ethylenediamine,[1] (*B*-I)-9-BBN,[2] N_2CPh_2,[3] $CeI_3(thf)_4$,[4] $CeCl_3(thf)_3$, $ScCl_3(thf)_3$, $UI_3(thf)_4$,[5,6] $YCl_3(thf)_{3.5}$, CeN''_3,[7] KN'',[8] $MgN''_2(thf)_2$,[9] ScN''_3,[10]

UN''_3,[6] YN''_3,[7] ZnN''_2,[11] CeN''_3Cl,[12] UN''_3Cl,[13] $U(2,6\text{-}^tBu\text{-}OC_6H_3)_3$,[14] KBn',[15] KBn,[16,17] LiNp,[18] $Ce(BH_4)_3(thf)_3$,[19] $Sc(BH_4)_3(thf)_2$,[19] $Y(BH_4)_3(thf)_3$,[19] $Sc(CH_2SiMe_3)_3(thf)_2$,[20] $Sc(CH_2CMe_3)_3(thf)_2$,[20] $U(CH\{SiMe_3\}_2)_3$,[21] $Y(CH_2SiMe_3)_3(thf)_2$,[20] $[Y(CH_2SiMe_3)_4][Li(thf)_4]$[22] and $Y(CH\{SiMe_3\}_2)_3(thf)_2$[23] were prepared with reference to published methods. LiN'' was purchased from Sigma Aldrich, recrystallised from hexanes and sublimed (10^{-4} mbar, 110 ºC), 2,6-^{t}Bu-C_6H_3OH was purchased from Sigma Aldrich and sublimed (10^{-4} mbar, 80 ºC), Ph_3CCl was recrystallised from toluene and washed with hexanes, Me_3SiCl and Me_3SiN_3 were distilled under reduced pressure, Me_3SiI was distilled under reduced pressure and stored in the absence of light, BnBr was dried over activated alumina and distilled under reduced pressure and then stored in the absence of light, Ph_3SnCl was sublimed (10^{-4} mbar, 90 ºC) and Ph_2PCl was distilled under reduced pressure (10^{-1} mbar, 120 ºC) prior to use. All other reagents were purchased and used without further purification.

6.2 Synthetic procedures described in Chapter Two

6.2.1 Synthesis of $[H_2L^D]Cl$

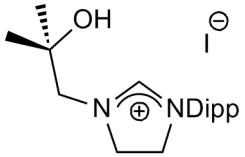


a. *N*-(2,6-di-*iso*-propylphenyl)ethylenediamine (7.28 mL, 33.0 mmol) and 1,2-*iso*-butylene oxide (2.50 g, 34.7 mmol) were combined in an ampoule. The reaction mixture was then heated to 90 °C and stirred for 2 days. The volatiles were removed *in vacuo* to afford $HOCMe_2CH_2NHCH_2CH_2N(H)Dipp$ as a clear, yellow oil. To a stirred solution of $HOCMe_2CH_2NHCH_2CH_2N(H)Dipp$ (5.59 g, 19.11 mmol) in Et_2O (25 mL) at 0 °C was added HCl (9.60 mL, 19.11 mmol; 2 M in diethyl ether). This resulted in the immediate formation of a white precipitate and the reaction mixture was stirred for 1.5 h at room temperature. The solid was isolated by filtration, washed with Et_2O (3 x 10 mL) and dried under reduced pressure to afford $[HOCMe_2CH_2(1\text{-}HC\{NCH_2CH_2NDipp\})]Cl$ which was reacted *in situ*. The white solid was slurried in toluene (30 mL) and to this was added $HC(OMe_3)$ (10.14 g, 95.57 mmol). The reaction mixture was heated to 90 °C under a partial static vacuum for 2 days to give a yellow solution. The volatiles were removed *in vacuo* to give a pale yellow solid, which was washed with acetone (3 x 20 mL) and then dried to afford $[H_2L^D]Cl$ as a white solid. Yield: 3.89 g (60 %). Diffraction-quality crystals were grown from an acetone solution at -80 °C. ^1H NMR ($CDCl_3$, 360 MHz): 9.47 (1 H, s, NCHN), 7.40 (1 H, t, $^3J_{HH}$ = 7 Hz, 4-C_6H_3), 7.21 (2 H, d, $^3J_{HH}$ = 7 Hz, 3,5-C_6H_3) 5.18 (1 H, s, OH), 4.44 and 4.13 (2 H each, m, NCH_2CH_2N), 3.95 (2 H, s, $HOCMe_2C\underline{H}_2$), 2.88 (2 H, sept, $^3J_{HH}$ = 2 Hz, $\underline{H}CMe_2$), 1.30 (6 H, s, CMe_2), 1.27 and 1.24 (6 H, d, $^3J_{HH}$ = 2 Hz, $HC\underline{Me}_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 90 MHz): 160.4 (NCHN), 146.5 (2-C_6H_3), 131.0 (4-C_6H_3), 130.0 (1-

C_6H_3), 124.8 (3,5-C_6H_3), 69.7 ($\underline{C}Me_2$), 57.3 ($OCMe_2\underline{C}H_2$) 53.1 and 51.7 (NCH_2CH_2N), 28.8 ($H\underline{C}Me_2$), 27.2 ($HC\underline{Me}_2$), 25.0 ($C\underline{Me}_2$), 23.9 ($HC\underline{Me}_2$) ppm. ESI-MS: *m/z*: 303.59 $[M\text{-}Cl]^+$ (17 %). Anal. Found (calcd for $C_{19}H_{31}ClN_2O$): C, 67.29 (67.33); H, 9.30 (9.22); N, 8.28 (8.27).

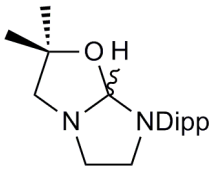
b. *N*-(2,6-di-*iso*-propylphenyl)ethylenediamine (7.28 mL, 33.0 mmol) and 1,2-*iso*-butylene oxide (2.50 g, 34.7 mmol) were combined in an ampoule. The reaction mixture was then heated to 90 °C and stirred for 2 days. The volatiles were removed *in vacuo* to afford $HOCMe_2CH_2NHCH_2CH_2N(H)Dipp$ as a clear, yellow oil. $HOCMe_2CH_2NHCH_2CH_2N(H)Dipp$ (23.46 g, 79.87 mmol) was combined with NH_4Cl (4.49 g, 83.67 mmol) and $HC(OMe_3)$ (127.10 g, 1198 mmol in a round bottomed flask. The flask was equipped with a condenser and purged with N_2. The reaction mixture was refluxed at 120 °C for 18 h under a positive pressure of N_2. After cooling to room temperature, the product was precipitated with diethyl ether, filtered off and washed with diethyl ether until the washings were colourless. Drying under reduced pressure afforded $[H_2L^D]Cl$ as a pale yellow solid. Yield: 17.10 g (63 %).

6.2.2 Synthesis of $[H_2L^D]I$



To a solution of $[H_2L^D]Cl$ (1.06 g, 3.13 mmol) in acetone (20 mL) was added a solution of NaI (0.94 g, 6.26 mmol) in acetone (10 mL) to yield a white precipitate immediately. The reaction mixture was stirred for 30 minutes. Solids were isolated by filtration and dried under reduced pressure. Extraction into CH_2Cl_2 (3 x 10 mL) and subsequent removal of the volatiles *in vacuo* afforded $[H_2L^D]I$ as an off-white solid. Yield: 1.00 g (73 %). ^1H NMR ($CDCl_3$, 360 MHz): 9.07 (1 H, s, NCHN), 7.40 (1 H, t, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 7.20 (2 H, d, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 5.18 (1 H, s, OH), 4.55 and 4.17 (2 H each, m, NCH_2CH_2N), 4.00 (2 H, s, $HOCMe_2C\underline{H}_2$), 2.91 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 1.32 (6 H, s, CMe_2), 1.25 and 1.22 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 90 MHz): 157.7 (NCHN), 145.6 (2-C_6H_3), 130.1 (4-C_6H_3), 129.8 (1-C_6H_3), 123.9 (3,5-C_6H_3), 69.6 ($\underline{C}Me_2$), 56.5 ($HOCMe_2\underline{C}H_2$) 52.3 and 51.5 (NCH_2CH_2N), 27.9 ($H\underline{C}Me_2$), 26.3 ($HC\underline{Me}_2$), 24.3 ($C\underline{Me}_2$), 23.1 ($HC\underline{Me}_2$) ppm. Anal. Found (calcd for $C_{19}H_{31}IN_2O$): C, 53.07 (53.03); H, 7.28 (7.26); N, 6.59 (6.51).

6.2.3 Synthesis of HL^D



a. Using ^{n}BuLi: To a cold (-78 °C) slurry of $[H_2L^D]Cl$ (6.47 g, 19.1 mmol) in thf (35 mL) was added dropwise ^{n}BuLi (14.3 mL, 22.9 mmol; 1.6 M in hexanes). The reaction mixture was stirred for 2 h before being allowed to warm up to room temperature at stirred for a further 3 h. The volatiles were removed *in vacuo* to give a white solid. Extraction into toluene (3 x 10 mL) was followed by drying under reduced pressure and washing of the solid with hexanes (3 x 10 mL). The solid was dried to afford HL^D as a white solid. A second crop was yielded by precipitation from the hexanes washings at -80 °C. Yield: 5.60 g (97 %). ^{1}H NMR (C_6D_6, 360 MHz): 7.28 - 7.04 (3 H, overlapping m, 3,4,5-C_6H_3), 5.78 (1 H, s, NCHN), 4.09 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.53 - 2.95 (4 H, overlapping m, NCH_2CH_2N), 3.36 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 2.91 and 2.52 (2 H each, d, $^2J_{HH}$ = 11 Hz, $OCMe_2C\underline{H}_2$), 1.42 and 1.30 (3 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.30 (3 H, s, CMe_2), 1.18 and 1.14 (3 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.11 (3 H, s, CMe_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 90 MHz): 151.6, 148.8, 140.2, 127.8, 124.9 and 124.0 (C_6H_3), 109.4 (NCHN), 77.6 ($\underline{C}Me_2$), 63.9 ($OCMe_2\underline{C}H_2$), 54.5 and 52.9 (NCH_2CH_2N), 29.3 ($H\underline{C}Me_2$), 28.3 ($C\underline{Me}_2$), 27.9 ($H\underline{C}Me_2$), 27.7 ($C\underline{Me}_2$), 25.3, 24.9 24.8, 24.5 ($HC\underline{Me}_2$) ppm. Anal. Found (calcd for $C_{19}H_{30}N_2O$): C, 75.51 (75.45); H, 10.07 (10.00); N, 9.20 (9.26).

b. Using KBn: $[H_2L^D]Cl$ (1.00 g, 2.95 mmol) and KBn (0.38 g, 2.95 mmol) were combined in a Schlenk and cooled to -78 °C. To this was added thf (15 mL) to yield a red suspension immediately and the reaction mixture was allowed to warm slowly to room temperature overnight. Extraction with thf (3 x 5 mL) resulted in a colourless solution. The volatiles were removed *in vacuo* to give a yellow-white solid. Sublimation (55 °C, 10^{-5} mbar) afforded HL^D as a white solid. Yield: 0.18 g (20 %).

c. Using KH: $[H_2L^D]I$ (1.1 g, 3.5 mmol) and KH (0.14 g, 3.5 mmol) were combined in a Schlenk and cooled to -78 °C. To this was added thf (20 mL). The reaction mixture was allowed to warm slowly to room temperature and stirred for 48 h during which time the solution became orange-yellow and a colourless precipitate formed. After extraction into thf (2 x 10 mL), recrystallisation from thf at -30 ºC afforded HL^D crudely as a pale yellow crystalline material. Yield: 0.68 g (64 %).

6.2.4 Attempted synthesis of $K(L^D)$

a. From HL^D and KN": To a solution of HL^D (0.61 g, 2.00 mol) in toluene (10 mL) was added a solution of KN" (0.42 g, 2.10 mmol). The reaction mixture was stirred for 16 h

and subsequently concentrated to 2 mL and cooled to -80 °C on which colourless crystalline material formed. This was washed with cold (- 80 °C) toluene (2 x 2 mL) and dried under reduced pressure to afford a white powder. ^{1}H NMR (C_6D_6, 360 MHz): 7.46 (1 H, m, 4-C_6H_3), 7.37 (2 H, m, 3,5-C_6H_3), 3.38 (2 H, s, $OCMe_2C\underline{H}_2$), 3.38 - 3.29 (4 H, overlapping m, NCH_2CH_2N), 3.15 (2 H, sept, $^{3}J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 1.31 and 1.23(6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.24 (6 H, s, CMe_2) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 90 MHz): 147.4 (2,6-C_6H_3), 139.3 (1-C_6H_3), 129.3 (4-C_6H_3), 124.2 (3,5-C_6H_3), 71.2 ($\underline{C}Me_2$), 67.4 ($OCMe_2\underline{C}H_2$), 53.4 and 52.8 (NCH_2CH_2N), 34.0 ($C\underline{Me}_2$), 29.3 ($H\underline{C}Me_2$), 25.3 and 21.4 ($HC\underline{Me}_2$) ppm.

b. From HL^D and KH: HL^D (0.010 g, 0.033 mmol) and KH (0.0020 g, 0.050 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature of on heating at 80 ºC for 16 h.

6.2.5 Attempted synthesis of Li(L^D)

a. From $[H_2L^D]Cl$ and ^{n}BuLi: At -78 ºC, to a slurry of $[H_2L^D]Cl$ (0.28 g, 0.83 mmol) in thf (10 mL) was added dropwise ^{n}BuLi (1.1 mL, 1.65 mmol; 1.6 M in hexanes) to yield a white suspension. The reaction mixture was allowed to warm to room temperature and stirred for 16 h to afford a yellow solution and white precipitate. The solution was filtered off and the volatiles removed *in vacuo* to afford a pale yellow solid. ^{1}H NMR spectroscopy only indicated the presence of HL^D.

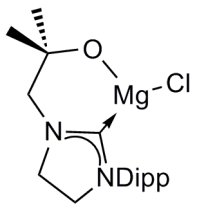
b. From HL^D and LiN": HL^D (0.024 g, 0.082 mmol) and LiN" (0.015 g, 0.087 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. The reaction mixture was stored at room temperature for 24 h. ^{1}H NMR (C_6D_6, 360 MHz): 7.22 – 7.14 (overlapping m, C_6H_3), 3.50 (2 H, br. s, $OCMe_2C\underline{H}_2$), 3.29 – 3.07 (6 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 1.46 and 1.15 (6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.96 (6 H, br. s, CMe_2) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 90 MHz): 147.4 139.9 and 124.0 (C_6H_3), 69.9 ($\underline{C}Me_2$), 65.4 ($OCMe_2\underline{C}H_2$), 54.3 and 52.5 (NCH_2CH_2N), 28.0 ($C\underline{Me}_2$) 26.0 ($H\underline{C}Me_2$), 24.7 ($HC\underline{Me}_2$) ppm.

c. From HL^D and ^{n}BuLi: To a solution of HL^D (0.021 g, 0.069 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^{n}BuLi (43 µL, 0.069 mmol; 1.6 M in hexanes) to afford a clear, yellow solution. The ^{1}H NMR spectrum indicated the formation of the same product seen in 6.2.5b.

6.2.6 Attempted synthesis of Tl(L^D)

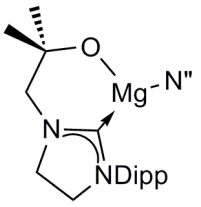
HL^D (0.016 g, 0.052 mmol) and TlCp (0.014 g, 0.052 mmol) were combined in C_6D_6/thf (0.5 mL) in a J-Young Teflon valve NMR tube. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature of on heating at 80 ºC for 16 h.

6.2.7 Synthesis of Mg(L^D)Cl



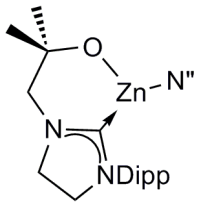
To a stirred solution of HL^D (0.39 g, 1.3 mmol) in toluene (10 mL) was added dropwise MeMgCl (0.43 mL, 1.3 mmol; 3.0 M in thf), resulting immediately in effervescence and generation of a white precipitate. The reaction mixture was stirred for 1 h at room temperature before being allowed to settle. The solid was filtered off, washed with toluene (2 x 5 mL) and dried in vacuo to afford Mg(L^D)Cl as a white powder. Yield: 0.47 g (100 %). ^{1}H NMR (C_5D_5N, 360 MHz): 7.41 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.21 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.64 (4 H, m, NCH_2CH_2N), 3.50 (2 H, s, $OCMe_2C\underline{H}_2$), 3.38 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 1.43 and 1.14 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.03 (6 H, s, CMe_2) ppm. $^{13}C\{^1H\}$ NMR (C_5D_5N, 90 MHz): 212.8 (NCN), 148.3 and 138.1 (1,2,6-C_6H_3), 129.4 (4-C_6H_3), 124.9 (3,5-C_6H_3), 70.7 ($\underline{C}Me_2$), 61.5 ($OCMe_2\underline{C}H_2$), 54.1 and 53.4 (NCH_2CH_2N), 29.7 ($C\underline{Me}_2$), 28.7 ($H\underline{C}Me_2$), 26.0 and 25.1 ($HC\underline{Me}_2$) ppm.

6.2.8 Synthesis of Mg(L^D)N"



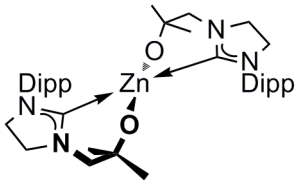
To a solution of $MgN"_2(thf)_2$ (0.53 g, 1.1 mmol) in benzene (5 mL) was added a solution of HL^D (0.33 g, 1.1 mmol) in benzene (5 mL) with stirring. The reaction mixture was stirred for 16 h at room temperature during which time a colourless precipitate formed. The solid was isolated by filtration, washed with toluene (3 × 5 mL) and dried *in vacuo* to afford Mg(L^D)N" as a colourless solid. Yield: 0.45 g (86 %). The compound was found to be too insoluble in common solvents to allow $^{13}C\{^1H\}$ NMR spectroscopic analysis and decomposes in pyridine. ^{1}H NMR (C_6D_6, 500 MHz, 333 K): 7.22 (1 H, m, 4-C_6H_3), 7.15 (2 H, m, 3,5-C_6H_3), 3.18 (8 H, overlapping m, NCH_2CH_2N, $\underline{H}CMe_2$ and $OCMe_2C\underline{H}_2$), 1.57 (6 H, s, CMe_2), 1.51 and 1.20 (6 H, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.24 (18 H, s, SiMe) ppm. Anal. Found (calcd for $C_{25}H_{47}MgN_3OSi_2$): C, 61.69 (61.77); H, 9.68 (9.74); N, 8.50 (8.64).

6.2.9 Synthesis of Zn(L^D)N"



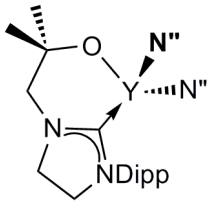
To a solution of ZnN"$_2$ (0.32 g, 0.82 mmol) in benzene (5 mL) was added a solution of HL^D (0.25 g, 0.82 mmol). The reaction mixture was stirred for 16 h at room temperature and subsequently the volatiles were removed *in vacuo* to afford Zn(L^D)N" as a white solid. Yield: 0.36 g (84 %). X-Ray quality single crystals were grown from a saturated toluene solution cooled to −20 °C. ^{1}H NMR (C_6D_6, 360 MHz): 7.18 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.05 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.02 (2 H, s, OCMe$_2$C$\underline{H}_2$), 3.11 – 2.85 (6 H, overlapping m, NCH$_2$CH$_2$N and $\underline{H}$CMe$_2$), 1.42 (6 H, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me}_2$), 1.38 (6 H, s, CMe$_2$), 1.07 (6 H, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me}_2$), 0.24 (18 H, s, SiMe) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 90 MHz): 196.1 (NCN), 146.8 (2-C_6H_3), 135.1 (1-C_6H_3), 129.9 (4-C_6H_3), 125.0 (3,5-C_6H_3), 70.4 ($\underline{C}$Me$_2$), 63.3 (OCMe$_2\underline{C}$H$_2$), 53.2 and 53.2 (NCH$_2$CH$_2$N), 31.0 (C$\underline{Me}_2$), 28.6 (H$\underline{C}$Me$_2$), 25.5 and 24.6 (HC$\underline{Me}_2$), 5.6 (SiMe) ppm. Anal. Found (calcd for $C_{25}H_{47}N_3OSi_2Zn$): C, 59.87 (59.95); H, 8.88 (8.99); N, 7.91 (7.97).

6.2.10 Synthesis of Zn(L^D)$_2$



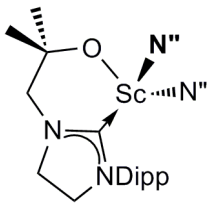
To a solution of ZnN"$_2$ (0.25 g, 0.66 mmol) in benzene (10 mL) was added a solution of HL^D (0.40 g, 1.3 mmol) in benzene (5 mL) with stirring to yield a clear, colourless solution. The reaction mixture was heated to 85 °C for 16 h during which time a colourless precipitate formed. The solid was isolated by filtration, washed with thf (3 × 5 mL) and dried *in vacuo* to afford Zn(L^D)$_2$ as a colourless solid. Yield: 0.33 g (76 %). ^{1}H NMR (C_5D_5N, 360 MHz): 7.54 – 7.31 (6 H, overlapping m, C_6H_3), 3.82 – 3.78 (8 H, overlapping m, NCH$_2$CH$_2$N), 3.16 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}$CMe$_2$), 2.97 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}$CMe$_2$), 2.73 and 2.08 (2 H each, d, $^2J_{HH}$ = 14 Hz, 2 H, s, OCMe$_2$C$\underline{H}_2$), 1.39, 1.35 and 1.25 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me}_2$), 1.22.(3 H, s, CMe$_2$), 1.14 (6 H, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me}_2$), 0.92, 0.63 and 0.15 (3 H each, s, CMe$_2$) ppm. ^{13}C{^{1}H} NMR (C_5D_5N, 90 MHz): 201.3 (NCN), 177.5, 160.8, 149.1, 147.4, 130.4, 129.5, 126.0 (C_6H_3), 70.7 ($\underline{C}$Me$_2$), 62.5 (OCMe$_2\underline{C}$H$_2$), 54.4 and 53.6 (NCH$_2$CH$_2$N), 32.1 and 29.4 (C$\underline{Me}_2$), 29.1 and 28.7 (H$\underline{C}$Me$_2$), 25.7 and 24.1 (HC$\underline{Me}_2$), 8.1 and 3.5 (C$\underline{Me}_2$) ppm. Anal. Found (calcd for $C_{38}H_{58}N_4O_2Zn$): C, 68.37 (68.30); H, 8.75 (8.77); N, 4.89 (4.79).

6.2.11 Synthesis of Y(L^D)N"$_2$



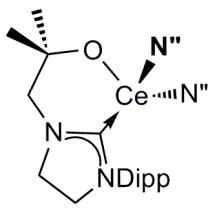
At room temperature, to a solution of YN"$_3$ (0.47 g, 0.82 mmol) in thf (2 ml) was added a solution of HL^D (0.25 g, 0.82 mmol) in thf (2 ml). The reaction mixture was stirred overnight at room temperature to afford a pale yellow solution. The volatiles were removed in vacuo and recrystallisation from toluene (~3 mL) at -30 ºC afforded Y(L^D)N"$_2$ as colourless plates. Yield: 0.30 g, 51 %. Diffraction-quality crystals were grown from a saturated toluene solution at -30 °C. ^{1}H NMR (C_6D_6, 360 MHz): 7.18 (1 H, m, 4-C_6H_3), 7.04 (2 H, m, 3,5-C_6H_3), 3.25 (2 H, s, OCMe$_2$C<u>H</u>$_2$), 3.15 (2 H, m, NCH$_2$CH$_2$N), 3.09 (2 H, sept, $^3J_{HH}$ = 7 Hz, <u>H</u>CMe$_2$), 2.90 (2 H, m, NCH$_2$CH$_2$N), 1.44 and 1.08 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC<u>Me</u>$_2$), 1.11 (6 H, s, CMe$_2$), 0.39 (36 H, s, SiMe) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 90 MHz): 216.3 (d, $^1J_{YC}$ = 42 Hz, NCN), 147.4 (1-C_6H_3), 136.3 (2,6-C_6H_3), 129.8 (4-C_6H_3), 125.0 (3,5-C_6H_3), 73.5 (<u>C</u>Me$_2$), 62.8 (OCMe$_2$<u>C</u>H$_2$), 53.6 and 53.2 (NCH$_2$CH$_2$N), 28.6 (C<u>Me</u>$_2$), 28.3 (H<u>C</u>Me$_2$), 26.2 and 24.7 (HC<u>Me</u>$_2$), 5.5 (SiMe) ppm. Anal. Found (calcd for $C_{31}H_{65}N_4OSi_4Y$): C, 52.27 (52.36); H, 9.28 (9.21); N, 7.73 (7.88).

6.2.12 Synthesis of Sc(L^D)N"$_2$



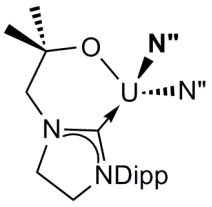
HL^D (0.016 g, 0.054 mmol) and ScN"$_3$ (0.029 g, 0.054 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube and heated to 80 ºC to afford a clear, colourless solution. The volatiles were removed *in vacuo* to yield a white solid. Recrystallisation from toluene at -20 ºC afforded Sc(L^D)N"$_2$ as colourless crystals. Yield: 0.015 g (41 %). Diffraction-quality crystals were grown from a saturated toluene solution at -20 ºC. ^{1}H NMR (C_6D_6, 600 MHz): 7.14 (1 H, t, $^3J_{HH}$ = 7 Hz, 4-C_6H_3), 7.02 (2 H, d, $^3J_{HH}$ = 7 Hz, 3,5-C_6H_3), 3.25 (2 H, s, OCMe$_2$C<u>H</u>$_2$), 3.11 (2 H, m, NCH$_2$CH$_2$N), 3.08 (2 H, sept, $^3J_{HH}$ = 7 Hz, <u>H</u>CMe$_2$), 2.90 (2 H, m, NCH$_2$CH$_2$N), 1.43 (6 H, d, $^3J_{HH}$ = 7 Hz, HC<u>Me</u>$_2$), 1.20 (6 H, s, CMe$_2$), 1.03 (6 H, d, $^3J_{HH}$ = 7 Hz, HC<u>Me</u>$_2$), 0.37 (36 H, s, SiMe) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): 212.3 (NCN), 147.2 (1-C_6H_3), 136.5 (2,6-C_6H_3), 129.8 (4-C_6H_3), 125.1 (3,5-C_6H_3), 75.1 (<u>C</u>Me$_2$), 61.9 (OCMe$_2$<u>C</u>H$_2$), 53.7 and 53.2 (NCH$_2$CH$_2$N), 28.4 (C<u>Me</u>$_2$), 27.9 (H<u>C</u>Me$_2$), 26.2 and 24.5 (HC<u>Me</u>$_2$), 6.1 (SiMe) ppm. Anal. Found (calcd for $C_{31}H_{65}N_4OSi_4Sc$): C, 55.73 (55.81); H, 9.73 (9.82); N, 8.28 (8.40).

6.2.13 Synthesis of Ce(L^D)N"$_2$



To a slurry of CeN"$_3$ (0.46 g, 0.73 mmol) in toluene (5 mL) was added a solution of HL^D (0.22 g, 0.73 mmol) in toluene (5 mL) at room temperature. The reaction mixture was stirred for 16 h to yield a yellow solution. On recrystallisation from toluene (5 mL) at -80 °C a yellow microcrystalline solid formed which was isolated by filtration, washed with hexanes (3 x 2 mL) and dried *in vacuo* to yield Ce(L^D)N"$_2$ as a yellow powder. Yield: 0.43 g (76 %). Diffraction-quality crystals were grown from a toluene solution at -30 °C. ^{1}H NMR (C_6D_6, 360 MHz): 46.03 (2 H, s, $OCMe_2CH_2$), 16.76 (6 H, s, $HCMe_2$ or CMe_2), 13.68 (2 H, s, NCH_2CH_2N), 3.84 (1 H, t, $^3J_{HH}$ = 7 Hz, 4-C_6H_3), 3.36 (2 H, s, NCH_2CH_2N), 1.73 (2 H, d, $^3J_{HH}$ = 7 Hz, 3,5-C_6H_3), -1.99 (6 H, s, $HCMe_2$ or CMe_2), -5.76 (36 H, s, SiMe), -9.11 (6 H, s, $HCMe_2$ or CMe_2) ppm. The resonance accounting for the $HCMe_2$ protons is too broad to be located. Anal. Found (calcd for $C_{31}H_{65}CeN_4OSi_4$) C, 48.84 (48.73); H, 8.59 (8.62); N, 7.35 (7.69).

6.2.14 Synthesis of U(L^D)N"$_2$



To a solution of UN"$_3$ (1.2 g, 1.6 mmol) in toluene (10 mL) was added a solution of HL^D (0.49 g, 1.6 mmol) to afford a dark blue solution immediately. The reaction mixture was allowed to stir at room temperature for 1 h before the volatiles were removed *in vacuo*. Recrystallisation from hexanes (10 mL) at -30 °C yielded U(L^D)N"$_2$ as dark blue, diffraction-quality crystals. Yield: 0.96 g (70 %). ^{1}H NMR (C_6D_6): 29.55 (6 H, s, $HCMe_2$ or CMe_2), 3.24 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 0.26 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), -3.31 (6 H, s, $HCMe_2$ or CMe_2), -5.64 (6 H, s, $HCMe_2$ or CMe_2), -7.79 (2 H, s, NCH_2CH_2N), -11.19 (36 H, s, SiMe), -19.30 (2 H, s, NCH_2CH_2N) ppm. The resonances accounting for the $OCMe_2CH_2$ and $HCMe_2$ protons are too broad to be located within the spectrum. Anal. Found (calcd for $C_{31}H_{65}N_4OSi_4U$) C, 43.36 (43.28); H, 7.67 (7.62); N, 6.58 (6.51).

6.2.15 Attempted synthesis of Y(L^D)$_2$N"

HL^D (0.50 g, 1.66 mmol) and YN"$_3$ (0.47 g, 0.83 mmol) were combined in toluene (15 mL) and heated to 85 °C for 16 h to yield a pale yellow solution. The volatiles were removed *in vacuo* resulting in a pale yellow solid. Analysis by ^{1}H NMR spectroscopy showed numerous small resonances which could not be assigned to a single product across a sweepwidth of 10 – 0 ppm. All attempted recrystallisations only afforded HL^D.

6.2.16 Attempted synthesis of $Sc(L^D)_2N''$

HL^D (0.025 g, 0.083 mmol) and ScN''_3 (0.022 g, 0.042 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. As identified by ^1H NMR spectroscopy; at room temperature unreacted HL^D and ScN''_3 are in solution; on heating to 80 ºC for 2 days, 1 equivalent of $Sc(L^D)N''_2$ is formed alongside 1 equivalent of unreacted HL^D.

6.2.17 Synthesis of $Ce(L^D)_2N''$

To a slurry of CeN''_3 (0.22 g, 0.60 mmol) in hexanes (5 mL) was added a solution of HL^D (0.36 g, 1.2 mmol) in hexanes (5 mL). The reaction mixture was stirred for 12 h during which time a pale yellow precipitate formed. This was isolated by filtration and dried *in vacuo* to afford $Ce(L^D)_2N''$ as a pale yellow powder. From the filtrate, a second crop of product was obtained by concentration of the solution and cooling to −30 °C. Yield: 0.47 g (81%). $Ce(L^D)_2N''$ is poorly soluble in C_6D_6 and the ^1H NMR spectrum showed broad overlapping resonances which could not be assigned. Anal. Found (calcd for $C_{24}H_{42}CeN_3O_2Si_2$) C, 50.67 (50.75); H, 7.44 (7.50); N, 7.24 (7.39).

6.2.18 Attempted synthesis of $U(L^D)_2N''$

a. From UN''_3 and 2 HL^D: HL^D (0.018 g, 0.061 mmol) and UN''_3 (0.022 g, 0.030 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a deep blue solution instantly. The ^1H NMR spectrum contained resonances for $U(L^D)_2N''$ and unreacted HL^D. Over the course of 36 h, the solution became clear, pale green-brown and the ^1H NMR spectrum contained resonances for HL^D alongside numerous small resonances over the a paramagnetic spectral width of 60 – -40 ppm.

b. From $U(L^D)N''_2$ and HL^D: HL^D (0.076 g, 0.25 mmol) and $U(L^D)_2N''$ (0.22 g, 0.25 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a deep blue solution. The ^1H NMR spectrum contained resonances for unreacted $U(L^D)_2N''$ and HL^D in a 1 : 1 ratio. Over the course of 36 h, the solution became clear, pale green-brown and HL^D was visible in the ^1H NMR spectrum alongside numerous small resonances over the a spectral width of 60 − -40 ppm.

6.2.19 Attempted synthesis of $U(L^D)_3$

HL^D (0.028 g, 0.093 mmol) and UN''_3 (0.022 g, 0.030 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a deep blue solution. The ^1H NMR spectrum contained resonances for crude $U(L^D)N''_2$ and HL^D. Over the course of 36 h,

the solution became clear, pale green-brown and HL^D, HN" and small resonances over the entire spectral width of the ^1H NMR spectrum were visible.

6.2.20 Synthesis of CeN"$_3$Cl

a. Preparation scale: To a mixture of CeN"$_3$ (0.64 g, 1.0 mmol) and Ph_3CCl (0.36 g, 1.3 mmol) was added toluene (10 mL) to afford a dark purple solution immediately. The reaction mixture was stirred for 1 h. The volatiles were removed *in vacuo* and recrystallisation from thf/hexanes (1/2) at -30 ºC afforded CeN"$_3$Cl as a dark purple microcrystalline solid. Yield: 0.54 g (81 %). ^1H NMR (C_6D_6, 400 MHz): 0.44 (54 H, s, SiMe) ppm.

b. NMR scale with internal standard: CeN"$_3$ (0.010 g, 0.016 mmol), Ph_3CCl (0.0056 g, 0.020 mmol) and 1,3,5-^{t}Bu-C_6H_3 (0.0040 g, 0.016 mmol) were combined and fully dissolved in C_6D_6 (0.5 mL) to afford a deep purple-red solution. The ^1H NMR spectrum indicated quantitative conversion of CeN"$_3$ to CeN"$_3$Cl and 0.5 equivalents of Gomberg's dimer, $Ph_3C(H)C_2H_4CPh_2$, by integration.

6.2.21 Synthesis of UN"$_3$Cl

a. Preparative scale: To a slurry of purple UN"$_3$ (0.51 g, 0.71 mmol) in toluene (10 mL) was added Ph_3CCl (0.25 g, 0.89 mmol) in toluene (5 mL) to afford a brown solution immediately. The reaction mixture was stirred for 1 h before the volatiles were removed *in vacuo*. Recrystallisation from thf/hexanes (1/2) at -30 ºC afforded UN"$_3$Cl as a brown microcrystalline solid. Yield: 0.27 g (50 %). ^1H NMR (C_6D_6, 400 MHz): -2.33 (54 H, s, SiMe) ppm.

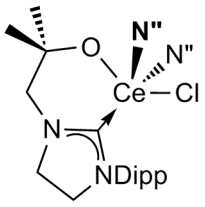
b. NMR scale with internal standard: UN"$_3$ (0.010 g, 0.014 mmol), Ph_3CCl (0.0048 g, 0.017 mmol) and 1,3,5-^{t}Bu-C_6H_3 (0.0034 g, 0.014 mmol) were combined and fully dissolved in C_6D_6 (0.5 mL) to afford a brown solution. The ^1H NMR spectrum indicated 65 % conversion of UN"$_3$ to UN"$_3$Cl and 0.5 equivalents of Gomberg's dimer $Ph_3C(H)C_2H_4CPh_2$ by integration. No other paramagnetic resonances were observed.

6.2.22 Synthesis of UN"$_3$ from UN"$_3$Cl

To Na/Hg (1 % Na, 0.0075 g, 0.33 mmol) was added a brown solution of UN"$_3$Cl (0.12 g, 0.16 mmol) in hexanes (10 mL). The reaction mixture was stirred for 15 h during which time the solution became dark purple in colour. The reaction mixture was decanted into a new flask and the amalgam washed with hexanes (3 x 5 mL). The combined washings

were dried *in vacuo* to afford $UN"_3$ as a purple solid. Yield: 0.062 g (63 %). ^{1}H NMR (C_6D_6, 400 MHz): -11.21 (54 H, s, SiMe) ppm.

6.2.23 Synthesis of $Ce(L^D)N"_2Cl$



a. From $Ce(L^D)N"_2$: To a slurry of $Ce(L^D)N"_2$ (0.62 g, 0.81 mmol) in toluene (5 mL) was added a solution of Ph_3CCl (0.22 g, 0.81 mmol) in toluene (5 mL). The reaction mixture was stirred for 12 h during which time it became deep orange-red in colour. Concentration to 5 mL and cooling to -30 ºC yielded red-orange microcrystalline material. This was isolated by filtration and the volatiles were then removed *in vacuo* to afford $Ce(L^D)N"_2Cl$ as a red-orange solid. Yield: 0.22 g (34 %). X-Ray diffraction-quality crystals were grown from a saturated toluene solution at -20 ºC. ^{1}H NMR (C_6D_6, 600 MHz): 7.17 (1 H, t, $^3J_{HH}$ = 7 Hz, 4-C_6H_3), 7.12 (1 H, t, $^3J_{HH}$ = 7 Hz, 3,5-C_6H_3), 3.29 (2 H, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 3.24 (2 H, sept. $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.01 (2 H, s, $OCMe_2C\underline{H}_2$), 2.83 (2 H, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 1.52 and 1.16 (6 H each, d, $^3J_{HH}$ = 7 Hz), 1.16 (6 H, s, CMe_2), 0.55 (36 H, s, SiMe) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 150 MHz): 237.4 (NCN), 145.9 (1-C_6H_3) 138.4 (2,6-C_6H_3), 124.5 (4-C_6H_3), 116.6 (3,5-C_6H_3), 85.8 ($\underline{C}Me_2$), 62.4 ($OCMe_2\underline{C}H_2$), 55.2 and 52.5 (NCH_2CH_2N), 28.6 ($H\underline{C}Me_2$), 28.4 ($C\underline{Me}_2$), 26.1 and 24.8 ($HC\underline{Me}_2$), 5.5 (SiMe) ppm. Anal. Found (calcd for $C_{31}H_{65}CeClN_4OSi_4$) C, 46.58 (46.67); H, 8.16 (8.21); N, 6.94 (7.02).

b. From $CeN"_3Cl$: To a dark red slurry of $CeN"_3Cl$ (0.068 g, 0.10 mmol) in toluene (2 mL) was added a solution of HL^D (0.031 g, 0.10 mmol) in toluene (0.5 mL). The reaction mixture became dark purple in colour and was stirred for 2 h at room temperature. Recrystallisation from toluene (0.5 mL) at -30 ºC afforded $Ce(L^D)N"_2Cl$ as a red-orange solid. Yield: 0.055 g (67 %).

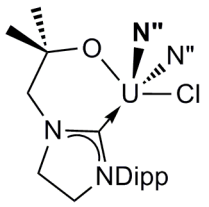
6.2.24 Attempted synthesis of $Ce(L^D)_2N"Cl$

a. From $CeN"_3Cl$ in C_6D_6: HL^D (0.022 g, 0.072 mmol) and $CeN"_3Cl$ (0.024 g, 0.036 mmol) were combined in C_6D_6 (0.5 mL) in J-Young Teflon valve NMR tube to afford a pale red-orange solution. The reaction mixture was allowed to stand for 4 hours. ^{1}H NMR (C_6D_6, 250 MHz): 7.27 - 7.20 (6 H, overlapping m, C_6H_3), 3.58 (4 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.28 (4 H, t, $^3J_{HH}$ = 10 Hz), 3.19 (4 H, s, $OCMe_2\underline{C}H_2$), 2.87 (4 H, t, $^3J_{HH}$ = 10 Hz), 1.85 and 1.18 (12 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.74 (18 H, s, SiMe) ppm. After standing for a further 8 h, the reaction mixture became blue. The ^{1}H NMR spectrum indicated

decomposition of the compound initially formed and there were resonances accounting for HL^D.

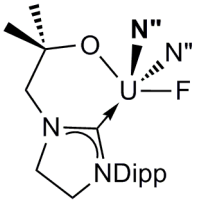
b. From $CeN"_3Cl$ in hexanes: To a slurry of $CeN"_3Cl$ (0.14 g, 0.21 mmol) in hexanes was added a solution of HL^D (0.13 g, 0.42 mmol). The reaction mixture was stirred for 2 days during which time the solution became orange-red in colour and a pale orange precipitate formed. The precipitate was isolated by filtration and dried under reduced pressure. Attempted recrystallisations did not afford a clean product. The compound decomposed in toluene and C_6D_6 solutions at room temperature.

6.2.25 Synthesis of $U(L^D)N"_2Cl$



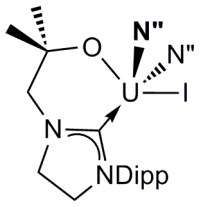
$UN"_3Cl$ (0.10 g, 0.13 mmol) and HL^D (0.040 g, 0.13 mmol) were combined in C_6D_6 (0.5 mL) to afford a brown solution. After 2 h, the volatiles were removed *in vacuo*. Recrystallisation from toluene afforded $U(L^D)N"_2Cl$ as a brown solid. Yield: 0.043 g (36 %). X-Ray diffraction-quality crystals were grown from a saturated toluene solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 77.39 (6 H, s, CMe_2 or $HC\underline{Me}_2$), 31.67 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N, $\underline{H}CMe_2$ or 3,5-C_6H_3), 12.93 (1 H, s, 4-C_6H_3), 7.47 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N, $\underline{H}CMe_2$ or 3,5-C_6H_3), -11.05 (6 H, s, CMe_2 or $HC\underline{Me}_2$), -12.69 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N, $\underline{H}CMe_2$ or 3,5-C_6H_3), -14.11 (6 H, s, CMe_2 or $HC\underline{Me}_2$), -17.61 (36 H, s, SiMe), -27.71 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N, $\underline{H}CMe_2$ or 3,5-C_6H_3) ppm. Satisfactory elemental analysis was not obtained from a sample of powdered single crystals.

6.2.26 Synthesis of $U(L^D)N"_2F$



To a dark blue solution of $U(L^D)N"_2$ (0.081 g, 0.094 mmol) in toluene (2 mL) was added F_3CSiMe_3 (14 µL, 0.094 mmol). The reaction mixture was heated to 80 °C for 24 h to afford a dark brown solution. Recrystallisation from toluene (0.5 mL) at -20 ºC afforded $U(L^D)N"_2F$ as a red-brown solid. Yield: 0.057 g (69 %). X-Ray diffraction-quality crystals were grown from a toluene solution at -30 ºC. ^{1}H NMR (C_6D_6, 360 MHz): 76.40 (6 H, s, CMe_2), 11.71 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N or $\underline{H}CMe_2$), 3.21 (1 H, t, $^3J_{HH}$ = 7 Hz, 4-C_6H_3)), 0.9 and 0.03 (1 H each, d, ^3J=7 Hz, 3,5-C_6H_3), -4.64 (12 H, s, $HC\underline{Me}_2$) -11.38 (36 H, s, SiMe), -24.1 and -31.2 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N or $\underline{H}CMe_2$), -47.64 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N or $\underline{H}CMe_2$) ppm. Satisfactory elemental analysis was not obtained from a sample of powdered single crystals.

6.2.27 Synthesis of $U(L^D)N''_2I$



a. ^{t}BuI: To a solution of $U(L^D)N''_2$ (0.16 g, 0.19 mmol) in toluene (10 mL) was added ^{t}BuI (22 µL, 0.19 mmol). The reaction mixture became pale brown in colour immediately. The volatiles were removed *in vacuo* and a pale pink solid containing $U(L^D)N''_2I$ as the major product was isolated from a toluene solution cooled to -20 ºC. Yield: 0.085 g (47 %). ^{1}H NMR (C_6D_6, 360 MHz): 64.83 (6 H, s, CMe_2), 43.16 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N or $\underline{H}CMe_2$), 8.31 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N or $\underline{H}CMe_2$), 7.08 (1 H, t, $^3J_{HH}$ = 7 Hz, 4-C_6H_3), 6.99 (1 H, d, $^3J_{HH}$ = 6.9 Hz, 3,5-C_6H_3), 3.75 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N or $\underline{H}CMe_2$), -10.77 (12 H, s, $HC\underline{Me}_2$), -11.23 (12 H, s, $HC\underline{Me}_2$), -17.19 (36 H, s, SiMe), -17.22 (2 H, s, $OCMe_2C\underline{H}_2$, NCH_2CH_2N or $\underline{H}CMe_2$) ppm.

b. PhI: To a solution of $U(L^D)N''_2$ (0.17 g, 0.021 mmol) in C_6D_6 (0.5 mL) was added PhI (2.3 µL, 0.021 mmol). The reaction mixture became pale brown in colour immediately. The ^{1}H NMR spectrum was shown to contain resonances corresponding to $U(L^D)N''_2I$.

6.3 Synthetic procedures described in Chapter Three

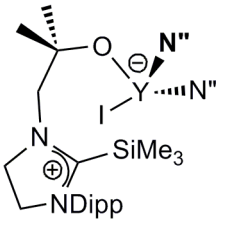
6.3.1 General polymerisation procedure of *rac*-lactide

Each polymerisation run was carried out at room temperature; a thf solution of the catalyst (3.00 mg) was added to a thf solution of *rac*-lactide monomer (300 mg), with vigorous stirring, to afford a total volume of 3 mL. The reaction was quenched by addition of wet THF and exposure to ambient atmosphere, followed by removal of the volatiles under reduced pressure. The polymers were characterised by ^{1}H, ^{13}C, ^{1}H{^{1}H} NMR spectroscopy ($CDCl_3$ solutions) and by Gel Permeation Chromatography (GPC).

6.3.2 Attempted synthesis of $Ce(L^D)_2I$

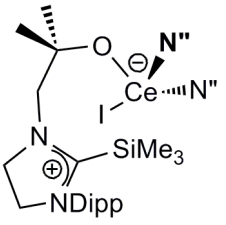
In a J-Young Teflon valve NMR tube, CeN''_3 (0.039 g, 0.063 mmol) and HL^D (0.038 g, 0.13 mmol) were combined in C_6D_6 and the reaction mixture stored for 45 minutes. To the reaction mixture was added LiI (0.0084 g, 0.063 mmol). The ^{1}H NMR spectrum (C_6D_6, 360 MHz) indicated no reaction at room temperature. The reaction mixture was heated to 80 ºC for 24 h until no LiI remained. The ^{1}H NMR spectrum showed a resonance accounting for LiN" alongside overlapping resonances in the range 9.80 – -8.52 ppm which could not be assigned. Attempted recrystallisations did not yield a pure product.

6.3.3 Synthesis of Y($L^{D, SiMe_3}$)N"$_2$I



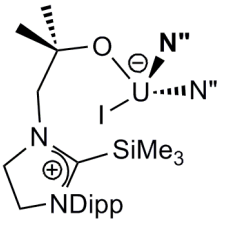
To a solution of Y(L^{D})N"$_2$ (0.15 g, 0.21 mmol) in benzene (10 mL) was added Me_3SiI (30 μL, 0.21 mmol) resulting in a clear, pale yellow solution. The reaction mixture was stirred at room temperature for 1 h before the volatiles were removed *in vacuo* to afford Y($L^{D, SiMe_3}$)N"$_2$I as a white powder. Yield: 0.19 g (100 %). Diffraction-quality crystals were grown from a saturated toluene solution cooled to -20 °C. ^{1}H NMR (C_6D_6, 360 MHz): 7.01 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.78 (2 H, d, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 4.83 and 3.51 (2 H each, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 3.41 (2 H, s, $OCMe_2CH_2$), 2.58 (2 H, sept, $^3J_{HH}$ = 7 Hz, $HCMe_2$), 1.51 (6 H, s, CMe_2), 0.98 and 0.97 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HCMe_2$), 0.68 (36 H, s, $N(SiMe_3)_2$), -0.38 (9 H, s, $CSiMe_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 90 MHz): 174.9 (NCN), 146.5 (3,5-C_6H_3), 132.7 (1-C_6H_3), 131.2 (2,6-C_6H_3), 125.2 (4-C_6H_3), 74.4 ($\underline{C}Me_2$), 60.9 ($OCMe_2\underline{C}H_2$), 55.3 (NCH_2CH_2N), 31.2 ($H\underline{C}Me_2$), 28.5 ($C\underline{Me}_2$), 25.9 and 23.3 ($HC\underline{Me}_2$), 6.3 ($N(SiMe_3)_2$), -0.95 ($CSi\underline{Me}_3$) ppm. Anal. Found (calcd for $C_{34}H_{74}IN_4OSi_5Y$) C, 44.74 (44.82); H, 8.20 (8.19); N, 6.07 (6.15).

6.3.4 Synthesis of Ce($L^{D, SiMe_3}$)N"$_2$I



To a solution of Ce(L^{D})N"$_2$ in toluene (0.50 g, 0.65 mmol) was added an excess of Me_3SiI (185 μL, 1.3 mmol) to yield a pale yellow solution and colourless crystalline material immediately. The reaction mixture was stirred for 4 h before being allowed to settle. The solid was then isolated by filtration, washed with hexanes (3 x 5 mL) and dried under reduced pressure to afford Ce($L^{D, SiMe_3}$)N"$_2$I as a white powder. Yield: 0.62 g (99 %). Diffraction-quality crystals could be grown from saturated solutions of toluene or benzene at room temperature. Ce($L^{D, SiMe_3}$)N"$_2$I was poorly soluble in C_6D_6 and the ^{1}H NMR spectrum showed broad overlapping resonances in the range 17.64 – -3.37 ppm which could not be assigned.

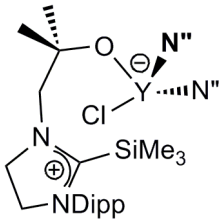
6.3.5 Synthesis of U($L^{D, SiMe_3}$)N"$_2$I



To a solution of U(L^{D})N"$_2$ (0.10 g, 0.12 mmol) was added Me_3SiI (17 μL, 0.12 mmol) to afford a dark brown solution immediately. The reaction mixture was stirred for 1 h before the volatiles were removed under reduced pressure to give a dark brown solid which was washed in hexanes and dried *in vacuo* to afford

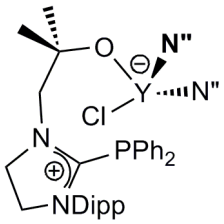
U($L^{D, SiMe_3}$)N"$_2$I as a dark brown solid. Yield: 0.088 g (73 %). Recrystallisation from toluene at -20 ºC yielded diffraction-quality crystals. ^{1}H NMR (C_6D_6, 360 MHz): 24.69 (1 H, s, HCMe$_2$), 19.81 (6 H, s, CMe$_2$), 19.51 (OCMe$_2$CH$_2$), 6.76 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.49 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 2.22 (2 H, s, NCH$_2$CH$_2$N), 1.50 (9 H, s, CSiMe$_3$), 1.36 (6 H, s, HCMe$_2$), 0.76 (2 H, s, NCH$_2$CH$_2$N), 0.13 (1 H, s, HCMe$_2$), -0.81 (6 H, s, HCMe$_2$), -10.78 (H, s, N(SiMe$_3$)$_2$) ppm. Anal. Found (calcd for $C_{34}H_{74}IN_4OSi_5U$): C, 38.47 (38.51); H, 6.96 (7.03); N, 5.19 (5.28).

6.3.6 Synthesis of Y($L^{D, SiMe_3}$)N"$_2$Cl



To J-Young Teflon valve NMR tube containing Y(L^D)N"$_2$ (0.021 g, 0.030 mmol) in C_6D_6 (0.5 mL) was added Me_3SiCl (3.8 μL, 0.030 mmol) resulting in a clear, colourless solution. The volatiles were removed *in vacuo* to afford Y($L^{D, SiMe_3}$)N"$_2$Cl as a white powder. Yield: 0.024 g (100 %). ^{1}H NMR (C_6D_6, 360 MHz): 7.00 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.77 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 4.83 and (2 H each, t, $^3J_{HH}$ = 11 Hz, NCH$_2$CH$_2$N), 3.51 (2 H, s, OCMe$_2$CH$_2$), 2.69 (2 H, sept, $^3J_{HH}$ = 7 Hz, HCMe$_2$), 1.54 (6 H, s, CMe$_2$), 1.01 and 0.99 (6 H each, d, $^3J_{HH}$ = 7 Hz, HCMe$_2$), 0.69 (36 H, s, N(SiMe$_3$)$_2$), -0.33 (9 H, s, CSiMe$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 90 MHz): 174.7 (NCN), 147.5 (3,5-C_6H_3), 132.7 (1-C_6H_3), 131.1 (2,6-C_6H_3), 125.1 (4-C_6H_3), 73.7 (CMe$_2$), 61.3 (OCMe$_2$CH$_2$), 55.2 and 52.5 (NCH$_2$CH$_2$N), 31.2 (HCMe$_2$), 28.4 (CMe$_2$), 25.7 and 23.2 (HCMe$_2$), 6.08 (N(SiMe$_3$)$_2$), -1.24 (CSiMe$_3$) ppm. Anal. Found (calcd for $C_{34}H_{74}ClN_4OSi_5Y$) C, 49.87 (49.81); H, 8.97 (9.10); N, 6.78 (6.83).

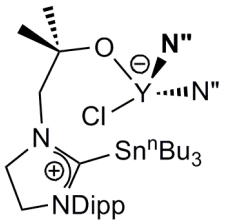
6.3.7 Synthesis of Y(L^{D, PPh_2})N"$_2$Cl



To a solution of Y(L^D)N"$_2$ (0.16 g, 0.22 mmol) in toluene (5 mL) was added Ph_2PCl (42 μL, 0.22 mmol) to yield a cloudy, colourless solution. The reaction mixture was concentrated to dryness to afford Y(L^{D, PPh_2})N"$_2$Cl as a white solid. Yield: 0.14 g (67 %). ^{1}H NMR (C_6D_6, 360 MHz): 7.15 – 6.86 (11 H, overlapping m, PPh$_2$ and 4-C_6H_3), 6.76 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 5.20 and 3.64 (2 H each, t, $^3J_{HH}$ = 11 Hz, NCH$_2$CH$_2$N), 3.34 (2 H, s, OCMe$_2$CH$_2$), 2.59 (2 H, sept, $^3J_{HH}$ = 7 Hz, HCMe$_2$), 1.12 (6 H, s, CMe$_2$), 0.93 and 0.77 (6 H each, d, $^3J_{HH}$ = 7 Hz, HCMe$_2$), 0.68 (36 H, s, SiMe) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 90 MHz): 170.6 ($^1J_{PC}$ = 151 Hz, NCN), 146.6 134.3 134.2 131.6 130.1 129.3 125.7 and 125.0 (C_6H_3 and PPh$_2$), 73.4 (CMe$_2$), 60.8 (OCMe$_2$CH$_2$), 53.7 (NCH$_2$CH$_2$N), 30.8

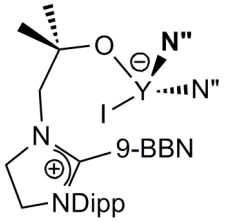
($C\underline{Me}_2$), 29.2 ($H\underline{C}Me_2$), 26.2 and 22.4 ($HC\underline{Me}_2$), 6.0 (SiMe) ppm. Anal. Found (calcd for $C_{43}H_{75}ClN_4OPSi_4Y$) C, 55.46 (55.43); H, 8.03 (8.11); N, 5.92 (6.01).

6.3.8 Synthesis of Y(L^{D, Sn^nBu_3})N"$_2$Cl



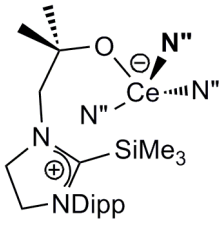
To a solution of Y(L^D)N"$_2$ (0.10 g, 0.14 mmol) in toluene (5 mL) was added $^nBu_3SnCl$ (39 μL, 0.14 mmol) to yield a clear, colourless solution. The volatiles were removed *in vacuo* to afford Y(L^{D, Sn^nBu_3})N"$_2$Cl as a white solid. Yield: 0.11 g (76 %) ^{1}H NMR (C_6D_6, 90 MHz): 7.07 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.84 (2 H, d, $^3J_{HH}$ = 8 Hz, 2,5-C_6H_3), 4.90 and 3.53 (2 H , t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 3.51 (2 H, s, $OCMe_2C\underline{H}_2$), 2.66 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 1.60 (6 H, s, CMe_2), 1.26 – 1.01 (15 H, overlapping m, Sn^{n}Bu$_3$), 1.00 and 0.98 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.81 – 0.79 (12 H, overlapping m, Sn^{n}Bu$_3$), 0.68 (36 H, s, SiMe) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 90 MHz): 182.6 (NCN), 147.1, 133.1, 131.2, 125.3 (C_6H_3), 73.7 ($\underline{C}Me_2$), 63.1 ($OCMe_2\underline{C}H_2$), 55.2 and 52.8 (NCH_2CH_2N), 31.0 28.6 27.1 25.5 23.8 13.5 ($C\underline{Me}_2$, $\underline{C}HMe_2$, $CH\underline{Me}_2$ and Sn^{n}Bu$_3$), 6.3 (SiMe) ppm. Anal. Found (calcd for $C_{43}H_{92}ClN_4OSi_4SnY$) C, 49.74 (49.82); H, 8.88 (8.95); N, 5.35 (5.40).

6.3.9 Synthesis of Y($L^{D, 9\text{-}BBN}$)N"$_2$I



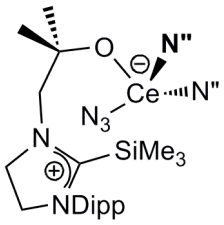
To a solution of Y(L^D)N"$_2$ (0.15 g, 0.36 mmol) in toluene (5 mL) was added a solution of (*B*-I)-9-BBN in hexanes (0.77 mL, 0.36 mmol) to give a cloudy. colourless solution. The volatiles were removed *in vacuo* and the resulting white solid was washed with hexanes (2 x 5 mL) and dried to afford Y($L^{D, 9\text{-}BBN}$)N"$_2$I as a white solid. Yield: 0.10 g (49 %). ^{1}H NMR (C_6D_6/thf, 500 MHz): 7.19 – 6.96 (3 H, overlapping m, 3,4,5-C_6H_3), 4.70 and 3.97 (1 H each, d, $^3J_{HH}$ = 11 Hz), 3.24 (2 H, s, $OCMe_2CH_2$), 3.17 (2 H, sept, $^3J_{HH}$ = 7 Hz, $HCMe_2$), 2,.29, 1.75, 1.31, 0.77 and 0.50 (2 H each, m, CH_2-9-BBN), 2.14 (1 H, CH-9-BBN), 1.21 and 1.01 (6 H each, d, $^3J_{HH}$ = 7 Hz), 1.13 (36 H, s, SiMe) ppm. The resonances accounting for the, CMe_2 CH-9-BBN and final CH_2-9-BBN protons could not be located as a result of the presaturation NMR experiment utilised. Here, these resonances are likely to be obscured by residual protio-thf still prominent in the ^{1}H NMR spectrum. Anal. Found (calcd for $C_{39}H_{79}BIN_4Si_4Y$) C, 48.81 (48.84); H, 8.30 (8.25); N, 5.84 (5.73).

6.3.10 Synthesis of Ce(L$^{D, SiMe_3}$)N"$_3$



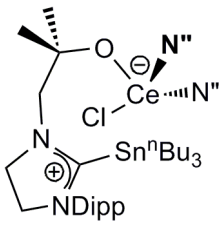
To a J-Young Teflon valve NMR tube containing Ce(L$^{D, SiMe_3}$)N"$_2$I (0.034 g, 0.035 mmol in C_6D_6 (0.5 mL) was added KN" (0.0070 g, 0.035 mmol) in C_6D_6 (0.5 mL). A white precipitate was observed to form instantly and the solution became pale yellow. ^{1}H NMR spectral analysis is fully consistent with the formation of Ce(L$^{D, SiMe_3}$)N"$_3$ in quantitative yield. The solution was filtered into a new NMR tube which was placed under a partial static vacuum and heated to 80 °C for 24 h. After this time, only Ce(L^D)N"$_2$ and N"' were visible in the ^{1}H NMR spectrum. ^{1}H NMR (C_6D_6, 360 MHz): 29.42 and 18.37 (2 H each, s, NCH_2CH_2N), 8.36 (2 H, s, $OCMe_2\underline{C}H_2$), 7.90 - 7.67 (3 H, overlapping m, 3,5-C_6H_3 and 4-C_6H_3), 5.79 (2 H, sept, $^3J_{HH}$ = 6 Hz, $\underline{H}CMe_2$), 2.31 and 2.02 (6 H each, d, $^3J_{HH}$ = 6 Hz, $HC\underline{M}e_2$), -1.44 (6 H , s, CMe_2), -2.26 (54 H s, SiMe) ppm.

6.3.11 Synthesis of Ce(L$^{D, SiMe_3}$)N"$_2$(N$_3$)



To a solution of Ce(L^D)N"$_2$ (0.16 g, 0.21 mmol) in toluene (10 mL) was added a solution of Me_3SiN_3 (27 µL, 0.021 mmol). The reaction mixture was stirred for 2 h during which time a colourless precipitate formed. The reaction mixture was allowed to settle before the solid was filtered off, washed with toluene (3 x 5 mL) and dried *in vacuo* to afford [Ce(L$^{D, SiMe_3}$)N"$_2$(N$_3$)] as a white powder. Yield: 0.17 g (100 %). Recrystallisation from toluene yielded diffraction-quality crystals. The crystals were too insoluble in common deuterated solvents to allow for satisfactory NMR spectral analysis. Anal. Found (calcd for $C_{68}H_{148}Ce_2N_{14}O_2Si_{10}$) C, 46.41 (46.54); H, 8.48 (8.50); N, 11.14 (11.17).

6.3.12 Synthesis of Ce(L$^{D, Sn^nBu_3}$)N"$_2$Cl



Ce(L^D)N"$_2$ (0.061 g, 0.079 mmol) and ^{n}Bu$_3$SnCl (21.6 µL, 0.079 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. The reaction mixture became clear and colourless immediately on combination of the reagents. Ce(L$^{D, Sn^nBu_3}$)N"$_2$Cl was judged to have been formed by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6, 600 MHz): 11.8 (6 H, s, CMe_2 or $HC\underline{M}e_2$ or ^{n}Bu$_3$Sn), 9.17 (2 H, s, $OCMe_2CH_2$ or NCH_2CH_2N or $\underline{H}CMe_2$), 6.92 (1 H, t, $^3J_{HH}$ = 6 Hz), 6.73 (2 H, d, $^3J_{HH}$ = 6 Hz), 2.71 (2 H, s,

$OCMe_2CH_2$ or NCH_2CH_2N or $\underline{H}CMe_2$). 2.19 – 0.98 (33 H, overlapping m, Sn^nBu_3), 0.35 (6 H, s, CMe_2), -3.24 (36 H, s, SiMe) ppm.

6.3.13 Elimination reaction of $Ce(L^{D, SiMe_3})N"_2I$

A J-Young Teflon valve NMR tube containing solid $Ce(L^{D, SiMe_3})N"_2I$ (0.038 g, 0.040 mmol) and a colourless solution of an internal standard 1,3,5-^{t}Bu-C_6H_3 (0.0038 g, 0.015 mmol) in C_6D_6 (0.5 mL) was placed under a partial static vacuum and heated to 80 °C for 36 h. After this time, the solution became yellow and a mixture of $Ce(L^D)N"_2$ (~50 % of the paramagnetic species by integration), $Ce(L^D)I_2$ and N''' (N''' = $N(SiMe_3)_3$) was visible in the ^{1}H NMR spectrum. To this mixture was added KN'' (0.019 g, 0.020 mmol) which resulted in the instant precipitation of KI and full conversion of $Ce(L^D)I_2$ to $Ce(L^D)N"_2$ by analysis of the ^{1}H NMR spectrum. GC analysis of the reaction solution also indicated the presence of N''', identified by comparison with a pure sample of N'''.

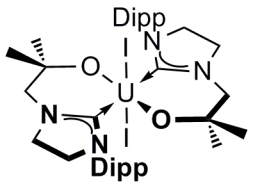
6.3.14 Elimination reaction of $Ce(L^{D, SiMe_3})N"_3$

A J-Young Teflon valve NMR tube containing $Ce(L^{D, SiMe_3})N"_3$ (0.035 g, 0.035 mmol) in C_6D_6 (0.5 mL) was placed under a partial static vacuum and heated to 80 °C for 24 h. After this time, $Ce(L^D)N"_2$ and N''' were visible in the ^{1}H NMR spectrum.

6.3.15 Elimination reaction of $U(L^{D, SiMe_3})N"_2I$ to form $U(L^D)_2I_2$

A solution of $U(L^{D, SiMe_3})N"_2I$ (0.082 g, 0.94 mmol) in toluene (5 mL) was heated to 80 °C for 24 h. During this time, diffraction-quality purple crystals formed which were isolated by filtration, washed with hexane (3 x 5 mL) and dried under reduced pressure to afford $U(L^D)_2I_2$. Yield: 0.018 g (21 %). The crystals were too insoluble in all common deuterated solvents to allow for NMR spectral analysis. Anal. Found (calcd for $C_{38}H_{58}I_2N_4O_2U$): C, 41.58 (41.69); H, 5.40 (5.34); N, 5.03 (5.12).

6.3.16 Alternative synthesis of $U(L^D)_2I_2$

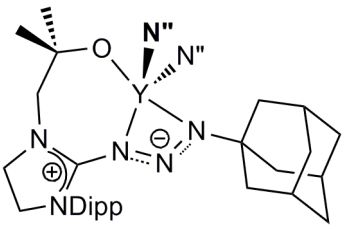


$U(L^D)_2N"$ (0.024 g, 0.027 mmol) and excess I_2 (0.053 g, 0.21 mmol) were combined in C_6D_6 in a J-Young Teflon valve NMR tube to afford a pale brown solution immediately. The reaction mixture was stored for 24 h during which time a pale brown precipitate and purple crystals formed. The crystals were shown to be $U(L^D)_2I_2$ by measurement of the unit cell.

6.3.17 Attempted synthesis of $UL_2(N_3)_2$

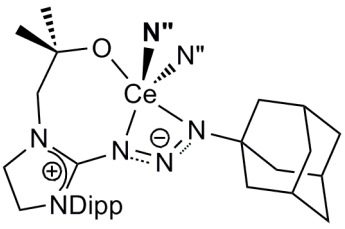
$U(L^D)_2I_2$ (0.010 g, 0.0091 mmol) and NaN_3 (0.0012 g, 0.018 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature. On heating the reaction mixture to 80 ºC, a grey solid was deposited in the NMR tube and the NMR spectrum showed resonances across a diamagnetic sweep width indicative of decomposition.

6.3.18 Synthesis of $Y(L^{D, AdN_3})N''_2$



To a mixture of $Y(L^D)N''_2$ (0.20 g, 0.28 mmol) and AdN_3 (0.10 g, 0.56 mmol) was added toluene. The reaction mixture was heated to 90 °C for 16 h, during which time it became a viscous, yellow solution. The volatiles were removed *in vacuo* to yield a yellow solid. Recrystallisation from toluene (2 mL) at -20 °C afforded $Y(L^{D,AdN_3})N''_2$ as diffraction-quality colourless crystals. Yield: 0.19 g (76 %). ^{1}H NMR (C_6D_6, 600 MHz): 7.30 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.93 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 4.03 (1 H , d, $^3J_{HH}$ = 14 Hz, $OCMe_2C\underline{H}_2$), 3.13 – 3.03 (overlapping m, 4 H, NCH_2CH_2N), 2.99 and 2.84 (1 H each, sept, $^3J_{HH}$ = 6 Hz, $\underline{H}CMe_2$), 2.61 (1 H , d, $^3J_{HH}$ = 14 Hz, $OCMe_2C\underline{H}_2$), 1.89 and 1.77 (6 H each, s, CMe_2), 1.63 – 1.58 (6 H each, overlapping m, $HC\underline{Me}_2$), 1.57 – 1.03 (18 H, overlapping m, CH_2-Ad and CH-Ad), 0.54 (36 H, s, SiMe) ppm. Anal. Found (calcd for $C_{41}H_{80}N_7OSi_4Y$) C, 55.40 (55.43); H, 8.98 (9.08); N, 10.95 (11.04).

6.3.19 Synthesis of $Ce(L^{D, AdN_3})N''_2$



To a mixture of $Ce(L^D)N''_2$ (0.25 g, 0.33 mmol) and AdN_3 (0.12 g, 0.66 mmol) was added toluene (10 mL). The reaction mixture was heated to 90 °C for 16 h to afford an orange solution. The volatiles were removed under reduced pressure to give a glassy solid. Recrystallisation from toluene (0.5 mL) at -20 °C afforded diffraction-quality, orange crystals of $Ce(L^{D,AdN_3})N''_2$. Yield: 0.20 g (65 %). ^{1}H NMR (C_6D_6, 600 MHz): 26.51 (2 H, s, $OCMe_2C\underline{H}_2$), 8.98 (2 H, s, NCH_2CH_2N) 7.59 (2 H, s, $\underline{H}CMe_2$), 4.80 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 4.63 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 4.16 and 3.29 (6 H each, d, $^3J_{HH}$ = 12 Hz, $HC\underline{Me}_2$), 2.45 (2 H, s, NCH_2CH_2N), -11.72 (36 H, s, SiMe) ppm. The resonances associated with the CH- and CH_2-Ad protons could not be assigned. Anal. Found (calcd for $C_{41}H_{80}CeN_7OSi_4$) C, 52.36 (52.41); H, 8.49 (8.58); N, 10.38 (10.44).

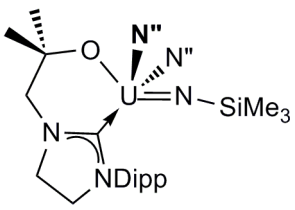
6.3.20 Attempted N_2 elimination from Ce(L^{D, AdN_3})N"$_2$

In a J-Young Teflon valve NMR tube, an orange solution of Ce(L^{D, AdN_3})N"$_2$ (0.025 g, 0.026 mmol) in C_6D_6 (0.5 mL) was placed under a partial static vacuum and heated to 80 ºC. The ^{1}H NMR spectrum showed that no reaction had taken place over the course of 6 days.

6.3.21 Reaction of Ce(L^{D, AdN_3})N"$_2$ with PhCCPh

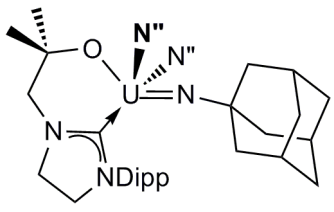
In a J-Young Teflon valve NMR tube, an orange solution of Ce(L^{D, AdN_3})N"$_2$ (0.025 g, 0.026 mmol) in C_6D_6 (0.5 mL) was placed under a partial static vacuum and heated to 80 ºC. No reaction was shown to have taken place over the course of 6 days by NMR spectroscopy.

6.3.22 Synthesis of U(L^D)N"$_2$(=NSiMe$_3$)



To a solution of U(L^D)$_2$N" (0.15 g, 0.18 mmol) in toluene (5 mL) was added a solution of Me_3SiN_3 (23.3 µL, 0.18 mmol) in toluene (2 mL). On addition, the solution became red-brown in colour and N_2 was evolved. The reaction mixture was stirred for 16 h and then the volatiles were removed under reduced pressure to yield a red-brown solid. Recrystallisation from a toluene solution at -20 ºC afforded U(L^D)N"$_2$(=NSiMe$_3$) as dark red, crystalline material. Yield: 0.085 g (52 %). Diffraction-quality single crystals were grown from a saturated toluene solution at -20 ºC. ^{1}H NMR (C_6D_6, 360 MHz): 77.32 and 32.41 (2 H each, s, $\underline{H}CMe_2$, $OCMe_2C\underline{H}_2$ or 3,5-C_6H_3), 28.22 (6 H, s, CMe_2), 2.51 (4 H, s, NCH_2CH_2N), -9.17 (36 H, s, $N(SiMe_3)_2$), -12.54 (2 H, s, $\underline{H}CMe_2$, $OCMe_2C\underline{H}_2$ or 3,5-C_6H_3), -13.01 (9 H, s, =$NSiMe_3$), -16.37 (12 H, s, $HC\underline{Me}_2$) ppm. The resonance accounting for the 4-C_6H_3 proton could not be identified. Anal. Found (calcd for $C_{34}H_{74}N_5OSi_5U$): C, 42.86 (43.10); H, 7.80 (7.87); N, 7.37 (7.39).

6.3.23 Synthesis of U(L^D)N"$_2$(=NAd)



To a solution of U(L^D)$_2$N" (0.14 g, 0.16 mmol) in toluene (5 mL) was added a solution of AdN_3 (0.028 g, 0.16 mmol) in toluene (5 mL). On addition, the solution became red-brown in colour and N_2 was evolved. The reaction mixture was stirred for 16 h and then the volatiles were removed under reduced pressure to afford U(L^D)N"$_2$(=NAd) as a red-brown solid. Yield: 0.10 g (62 %). Diffraction-quality single crystals were grown from a saturated toluene

solution at -20 ºC. ^{1}H NMR (C_6D_6, 600 MHz): 33.80 19.32 15.47 and 12.56 (6 H each, s, CMe_2, $HC\underline{Me}_2$ or CH_2-Ad), 9.46 (2 H, s, $OCMe_2C\underline{H}_2$ or 3,5-C_6H_3), 7.96 (4 H, s, NCH_2CH_2N), -4.41 (3 H, s, CH-Ad), -8.81 (6 H, s, CMe_2, $HC\underline{Me}_2$ or CH_2-Ad), - 10.98 (1 H, s, 4-C_6H_3), -11.19 (2 H, s, $OCMe_2C\underline{H}_2$ or 3,5-C_6H_3), -17.19 (36 H, s, SiMe) ppm. Anal. Found (calcd for $C_{41}H_{80}N_5OSi_4U$): C, 48.70 (48.78); H, 8.05 (7.99); N, 6.87 (6.94).

6.3.24 Attempted addition reactions of Y(L^D)N"$_2$ with other E-X

a. ^{t}BuI: Y(L^D)N"$_2$ (0.020 g, 0.028 mmol) and ^{t}BuI (3.4 µL, 0.028 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

b. Ph_3CCl: Y(L^D)N"$_2$ (0.018 g, 0.025 mmol) and Ph_3CCl (0.0070 g, 0.025 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a pale pink solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

c. PhI: Y(L^D)N"$_2$ (0.022 g, 0.031 mmol) and PhI (3.5 µL, 0.031 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature. On heating to 80 ºC, the solution became pale yellow in colour but no further reaction was judged to have occurred after 16 h.

d. C_6F_5I: Y(L^D)N"$_2$ (0.023 g, 0.032 mmol) and C_6F_5I (4.3 µL, 0.032 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature. On heating to 80 ºC for 4 h, a dark brown oily precipitate was deposited and the NMR spectrum showed only a single resonance at 0.29 ppm. This is assigned as C_6F_5N" based on the established addition-elimination mechanism.

6.3.25 Attempted addition reactions of Ce(L^D)N"$_2$ with other E-X

a. ^{t}BuI: Ce(L^D)N"$_2$ (0.018 g, 0.024 mmol) and ^{t}BuI (2.9 µL, 0.024 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, yellow solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

b. PhI: Ce(L^D)N"$_2$ (0.028 g, 0.037 mmol) and PhI (4.1 µL, 0.028 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, yellow

solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature or on heating to 80 ºC.

c. PhCl: Ce(L^{D})N"$_2$ (0.017 g, 0.022 mmol) and PhCl (2.1 µL, 0.022 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, yellow solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

d. PhF: Ce(L^{D})N"$_2$ (0.025 g, 0.033 mmol) and PhF (3.1 µL, 0.033 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, yellow solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

e. C_6F_5I: Ce(L^{D})N"$_2$ (0.026 g, 0.033 mmol) and C_6F_5I (4.5 µL, 0.033 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, yellow solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature. On heating to 80 ºC for 4 h, a dark brown oily precipitate was deposited and the NMR spectrum showed only a single resonance at 0.30 ppm. This is assigned as C_6F_5N" based on the established addition-elimination mechanism.

f. H_2CCHCH_2Cl: Ce(L^{D})N"$_2$ (0.023 g, 0.030 mmol) and H_2CCHCH_2Cl (2.4 µL, 0.030 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, yellow solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

6.3.26 Attempted addition reactions of U(L^{D})N"$_2$ with other E-X

a. PhCl: U(L^{D})N"$_2$ (0.033 g, 0.038 mmol) and PhCl (3.9 µL, 0.038 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a dark blue solution. The ^{1}H NMR spectrum showed that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

6.3.27 Reaction of Y(L^{D})N"$_2$ with E-H

a. $PhSiH_3$: To a solution of Y(L^{D})N"$_2$ (0.026 g, 0.036 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $PhSiH_3$ (4.4 µL, 0.036 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

b. $HCCSi^{i}Pr_3$: To a solution of Y(L^{D})N"$_2$ (0.022 g, 0.031 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $HCCSi^{i}Pr_3$ (4.4 µL, 0.031 mmol) to afford a

clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

c. ^{n}Bu$_3$SnH: To a solution of Y(L^D)N"$_2$ (0.022 g, 0.030 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^{n}Bu$_3$SnH (8.1 µL, 0.030 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature. On heating to 80 ºC, the solution became pale yellow but no further reaction was judged to have occurred after 16 h.

d. Ph_2PH: To a solution of Y(L^D)N"$_2$ (0.024 g, 0.034 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Ph_2PH (5.9 µL, 0.034 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC.

e. $H_2CCHCH_2SiMe_3$: To a solution of Y(L^D)N"$_2$ (0.023 g, 0.032 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $H_2CCHCH_2SiMe_3$ (5.2 µL, 0.032 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

6.3.28 Reaction of Ce(L^D)N"$_2$ with E-H

a. $PhSiH_3$: To a solution of Ce(L^D)N"$_2$ (0.041 g, 0.054 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $PhSiH_3$ (6.7 µL, 0.054 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

b. HCCSi^{i}Pr$_3$: To a solution of Ce(L^D)N"$_2$ (0.055 g, 0.072 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added HCCSi^{i}Pr$_3$ (16 µL, 0.072 mmol) to afford a clear, pale yellow solution. ^{1}H NMR spectroscopy indicated that no starting material remained and a number of resonances over a sweep width of 20 – -3ppm which could not be assigned.

c. ^{n}Bu$_3$SnH: To a solution of Ce(L^D)N"$_2$ (0.022 g, 0.028 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^{n}Bu$_3$SnH (7.8 µL, 0.028 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

d. Ph_2PH: To a solution of Ce(L^D)N"$_2$ (0.033 g, 0.044 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Ph_2PH (7.5 µL, 0.044 mmol) to afford a clear,

yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

e. $H_2CCHCH_2SiMe_3$: To a solution of Ce(L^D)N"$_2$ (0.029 g, 0.038 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $H_2CCHCH_2SiMe_3$ (6.1 µL, 0.038 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

f. PhCCH: To a solution of Ce(L^D)N"$_2$ (0.027 g, 0.035 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added PhCCH (3.8 µL, 0.035 mmol) to afford a clear, yellow solution which became brown over the course of 3 days. ^{1}H NMR spectroscopy indicated mainly unreacted Ce(L^D)N"$_2$ and PhCCH but also some new resonances over a sweep with of 35 – -30 ppm which could not be assigned.

6.3.29 Reaction of U(L^D)N"$_2$ with E-H

a. $PhSiH_3$: To a solution of U(L^D)N"$_2$ (0.024 g, 0.028 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $PhSiH_3$ (3.5 µL, 0.028 mmol) to afford a dark blue solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature initially. Over the course of 2 days, the solution became greener in colour but there were no significant changes in the ^{1}H NMR spectrum.

b. $HCCSi^iPr_3$: To a solution of U(L^D)N"$_2$ (0.026 g, 0.023 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $HCCSi^iPr_3$ (5.2 µL, 0.023 mmol) to afford a dark blue solution. ^{1}H NMR spectroscopy indicated a small amount of unreacted U(L^D)$_2$N" alongside numerous small resonances across a sweep width of 76.08 – -40.77 ppm which could not be assigned.

d. PhCCH: To a solution of U(L^D)N"$_2$ (0.017 g, 0.020 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added PhCCH (2.2 µL, 0.020 mmol) to afford a red-brown solution. ^{1}H NMR spectroscopy showed that U(L^D)$_2$N" was fully consumed and new resonances over a sweep with of 85.58 – -65.74 ppm which could not be assigned.

e. Naphthalene: U(L^D)$_2$N" (0.010 g, 0.012 mmol) and naphthalene (0.0015 g, 0.012 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a dark blue solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

f. PhHNNHPh: U(L^D)$_2$N" (0.032 g, 0.037 mmol) and PhHNNHPh (0.0068 g, 0.037 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a

red-brown solution. ^{1}H NMR spectroscopy showed that U(L^D)$_2$N" was fully consumed and new resonances over a sweep with of 36.09 – -16.59 ppm which could not be assigned.

6.3.30 Reaction of Y(L^D)N"$_2$ with E-E'

a. $Me_3SnSnMe_3$: To a solution of Y(L^D)N"$_2$ (0.019 g, 0.026 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Me_3SnSnMe_3$ (5.5 µL, 0.026 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

b. $Et_3GeGeEt_3$: To a solution of Y(L^D)N"$_2$ (0.021 g, 0.029 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Et_3GeGeEt_3$ (8.2 µL, 0.029 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

c. $Me_2PhSiB(OCMe_2CMe_2O)$: To a solution of Y(L^D)N"$_2$ (0.035 g, 0.049 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Me_2PhSiB(OCMe_2CMe_2O)$ (13.4 µL, 0.049 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

d. 1,1-Me_2-Si-$(CH_2)_3$: To a solution of Y(L^D)N"$_2$ (0.010 g, 0.014 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added 1,1-Me_2-Si-$(CH_2)_3$ (1.8 µL, 0.014 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

e. P_4: Y(L^D)N"$_2$ (0.010 g, 0.014 mmol) and P_4 (0.0018 g, 0.014 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

f. $Ph_3P{=}S$: Y(L^D)N"$_2$ (0.021 g, 0.030 mmol) and $Ph_3P{=}S$ (0.0087 g, 0.030 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

g. ^{t}BuNC: To a solution of Y(L^D)N"$_2$ (0.014 g, 0.019 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^{t}BuNC (0.0029, 0.014 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature. On heating to 80 ºC, the ^{1}H NMR spectrum indicated that all Y(L^D)N"$_2$ had

been consumed and new overlapping resonances between 1.92 – 0.77 ppm which could not be assigned.

6.3.31 Reaction of Ce(L^D)N"$_2$ with E-E'

a. $Me_3SnSnMe_3$: To a solution of Ce(L^D)N"$_2$ (0.019 g, 0.024 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Me_3SnSnMe_3$ (5.0 µL, 0.024 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

b. $Et_3GeGeEt_3$: To a solution of Ce(L^D)N"$_2$ (0.025 g, 0.032 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Et_3GeGeEt_3$ (9.1 µL, 0.032 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

c. $Me_2PhSiB(OCMe_2CMe_2O)$: To a solution of Ce(L^D)N"$_2$ (0.026 g, 0.034 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Me_2PhSiB(OCMe_2CMe_2O)$ (9.4 µL, 0.034 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

d. 1,1-Me_2-Si-$(CH_2)_3$: To a solution of Ce(L^D)N"$_2$ (0.019 g, 0.025 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added 1,1-Me_2-Si-$(CH_2)_3$ (3.3 µL, 0.025 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

e. $BnSiMe_3$ To a solution of Ce(L^D)N"$_2$ (0.024 g, 0.031 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $BnSiMe_3$ (6.0 µL, 0.031 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

f. F_3CSiMe_3: To a solution of Ce(L^D)N"$_2$ (0.031 g, 0.039 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $BnSiMe_3$ (5.9 µL, 0.039 mmol) to afford a clear, yellow solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

6.3.32 Reaction of U(L^D)N"$_2$ with E-E'

a. $Me_3SnSnMe_3$: To a solution of U(L^D)N"$_2$ (0.017 g, 0.020 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Me_3SnSnMe_3$ (4.1 µL, 0.020 mmol) to afford a dark green solution. ^{1}H NMR spectroscopy indicated numerous new resonances between 85.42 – -34.30 ppm which could not be assigned.

b. $Et_3GeGeEt_3$: To a solution of $U(L^D)N''_2$ (0.021 g, 0.024 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Et_3GeGeEt_3$ (6.6 µL, 0.024 mmol) to afford a dark green solution solution. ^{1}H NMR spectroscopy indicated numerous new resonances between 86.46 – -54.23 ppm which could not be assigned.

c. $Me_2PhSiB(OCMe_2CMe_2O)$: To a solution of $U(L^D)N''_2$ (0.020 g, 0.023 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Me_2PhSiB(OCMe_2CMe_2O)$ (6.4 µL, 0.023 mmol) to afford a dark green solution. ^{1}H NMR spectroscopy indicated numerous new resonances between 36.09 – -35.57 ppm which could not be assigned. After 3 days, the solution became pale brown in colour but the ^{1}H NMR spectrum indicated no change in composition.

d. 1,1-Me_2-Si-$(CH_2)_3$: To a solution of $U(L^D)N''_2$ (0.027 g, 0.031 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added 1,1-Me_2-Si-$(CH_2)_3$ (4.0 µL, 0.031 mmol) to afford a dark blue solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

e. $BnSiMe_3$: To a solution of $U(L^D)N''_2$ (0.021 g, 0.024 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $BnSiMe_3$ (4.6 µL, 0.024 mmol) to afford a dark blue solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

f. P_4: $U(L^D)N''_2$ (0.024 g, 0.027 mmol) and P_4 (0.00086 g, 0.0070 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no $U(L^D)_2N''$ remained and small resonances across a spectral width of 80.60 – -80.50 ppm.

g. PhCCPh: $U(L^D)N''_2$ (0.028 g, 0.032 mmol) and PhCCPh (0.0057 g, 0.032 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a red-brown solution. ^{1}H NMR spectroscopy indicated that no $U(L^D)_2N''$ remained and small resonances across a spectral width of 85.58 – -58.33 ppm.

6.3.33 Attempted addition reactions of $Ce(L^D)_2N''_2$ with E-X

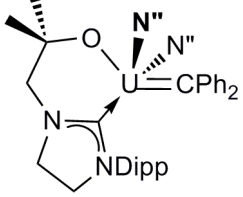
a. Me_3SiCl: To a solution of $Ce(L^D)_2N''$ (0.23 g, 0.25 mmol) in toluene (5 mL) was added Me_3SiCl (64 µL, 0.50 mmol) to afford a clear, pale yellow solution. The reaction mixture was stirred for 3 h and then the volatiles were removed under reduced pressure to afford a pale yellow solid. Attempted recrystallisation from toluene at -20 ºC afforded a pale yellow precipitate which was isolated by filtration and dried under reduced pressure. Yield: 0.10 g. ^{1}H NMR (C_6D_6, 500 MHz): 7.27 – 7.01 (3 H, overlapping m, 3,4,5-C_6H_3), 3.60 (2 H,

t, $^{3}J_{HH}$ = 10 Hz, NCH_2CH_2N), 3.57 (2 H, s, $OCMe_2C\underline{H}_2$), 3.43 (2 H, t, $^{3}J_{HH}$ = 10 Hz, NCH_2CH_2N), 3.29 (2 H, sept, $^{3}J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 1.35 (6 H, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.27 (6 H, s, CMe_2), 1.26 (6 H, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz): 243.5 (NCN), 150.0 138.5 130.4 and 124.0 (C_6H_3), 72.8 ($\underline{C}Me_2$), 62.5 ($OCMe_2\underline{C}H_2$), 54.3 and 51.1 (NCH_2CH_2N), 28.7 ($C\underline{Me}_2$), 28.0 ($H\underline{C}Me_2$), 25.2 and 23.9 ($HC\underline{Me}_2$) ppm.

b. Me_3SiI: To a solution of $Ce(L^D)_2N''$ (0.030 g, 0.033 mmol) in C_6D_6 (0.5 mL) was added Me_3SiI (4.8 µL, 0.033 mmol) to afford a clear, pale yellow solution. ^{1}H NMR (C_6D_6, 500 MHz): 7.27 – 7.01 (3 H, overlapping m, 3,4,5-C_6H_3), 3.60 (2 H, t, $^{3}J_{HH}$ = 10 Hz, NCH_2CH_2N), 3.57 (2 H, s, $OCMe_2C\underline{H}_2$), 3.43 (2 H, t, $^{3}J_{HH}$ = 10 Hz, NCH_2CH_2N), 3.30 (2 H, sept, $^{3}J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 1.35 (6 H, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.27 (6 H, s, CMe_2), 1.26 (6 H, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) ppm.

c. Me_3SiN_3: To a slurry of $Ce(L^D)_2N''$ (0.20 g, 0.23 mmol) in hexane (5 mL) was added Me_3SiN_3 (30.8 µL, 0.23 mmol) to afford a clear, pale yellow solution. The reaction mixture was stirred for 2 h and then the volatiles were removed under reduced pressure to afford a pale yellow solid. Attempted recrystallisation from toluene at -20 ºC afforded a pale yellow precipitate which was isolated by filtration and dried under reduced pressure. ^{1}H NMR (C_6D_6, 360 MHz): 7.28 – 7.00 (3 H, overlapping m, 3,4,5-C_6H_3), 3.60 (2 H, m, NCH_2CH_2N), 3.57 (2 H, s, $OCMe_2C\underline{H}_2$), 3.42 (2 H, m, NCH_2CH_2N), 3.29 (2 H, sept, $^{3}J_{HH}$ = 7 Hz), 1.35 (6 H, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.27 (6 H, s, CMe_2), 1.26 (6 H, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) ppm.

6.3.34 Synthesis of $U(L^D)N''_2(=NCHPh_2)$



To a solution of $U(L^D)_2N''$ (0.15 g, 0.17 mmol) in hexanes (10 mL) was added a solution of Ph_2CN_2 (0.035 g, 0.17 mmol) in hexanes (2 mL) to afford a dark brown solution. The reaction mixture was stirred for 2 h and then the volatiles were removed under reduced pressure to yield a brown solid. Attempted recrystallisation from toluene at -20 ºC afforded both pale brown $U(L^D)N''_2(=NCHPh_2)$ and colourless H_2NCHPh_2 as diffraction-quality single crystals which were unable to be separated by subsequent recrystallisations.

6.3.35 Reaction of $Y(L^D)N''_2$ with CO_2

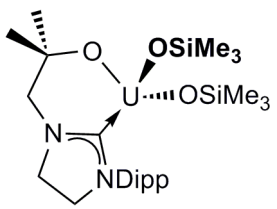
To a freeze-pump-thaw degassed solution of $Y(L^D)_2N''$ (0.011 g, 0.015 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CO_2 (1 atm) to afford clear, colourless solution and colourless precipitate immediately. ^{1}H NMR spectral analysis of the

solution showed broad, unassignable resonances across the range 10.00 – 0.00 ppm and traces of HL^D. The solid was isolated by filtration, dried *in vacuo* and redissolved in C_5D_5N. The ^1H NMR spectrum indicated only HL^D and some broad resonances which could not be assigned.

6.3.36 Reaction of Ce(L^D)N"$_2$ with CO_2

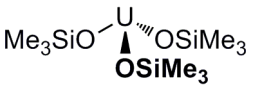
To a freeze-pump-thaw degassed solution of Ce(L^D)$_2$N" (0.015 g, 0.020 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CO_2 (1 atm) to afford a yellow solution and pale yellow precipitate immediately. ^1H NMR spectral analysis of the solution showed two broad resonances across a range of 10.00 – 0.00 ppm. The solid was isolated by filtration, dried *in vacuo* and redissolved in C_5D_5N. The ^1H NMR spectrum indicated only HL^D.

6.3.37 Reaction of U(L^D)N"$_2$ with CO_2; synthesis of U(L^D)N"(OSiMe$_3$)



To a freeze-pump-thaw degassed solution of U(L^D)$_2$N" (0.20 g, 0.24 mmol) in benzene (5 mL) was added CO_2 (1 atm) to afford a brown-green solution. The reaction mixture was stirred for 24 h before the volatiles were removed *in vacuo* to afford U(L^D)N"(OSiMe$_3$) as a pale green solid. Yield: 0.053g (32 %). IR (ν, nujol mull): 2183 cm-^{1}.

6.3.38 Reaction of UN"$_3$ with CO_2; Synthesis of U(OSiMe$_3$)$_3$



To a freeze-pump-thaw degassed solution of UN"$_3$ (0.30 g, 0.42 mmol) in toluene (10 mL) was added CO_2 (1 atm) to afford clear, pale green solution. The volatiles were removed *in vacuo* and attempted recrystallisation from toluene at -20 ºC afforded a pale green powder. Anal. Found (calcd for $C_{24}H_{72}O_8Si_8U_2$): C, 24.18 (24.23); H, 6.03 (6.10).

6.3.39 Reaction of Y(L^D)N"$_2$ with CO

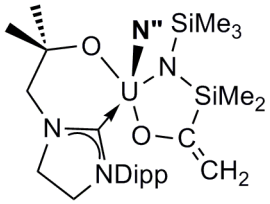
To a freeze-pump-thaw degassed solution of Y(L^D)N"$_2$ (0.024 g, 0.034 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm) to afford a clear, yellow solution. The ^1H NMR spectrum indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

6.3.40 Reaction of Ce(L^D)N"$_2$ with CO

To a freeze-pump-thaw degassed solution of Ce(L^D)N"$_2$ (0.024 g, 0.031 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm) to afford a clear,

yellow solution. The ^{1}H NMR spectrum indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

6.3.41 Reaction of U(L^D)N"$_2$ with CO; synthesis of U(L^D)N"(OC{CH$_2$}SiMe$_2$N{SiMe$_3$})

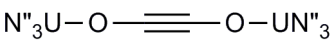


To a freeze-pump-thaw degassed solution of U(L^D)$_2$N" (0.23 g, 0.26 mmol) in benzene (10 mL) was added CO (1 atm). The reaction mixture was heated to 80 ºC for 7.5 days during which time the solution became dark brown in colour. The volatiles were removed *in vacuo* to afford a brown solid. Recrystallisation from toluene at -20 ºC afforded U(L^D)N"(OC{CH$_2$}SiMe$_2$N(SiMe$_3$}) as a pale brown microcrystalline solid. Yield: 0.16 g, (68 %). Single crystals suitable for an X-ray diffraction study were grown from a saturated toluene solution at -20 ºC. Anal. Found (calcd for $C_{32}H_{64}N_4O_2Si_4U$): C, 43.22 (43.32); H, 7.20 (7.27); N, 6.41 (6.31).

6.3.42 Attempted synthesis of U(L^D)N"({CH$_2$}SiMe$_2$N(SiMe$_3$})

A solution of U(L^D)$_2$N" (0.021 g, 0.024 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was placed under a partial static vacuum and heated to 80 ºC for 7 days. The ^{1}H NMR spectrum indicated U(L^D)N"$_2$ as the major product, small new resonances across a range of 86.53 – -68.00 ppm and no resonance corresponding to H_2.

6.3.43 Reaction of UN"$_3$ with CO; synthesis of N"$_3$UOC≡COUN"$_3$



a. In toluene: To a freeze-pump-thaw degassed solution of UN"$_3$ (1.0 g, 1.4 mmol) in toluene (20 mL) was added CO (1 atm) at room temperature. After 1 h, golden-coloured microcrystalline solid started to precipitate and the reaction mixture was then stored at room temperature for 3 days. The solid was isolated by filtration, washed with hexanes (3 x 10 mL) and then dried in vacuo to afford N"$_3$UOC≡COUN"$_3$ as a golden-coloured solid. Yield: 0.85 g (82 %). Crystals suitable for an X-ray diffraction study were grown from a C_6D_6 solution at room temperature. ^{1}H NMR (C_6D_6, 600 MHz): -8.55 (108 H, s, fwhm = 1297 Hz, SiMe) ppm. IR (ν, nujol mull): 2478 (vw), 2214 (vw), 2083 (vw), 1921 (w), 1856 (w), 1400 (s), 1359 (w) 1289 (m), 1250 (s) 930 (s), 835 (s), 769 (s), 670 (m), 654 (m), 609 (s), 502 (vw) cm^{-1}. Anal. Found (calcd for $C_{38}H_{108}N_6O_2Si_{12}U_2$): C, 30.37 (30.54); H, 7.35(7.28); N, 5.55 (5.62).

b. In hexanes: To a freeze-pump-thaw degassed solution of UN"$_3$ (0.049 g, 0.068 mmol) in hexanes (2 mL) was added CO (1 atm) at room temperature. After 15 minutes, golden-coloured microcrystalline solid started to precipitate and the reaction

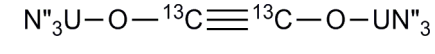
mixture was then stored at room temperature for 3 days. The solid was isolated by filtration, washed with hexanes (3 x 1 mL) and then dried *in vacuo* to afford N"$_3$UOC≡COUN"$_3$ as a golden solid. Yield: 0.29 g (58 %).

c. In thf: To a freeze-pump-thaw degassed solution of UN"$_3$ (0.018 g, 0.025 mmol) in C_4D_8O (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm) at room temperature. No reaction was shown to have taken place by ^{1}H NMR spectroscopy.

d. In C_5D_5N: To a freeze-pump-thaw degassed solution of UN"$_3$ (0.016 g, 0.022 mmol) in C_5D_5N (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm) at room temperature. No reaction was shown to have taken place by ^{1}H NMR spectroscopy.

6.3.44 Synthesis of N"$_3$UO^{13}C≡^{13}COUN"$_3$

To a freeze-pump-thaw degassed solution of UN"$_3$ (0.0502 g, 0.0698 mmol) in toluene (2 mL) was added ^{13}CO (1 atm) at room temperature. After 1 h, golden coloured microcrystalline solid started to precipitate and the reaction mixture was then stored at room temperature for 3 days. The solid was isolated by filtration, washed with hexanes (3 x 2 mL) and then dried *in vacuo* to afford N"$_3$UO^{13}C≡^{13}COUN"$_3$ as a golden-coloured solid. ^{1}H NMR (C_6D_6, 600 MHz): -8.55 (108 H, s, SiMe) ppm. ^{13}C{^{1}H} (C_6D_6, 150 MHz) 171.0 (O^{13}C^{13}CO) ppm. The resonance associated with the SiMe carbons was not visible in the spectrum. IR (ν, nujol mull): 2478 (vw), 2154 (vw), 2082 (vw), 1921 (vw), 1856 (vw), 1332 (s), 1250 (s), 1156 (vw), 930 (s), 836 (s), 770 (s), 734 (m), 672 (m), 656 (m), 610 (s), 505 (vw) cm^{-1}.



6.3.45 Attempted reaction of UN"$_3$ with H_2/CO (2/1)

a. Room temperature in C_6D_6: To a freeze-pump-thaw degassed solution of UN"$_3$ (0.017 g, 0.024 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added H_2/CO (1 atm) at room temperature. Slow reaction to form only N"$_3$UOC≡COUN"$_3$ was shown to have taken place by ^{1}H NMR spectroscopy.

b. 0 ºC in toluene: To a freeze-pump-thaw degassed solution of UN"$_3$ (0.21 g, 0.29 mmol) in toluene (10 mL) was added H_2/CO (1 atm) at -78 ºC. The reaction mixture was stirred at this temperature for 16 h and then 0 ºC for a further 24 h. A pale brown solid was isolated by filtration and dried *in vacuo*. Formation of N"$_3$UOC≡COUN"$_3$ was shown to have taken place by ^{1}H NMR spectroscopy.

b. -78 ºC in toluene: To a freeze-pump-thaw degassed solution of UN"$_3$ (0.19 g, 0.26 mmol) in toluene (10 mL) was added H_2/CO (1 atm) at -78 ºC. The reaction mixture was stirred at this temperature for 20 h. Formation of N"$_3$UOC≡COUN"$_3$ was shown to have taken place by ^{1}H NMR spectroscopy.

6.3.46 Reaction of N"$_3$UOC≡COUN"$_3$ with CO

To a J-Young Teflon valve NMR tube containing a freeze-pump-thaw degassed mixture of N"$_3$UOC≡COUN"$_3$ (0.010 g, 0.0067 mmol) and C_6D_6 (0.5 mL) was added CO (1 atm). No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature after 16 h.

6.3.47 Reaction of N"$_3$UOC≡COUN"$_3$ with Me_3SiX

a. Me_3SiCl: To a J-Young Teflon valve NMR tube containing a mixture of N"$_3$UOC≡COUN"$_3$ (0.0084 g, 0.0056 mmol) and C_6D_6 (0.5 mL) was added Me_3SiCl (1.4 µL, 0.011 mmol). No reaction was shown to have taken place by ^{1}H NMR spectroscopy after 16 h.

b. Me_3SiI: To a J-Young Teflon valve NMR tube containing a mixture of N"$_3$UOC≡COUN"$_3$ (0.0050 g, 0.0033 mmol) and C_6D_6 (0.5 mL) was added Me_3SiI (0.95 µL, 0.0066 mmol). No reaction was shown to have taken place by ^{1}H NMR spectroscopy after 16 h.

6.3.48 Reaction of N"$_3$UOC≡COUN"$_3$ with LiI/Me_3SiCl

To a J-Young Teflon valve NMR tube containing a mixture of N"$_3$UOC≡COUN"$_3$ (0.043 g, 0.029 mmol) and C_6D_6 (0.5 mL) was added LiI (0.0020 g, 0.0015 mmol) and Me_3SiCl (7.5 µL, 0.059 mmol). No reaction was shown to have taken place by ^{1}H NMR spectroscopy after 16 h.

6.3.49 Reaction of N"$_3$UOC≡COUN"$_3$ with MeI

To a J-Young Teflon valve NMR tube containing N"$_3$UOC≡COUN"$_3$ (0.014 g, 0.0095 mmol) and C_6D_6 (0.5 mL) was added MeI (1.2 µL, 0.019 mmol). No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature. Heating to 80 ºC resulted in the formation of N"$_3$UOC=C(H)OU(N{$SiMe_2CH_2$}{$SiMe_3$})N"$_2$ which did not subsequently react with MeI.

6.3.50 Reaction of N"$_3$UOC≡COUN"$_3$ with H_2

To a freeze-pump-thaw degassed solution of N"$_3$UOC≡COUN"$_3$ (0.010 g, 0.0067 mmol) in C_6D_6 (0.5 mL) was added H_2 (1 atm). By NMR spectroscopy, at room temperature after 4 days, H_2 and unreacted N"$_3$UOC≡COUN"$_3$ are visible within the ^{1}H NMR spectrum. Some broad resonances between 2.06 – -1.35 ppm are also present.

6.3.51 Reaction of N"$_3$UOC≡COUN"$_3$ with CH_4

To a freeze-pump-thaw degassed solution of N"$_3$UOC≡COUN"$_3$ (0.010 g, 0.0067 mmol) in C_6D_6 (0.5 mL) was added CH_4 (1 atm). No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature. Heating to 80 ºC resulted in the formation of N"$_3$UOC=C(H)OU(N{$SiMe_2CH_2$}{$SiMe_3$})N"$_2$ which did not subsequently react with CH_4.

6.3.52 Reaction of N"$_3$UOC≡COUN"$_3$ with $SiMe_4$

To a J-Young Teflon valve NMR tube containing a mixture of N"$_3$UOC≡COUN"$_3$ (0.018 g, 0.012 mmol) and C_6D_6 (0.5 mL) was added $SiMe_4$ (1.6 µL, 0.0012 mmol). No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature. Heating to 80 ºC resulted in the formation of N"$_3$UOC=C(H)OU(N{$SiMe_2CH_2$}{$SiMe_3$})N"$_2$ which did not subsequently react with $SiMe_4$.

6.3.53 Reaction of N"$_3$UOC≡COUN"$_3$ with $PhSiH_3$

To a J-Young Teflon valve NMR tube containing a mixture of N"$_3$UOC≡COUN"$_3$ (0.014 g, 0.00094 mmol) and C_6D_6 (0.5 mL) was added $PhSiH_3$ (1.1 µL, 0.00094 mmol). No reaction was shown to have taken place by ^{1}H NMR spectroscopy. Heating to 80 ºC resulted in the formation of N"$_3$UOC=C(H)OU(N{$SiMe_2CH_2$}{$SiMe_3$})N"$_2$ which did not subsequently react with $SiMe_4$.

6.3.54 Reaction of N"$_3$UOC≡COUN"$_3$ with Et_2O

N"$_3$UOC≡COUN"$_3$ (0.011 g, 0.00074 mmol) and biphenylene (0.0026 g, 0.017 mmol) were combined in C_6D_6 (0.5 mL) was added 1 drop of Et_2O. No reaction was shown to have taken place by ^{1}H NMR spectroscopy. Heating to 80 ºC resulted in the formation of N"$_3$UOC=C(H)OU(N{$SiMe_2CH_2$}{$SiMe_3$})N"$_2$ which did not subsequently react with Et_2O.

6.3.55 Reaction of N"$_3$UOC≡COUN"$_3$ with biphenylene

N"$_3$UOC≡COUN"$_3$ (0.026 g, 0.017 mmol) and biphenylene (0.0026 g, 0.017 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature. Heating to 80 ºC resulted in the formation of N"$_3$UOC=C(H)OU(N{$SiMe_2CH_2$}{$SiMe_3$})N"$_2$ which did not subsequently react with biphenylene.

6.3.56 Reaction of N"$_3$UOC≡COUN"$_3$ with $H_3N{:}BH_3$

N"$_3$UOC≡COUN"$_3$ (0.024 g, 0.016 mmol) and $H_3N{:}BH_3$ (0.00050 g, 0.016 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature. Heating to 80 ºC resulted in the formation of N"$_3$UOC=C(H)OU(N{$SiMe_2CH_2$}{$SiMe_3$})N"$_2$ which did not subsequently react with $H_3N{:}BH_3$.

6.3.57 Reaction of N"$_3$UOC≡COUN"$_3$ with PhCCH

N"$_3$UOC≡COUN"$_3$ (0.012 g, 0.0080 mmol) and PhCCH (0.85 µL, 0.0080 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature. Heating to 80 ºC resulted in the formation of N"$_3$UOC=C(H)OU(N{$SiMe_2CH_2$}{$SiMe_3$})N"$_2$ which did not subsequently react with PhCCH.

6.3.58 Reaction of N"$_3$UOC≡COUN"$_3$ with $BAr^F{}_3$

N"$_3$UOC≡COUN"$_3$ (0.024 g, 0.016 mmol) and $BAr^F{}_3$ (0.016 g, 0.032 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature. Single crystals formed were shown to be N"$_3$UOC≡COUN"$_3$ by inspection of the unit cell parameters.

6.3.59 Reaction of N"$_3$UOC≡COUN"$_3$ with 9-BBN

N"$_3$UOC≡COUN"$_3$ (0.010 g, 0.0070 mmol) and 9-BBN (0.0017 g, 0.0070 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a pale brown solution and a brown solid. The ^{1}H NMR spectrum indicated mainly unreacted 9-BBN and N"$_3$UOC≡COUN"$_3$. ^{1}H NMR (C_6D_6, 250 MHz): 2.97 – 0.96 (overlapping m, 9-BBN), 2.50 (s), 2.95 (s), -8.71 (SiMe) ppm. Relative integrations could not be accurately recorded due to the lack of a homogenous solution. Single crystals grown within in the solution were shown to be N"$_3$UOC≡COUN"$_3$ by measurement of the unit cell.

6.3.60 Reaction of N"$_3$UOC≡COUN"$_3$ with (*B*-I)-9-BBN

N"$_3$UOC≡COUN"$_3$ (0.023 g, 0.016 mmol) and (*B*-I)-9-BBN (31 µL, 0.0031 mmol, 1.0 M in hexanes) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. At room temperature, a new resonance at -0.98 ppm, unreacted (*B*-I)-9-BBN and N"$_3$UOC≡COUN"$_3$ are visible within the ^{1}H NMR spectrum.

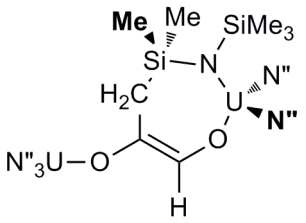
6.3.61 Reaction of N"$_3$UOC≡COUN"$_3$ with PhCOCl

N"$_3$UOC≡COUN"$_3$ (0.013 g, 0.0087 mmol) and PhCOCl (2.0 µL, 0.017 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. No reaction was shown to have taken place by ^{1}H NMR spectroscopy at room temperature.

6.3.62 Reaction of N"$_3$UOC≡COUN"$_3$ with HNEt$_3$Cl

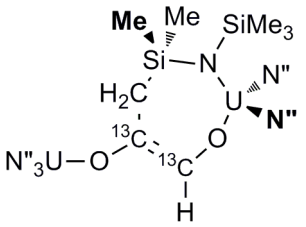
N"$_3$UOC≡COUN"$_3$ (0.075 g, 0.050 mmol) and HNEt$_3$Cl (0.014 g, 0.10 mmol) were combined in thf (3 mL) to afford a clear, yellow solution. The reaction mixture was stirred for 2 h before the volatiles were removed *in vacuo* to yield a pale orange solid. ^{1}H NMR spectral analysis indicated unreacted N"$_3$UOC≡COUN"$_3$ and HNEt$_3$Cl, UN"$_3$Cl and some new resonances over a range -1.00 – -11.00 ppm which could not be assigned.

6.3.63 Synthesis of N"$_3$UOC=C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$



A slurry of N"$_3$UOC≡COUN"$_3$ (0.11 g, 0.072 mmol) in toluene (10 mL) was heated to 80 ºC for 24 h. The volatiles were removed under reduced pressure to afford N"$_3$UOC=C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$ as a golden-coloured solid. Yield: 0.071 g (67 %) ^{1}H NMR (C_6D_6, 600 MHz): 1.32 (6 H, s, NSiMe$_2$), 0.10 (2 H, s, CHC<u>H</u>$_2$), -5.66 (36 H, s, U(N{SiMe$_3$}$_2$)$_2$), -7.47 (54 H, s, U(N{SiMe$_3$}$_2$)$_3$), -14.85 (9 H, s, NSiMe$_3$), -60.70 (1 H, s, C<u>H</u>CH$_2$) ppm. IR (ν, KBr): 2954 (m), 2897 (m), 2799 (w), 1634 (m), 1410 (w), 1357 (w), 1248 (s), 1183 (w), 1099 (m), 1051(m), 930 (s), 838 (s), 792 (m), 645 (w) cm^{-1}.

6.3.64 Synthesis of N"$_3$UO^{13}C=^{13}C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$



N"$_3$UO^{13}C^{13}COUN"$_3$ (0.061 g, 0.041 mmol) was partially dissolved in C_6D_6 in a J-Young Teflon valve NMR tube. The reaction mixture was heated to 80 ºC for 48 h. The volatiles were removed under reduced pressure to afford N"$_3$UO^{13}C=^{13}C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$ as a golden-coloured solid. Yield: 0.051 g (84 %). ^{1}H NMR (C_6D_6, 400 MHz): 1.32 (6 H, s, NSiMe$_2$),

0.10 (2 H, s, $^{13}CH^{13}CC\underline{H}_2$), -5.66 (36 H, s, $U(N\{SiMe_3\}_2)_2$), -7.47 (54 H, s, $U(N\{SiMe_3\}_2)_3$), -14.85 (9 H, s, $NSiMe_3$), -60.70 (1 H, s,$^{13}C\underline{H}^{13}C$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): 30.4 (d, $^1J_{CC}$ = 98 Hz, $^{13}CH^{13}\underline{C}$), 23.9 (d, $^1J_{CC}$ = 98 Hz, $^{13}\underline{C}H^{13}C$) ppm. ^{13}C NMR (C_6D_6, 100 MHz): 30.4 (d, $^1J_{CC}$ = 98 Hz, $^{13}CH^{13}\underline{C}$), 23.7 (dd, $^1J_{CH}$ = 182 Hz, $^1J_{CC}$ = 98 Hz, $^{13}\underline{C}H^{13}C$) ppm. IR (ν, KBr): 2956 (m), 2900 (m), 2790 (w), 1635 (m), 1410 (w), 1360 (w), 1252 (s), 1184 (w), 1086 (m), 1041(m), 933 (s), 841 (s), 800 (m), 752 (w), 669 (w) cm^{-1}.

6.3.65 Synthesis of N"$_3$UOC=C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$:N"$_3$UOC≡COUN"$_3$

A slurry of N"$_3$UOC≡COUN"$_3$ (0.15 g, 0.10 mmol) in toluene (10 mL) was heated to 80 ºC for 5.5 h. The clear, orange solution was cooled slowly to room temperature to afford single crystals of N"$_3$UOC=C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$:N"$_3$UOC≡COUN"$_3$ suitable for an X-ray diffraction study. Yield: 0.12 g (81 %). The study confirmed the contents of the crystal to be a 1:1 co-crystal of N"$_3$UOC=C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$:N"$_3$UOC≡COUN"$_3$. This was confirmed by solution ^1H NMR spectroscopy of a sample of isolated single crystals.

6.3.66 Reaction of N"$_3$UOC=C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$ with Me$_3$SiX

a. Me_3SiCl: To a J-Young Teflon valve NMR tube containing a solution of N"$_3$UOC=C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$ (0.010 g, 0.0067 mmol) was added Me_3SiCl (1.7 µL, 0.013 mmol) to afford a golden-coloured solution. No reaction was shown to have taken place by ^1H NMR spectroscopy at room temperature or after heating to 80 ºC for 12 h.

b. Me_3SiN_3: To a J-Young Teflon valve NMR tube containing a solution of N"$_3$UOC=C(H)OU(N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$ (0.010 g, 0.0069 mmol) was added Me_3SiN_3 (1.8 µL, 0.014 mmol) to afford a golden-coloured solution. No reaction was shown to have taken place by ^1H NMR spectroscopy at room temperature or after heating to 80 ºC for 12 h.

6.3.67 Reaction of UN"$_3$ with Me$_3$SiCl

To a J-Young Teflon valve NMR tube containing a solution of UN"$_3$ (0.018 g, 0.024 mmol) in C_6D_6 (0.5 mL) was added Me_3SiCl (6.2 µL, 0.049 mmol). No reaction was shown to have taken place by ^1H NMR spectroscopy at room temperature after 14 days.

6.3.68 Reaction of UN"$_3$ with Me$_3$SiCl /CO

To a freeze-pump-thaw degassed solution of UN"$_3$ (0.013 g, 0.018 mmol) and Me_3SiCl (4.5 µL, 0.035 mmol) was added CO (1 atm) at room temperature. The slow

formation of $N"_3UOC{\equiv}COUN"_3$ and $UN"_3Cl$ was shown to be taking place by ^1H NMR spectroscopy.

6.3.69 Reaction of $UN"_3$ with Ph_3SiCl /CO

$UN"_3$ (0.018 g, 0.024 mmol) and Ph_3SiCl (0.014 g, 0.049 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. No reaction was shown to take place at room temperature by ^1H NMR spectroscopy. The reaction mixture was freeze-pump-thaw degassed and to this was added CO (1 atm) at room temperature. The slow formation of $N"_3UOC{\equiv}COUN"_3$ was shown to be taking place by ^1H NMR spectroscopy.

6.3.70 Reaction of $UN"_3$ with Ph_2SiHCl

To a J-Young Teflon valve NMR tube containing a solution of $UN"_3$ (0.010 g, 0.014 mmol) in C_6D_6 (0.5 mL) was added Ph_2SiHCl (2.7 µL, 0.014 mmol). The solution became dark brown in colour and ^1H NMR spectroscopy indicated the slow formation of $UN"_3Cl$ only. After 2 days the ratio of $UN"_3Cl:UN"_3$ = 0.79:1.00.

6.3.71 Reaction of $UN"_3$ with $Co_2(CO)_8$

$UN"_3$ (0.055 g, 0.076 mmol) and $Co_2(CO)_8$ (0.013 g, 0.038 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. Immediately the solution became pale brown in colour and a brown precipitate formed. ^1H NMR (C_6D_6, 500 MHz): -4.16 ppm.

6.3.72 Reaction of $CeN"_3$ with CO

To a freeze-pump-thaw degassed solution of $CeN"_3$ (0.011 g, 0.018 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm). No reaction was shown to take place at room temperature or on heating to 80 ºC for 16 h.

6.3.73 Reaction of $UN"_3Cl$ with CO

To a freeze-pump-thaw degassed solution of $UN"_3Cl$ (0.009 g, 0.012 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm). No reaction was shown to take place at room temperature.

6.3.74 Attempted synthesis of $Ce(L^D)N"_2R$

a. MeMgCl In a J-Young Teflon valve NMR tube, $Ce(L^D)N"_2Cl$ (0.018 g, 0.022 mmol) and MeMgCl (7.5 µL, 0.022 mmol, 3.0 M in thf) were combined in C_6D_6 (0.5 mL) to afford a pale red-orange, clear solution which became yellow over the course of 2 h. The ^1H NMR spectrum showed no remaining $Ce(L^D)N"_2Cl$ and overlapping resonances in the range 7.36 – 0.10 ppm which could not be assigned.

b. LiNp: In a J-Young Teflon valve NMR tube, Ce(L^D)N"$_2$Cl (0.028 g, 0.035 mmol) and LiNp (0.0027 g, 0.035 mmol) were combined in C_6D_6 (0.5 mL) to afford a pale red-orange, clear solution. The ^{1}H NMR spectrum (C_6D_6, 400 MHz) showed resonances over the range 7.77 – 0.10 ppm along with resonances for Ce(L^D)N"$_2$.

6.3.75 Synthesis of N"(L^D)$_2$Ce(bnq)Ce(L^D)$_2$N"

To a slurry of Ce(L^D)$_2$N" (0.20 g, 0.22 mmol) in toluene (2 mL) was added benzoquinone (bnq = C_6H_4O) (0.024 g, 0.22 mmol) in toluene (2 mL) to afford a dark purple precipitate immediately. The reaction mixture was stirred for 18 h before the solid was filtered off, washed with hexanes (2 x 5 mL) and dried *in vacuo* to afford N"(L^D)$_2$Ce(bnq)Ce(L^D)$_2$N" as a dark purple solid. Yield: 0.096 g (45 %). The solid was too insoluble in all common deuterated solvents to allow for a satisfactory ^{1}H NMR spectral analysis. Anal. Found (calcd for $C_{94}H_{156}Ce_2N_{10}O_6Si_4$) C, 59.08 (58.96); H, 8.30 (8.21); N, 7.27 (7.31).

6.3.76 Attempted preparation of [Ce(L^D)N"$_2$][X]

a. BAr^F_3: Ce(L^D)N"$_2$Cl (0.051 g, 0.064 mmol) and BAr^F_3 (0.033 g, 0.064 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a deep red solution. The volatiles were removed *in vacuo* to afford a glassy, dark red solid. The NMR spectra contained resonances for 0.33 equivalents of toluene and CeN"$_3$ which were not present within in the original starting material; these data are omitted for clarity. Attempted recrystallisation from toluene did not yield a pure material and addition of a second equivalent of BAr^F_3 did not result in any further reaction at room temperature. Yield: 0.059 g (71 %). ^{1}H NMR (C_6D_6, 600 MHz): 6.94 – 6.86 (2 H, overlapping m, 3,4,5-C_6H_3), 6.44 (1 H, d, $^3J_{HH}$ = 7 Hz, 3,5-C_6H_3), 4.70 and 4.28 (1 H each, m, NCH_2CH_2N), 4.00 (1 H, d, $^3J_{HH}$ = 15 Hz, $OCMe_2C\underline{H}_2$), 3.93 and 3.65 (1 H each, m, NCH_2CH_2N), 3.62 (1 H, d, $^3J_{HH}$ = 15 Hz, $OCMe_2C\underline{H}_2$), 3.32 and 3.13 (1 H each, sept, $^3J_{HH}$ = 6 Hz, $\underline{H}CMe_2$), 1.40 (3 H, d, $^3J_{HH}$ = 6 Hz, $HC\underline{Me}_2$), 1,14 (3 H, s, CMe_2), 1.11 and 0.93 (3 H each, d, $^3J_{HH}$ = 6 Hz, $HC\underline{Me}_2$), 0.83 (3 H, s, CMe_2), 0.64 (3 H, d, $^3J_{HH}$ = 6 Hz, $HC\underline{Me}_2$), 0.39 and 0.33 (18 H each, s, SiMe) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): 149.2 - 146.8 (br) 148.6 147.6 144.2 139.7 - 135.2 (br) and 133.2 (Ar), 130.6 (3,5-C_6H_3), 124.1 (Ar), 123.0 (4-C_6H_3), 88.4 ($\underline{C}Me_2$), 61.1 ($OCMe_2C\underline{H}_2$), 55.9 and 51.1 (NCH_2CH_2N), 31.8 ($C\underline{Me}_2$), 28.5 ($\underline{H}CMe_2$), 28.0 ($HC\underline{Me}_2$), 27.8 ($\underline{H}CMe_2$), 27.7 ($HC\underline{Me}_2$), 26.3 ($C\underline{Me}_2$), 21.9 and 21.1 ($HC\underline{Me}_2$) ppm. ^{11}B NMR (C_6D_6, 128 MHz): -16.4 ppm. Satisfactory elemental analysis was not obtained.

b. $AlMe_3$: In a J-Young Teflon valve NMR tube, $Ce(L^D)N"_2Cl$ (0.022 g, 0.028 mmol) and $AlMe_3$ (13.8 µL, 0.028 mmol, 3.0 M in toluene) were combined in C_6D_6 (0.5 mL) to afford a yellow, clear solution. Addition of a second equivalent of $AlMe_3$ did not result in any change at room temperature or after heating to 80 ºC for 16 h. ^1H NMR (C_6D_6, 600 MHz): 7.13 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.96 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.06 (2 H each, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 2.82 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 2.62 (2 H each, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 1.43 (6 H, s, CMe_2), 1.27 and 1.01 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.56 ($OCMe_2C\underline{H}_2$) ppm. $^{13}C\{^1H\}$ (C_6D_6, 150 MHz): 146.7 133.8 131.7 130.3 129.2 126.3 and 124.7 (C_6H_3), 76.8 ($\underline{C}Me_2$), 58.5 ($OCMe_2\underline{C}H_2$), 53.2 and 51.7 (NCH_2CH_2N), 28.5 ($C\underline{Me}_2$) 27.3 ($H\underline{C}Me_2$) 26.1 and 23.6 ($HC\underline{Me}_2$) ppm.

c. $AgBF_4$: In a J-Young Teflon valve NMR tube, $Ce(L^D)N"_2Cl$ (0.021 g, 0.025 mmol) and $AgBF_4$ (0.0050 g, 0.025 mmol) were combined in C_6D_6 (0.5 mL) to afford a dark red solution. The ^1H NMR spectrum indicated that no reaction had taken place at room temperature.

d. $[NEt_3H][BPh_4]$: In a J-Young Teflon valve NMR tube, $Ce(L^D)N"_2Cl$ (0.050 g, 0.063 mmol) and $[NEt_3H][BPh_4]$ (0.026 g, 0.062 mmol) were combined in C_6D_6 (0.5 mL) to afford a red solution. The ^1H NMR spectrum indicated that no reaction had taken place at room temperature.

6.3.77 Attempted synthesis of $[Ce(L^D)_2][BAr^F_4]$

$Ce(L^D)_2N"$ (0.029 g, 0.032 mmol) and $[Ph_3C][BAr^F_4]$ (0.030 g, 0.032 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a red-orange solution and unreacted solids of $Ce(L^D)_2N"$ and $[Ph_3C][BAr^F_4]$. The ^1H NMR spectrum indicated that no reaction had taken place after 2 days at room temperature.

6.3.78 Synthesis of $N"_2(L^D)Ce(bnq)Ce(L^D)N"_2$

To a slurry of $Ce(L^D)N"_2$ (0.20 g, 0.27 mmol) in hexanes (2 mL) was added benzoquinone (bnq = C_6H_4O) (0.029 g, 0.27 mmol) in hexanes/toluene (2 mL/1 mL) to afford a dark purple precipitate immediately. The reaction mixture was stirred for 18 h before the solid was filtered off, washed with hexanes (2 x 5 mL) and dried *in vacuo* to afford $N"_2(L^D)Ce(bnq)Ce(L^D)N"_2$ as a dark purple solid. Yield: 0.13 g (60 %). ^1H NMR (C_6D_6, 500 MHz): 7.37 (1 H, t, $^3J_{HH}$ = 7 Hz, 4-C_6H_3), 7.12 (2 H, d, $^3J_{HH}$ = 7 Hz, 3,5-C_6H_3), 5.54 (4 H, s, C_6H_4), 3.33 (2 H, m, $\underline{H}CMe_2$), 3.56 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 3.12 (2 H, s, $OCMe_2C\underline{H}_2$), 2.85 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 1.40 (6 H, d, $^3J_{HH}$ = 7 Hz,

HC<u>Me$_2$</u>), 1.18 (6 H, s, CMe$_2$), 1.13 (6 H, d, $^3J_{HH}$ = 7 Hz, HC<u>Me$_2$</u>) ppm. Anal. Found (calcd for $C_{68}H_{134}Ce_2N_8O_4Si_8$) C, 49.97 (50.02); H, 8.19 (8.27); N, 6.79 (6.86).

6.3.79 Attempted synthesis of Ce(L^D)$_2$NPh$_2$

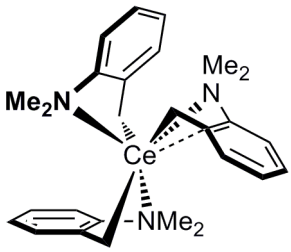
Ce(L^D)$_2$N" (0.051 g, 0.056 mmol) and HNPh$_2$ (0.0095 g, 0.056 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, orange solution immediately. By NMR spectroscopy, a resonance accounting for HN" and overlapping resonances in the range 24.9 – -20.7 ppm, which could not be assigned, were visible. The volatiles were removed *in vacuo* to yield a pale orange powder. Further recrystallisations did not yield a pure product.

6.3.80 Attempted synthesis of Ce(L^D)N"$_2$(N-2,6-^{t}Bu-C$_6$H$_3$)

In a J-Young Teflon valve NMR tube, Ce(L^D)N"$_2$Cl (0.021 g, 0.026 mmol) and K(H)N-2,6-^{t}Bu-C_6H_3 (0.0056 g, 0.026 mmol) were combined in C_6D_6 (0.5 mL) to afford a dark red-brown, clear solution. ^{1}H NMR spectroscopy indicated no remaining Ce(L^D)N"$_2$Cl, new resonances between 7.34 – -0.17 ppm which could not be assigned, and HN".

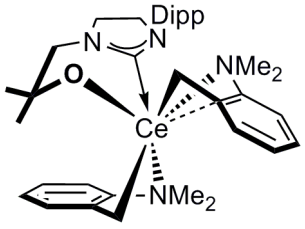
6.4 Synthetic procedures described in Chapter Four

6.4.1 Synthesis of CeBn'$_3$



At -78 ºC, to the combined solids of CeCl$_3$(thf)$_{3.5}$ (2.0 g, 4.3 mmol) and KBn' (2.2 g, 13 mmol) was added thf (40 mL) to afford a brown suspension. The reaction mixture was stirred for 1.5 h before being allowed to warm to room temperature and stirred for 16 h. The precipitate was allowed to settle, the solution filtered off and the solid washed with thf (3 x 10 mL). The combined washings were dried under reduced pressure to yield an orange solid. Recrystallisation from toluene (25 mL) at -30 ºC afforded CeBn'$_3$ as large, bright orange single crystals. Yield: 1.7 g (73 %). ^{1}H NMR (C_6D_6, 360 MHz): 15.50 (1 H, s, CH$_2$), 8.88 and 4.07 (2 H each, s, 2,5-C_6H_3 and 3,4-C_6H_3), -1.54 (1 H, s, CH$_2$), -8.75 (6 H, s, NMe$_2$) ppm. Anal. Found (calcd for $C_{27}H_{36}CeN_3$): C, 59.62 (59.75); H, 6.58 (6.69); N, 7.72 (7.74).

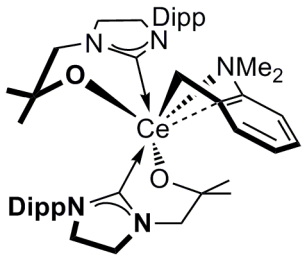
6.4.2 Synthesis of Ce(L^D)Bn'$_2$



At -78 ºC, to a slurry of CeBn'$_3$ (0.23 g, 0.41 mmol) in hexanes (2 mL) was added dropwise a solution of HL^D (0.13 g, 0.41 mmol) in hexanes (10 mL). The reaction mixture was

allowed to warm to room temperature and stirred for 16 h to afford an orange solution and pale orange precipitate. The precipitate was filtered off, washed with hexanes (3 x 3 mL) and dried *in vacuo* to afford $Ce(L^D)Bn'_2$ as a pale orange solid. Yield: 0.14 g (42 %). $Ce(L^D)_2Bn'$ was poorly soluble in C_6D_6 and the ^1H NMR spectrum showed broad resonances across the range 35 – -30 ppm. Anal. Found (calcd for $C_{37}H_{53}CeN_4O$): C, 62.67 (62.59); H, 7.55 (7.52); N, 7.79 (7.89).

6.4.3 Synthesis of $Ce(L^D)_2Bn'$

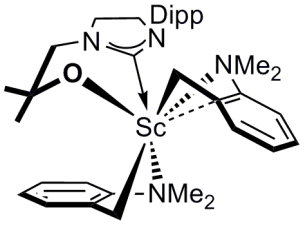


At -78 ºC, to a slurry of $CeBn'_3$ (0.20 g, 0.37 mmol) in hexanes (2 mL) was added dropwise a solution of HL^D (0.22 g, 0.74 mmol) in hexanes (10 mL). The reaction mixture was allowed to warm to room temperature and stirred for 16 h to afford an orange solution and bright yellow-orange precipitate. The precipitate was filtered off, washed with hexanes (2 x 5 mL) and dried *in vacuo* to afford $Ce(L^D)_2Bn'$ as a yellow solid. Yield: 0.15 g (47 %). $Ce(L^D)_2Bn'$ was poorly soluble in C_6D_6 and the ^1H NMR spectrum showed broad resonances across the range 30 – -25 ppm. Anal. Found (calcd for $C_{47}H_{70}CeN_5O_2$): C, 64.25 (64.35); H, 8.13 (8.04); N, 7.88 (7.98).

6.4.4 Attempted synthesis of $Y(L^D)Bn'_2$

YBn'_3 (0.030 g, 0.060 mmol) and HL^D (0.018 g, 0.060 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. The reaction mixture was heated to 80 ºC for 16 h to yield a dark orange solution. The ^1H NMR spectrum showed several broad resonances in a range 10 – 0 ppm and full consumption of the starting materials.

6.4.5 Synthesis of $Sc(L^D)Bn'_2$

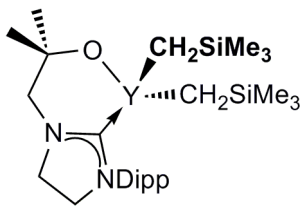


$ScBn'_3$ (0.022 g, 0.049 mmol) and HL^D (0.015 g, 0.049 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. The reaction mixture was heated to 80 ºC for 16 h to yield a dark orange solution. The volatiles were removed *in vacuo* and the orange solid was recrystallised from toluene at -20 ºC to afford $Sc(L^D)Bn'_2$ as pale orange crystals suitable for an X-ray diffraction study. Yield: 0.048 g (17 %). In subsequent repetition of this reaction, when the reaction mixture was heated for only 5 h, the reaction was incomplete and $ScBn'_3$ was isolated as single crystals suitable for a diffraction study.

6.4.6 Attempted synthesis of Sc(L^D)$_2$Bn'

ScBn'$_3$ (0.020 g, 0.045 mmol) and HL^D (0.027 g, 0.091 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. The reaction mixture was heated to 80 ºC for 16 h to yield a yellow-orange solution. The volatiles were removed *in vacuo* and the yellow-orange solid was recrystallised from toluene at -20 ºC. ^{1}H NMR spectral analysis indicated the formation of only Sc(L^D)Bn'$_2$.

6.4.7 Synthesis of Y(L^D)(CH_2SiMe_3)$_2$



At 0 ºC, to a solution of Y(CH_2SiMe_3)$_3$(thf)$_2$ (0.55 g, 1.1 mmol) in hexanes (15 mL) was added dropwise a solution of HL^D (0.34, 1.1 mmol) in hexanes (10 mL) to afford a clear, pale yellow solution. The reaction mixture was stirred for 1 h to yield a white precipitate which was collected by filtration, washed with hexanes (3 x 5 mL) and dried *in vacuo* to afford Y(L^D)(CH_2SiMe_3)$_2$ as a white powder. Storage at room temperature, both in the solid state and in solution led to decomposition over the course of 24 h. Yield: 0.32 g (51 %). Diffraction-quality crystals were grown from a saturated toluene solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 7.27 –7.02 (3 H, overlapping m, 4-C_6H_3 and 3,5-C_6H_3), 3.20 (2 H, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 3.14 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 2.89 (2 H, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 2.11 (2 H, s, $OCMe_2C\underline{H}_2$), 1.56 (6 H, s, $OC\underline{Me}_2CH_2$), 1.50 and 1.15 (6 H each, d, $^3J_{HH}$ = 7, $HC\underline{Me}_2$), 0.26 (18 H, s, $CH_2Si\underline{Me}_3$), -0.65 – -0.96 (2 H, br. m, $C\underline{H}_2SiMe_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): 215.4 (d, $^1J_{YC}$ = 30 Hz, NCN), 146.3 (1-C_6H_3), 136.5 (2,6-C_6H_3), 129.3 (4-C_6H_3) 124.7 (3,5-C_6H_3), 74.5 ($\underline{C}Me_2$), 60.8 ($OCMe_2\underline{C}H_2$), 54.0 and 52.4 (NCH_2CH_2N), 37.6 ($^1J_{YC}$ = 38 Hz, $\underline{C}H_2SiMe_3$), 30.5 (CMe_2), 28.4 ($H\underline{C}Me_2$), 25.8 and 24.8 ($HC\underline{Me}_2$), 4.8 ($CH_2Si\underline{Me}_3$) ppm. Anal. Found (calcd for $C_{27}H_{51}N_2OSi_2Y$): C, 57.35 (57.42); H, 8.98 (9.10); N 5.03 (4.96).

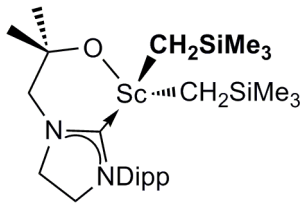
6.4.8 Attempted synthesis of Y(L^D)(CH{$SiMe_3$}$_2$)$_2$

Y(L^D)(CH{$SiMe_3$}$_2$)$_2$ (0.010 g, 0.014 mmol) and HL^D (0.043 g, 0.014 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. The ^{1}H NMR spectrum indicated broad resonances over a diamagnetic sweep width which could not be assigned. Subsequent attempts at larger scale reactions did not result in a clean compound.

6.4.9 Attempted synthesis of $Y(L^D)_2CH(SiMe_3)_2$

$Y(L^D)(CH\{SiMe_3\})_2$ (0.010 g, 0.015 mmol) and HL^D (0.088 g, 0.029 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. The ^1H NMR spectrum indicated broad resonances over a diamagnetic sweep width which could not be assigned. Subsequent attempts at larger scale reactions did not result in a clean compound.

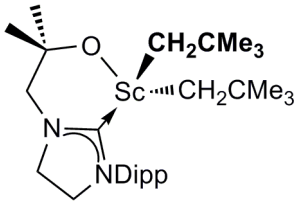
6.4.10 Synthesis of $Sc(L^D)(CH_2SiMe_3)_2$



a. From $Sc(CH_2SiMe_3)_3(thf)_2$: At 0 ºC , to a slurry of $Sc(CH_2SiMe_3)_3(thf)_2$ (1.1 g, 2.4 mmol) in hexanes (15 mL) was added a solution of HL^D (0.72 g, 2.4 mmol) in hexanes (10 mL). The reaction mixture was stirred for 3 h during which time a white precipitate formed. The precipitate was collected by filtration and dried *in vacuo* for afford $Sc(L^D)(CH_2SiMe_3)_2$ as a white powder. Storage at room temperature in the solid state or in solution led to decomposition over a period of 24 h. Yield: 0.77 g (62 %). Diffraction-quality crystals were grown from a toluene solution at -20 ºC. ^1H NMR (C_6D_6, 500 MHz): 7.26 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.16 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.33 – 3.20 (2 H, br. m, $\underline{H}CMe_2$), 3.25 and 2.92 (2 H each, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 1.61 (6 H, s, CMe_2), 1.53 and 1.14 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.21 (9 H, s, $CH_2Si\underline{Me}_3$), -0.21 (2 H, br. s, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 500 MHz): 147.0 (1-C_6H_3), 137.3 (2,6-C_6H_3), 129.5 (4-C_6H_3), 125.2 (3,5-C_6H_3), 75.9 ($\underline{C}Me_2$), 54.3 and 52.0 (NCH_2CH_2N), 28.3 ($H\underline{C}Me_2$), 26.4 and 24.1 ($HC\underline{Me}_2$), 4.6 ($CH_2Si\underline{Me}_3$) ppm. Anal. Found (calcd for $C_{27}H_{51}N_2OScSi_2$): C, 62.18 (62.26); H, 8.77 (9.87); N, 5.48 (5.38).

b. *in situ* preparation from $ScCl_3(thf)_3$: At -78 ºC, to a slurry of $ScCl_3(thf)_3$ (0.28 g, 0.77 mmol) in hexanes/thf (15 mL/20 mL) was added dropwise a solution of $LiCH_2SiMe_3$ (0.29 g, 3.1 mmol) in hexanes (20 mL) to afford a clear, colourless solution. The reaction mixture was stirred at 0 ºC for 2 h and then a slurry of $[H_2L^D]Cl$ (0.26 g, 0.77 mmol) in thf (20 mL) was added in one portion to afford a clear, colourless solution. The reaction mixture was stirred for 2 h and the volatiles were then removed *in vacuo* to yield a white solid. Extraction into cold (0 ºC) toluene (2 x 10 mL) afforded a clear, pale yellow solution. The volatiles were removed *in vacuo* afford a white solid. The synthesis of $Sc(L^D)(CH_2SiMe_3)_2$ was confirmed by ^1H NMR spectroscopy.

6.4.11 Synthesis of $Sc(L^D)(CH_2CMe_3)_2$



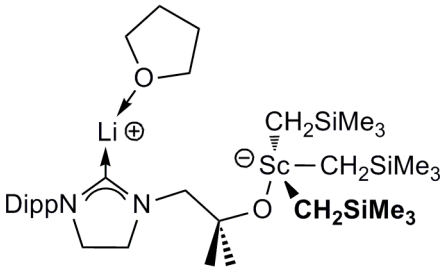
At 0 ºC, to a solution of $Sc(CH_2CMe_3)_3(thf)_{0.65}$ (0.69 g, 0.22 mmol) in hexanes (0.5 mL) was added dropwise a solution of HL^D (0.051 g, 0.17 mmol) in hexanes (0.5 mL). The reaction mixture was stirred for 3 h during which time a white precipitate formed. This was isolated by filtration and the volatiles removed *in vacuo* to afford crude $Sc(L^D)(CH_2CMe_3)_2$ as a white solid. Yield: 0.023 g (28 %). ^{1}H NMR (C_6D_6, 500 MHz): 7.27 – 7.08 (3 H, overlapping m, C_6H_3), 3.58 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.28 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 3.19 (2 H, s, $OCMe_2CH_2$), 2.87 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 1.84 and 1.17 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.73 (6 H, s, CMe_2), 0.52 (2 H, s, $C\underline{H}_2CMe_3$), 0.09 (9 H, s, $CH_2C\underline{Me}_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 236.1 (NCN), 148.1 (2,6-C_6H_3), 137.1 (1-C_6H_3), 128.9 (4-C_6H_3), 124.5 (3,5-C_6H_3), 87.1 ($\underline{C}Me_2$), 61.9 ($OCMe_2\underline{C}H_2$), 53.3 (NCH_2CH_2N), 27.5 ($C\underline{Me}_2$), 26.7 ($HC\underline{Me}_2$), 24.7 ($HC\underline{Me}_2$), 5.63 ($CH_2\underline{C}Me_3$), 4.91 ($\underline{C}H_2CMe_3$), -2.65 ($CH_2C\underline{Me}_3$) ppm. Satisfactory elemental analysis was not obtained.

6.4.12 Attempted synthesis of $Y(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$

a. *in situ* preparation from $YCl_3(thf)_{3.5}$: To a slurry of $YCl_3(thf)_{3.5}$ (0.40 g, 0.98 mmol) in thf (35 mL) at -78 ºC was added dropwise a solution of $LiCH_2SiMe_3$ (2.9 mL, 2.9 mmol, 1.0 M in pentane) diluted in hexanes (15 mL) to afford a clear, colourless solution. The reaction mixture was allowed to warm to 0 ºC and stirred for 2 h. To the reaction mixture was added a solution of HL^D (0.30 g, 0.98 mmol) and it was then stirred for a further 2 h. The volatiles were removed *in vacuo* to yield a pale yellow solid. Extraction into toluene (2 x 10 mL) and removal of the volatiles under reduced pressure afforded a pale yellow powder. Yield: 0.24 g (33 %). The ^{1}H NMR spectrum contained broad resonances between 3.50 – 0.00 ppm and other small resonances which could not be assigned.

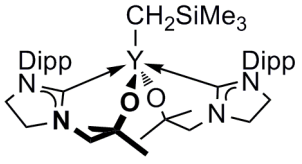
b. From $[Y(CH_2SiMe_3)_4][Li(thf)_4]$: $[Y(CH_2SiMe_3)_4][Li(thf)_4]$ (0.016 g, 0.021 mmol) and HL^D (0.0065 g, 0.021 mmol) were combined in C_6D_6/thf (0.5 mL) to afford a clear, pale yellow solution. The ^{1}H NMR spectrum contained resonances assigned as unreacted $[Y(CH_2SiMe_3)_4][Li(thf)_4]$ and broad resonances across the spectral width which could not be assigned.

6.4.13 Synthesis of $Sc(CH_2SiMe_3)_3(L^{D, Li\{thf\}})$



To a slurry of $ScCl_3(thf)_3$ (1.0 g, 2.8 mmol) in thf (40 mL) at -78 ºC was added dropwise a solution of $LiCH_2SiMe_3$ (1.1 g, 11 mmol). The reaction mixture was allowed to warm to 0 ºC and stirred for 2 h. To the reaction mixture was added a solution of HL^D (0.85 g, 2.8 mmol) and it was then stirred for a further 2 h. The volatiles were removed *in vacuo* to yield a white powder. Extraction into toluene (3 x 15 mL) and removal of the volatiles under reduced pressure gave a white powder which was washed with hexanes (3 x 15 mL) and dried once more to afford $Sc(CH_2SiMe_3)_3(L^{D, Li\{thf\}})$ as a white solid. Yield: 1.45 g (75 %). ^{1}H NMR (C_6D_6, 600 MHz): 7.08 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.96 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.13 (2 H, t, $^3J_{HH}$ = 6 Hz, C_2H_4O), 3.12 (2 H, s, $OCMe_2\underline{C}H_2$), 2.85 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 2.90 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.05 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 1,51 (6 H, s, CMe_2), 1.21 (2 H, t, $^3J_{HH}$ = 6 Hz, C_2H_4O), 1.15 and 1.09 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.42 (27 H, s, $CH_2Si\underline{Me}_3$), -0.16 (6 H, s, $C\underline{H}_2SiMe_3$) ppm.^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): 221.1 (NCN), 147.6 and 147.4 (2,6-C_6H_3), 138.2 and 137.8 (1-C_6H_3), 128.9 and 128.8 (4-C_6H_3), 124.3 (3,5-C_6H_3), 74.0 ($\underline{C}Me_2$), 68.0 (C_2H_4O), 62.2 ($OCMe_2\underline{C}H_2$), 52.8 and 51.7 (NCH_2CH_2N), 35.4 ($\underline{C}H_2SiMe_3$), 30.9 ($C\underline{Me}_2$), 28.4 and 28.3 ($H\underline{C}Me_2$), 25.3 (C_2H_4O), 24.8 and 24.7 ($HC\underline{Me}_2$), 4.39 ($CH_2Si\underline{Me}_3$) ppm. Anal. Found (calcd for $C_{35}H_{70}LiN_2O_2ScSi_3$): C, 60.12 (61.18); 10.09 (10.27); N, 4.45 (4.66).

6.4.14 Synthesis of $Y(L^D)_2CH_2SiMe_3$



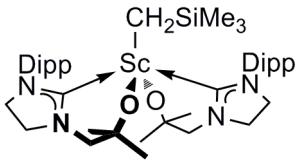
To a clear, colourless solution of $Y(CH_2SiMe_3)_3(thf)_2$ (0.27 g, 0.55 mmol) in hexanes (10 mL) was added a solution of HL^D (0.33 g, 1.11 mmol) in hexanes (5 mL) to afford a pale yellow solution. The reaction mixture was stirred for 12 h at room temperature and the volatiles were then removed under reduced pressure to yield a pale yellow solid which was washed with hexanes (3 x 5 mL) and dried under reduced pressure to afford $Y(L^D)_2CH_2SiMe_3$ as a white solid. Yield: 0.14 g (33 %). ^{1}H NMR (C_6D_6, 600 MHz): 7.29 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3) 7.17 (4 H, m, 3,5-C_6H_3), 3.63 (2 H, d, $^3J_{HH}$ = 14 Hz, $OCMe_2C\underline{H}_2$), 3.38 – 2.85 (12 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.67 (2 H, d, $^3J_{HH}$ = 14 Hz, $OCMe_2C\underline{H}_2$), 1.57 1.49 and 1.19 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.87 and 0.79 (6 H each, s, CMe_2), 0.41 (9 H, s, $CH_2Si\underline{Me}_3$), -0.48 and -1.04 (1 H each, dd, $^1J_{HH}$ = 11 Hz, $^1J_{YH}$ = 3 Hz, $C\underline{H}_2SiMe_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): 217.9 (d, $^1J_{YC}$ = 33 Hz,

NCN), 147.6 and 147.2 (2,6-C_6H_3), 137.7 (1-C_6H_3), 128.6 (4-C_6H_3), 124.1 and 124.0 (2,6-C_6H_3), 67.9 and 63.2 ($OCMe_2\underline{C}H_2$), 53.2 and 53.0 ($NCH_2\underline{C}H_2N$), 31.2 and 28.7 ($C\underline{Me}_2$), 28.3 and 28.0 ($H\underline{C}Me_2$), 25.9 25.6 25.1 and 25.0 ($HC\underline{Me}_2$) 5.0 ($CH_2Si\underline{Me}_3$) ppm. The resonance accounting for the $\underline{C}H_2SiMe_3$ carbon could not be found within the spectrum. Satisfactory elemental analysis was not gained from powdered single crystals.

6.4.15 Decomposition of $Y(L^D)_2CH_2SiMe_3$

To a clear, colourless solution of $Y(CH_2SiMe_3)_3(thf)_2$ (0.65 g, 1.3 mmol) in toluene (10 mL) was added a solution of HL^D (0.79 g, 2.6 mmol) in toluene (5 mL) to afford a pale yellow solution. The reaction mixture was stirred for 3 h at room temperature and then the volatiles were removed under reduced pressure to yield a pale yellow solid. The ^{1}H NMR spectrum of this solid showed resonances for $Y(L^D)_2CH_2SiMe_3$ and small amounts of impurities. Attempted recrystallisation from hexanes at -30 ºC led to the precipitation of a white solid which was isolated by filtration and dried *in vacuo*. ^{1}H (C_6D_6, 400 MHz): 7.36 (2 H, t, $^3J_{HH}$ = 7 Hz, 4-C_6H_3), 7.29 and 7.24 (2 H each, d, $^3J_{HH}$ = 7 Hz, 3,5-C_6H_3), 3.61 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.37 – 3.13 (12 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.77 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.58 1.53 1.37 and 1.27 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.95 and 0.82 (6 H each, s, CMe_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 400 MHz): 221.1 (d, $^1J_{YC}$ = 36 Hz, NCN), 147.6 and 147.1 (2,6-C_6H_3), 138.5 (1-C_6H_3) 123.9 (4-C_6H_3), 123.6 and 128.4 (3,5-C_6H_3), 71.3 ($\underline{C}Me_2$), 64.1 ($OCMe_2\underline{C}H_2$), 53.6 and 53.1 ($H\underline{C}Me_2$ and NCH_2CH_2N), 31.9 and 29.3 ($C\underline{Me}_2$), 28.5 ($H\underline{C}Me_2$ and NCH_2CH_2N), 26.9 25.9 25.6 and 25.0 ($HCMe_2$) ppm. The reaction could not be subsequently reproduced.

6.4.16 Synthesis of $Sc(L^D)_2CH_2SiMe_3$

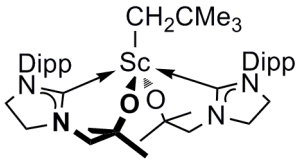


a. From $Sc(CH_2SiMe_3)_3(thf)_2$: At 0 ºC, to a clear, colourless solution of $Sc(CH_2SiMe_3)_3(thf)_2$ (0.86 g, 1.9 mmol) in hexanes (20 mL) was added a solution of HL^D (1.2 g, 3.8 mmol) in hexanes (10 mL). The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 1.5 h to afford a clear, colourless solution. The volatiles were removed under reduced pressure to afford $Sc(L^D)_2CH_2SiMe_3$ as a white solid. Yield: 1.1 g (81 %). Diffraction-quality crystals were grown from a hexanes solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 7.27 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.26 (4 H, d , $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.74 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.32 (2 H, m, $\underline{H}CMe_2$), 3.25 – 2.28 (10 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.56 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.58 1.51 1.21 and 1.16 (6 H each, d, $^3J_{HH}$

= 7 Hz, HC<u>Me</u>$_2$) 0.87 and 0.60 (6 H each, s, CMe$_2$), 0.37 (9 H, s, CH$_2$Si<u>Me</u>$_3$), -0.33 and -0.72 (1 H each, d, $^1J_{HH}$ = 11 Hz, CH$_2$SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): 147.8 and 147.1 (2,6-C_6H_3), 138.4 (1-C_6H_3), 128.4 (4-C_6H_3), 124.02 (3,5-C_6H_3), 72.7 (<u>C</u>Me$_2$) 62.41 (OCMe$_2$<u>C</u>H$_2$), 53.3 and 52.7 (H<u>C</u>Me$_2$ and NCH$_2$CH$_2$N), 30.2 (C<u>Me</u>$_2$), 28.7 (<u>C</u>H$_2$SiMe$_3$), 28.3 (C<u>Me</u>$_2$), 27.6 25.9 25.3 and 25.1 (HC<u>Me</u>$_2$), 4.7 (CH$_2$Si<u>Me</u>$_3$) ppm. Anal. Found (calcd for $C_{42}H_{69}N_4O_2ScSi$): C, 68.50 (68.63); H, 9.26 (9.46); N, 7.74 (7.62).

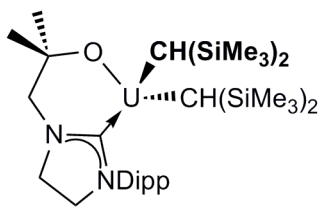
b. From Sc(L^D)$_2$Cl (see 6.4.34): Sc(L^D)$_2$Cl (0.014 g, 0.020 mmol) and LiCH$_2$SiMe$_3$ (0.0019 g, 0.020 mmol) were combined in C_6D_6 in a J-Young Teflon valve NMR tube. The reaction mixture was heated to 80 ºC for 12 h. The formation of Sc(L^D)$_2$CH$_2$SiMe$_3$ was confirmed by ^{1}H NMR spectroscopy.

6.4.17 Synthesis of Sc(L^D)$_2$CH$_2$CMe$_3$



At 0 ºC, to a clear, colourless solution of Sc(CH$_2$CMe$_3$)$_3$(thf)$_{0.65}$ (0.10 g, 0.34 mmol) in hexanes (5 mL) was added a solution of HL^D (0.15 g, 0.51 mmol) in hexanes (5 mL). The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 1.5 h at room temperature to afford a clear, colourless solution. The volatiles were removed under reduced pressure to afford Sc(L^D)$_2$CH$_2$CMe$_3$ as a white solid. Yield: 0.11 g (47 %). Diffraction-quality crystals were grown from a hexanes solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 7.30 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.18 (4 H, m, 2,6-C_6H_3) , 3.92 (2 H, d, $^3J_{HH}$ = 13 Hz, OCMe$_2$C<u>H</u>$_2$), 3.46 (2 H, sept, $^3J_{HH}$ = 7 Hz, <u>H</u>CMe$_2$), 3.27 (2 H, m, NCH$_2$CH$_2$N), 3.11 – 2.87 (6 H, overlapping m, <u>H</u>CMe$_2$ and NCH$_2$CH$_2$N), 2.64 (2 H, d, $^3J_{HH}$ = 13 Hz, OCMe$_2$C<u>H</u>$_2$), 1.62 and 1.52 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC<u>Me</u>$_2$), 1.41 (9 H, s, CH$_2$C<u>Me</u>$_3$), 1.22 and 1.16 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC<u>Me</u>$_2$), 0.91 and 0.67 (6 H each, s, CMe$_2$), 0.50 and 0.37 (1 H each, d, $^1J_{HH}$= 12 Hz, C<u>H</u>$_2$CMe$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 500 MHz): 147.9 and 147.1 (2,6-C_6H_3), 138.6 (1-C_6H_3), 124.0 (3,5-C_6H_3), 72.5 (<u>C</u>Me$_2$), 62.3 (OCMe$_2$<u>C</u>H$_2$), 53.3 ad 52.8 (NCH$_2$CH$_2$N), 36.9 (CH$_2$<u>C</u>Me$_3$), 31.6 (C<u>Me</u>$_2$), 28.7 and 28.2 (H<u>C</u>Me$_2$), 27.8 (C<u>Me</u>$_2$), 26.0 25.8 25.5 and 25.1 (HC<u>Me</u>$_2$) ppm. The resonance for the 4-C_6H_3 carbon was obscured by the C_6D_6 resonance. Anal. Found (calcd for $C_{43}H_{69}N_4O_2Sc$): C, 71.74 (71.83); H, 9.75 (9.67); N, 7.61 (7.79).

6.4.18 Synthesis of $U(L^D)(CH\{SiMe_3\}_2)_2$



At 0 ºC, to a solution of $U(CH\{SiMe_3\}_2)_3$ (0.083 g, 0.12 mmol) in hexanes (5 mL) was added a solution of HL^D (0.035 g, 0.12 mmol) in hexanes (5 mL) to afford a dark green-brown solution. The volatiles were removed in vacuo to afford a dark green-brown solid. Storage in solution or the solid state at room temperature led to full decomposition over the course of 1 h to $CH_2(SiMe_3)_2$ and small unidentified paramagnetic resonances over a range of 37.2 – -38.1 ppm. An accurate yield was not recorded for this reason. ^{1}H NMR (C_6D_6, 400 MHz): 26.25 (2 H, s, $OCMe_2C\underline{H}_2$ or $\underline{H}CMe_2$, or $C\underline{H}(SiMe_3)_2$), 17.59 (6 H, s, CMe_2), 12.53 (2 H, s, $OCMe_2C\underline{H}_2$ or $\underline{H}CMe_2$ or $C\underline{H}(SiMe_3)_2$), 7.75 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.65 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 5.15 and 4.90 (2 H each, s, NCH_2CH_2N), 2.48 and 1.59 (6 H each, d, $^3J_{HH}$ = 6 Hz, $HC\underline{Me}_2$), -5.82 (2 H, s, $OCMe_2C\underline{H}_2$ or $\underline{H}CMe_2$ or $C\underline{H}(SiMe_3)_2$), -6.26 (36 H, s, $CH(Si\underline{Me}_3)_2$) ppm.

6.4.19 Attempted synthesis of $U(L^D)_2CH(SiMe_3)_2$

HL^D (0.0080 g, 0.026 mmol) and $U(CH\{SiMe_3\}_2)_3$ (0.0095 g, 0.0013 mmol) were combined in C_6D_6 to afford a dark green-brown solution immediately. Analysis by ^{1}H NMR spectroscopy indicated 1 equivalent of $U(L^D)(CH\{SiMe_3\}_2)_2$ and 1 equivalent of unreacted HL^D. Storage in solution at room temperature led to full decomposition over the course of 1 h to $H_3CH(SiMe_3)_2$, HL^D and paramagnetic resonances over the range 37.2 – - 38.1 ppm.

6.4.20 Attempted synthesis of $Y(L^D)(BH_4)_2(thf)_2$

$Y(BH_4)_3(thf)_3$ (0.090 g, 0.26 mmol) and HL^D (0.076 g, 0.26 mmol) were combined in C_6D_6 and heated to 80 ºC for 3 h to afford a clear, colourless solution. The volatiles were removed *in vacuo* to afford a gluey, white solid. Yield: 0.045 g. ^{1}H NMR (C_6D_6, 500 MHz): 7.18 – 7.05 (3 H, overlapping m, C_6H_3), 3.88 (8 H, s, C_4H_8O), 3.35 (2 H, sept, $^3J_{HH}$ = 6.91 Hz), 3.06 (4 H, m, NCH_2CH_2N), 2.73 (2 H, s, $OCMe_2C\underline{H}_2$), 1.72 – 0.84 (22 H overlapping m, BH_4, CMe_2 and C_4H_8O) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 148.99 (1-C_6H_3), 147.29 (2,6-C_6H_3), 127.06 (4-C_6H_3) and 124.56 (3,5-C_6H_3), 80.55 ($\underline{C}Me_2$), 72.24 (C_4H_8O), 61.13 and 57.08 (NCH_2CH_2N), 49.09,. 46.14,.43.00, 29.70, 28.62, 28.25, 25.28, 25.00, 24.45 ppm.

6.4.21 Attempted synthesis of $Sc(L^D)(BH_4)_2(thf)_2$

$Sc(BH_4)_3(thf)_2$ (0.17 g, 0.74 mmol) and HL^D (0.22 g, 0.74 mmol) were combined in C_6D_6 and heated to 80 ºC for 3 h to afford a clear, colourless solution. The volatiles were removed *in vacuo* to afford a gluey, white solid. Yield: 0.15 g. ^{1}H NMR (C_6D_6, 500 MHz): 7.16 – 7.10 (3 H, overlapping m, C_6H_3), 3.61 (8 H, s, C_4H_8O), 3.42 (2 H, m, $\underline{H}CMe_2$), 3.23 (4 H, overlapping m, NCH_2CH_2N), 2.67 (2 H, s $OCMe_2C\underline{H}_2$), 2.0 – 1.0 (22 H, overlapping m, BH_4, CMe_2, C_4H_8O).

6.4.22 Attempted synthesis of $Ce(L^D)(BH_4)_2$

To a slurry of $Ce(BH_4)_3(thf)_3$ (0.27 g, 0.66 mmol) in toluene (10 mL) was added a solution of HL^D (0.40 g, 1.3 mmol) in toluene (5 mL). The reaction mixture was heated to 80 ºC to afford a turbid solution. The volatiles were removed *in vacuo* to afford a white powder. ^{1}H NMR (C_6D_6, 360 MHz): 32.35 (8 H, br. s, BH_4) ppm.

6.4.23 Attempted synthesis of $Ce(L^D)_2(BH_4)$

To a slurry of $Ce(BH_4)_3(thf)_3$ (0.39 g, 0.96 mmol) in toluene (10 mL) was added a solution of HL^D (0.29 g, 0.96 mmol) in toluene (5 mL).The reaction mixture was heated to 80 ºC to afford a turbid solution. The volatiles were removed *in vacuo* to afford a white powder. ^{1}H NMR (C_6D_6, 360 MHz): 36.23(8 H, br. s, BH_4) ppm. Subsequent attempts of recrystallisation from thf at -20 ºC yielded only $[Ce(BH_4)_2(thf)_5][Ce(BH_4)_4(thf)_2]$ as single crystals.

6.4.24 Attempted synthesis of $[Ce(L^D)Bn'][BAr^F{}_3Bn']$

At -78 ºC, to the combined solids of $Ce(L^D)Bn'_2$ (0.13 g, 0.18 mmol) and $BAr^F{}_3$ (0.094 g, 0.18 mmol) was added thf (10 mL). The reaction mixture was allowed to warm to room temperature and stirred for 16 h to afford an orange solution. The volatiles were removed *in vacuo* to afford an orange solid. The compound was poorly soluble in C_6D_6 and satisfactory elemental analysis was not obtained.

6.4.25 Attempted synthesis of $[Ce(L^D)_2][BAr^F{}_3Bn']$

At -78 ºC, to the combined solids of $Ce(L^D)Bn'_2$ (0.12 g, 0.14 mmol) and $BAr^F{}_3$ (0.072 g, 0.14 mmol) was added thf (10 mL). The reaction mixture was allowed to warm to room temperature and stirred for 16 h to afford an orange solution. The volatiles were removed *in vacuo* to afford a yellow solid. The product was poorly soluble in C_6D_6. Anal. Found (calcd for $C_{65}H_{70}BCeF_{15}N_5O_2$): C, 51.59 (56.20); H, 4.30 (5.08); N, 4.32 (5.04).

6.4.26 Reaction of $Ce(L^D)Bn'_2$ with H_2

To a freeze-pump-thaw degassed solution of $Ce(L^D)Bn'_2$ (0.20 g, 0.028 mmol) in toluene (5 mL) was added H_2 (1 atm) to afford a dark orange solution. The reaction mixture was stirred for 2 h before the volatiles were removed *in vacuo* to afford a dark orange solid. ^{1}H NMR spectral analysis indicated the presence of HBn' and HL^D, indicative of decomposition.

6.4.27 Reaction of $Ce(L^D)_2Bn'$ with H_2

To a freeze-pump-thaw degassed solution of $Ce(L^D)_2Bn'$ (0.20 g, 0.023 mmol) in toluene (5 mL) was added H_2 (1 atm) to afford a dark orange solution. The reaction mixture was stirred for 2 h before the volatiles were removed *in vacuo* to afford a dark orange solid. ^{1}H NMR spectral analysis indicated the presence of HBn' and HL^D, indicative of decomposition.

6.4.28 Reaction of $Ce(L^D)Bn'_2$ with AdN_3

$Ce(L^D)Bn'_2$ (0.016 g, 0.22 mmol) and AdN_3 (0.039 g, 0.022 mmol) were combined in toluene (5 mL) to afford an orange solution. The reaction mixture was stirred for 2 h before the volatiles were removed *in vacuo* to yield an orange solid. The ^{1}H NMR spectrum showed overlapping resonances in the range 20 – -20 ppm which could not be assigned.

6.4.29 Reaction of $Y(L^D)(CH_2SiMe_3)_2$ with Me_3SiCl

To a solution of $Y(L^D)(CH_2SiMe_3)_2$ (0.019 g, 0.034 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Me_3SiCl (4.3 µL, 0.034 mmol) to afford a clear, pale yellow solution. Immediately, the formation of $Me_3SiCH_2SiMe_3$ was indicated by ^{1}H NMR spectroscopy. There was no evidence of the reformation of $Y(L^D)(CH_2SiMe_3)_2$.

6.4.30 Reaction of $Sc(L^D)(CH_2SiMe_3)_2$ with E-X

a. Me_3SiCl: To a solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.019 g, 0.036 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Me_3SiCl (4.6 µL, 0.036 mmol) to afford a clear, colourless solution. Over the course of 3 h the reaction was monitored by ^{1}H NMR spectroscopy and the formation of $Me_3SiCH_2SiMe_3$ was observed. There was no evidence of the reformation of $Sc(L^D)(CH_2SiMe_3)_2$.

b. MeI: To a solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.014 g, 0.027 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added MeI (1.7 µL, 0.027 mmol) to afford a clear, colourless solution. The ^{1}H NMR spectrum indicated no reaction at room temperature.

On heating to 80 ºC for 2 h, $Sc(L^D)(CH_2SiMe_3)_2$ was fully consumed but the resulting products could not be identified.

c. CH_2CHCH_2Cl: To a solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.023 g, 0.045 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CH_2CHCH_2Cl (3.6 µL, 0.045 mmol) to afford a clear, colourless solution. The ^1H NMR spectrum indicated no reaction at room temperature. On heating to 80 ºC for 2 h, $Sc(L^D)(CH_2SiMe_3)_2$ was fully consumed but the resulting products could not be identified.

e. $^nBu_3SnCl$: To a solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.0096 g, 0.018 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $^nBu_3SnCl$ (5.0 µL, 0.018 mmol) to afford a clear, colourless solution. On heating to 80 ºC for 2 h, $Sc(L^D)(CH_2SiMe_3)_2$ was fully consumed but the resulting products could not be identified.

f. Ph_3CCl: $Sc(L^D)(CH_2SiMe_3)_2$ (0.0078 g, 0.015 mmol) and Ph_3CCl (0.0012 g, 0.015 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. After 16 h, the ^1H NMR spectrum indicated $Sc(L^D)_2CH_2SiMe_3$ and multiple products which could not be identified.

6.4.31 Reaction of $Sc(L^D)(CH_2SiMe_3)_2$ with E-H

a. $^nBu_3SnH$: To a solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.0097 g, 0.019 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $^nBu_3SnH$ (5.0 µL, 0.019 mmol) to afford a clear, colourless solution. The ^1H NMR spectrum indicated that no reaction had taken place at room temperature.

b. $PhSiH_3$: To a solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.0033 g, 0.0063 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $PhSiH_3$ (0.78 µL, 0.0063 mmol) to afford a clear, pale yellow solution. The ^1H NMR spectrum indicated that no reaction had taken place at room temperature. On heating to 80 ºC for 2 h, decomposition of $Sc(L^D)(CH_2SiMe_3)_2$ to $SiMe_4$ and other unidentified products occurred.

c. H_2: To a freeze-pump-thaw degassed solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.010 g, 0.019 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added H_2 (1 atm) to afford a clear, colourless solution. ^1H NMR spectroscopy indicated the slow formation of $SiMe_4$ at room temperature and the growth of some additional resonances which could not be assigned.

.4.31.1 Reaction of $Sc(L^D)(CH_2SiMe_3)_2$ with E-E'

a. PhSSPh: $Sc(L^D)(CH_2SiMe_3)_2$ (0.015 g, 0.029 mmol) and PhSSPh (0.0063 g, 0.029 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature. On heating to 80 ºC for 16 h, the solution became yellow-orange in colour. (The ^{1}H NMR spectrum contained the same resonances observed in 6.4.51a). ^{1}H NMR (C_6D_6, 500 MHz): 7.73 (1 H, d, $^3J_{HH}$ = 7 Hz), 7.25 (4 H, d, $^3J_{HH}$ = 7 Hz), 7.08 (4 H, m), 6.95 (2 H, m), 3.58 (1 H, d, $^3J_{HH}$ = 13 Hz), 3.56 and 3.25 (1 H each, m), 3.10 – 3.00 (2 H, overlapping m), 2.85 (2 H, t, $^3J_{HH}$ = 11 Hz), 2.42 (1 H, d, $^3J_{HH}$ = 13 Hz), 1.93 (4 H, s), 1.65 1.62 1.21 and 1.17 (3 H each, d, $^3J_{HH}$ = 7 Hz), 0.93 and 0.49 (3 H each, s) 0.07 (18 H, s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 215.5 147.9 147.3 138.0 134.1 129.0 128.6 127.3 126.5 124.8 124.2 121.8 73.3 61.9 53.5 52.5 29.5 28.7 28.4 27.1 25.6 25.5 24.6 18.18 and -1.67 ppm.

b. B_2cat_2: $Sc(L^D)(CH_2SiMe_3)_2$ (0.0098 g, 0.019 mmol) and B_2cat_2 (0.0045 g, 0.019 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a turbid, pale orange solution. ^{1}H NMR spectroscopy indicated the formation of $SiMe_4$ and small overlapping resonances across the diamagnetic spectral width which could not be assigned.

c. $Me_3SnSnMe_3$: $Sc(L^D)(CH_2SiMe_3)_2$ (0.015 g, 0.029 mmol) and $Me_3SnSnMe_3$ (6.0 µL, 0.029 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated that no reaction had taken place at room temperature. On heating to 80 ºC, the solution became pale yellow in colour and $Sc(L^D)(CH_2SiMe_3)_2$ was fully consumed but the resulting products could not be identified.

d. 1,1-Me_2-Si-$(CH_2)_3$: To a solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.011 g, 0.020 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added 1,1-Me_2-Si-$(CH_2)_3$ (2.6 µL, 0.020 mmol) to afford a clear, colourless solution. The ^{1}H NMR spectrum indicated that no reaction had taken place at room temperature.

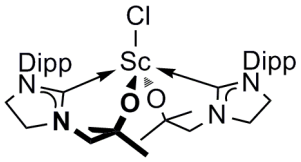
6.4.32 Reaction of $Y(L^D)_2CH_2SiMe_3$ with Me_3SiCl

To a solution of $Y(L^D)_2CH_2SiMe_3$ (0.015 g, 0.019 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Me_3SiCl (2.5 µL, 0.019 mmol) to afford a clear, pale yellow solution. The ^{1}H NMR spectrum indicated the formation of $Me_3SiCH_2SiMe_3$. The inorganic reaction product could not be identified.

6.4.33 Reaction of $Sc(L^D)_2CH_2SiMe_3$ with Me_3SiCl

: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.024 g, 0.032 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Me_3SiCl (4.2 µL, 0.032 mmol) to afford a clear, colourless solution. Over the course of 5 days the reaction was monitored by ^1H NMR spectroscopy and the formation of $Sc(L^D)_2Cl$ and $Me_3SiCH_2SiMe_3$.

6.4.34 Synthesis of $Sc(L^D)_2Cl$



$Sc(L^D)_2CH_2SiMe_3$ (0.17 g, 0.23 mmol) and Me_3SiCl (29 µL, 0.23 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. After 5 days, colourless crystals had formed and these were isolated by filtration, washed with hexanes (3 x 2 mL) and dried *in vacuo* to afford $Sc(L^D)_2Cl$ as a colourless solid. Yield: 0.071 g (45 %). Diffraction-quality crystals were grown from a saturated C_6D_6 solution. ^1H NMR (C_6D_6, 500 MHz): 7.25 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.19 and 7.14 (2 H each, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 3,5-C_6H_3), 3.69 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.59 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.25 – 3.19 (2 H, m, NCH_2CH_2N), 3.11 – 3.03 (4 H, overlapping m, $\underline{H}CMe_2$ and $NCH_2\underline{C}H_2N$), 2.92 – 2.82 (4 H, m, NCH_2CH_2N), 2.49 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.72 1.60 1.21 and 1.21 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.98 and 0.50 (CMe_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): ppm. 215.2 (NCN), 147.8 147.6 and 129.3 (1,2,6-C_6H_3), 128.6 (4-C_6H_3), 124.3 and 124.1 (3,5-C_6H_3), 73.3 ($\underline{C}Me_2$), 62.3 ($OCMe_2\underline{C}H_2$), 52.3 and 52.6 (NCH_2NCH_2), 29.4 ($C\underline{Me}_2$), 28.8 and 28.2 ($H\underline{C}Me_2$), 27.2 ($C\underline{Me}_2$), 25.8 25.4 and 25.0 ($HC\underline{Me}_2$) ppm. Anal. Found (calcd for $C_{38}H_{58}ClN_4O_2Sc$): C, 67.16 (66.79); H, 8.91 (8.56); N, 7.85 (8.20).

6.4.35 Reaction of $Sc(L^D)_2CH_2CMe_3$ with $SiMe_3Cl$

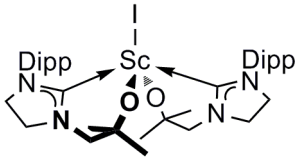
To a solution of $Sc(L^D)_2CH_2CMe_3$ (0.012 g, 0.017 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Me_3SiCl (2.1 µL, 0.017 mmol) to afford a clear, colourless solution. Over the course of 10 days the reaction was monitored by ^1H NMR spectroscopy and the formation of $Sc(L^D)_2Cl$ and $Me_3CCH_2SiMe_3$ was observed. ^1H NMR: (C_6D_6, 400 MHz): 1.26 (CMe_3), 0.14 (9 H, s, $CH_2Si\underline{Me}_3$), 0.07 (2 H, s, $C\underline{H}_2SiMe_3$) ppm. Accurate integration of the CMe_3 resonance could not be performed due to overlapping resonances.

6.4.36 Reaction of $Sc(L^D)_2CH_2CMe_3$ with Me_3SiI

To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.066 g, 0.090 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Me_3SiI (12.8 µL, 0.090 mmol) to afford a clear,

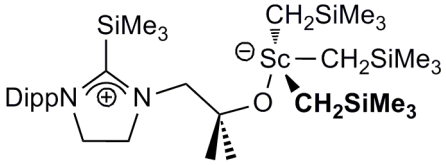
colourless solution. Over the course of 5 days the reaction was monitored by ^{1}H NMR spectroscopy and the formation of $Sc(L^{D})_2I$ was observed. The volatiles were distilled off and were shown to contain $Me_3SiCH_2SiMe_3$.

6.4.37 Synthesis of $Sc(L^{D})_2I$



$Sc(L^{D})_2CH_2SiMe_3$ (0.16 g, 0.22 mmol) and MeI (13.9 µL, 0.22 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. The reaction mixture was heated to 80 ºC for 2 h to afford a clear, pale yellow solution. Removal of the volatiles *in vacuo* afforded $Sc(L^{D})_2I$ as a white powder. Yield: 0.061 g (35 %). Diffraction-quality crystals were grown by slow evaporation of a toluene solution. ^{1}H NMR (C_6D_6, 500 MHz): 7.24 (2 H, t, $^{3}J_{HH}$ = 8 Hz, 4-C_6H_3), 7.17 and 7.13 (2 H each, dd, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 1 Hz, 3,5-C_6H_3), 3.87 (2 H, d, $^{3}J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.68 (2 H, sept, $^{3}J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.31 – 3.23 (2 H, m, NCH_2CH_2N), 3.08 – 2.78 (4 H, overlapping m, $\underline{H}CMe_2$ and NCH_2CH_2N), 2.92 - 2.82 (4 H, m, NCH_2CH_2N), 2.49 (2 H, d, $^{3}J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.75 1.59 1.21 and 1.17 (6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.94 and 0.48 (CMe_2) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz): 147.9 and 147.8 (2,6-C_6H_3), 137.7 (1-C_6H_3), 128.7 (4-C_6H_3), 124.3 and 124.2 (3,5-C_6H_3), 74.1 ($\underline{C}Me_2$), 61.9 ($OCMe_2\underline{C}H_2$), 53.4 and 52.8 (NCH_2NCH_2), 29.1 ($C\underline{Me}_2$), 28.7 and 28.1 ($H\underline{C}Me_2$), 26.9 ($C\underline{Me}_2$), 26.4 26.0 and 25.3 24.6 ($HC\underline{Me}_2$) ppm. Anal. Found (calcd for $C_{38}H_{58}IN_4O_2Sc$): C, 58.72 (58.91); H, 7.39 (7.55); N, 7.23 (7.16).

6.4.38 Synthesis of $Sc(CH_2SiMe_3)_3(L^{D,\ SiMe_3})$



At 0 ºC, to a solution of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (0.34 g, 0.51 mmol) in toluene (5 mL) was added a solution of Me_3SiCl (64 µL, 0.51 mmol) in toluene (5 mL). The reaction mixture was stirred for 2 h. The volatiles were removed *in vacuo* to afford $Sc(CH_2SiMe_3)_3(L^{D,\ SiMe_3})$ as a white powder. Storage at room temperature in solution resulted in further elimination reactivity (see 6.4.39) or decomposition in the solid state. Yield: 0.27 g (78 %). ^{1}H NMR (C_6D_6, 500 MHz): 6.99 (1 H, t, $^{3}J_{HH}$ = 8 Hz, 4-C_6H_3), 6.75 (2 H, d, $^{3}J_{HH}$ = 8 Hz, 3,5-C_6H_3), 4.58 and 3.35 (2 H each, t, $^{3}J_{HH}$ = 12 Hz, NCH_2CH_2N), 2.46 (2 H, sept, $^{3}J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.30 (2 H, s, $OCMe_2C\underline{H}_2$), 1.52 (6 H, s, CMe_2), 0.93 (12 H, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.58 (27 H, s, $CH_2Si\underline{Me}_3$), 0.16 (6 H, br. s, $C\underline{H}_2SiMe_3$), -0.43 (9 H, s, $CSiMe_3$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz): ppm. 174.8 (NCN), 146.3(1-C_6H_3), 132.4

(2,6-C_6H_3), 131.3(4-C_6H_3), 125.2 (3,5-C_6H_3), 73.02 ($\underline{C}Me_2$), 64.2 ($OCMe_2\underline{C}H_2$), 54.7 and 51.5 (NCH_2CH_2N), 31.5 ($C\underline{Me}_2$), 28.5 ($H\underline{C}Me_2$), 25.6 and 23.3 ($HC\underline{Me}_2$), 4.91 ($CH_2Si\underline{Me}_3$ and $\underline{C}H_2SiMe_3$),1.48 ($CSi\underline{Me}_3$) ppm. Anal. Found (calcd for $C_{34}H_{71}N_2OScSi_4$): C, 59.89 (59.94); H, 10.41 (10.50); N, 4.14 (4.11).

6.4.39 Elimination reaction of $Sc(CH_2SiMe_3)_3(L^{D, SiMe_3})$

$Sc(CH_2SiMe_3)_3(L^{D, SiMe_3})$ (0.021 g, 0.031 mmol) was dissolved in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. The reaction mixture was stored at room temperature for 2 h after which time the ^{1}H NMR spectrum contained resonances for approximately 1 equivalent of $Me_3SiCH_2SiMe_3$, 0.9 equivalents of $Sc(L^D)(CH_2SiMe_3)_2$ and 0.05 equivalents $Sc(L^D)_2CH_2SiMe_3$ arising from ligand redistribution.

6.4.40 Reaction of $Sc(L^D)_2CH_2SiMe_3$ with Sn-X

a. $^nBu_3SnCl$: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.037 g, 0.051 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $^nBu_3SnCl$ (14 µL, 0.051 mmol) to afford a clear, colourless solution. Over the course of 17 h the reaction was monitored by ^{1}H NMR spectroscopy and the formation of 1 equivalent of $Sc(L^D)_2Cl$ and 1 equivalent of $^nBu_3SnCH_2SiMe_3$ were observed. ^{1}H NMR (C_6D_6, 500 MHz): 1.67 (6 H, m, $(C\underline{H}_2)_3CH_3$), 1.49 (6 H, m, $(C\underline{H}_2)_3CH_3$)), 1.06 - 0.94 (36 H, overlapping m, 4-$(C\underline{H}_2)_3CH_3$ and 1-$(CH_2)_3C\underline{H}_3$), 0.24 (9 H, s, $CH_2Si\underline{Me}_3$), -0.13 (2 H, s, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 29.7 ((2,3-$C\underline{H}_2)_3CH_3$), 27.9 ((2,3-$C\underline{H}_2)_3CH_3$), 14.0 (4-$C\underline{H}_2)_3CH_3$), 10.7 (1-$(C\underline{H}_2)_3CH_3$, $^2J_{^{119}SnC}$ = 162 Hz, $^2J_{^{117}SnC}$ = 155 Hz), 1.9 ($CH_2Si\underline{Me}_3$), -7.1 ($\underline{C}H_2SiMe_3$) ppm. EI-MS: *m/z*: 363.1 $[M\text{-}Me]^+$ (5 %), 321.1 $[M\text{-}^nBu]^+$ (100 %), 264.0 $[M\text{-}2^nBu]^+$ (18 %), 207.0 $[M\text{-}3^nBu]^+$ (66 %).

b. Ph_3SnCl: $Sc(L^D)_2CH_2SiMe_3$ (0.019 g, 0.026 mmol) and Ph_3SnCl (0.010 g, 0.026 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. Over the course of 5 days the reaction was monitored by ^{1}H NMR spectroscopy and the formation of $Sc(L^D)_2Cl$ and $Ph_3SnCH_2SiMe_3$ were observed. ^{1}H NMR (C_6D_6, 500 MHz): 7.62 – 7.60 (3 H, overlapping m, C_6H_4), 7.21 – 7.13 (overlapping m, -C_6H_4), 0.36 (2 H, s, $\underline{C}H_2SiMe_3$), 0.01 (9 H, s, $CH_2Si\underline{Me}_3$) ppm. Integration of the aromatic protons could not be performed accurately due to overlap with both the residual $Sc(L^D)_2Cl$ and C_6D_6 resonances. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 137.3 and 128.7 (C_6H_4), 1.7 ($\underline{C}H_2SiMe_3$), -5.0 ($CH_2Si\underline{Me}_3$) ppm. The remaining –C_6H_4 resonances are obscured by $Sc(L^D)_2Cl$ and C_6D_6 resonances. EI-MS: *m/z*: 423.1 $[M\text{-}Me]^+$ (10 %), 361.1 $[M\text{-}Ph]^+$ (14 %), 351.0 $[M\text{-}CH_2SiMe_3]^+$ (100 %).

6.4.41 Reaction of $Sc(L^D)_2CH_2SiMe_3$ with Ph_2PCl

To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.051 g, 0.069 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Ph_2PCl (12.3 µL, 0.069 mmol) to afford a clear, colourless solution. Over the course of 5 days the reaction was monitored by ^1H NMR spectroscopy and the formation of $Sc(L^D)_2Cl$ and $Ph_2PCH_2SiMe_3$ was observed. ^1H NMR (C_6D_6, 500 MHz): 7.45 (12 H, m, C_6H_4), 0.36 ($C\underline{H}_2SiMe_3$) ppm. The $-C_6H_4$ resonances were obscured by those of $Sc(L^D)_2Cl$ and C_6D_6. EI-MS: *m/z*: 272.1 $[M]^+$ (100 %).

6.4.42 Reaction of $Y(L^D)_2CH_2SiMe_3$ with ^iPrCl

To a solution of $Y(L^D)_2CH_2SiMe_3$ (0.014 g, 0.018 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^iPrCl (1.6 µL, 0.018 mmol) to afford a clear, colourless solution. The ^1H NMR spectrum indicated that no reaction had taken place at room temperature or on heating at 80 ºC.

6.4.43 Reaction of $Sc(L^D)_2CH_2SiMe_3$ with C-X

a. MeI:To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.040 g, 0.054 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added MeI (3.4 µL, 0.054 mmol) to afford a clear, colourless solution. The reaction mixture was heated to 80 ºC for 2 h. ^1H NMR spectroscopy indicated the formation of $Sc(L^D)_2I$.

b. ^iPrCl: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.012 g, 0.016 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^iPrI (1.5 µL, 0.016 mmol) to afford a clear, colourless solution. ^1H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

c. ^iPrI: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.021 g, 0.028 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^iPrI (3.4 µL, 0.040 mmol) to afford a clear, colourless solution. ^1H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

d. ^tBuI: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.025 g, 0.034 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^tBuI (4.1 µL, 0.034 mmol) to afford a clear, colourless solution. ^1H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

e. Ph_3CCl: $Sc(L^D)_2CH_2SiMe_3$ (0.011 g, 0.014 mmol) and Ph_3CCl (0.0040, 0.014 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to

afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

f. CH_2CHCH_2Cl: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.028 g, 0.038 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CH_2CHCH_2Cl (3.1 µL, 0.038 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

g. BnBr: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.010 g, 0.014 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added BnBr (1.6 µL, 0.014 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

h. PhCl: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.014 g, 0.020 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added PhCl (2.0 µL, 0.020 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

i. PhI: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.027 g, 0.037 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added PhI (4.1 µL, 0.037 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC.

6.4.44 Reaction of $Sc(L^D)_2CH_2CMe_3$ with MeI

To a solution of $Sc(L^D)_2CH_2CMe_3$ (0.015 g, 0.021 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added MeI (1.3 µL, 0.021 mmol) to afford a clear, colourless solution. The reaction mixture was heated to 80 ºC for 2 h. ^{1}H NMR spectroscopy indicated the formation of $Sc(L^D)_2I$.

6.4.45 Reaction of $Sc(CH_2SiMe_3)_3(L^{D, Li\{thf\}})$ with C-X

a. Ph_3CCl: To a solution of $Sc(CH_2SiMe_3)_3(L^{D, Li\{thf\}})$ (0.11 g, 0.16 mmol) in toluene (2 mL) was added a solution of Ph_3CCl (0.045 g 0.16 mmol) in toluene (0.5 mL) to afford a pale orange solution immediately. The reaction mixture was allowed to stir for 1 h during which time a white precipitate formed. The solution was filtered off and the precipitate was washed with toluene (3 x 1 mL). The combined washings were dried *in vacuo* to afford an orange solid. ^{1}H NMR spectral analysis showed this to be a combination of $Sc(L^D)(CH_2SiMe_3)_2$ and $Ph_3CCH_2SiMe_3$. ^{1}H NMR (C_6D_6, 400 MHz): 7.32 – 7.30 and 7.15 –

6.86 (overlapping m, C_6H_4), -0.8 (2 H, s, $C\underline{H}_2SiMe_3$), -0.21 ($CH_2Si\underline{Me}_3$) ppm. EI-MS: *m/z*: 330.2 $[M]^+$ (25 %), 315.2 $[M\text{-}Me]^+$ (6 %), 243.1 $[M\text{-}CH_2SiMe_3]^+$ (100 %).

b. ^{i}PrCl: To a solution of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (0.026 g, 0.037 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^{i}PrCl (3.4 µL, 0.037 mmol) to afford a clear, pale yellow solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature. On heating to 80 ºC for 2 h, unreacted ^{i}PrCl, free thf and 3 equivalents of $SiMe_4$ were observed alongside some broad resonances in the range 2.0 – 0.5 ppm.

c. ^{i}PrI: To a solution of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (0.018 g, 0.027 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^{i}PrI (2.7 µL, 0.027 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

d. ^{t}BuI: To a solution of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (0.035 g, 0.051 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added ^{t}BuI (6.2 µL, 0.051 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature. On heating to 80 ºC the solution became orange in colour and a small amount of white precipitate was formed. The solution was shown to contain unreacted ^{t}BuI, free thf and $SiMe_4$. The ^{1}H NMR spectrum also contained some broad resonances in the range 2.5 – 0.5 ppm.

e. BnBr: To a solution of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (0.014 g, 0.020 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added BnBr (2,4 µL, 0.020 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed free thf, $SiMe_4$ and broad resonances in the range 4.0 – 0.5 ppm.

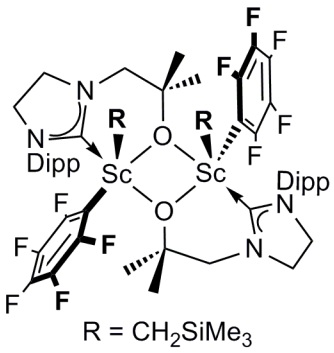
f. PhCl: To a solution of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (0.023 g, 0.034 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added PhCl (3.4 µL, 0.034 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

g. PhI: To a solution of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (0.021 g, 0.031 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added PhI (3.4 µL, 0.031 mmol) to afford a clear, colourless solution. After 24 h, ^{1}H NMR spectroscopy showed unreacted $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$, free thf, $SiMe_4$ and some broad resonances in the range 2.0 – -0.5 ppm.

6.4.46 Reaction of $Sc(L^D)_2CH_2SiMe_3$ with (*B*-I)-9-BBN

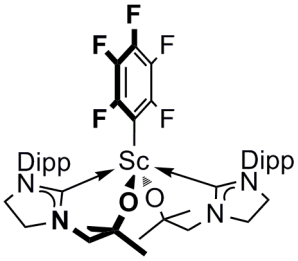
To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.055 g, 0.075 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added (*B*-I)-9-BBN (75 µL, 0.075 mmol) to afford a clear, pale yellow solution. Over the course of 16 h the reaction was monitored by ^{1}H NMR spectroscopy and the formation of $Sc(L^D)_2I$ and BBN-CH_2SiMe_3 was observed.^{1}H NMR (C_6D_6, 500 MHz): 0.09 (9 H, s, $CH_2Si\underline{Me}_3$), 0.00 (2 H, s, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 500 MHz): 1.4 ($CH_2Si\underline{Me}_3$), 0.0 ($\underline{C}H_2SiMe_3$) ppm.

6.4.47 Reaction of $Sc(L^D)(CH_2SiMe_3)_2$ with C_6F_5I



To a solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.021 g, 0.040 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added C_6F_5I (5.3 µL, 0.040 mmol) to afford a clear, colourless solution. Recrystallisation from toluene at -20 ºC afforded diffraction quality crystals of $[Sc(L^D)(CH_2SiMe_3)Ar^F]_2$. ^{1}H NMR ($C_6D_6$, 400 MHz): 7.00 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.86 and 6.81 (1 H each, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 4.34 (1 H, d, $^3J_{HH}$ = 15 Hz, $OCMe_2CH_2$), 3.32 – 2.62 (6 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.32 (1 H, d, $^3J_{HH}$ = 15 Hz, $OCMe_2CH_2$), 1.55 1.42 0.94 and 0.84 (3 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) ppm.

6.4.48 Synthesis of $Sc(L^D)_2Ar^F$



$Sc(L^D)_2CH_2SiMe_3$ (0.15 g, 0.21 mmol) and C_6F_5I (27.6 µL, 0.21 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. Immediately a colourless solid precipitated from the reaction mixture. This solid was washed with hexanes (3 x 1 mL) and the volatiles were removed *in vacuo* to afford $Sc(L^D)_2Ar^F$ as a colourless solid. Yield: 0.15 g (86 %). Diffraction-quality crystals were grown from a toluene solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 7.18 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.13 and 6.92 (2 H each, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 2,6-C_6H_3) , 3.41 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.25 – 2.91 (12 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.80 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.63 (6 H, s, CMe_2), 1.60 and 1.16 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.11 (6 H, s, CMe_2), 0.99 and 0.94 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 215.3 (NCN), 147.4 (3,5-C_6H_3), 146.9 (1-C_6H_3), 137.7 (4-C_6H_3), 124.4 and 123.7 (2,6-C_6H_3), 73.6 ($\underline{C}Me_2$), 62.5 ($OCMe_2\underline{C}H_2$), 53.0 and 52.8 (NCH_2CH_2N), 28.6 ($H\underline{C}Me_2$), 28.2 ($C\underline{Me}_2$), 28.1

(H<u>C</u>Me$_2$), 26.0, 25.5, 24.9 and 23.1 (HC<u>Me</u>$_2$) ppm. Anal. Found (calcd for $C_{44}H_{58}F_5N_4O_2Sc$): C, 64.70 (64.85); H, 7.07 (7.17); N, 6.78 (6.88).

6.4.49 Reaction of Y(L^D)$_2$CH$_2$SiMe$_3$ with E-H

a. $PhSiH_3$: To a solution of Y(L^D)$_2$CH$_2$SiMe$_3$ (0.018 g, 0.022 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $PhSiH_3$ (2.8 µL, 0.022 mmol) to afford a clear, pale yellow solution. The ^{1}H NMR spectrum indicated full consumption of $PhSiH_3$ and resonances associated with Y(L^D)$_2$CH$_2$SiMe$_3$, some broad resonances between 3.50 - 2.50 and 1.75 - 1.00 and two addition triplets at 4.58 and -0.08 (2 H, t, J_{HH} = 5 Hz) which show only mutual coupling in a ^{1}H-^{1}H COSY spectrum. Addition of a second equivalent of $PhSiH_3$ (2.8 µL, 0.022 mmol) resulted only in decomposition of Y(L^D)$_2$CH$_2$SiMe$_3$.

b. 1,1-Me$_2$-Si-(CH$_2$)$_3$: To a solution of Y(L^D)$_2$CH$_2$SiMe$_3$ (0.012 g, 0.016 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added 1,1-Me$_2$-Si-(CH$_2$)$_3$ (2.0 µL, 0.016 mmol) to afford a clear, colourless solution. The ^{1}H NMR spectrum indicated that no reaction had taken place at room temperature or on heating at 80 ºC.

6.4.50 Reaction of Sc(L^D)$_2$CH$_2$SiMe$_3$ with E-H

a. CH_4: To a freeze-pump-thaw degassed solution of Sc(L^D)$_2$CH$_2$SiMe$_3$ (0.014 g, 0.019 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added CH_4 (1 atm) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

b. Ph_3CH: Sc(L^D)$_2$CH$_2$SiMe$_3$ (0.011 g, 0.015 mmol) and Ph_3CH (0.0037 g, 0.015 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

c. C_6F_5H: Sc(L^D)$_2$CH$_2$SiMe$_3$ (0.010 g, 0.014 mmol) and C_6F_5H (1.6 µL, 0.014 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC.

d. PhCCH: To a solution of Sc(L^D)$_2$CH$_2$SiMe$_3$ (0.012 g, 0.016 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added PhCCH (1.8 µL, 0.016 mmol) to afford a clear, pale yellow solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

d. $^{n}Bu_3SnH$: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.011 g, 0.015 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $^{n}Bu_3SnH$ (4.1 µL, 0.015 mmol) to afford a clear, colourless solution. ^1H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

e. $H_2CCHSiMe_3$: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.019 g, 0.026 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $H_2CCHSiMe_3$ (3.7 µL, 0.026 mmol) to afford a clear, colourless solution. ^1H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

f. $PhSiH_3$: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.021 g, 0.029 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $PhSiH_3$ (3.6 µL, 0.029 mmol) to afford a clear, pale yellow solution. The ^1H NMR spectrum indicated full consumption of $PhSiH_3$ and resonances associated with $Sc(L^D)_2CH_2SiMe_3$, some broad resonances between 3.50 – 2.50 and 1.75 – 1.00 and two addition triplets at 4.58 and -0.08 (2 H, t, J_{HH} = 5 Hz) which show coupling only to each other in a COSY spectrum. Addition of a second equivalent of $PhSiH_3$ (3.6 µL, 0.029 mmol) resulted in no further reaction at room temperature or on heating to 80 ºC for 16 h.

g. Ph_2SiH_2: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.025 g, 0.034 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added Ph_2SiH_2 (6.3 µL, 0.034 mmol) to afford a clear, colourless solution. ^1H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

6.4.51 Reaction of $Sc(L^D)_2CH_2SiMe_3$ with E-E'

a. PhSSPh: $Sc(L^D)_2CH_2SiMe_3$ (0.20 g, 0.28 mmol) and PhSSPh (0.060 g, 0.28 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a deep orange solution. The reaction mixture was stored for 16 h after with time the ^1H NMR spectrum indicated the presence of a single compound with resonances and integration matching those in .4.31.1a.

In a separate reaction, $Sc(L^D)_2CH_2SiMe_3$ (0.010 g, 0.014 mmol) and PhSSPh (0.015 g, 0.0070 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a pale yellow solution. The ^1H NMR spectrum indicated a single new compound. ^1H NMR (C_6D_6, 400 MHz): 7.24 (2 H, t, $^3J_{HH}$ = 8 Hz), 7.18 and 7.13 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.01 (1 H, d, $^3J_{HH}$ = 8 Hz), 3.86 (2 H, d, $^3J_{HH}$ = 13 Hz), 3.67 (2 H, sept , $^3J_{HH}$ = 7 Hz), 2.49 (2 H, d, $^3J_{HH}$ = 13 Hz), 3.31 – 2.27 (10 H, overlapping m), 2.11 (2 H, s),

1.75 1.56 1.21 and 1.17 (6 H each, d, $^3J_{HH}$ = 7 Hz), 0.93 (6 H, s), 0.47 (6 H, s), 0.09 (9 H, s) ppm.

b. B_2pin_2: $Sc(L^D)_2CH_2SiMe_3$ (0.0098 g, 0.013 mmol) and B_2pin_2 (0.0031 g, 0.013 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated no reaction at room temperature or on heating to 80 ºC for 16 h.

c. B_2cat_2: $Sc(L^D)_2CH_2SiMe_3$ (0.010 g, 0.014 mmol) and B_2cat_2 (0.0034 g, 0.014 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, pale yellow solution. ^{1}H NMR spectroscopy indicated the presence of $Sc(L^D)_2CH_2SiMe_3$ and several new resonances which could not be assigned.

d. $Et_3GeGeEt_3$: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.013 g, 0.017 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Et_3GeGeEt_3$ (4.9 µL, 0.017 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 90 ºC for 16 h.

e. $Me_3SnSnMe_3$: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.012 g, 0.017 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Me_3SnSnMe_3$ (3.4 µL, 0.017 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 90 ºC for 16 h.

f. $Me_2PhSiB(OCMe_2CMe_2O)$: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.022 g, 0.030 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $Me_2PhSiB(OCMe_2CMe_2O)$ (8.3 µL, 0.030 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

g. 1,1-Me_2-Si-$(CH_2)_3$: To a solution of $Sc(L^D)_2CH_2SiMe_3$ (0.019 g, 0.025 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added 1,1-Me_2-Si-$(CH_2)_3$ (3.2 µL, 0.025 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature or on heating at 80 ºC for 16 h.

6.4.52 Reaction of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ with H_2

To a freeze-pump-thaw degassed solution of $Sc(CH_2SiMe_3)_3(L^{D,\ Li\{thf\}})$ (0.24 g, 0.35 mmol) in toluene (10 mL) was added H_2 (1 atm) and heated to 80 ºC for 14 h to afford an glassy, orange solid. ^{1}H NMR spectroscopy indicated free thf, $SiMe_4$, and new resonances

between 7.5 – -0.5 ppm which could not be assigned. Attempted recrystallisation from toluene at -20 ºC did not yield a pure product.

6.4.53 Attempted synthesis of $Y(L^D)H_2$

To a freeze-pump-thaw degassed solution of $Y(L^D)(CH_2SiMe_3)_2$ (0.013 g, 0.022 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added H_2 to afford a clear, colourless solution. Over the course of 4 days, ^{1}H NMR spectroscopy showed that $Y(L^D)(CH_2SiMe_3)_2$ was fully consumed and contained new resonances which could not be assigned.

6.4.54 Attempted synthesis of $Sc(L^D)H_2$

To a freeze-pump-thaw degassed solution of $Sc(L^D)(CH_2SiMe_3)_2$ (0.010 g, 0.019 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added H_2 to afford a clear, colourless solution. Over the course of 3 days, ^{1}H NMR spectroscopy showed that unreacted $Sc(L^D)(CH_2SiMe_3)_2$ remained and the appearance of some small new resonances which could not be assigned.

6.4.55 Attempted synthesis of $Y(L^D)_2H$

To a freeze-pump-thaw degassed solution of $Y(L^D)_2(CH_2SiMe_3)$ (0.0085 g, 0.011 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added H_2 to afford a clear, colourless solution. Over the course of 2 days, ^{1}H NMR spectroscopy showed that $Y(L^D)_2CH_2SiMe_3$ was fully consumed, 1 equivalent of $SiMe_4$ and 2 equivalents of HL^D were produced as well as the presence of a number of small resonances which could not be assigned.

6.4.56 Attempted synthesis of $Sc(L^D)_2H$

a. From $Sc(L^D)_2CH_2SiMe_3$ with H_2: To a freeze-pump-thaw degassed solution of $Sc(L^D)_2(CH_2SiMe_3)$ (0.011 g, 0.015 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added H_2 to afford a clear, colourless solution. ^{1}H NMR spectroscopy showed that no reaction had taken place at room temperature. On heating to 80 ºC, $SiMe_4$ was slowly produced as is consistent with heating $Sc(L^D)_2CH_2SiMe_3$ in the absence of H_2.

b. From $Sc(L^D)_2Cl$ with $^nBu_3SnH$: To a solution of $Sc(L^D)_2Cl$ (0.012 g, 0.017 mmol) in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube was added $^nBu_3SnH$ (4.6 µL, 0.017 mmol) to afford a clear, colourless solution. ^{1}H NMR spectroscopy indicated no reaction at room temperature after 16 h.

c. From $Sc(L^D)_2Cl$ with KH: $Sc(L^D)_2Cl$ (0.011 g, 0.016 mmol) and an excess of KH (0.015 g, 0.38 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. ^1H NMR spectroscopy indicated that no reaction had taken place at room temperature or on heating to 80 ºC for 16 h.

6.4.57 Attempted synthesis of $[Y(L^D)CH_2SiMe_3][X]$

a. $Y(L^D)_2CH_2SiMe_3$ with $BAr^F{}_3$: $Y(L^D)(CH_2SiMe_3)_2$ (0.013 g, 0.023 mmol) and $BAr^F{}_3$ (0.012 g, 0.023 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a white precipitate and clear, colourless solution immediately. The ^1H NMR spectrum indicated full consumption of the starting material and new resonances across the spectral width which could not be assigned.

b. $Y(L^D)_2CH_2SiMe_3$ with $[NEt_3H][BPh_4]$: $Y(L^D)(CH_2SiMe_3)_2$ (0.011 g, 0.020 mmol) and $[NEt_3H][BPh_4]$ (0.0083 g, 0.020 mmol) were combined in C_6D_6 to afford a yellow solution and a tacky solid. The ^1H NMR spectrum only indicated the presence of $[NEt_3H][BPh_4]$ and broad resonances across a diamagnetic sweep width which could not be assigned.

6.4.58 Attempted synthesis of $[Sc(L^D)_2][X]$

a. $Sc(L^D)_2CH_2SiMe_3$ with BPh_3: $Sc(L^D)_2CH_2SiMe_3$ (0.0075 g, 0.010 mmol) and BPh_3 (0.0025 g, 0.010 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. After 4 days, the ^1H NMR spectrum indicated the presence of $Sc(L^D)_2CH_2SiMe_3$ as the major product but also several new resonances which could not be assigned.

b. $Sc(L^D)_2CH_2SiMe_3$ with $BAr^F{}_3$: $Sc(L^D)_2CH_2SiMe_3$ (0.055 g, 0.0075 mmol) and $BAr^F{}_3$ (0.0038 g, 0.0075 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a clear, colourless solution. The ^1H NMR indicated unreacted starting material, $Sc(L^D)_2CH_2SiMe_3$ and also decomposition into HL^D and $SiMe_4$.

c. $Sc(L^D)_2CH_2SiMe_3$ with $[NEt_3H][BPh_4]$: $Sc(L^D)_2CH_2SiMe_3$ (0.015 g, 0.020 mmol) and $[NEt_3H][BPh_4]$ (0.0086 g, 0.020 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. The ^1H NMR spectrum indicated that no reaction had taken place at room temperature of on heating to 80 ºC.

d. $Sc(L^D)_2CH_2SiMe_3$ with $[Ph_3C][BAr^F{}_4]$: $Sc(L^D)_2CH_2SiMe_3$ (0.024 g, 0.032 mmol) and $[Ph_3C][BAr^F{}_4]$ (0.039 g, 0.032 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a pale pink solution. After 16 h, the ^1H NMR indicated the

full consumption of $Sc(L^D)(CH_2SiMe_3)_2$ and the presence of several small resonances which could not be assigned.

e. $Sc(L^D)_2Cl$ with BAr^F_3: $Sc(L^D)_2Cl$ (0.011 g, 0.015 mmol) and BAr^F_3 (0.0079 g, 0.015 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. Sonication for 5 minutes afforded a clear, colourless solution. The ^1H NMR spectrum indicated full consumption of $Sc(L^D)_2Cl$ and very broad resonances which could not be assigned.

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X-ray crystallography tables

	$[H_2L^D]Cl$	$Zn(L^D)N''$	$Y(L^D)N''_2$
Chemical formula	$C_{19}H_{31}ClN_2O{\cdot}H_{1.2}O_{0.6}$	$C_{25}H_{47}N_3OSi_2Zn$	$C_{31}H_{65}N_4OSi_4Y$
M_r	349.72	527.21	711.14
Crystal system, space group	Monoclinic, *P*21/*c*	Monoclinic, *P*21/*n*	Monoclinic *P*21/*c*
Temperature (K)	150	150	150
a, *b*, *c* (Å)	11.9968(3),11.2624 (3), 14.8437(4)	11.2450(4), 11.7949 (5), 23.0602(8)	20.3348(16), 10.6423 (9), 20.1193(16)
α, β, γ (°)	90.000(0), 94.715(2), 90.000(0)	90.000(0), 101.339(1), 90.000(0)	90.000(0), 112.017(4), 90.000(0)
V (Å^3)	1998.79(9)	2998.9(2)	4036.5(6)
Z	4	4	4
μ (mm^{-1})	0.20	0.92	1.59
Crystal shape and colour	Colourless slab	Colourless block	Colourless block
Crystal size (mm)	0.40 × 0.20 × 0.17	0.30 × 0.30 × 0.25	0.83 x 0.57 x 0.10
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
Diffractometer	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector
Scan method	ω scans	ω scans	ω and φ scans
Absorption correction	Multi-scan SADABS	Multi-scan SADABS	Multi-scan SADABS
θ_{max}, θ_{min} (°)	29.7, 2.3	30.5, 1.8	30.6, 2.0
T_{min}, T_{max}	0.634, 0.746	0.701, 0.795	0.512, 0.746
Number of measured, independent and observed [I > 2s(I)] reflections	20598, 5212, 4360	30818, 8688, 7357	69743, 12185, 8188
R_{int}	0.042	0.034	0.091
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.081, 0.173, 1.19	0.055, 0.116, 1.20	0.049, 0.119, 1.06
Number of reflections	5212	8688	12185
Number of parameters	232	301	378
Number of restraints	2	0	0
H atom treatment	Mixture of constrained and independent refinement	Riding	Riding
$(\Delta/\sigma)_{max}$	< 0.001	0.001	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.40, -0.36	0.59, -0.35	0.95, -0.63

	Sc(L^D)N"$_2$	**U(L^D)N"$_2$**	**Ce(L^D)$_2$N"**
Chemical formula	$C_{31}H_{65}N_4OScSi_4$	$C_{31}H_{56}N_4OSi_4U$	$C_{47}H_{79}CeN_5O_2Si_2$
M_r	667.19	851.19	942.45
Crystal system, space group	Monoclinic, *P*21/*c*	Monoclinic, *P*12/*c*	Monoclinic, *P*21/*c*
Temperature (K)	170	150	150
a, *b*, *c* (Å)	20.4267(8), 10.5731 (3), 20.3496(7)	20.3248(10), 10.7829 (5), 19.9568(9)	19.9366(6), 12.7554 (4), 20.3716(6)
α, β, γ (º)	90.000(0), 114.147(4), 90.000(0)	90.000(0),110.601(2), 90.000(0)	90.000(0), 92.147(2), 90.000(0)
V (Å^3)	4010.4(2)	4094.1(3)	5176.8(3)
Z	4	4	4
μ (mm^{-1})	0.33	4.11	0.96
Crystal shape and colour	Colourless block	Dark blue block	Yellow shard
Crystal size (mm)	0.42 × 0.32 × 0.15	0.43 × 0.42 × 0.18	0.38 × 0.25 × 0.25
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
Diffractometer	Xcalibur, Eos	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector
Scan method	ω scans	ω and φ scans	ω and φ scans
Absorption correction	Multi-scan SCALE3 ABSPACK	Multi-scan *SADABS*	Multi-scan *SADABS*
θ_{max}, θ_{min} (°)	29.2, 2.9	29.6, 2.1	30.0, 1.9
T_{min}, T_{max}	0.985, 1.000	0.473, 0.746	0.609, 0.746
Number of measured, independent and observed [I > 2s(I)] reflections	27548, 9419, 5859	45592, 10643, 8900	66609, 14500, 11504
R_{int}	0.026	0.036	0.061
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.081, 0.87	0.034, 0.081, 1.07	0.046, 0.097, 1.10
Number of reflections	9419	10643	14500
Number of parameters	388	371	547
Number of restraints	0	0	48
H atom treatment	Riding	Riding	Riding
$(\Delta/\sigma)_{max}$	0.001	0.002	< 0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.76, −0.27	1.96, −0.87	1.38, −0.70

	Ce(L^D)N"$_2$Cl	**U(L^D)N"$_2$Cl**	**U(L^D)N"$_2$F**
Chemical formula	$C_{31}H_{65}CeClN_4OSi_4 \cdot C_7H_8$	$C_{31}H_{65}ClN_4OSi_4U$ C_7H_8	$C_{31}H_{65}FN_4OSi_4U$
M_r	889.93	987.84	879.26
Crystal system, space group	Monoclinic, *P*21/*n*	Monoclinic, *P*21/*n*	Monoclinic, *C*12/*c*
Temperature (K)	150	150	150
a, *b*, *c* (Å)	13.8020(4), 23.2055(6), 15.9418(4)	13.7930(4),23.2320 (7), 16.0212(5)	37.6889(9), 10.7517 (2), 20.6617(5)
α, β, γ (°)	90.000(0), 112.297(1), 90.000(0)	90.000(0), 112.169(1), 90.000(0)	90.000(0), 94.454(1), 90.000(0)
V (Å^3)	4724.1(2)	4754.3(2)	8347.2(3)
Z	4	4	8
μ (mm^{-1})	1.15	3.60	4.04
Crystal shape and colour	Dark red block	Brown block	Pale red block
Crystal size (mm)	0.48 × 0.25 × 0.15	0.39 × 0.38 × 0.32	0.56 × 0.38 × 0.21
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
Diffractometer	Bruker *SMART APEX* CCD area detector	Bruker SMART APEX CCD area detector	Bruker *SMART APEX* CCD area detector
Scan method	ω and φ scans	ω and φ scans	ω scans
Absorption correction	Multi-scan *SADABS*	Multi-scan SADABS	Multi-scan *SADABS*
θ_{max}, θ_{min} (°)	26.4, 2.2	26.4, 1.6	26.4, 1.1
T_{min}, T_{max}	0.677, 0.842	0.564, 0.745	0.252, 0.429
Number of measured, independent and observed [I > 2s(I)] reflections	34220, 9609, 8221	86378, 9712, 8578	44067, 8562, 7494
R_{int}	0.044	0.049	0.057
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.079, 1.02	0.021, 0.050, 1.03	0.046, 0.099, 1.22
Number of reflections	9609	9712	8562
Number of parameters	461	461	397
Number of restraints	0	0	0
H atom treatment	Riding	Riding	Riding
$(\Delta/\sigma)_{max}$	0.028	0.005	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.87, -0.42	0.91, -0.73	2.53, -2.51

	Y($L^{D, SiMe_3}$)N"$_2$I	**Ce($L^{D, SiMe_3}$)N"$_2$I**	**U($L^{D, SiMe_3}$)N"$_2$I**
Chemical formula	$C_{34}H_{74}IN_4OSi_5Y$	$C_{34}H_{74}CeIN_4OSi_5$	$C_{34}H_{74}IN_4OSi_5U$
M_r	911.23	962.44	1060.35
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1
Temperature (K)	150	150	150
a, *b*, *c* (Å)	9.6227(8), 16.3315 (13),16.4128(14)	9.7094(2), 16.4010 (4), 16.4221(4)	9.6898(2), 16.4169 (4), 16.4228(4)
α, β, γ (°)	106.924(4), 94.311(4), 106.275(4)	106.650(1), 94.867(1), 106.296(1)	106.812(1), 94.571(1), 106.326(1)
V (Å^3)	2334.0(3)	2365.67(10)	2362.84(13)
Z	2	2	2
μ (mm^{-1})	2.07	1.77	4.24
Crystal shape and colour	Colourless shard	Colourless shard	Dark red plate
Crystal size (mm)	0.54 × 0.44 × 0.30	0.50 × 0.38 × 0.28	0.62 × 0.42 × 0.16
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
Diffractometer	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector
Scan method	ω and φ scans	ω and φ scans	ω and φ scans
Absorption correction	Multi-scan *SADABS*	Multi-scan *SADABS*	Multi-scan *SADABS*
θ_{max}, θ_{min} (°)	30.6, 1.3	30.0, 2.2	3.05, 2.2
T_{min}, T_{max}	0.421, 0.538	0.507, 0.610	0.151, 0.507
Number of measured, independent and observed [I > 2s(I)] reflections	41184, 12734, 10822	42729, 12559, 11400	39450, 13201, 12222
R_{int}	0.029	0.035	0.046
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.073, 1.04	0.034, 0.073, 1.14	0.047, 0.098, 1.21
Number of reflections	12734	12559	13201
Number of parameters	436	436	436
Number of restraints	0	0	0
H atom treatment	Riding	Riding	Riding
$(\Delta/\sigma)_{max}$	0.007	0.003	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.76, -0.57	1.08, −0.53	2.74, −1.47

	Ce($L^{D, SiMe_3}$)N"$_2$(N_3)	**U(L^D)$_2$$I_2$**	**Y(L^{D, AdN_3})N"$_2$**
Chemical formula	$C_{68}H_{148}Ce_2N_{14}O_2Si_{10}$ 4(C_6H_6)	$C_{38}H_{58}I_2N_4O_2U$	$C_{41}YH_{80}N_7OSi_4$
M_r	2067.58	1094.71	-
Crystal system, space group	Triclinic, *P*-1	Monoclinic, *P*21/*n*	Triclinic, *P*-1
Temperature (K)	150	150	150
a, *b*, *c* (Å)	13.7100(6), 14.9679 (7), 14.9982(7)	9.2758(2), 12.5624 (3), 17.6005(3)	11.9338(17),17.9680 (25), 23.4500(34)
α, β, γ (º)	88.187(3), 81.333(2), 72.347(2)	90.000(0), 90.212(1), 90.000(0)	89.564(10), 89.214(9), 83.793(9)
V (Å^3)	2899.0(2)	2050.91(7)	4998.26(51)
Z	1	2	-
μ (mm^{-1})	0.93	5.50	-
Crystal shape and colour	Pale yellow shard	Pink prism	Colourless block
Crystal size (mm)	0.43 × 0.33 × 0.31	0.52 × 0.30 × 0.18	0.38 x 0.28 x 0.27
Radiation type	Mo *K*α	Mo *K*α	Mo Kα
Diffractometer	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector	Bruker SMART APEX CCD area detector
Scan method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan *SADABS*	Multi-scan *SADABS*	Multi-scan SADABS
θ_{max}, θ_{min} (°)	30.6, 1.4	30.5, 2.0	-
T_{min}, T_{max}	0.621, 0.746	0.241, 0.372	-
Number of measured, independent and observed [I > 2s(I)] reflections	58812, 16821, 14932	20792, 6091, 5478	-
R_{int}	0.042	0.033	-
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.107, 1.18	0.040, 0.089, 1.16	-
Number of reflections	16821	6091	-
Number of parameters	538	220	-
Number of restraints	0	0	-
H atom treatment	Riding	Riding	-
$(\Delta/\sigma)_{max}$	0.001	< 0.001	-
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	2.11, −0.70	2.63, −0.96	-

	Ce(L^{D, AdN_3})N"$_2$	**U(L^{D})N"$_2$(=NSiMe$_3$)**	**U(L^{D})N"$_2$(=NAd)**
Chemical formula	$C_{41}H_{80}CeN_7OSi_4$	$C_{34}H_{74}N_5OSi_5U$	$C_{89}H_{168}N_{10}O_2Si_8U_2$
M_r	939.60	947.46	2111.11
Crystal system, space group	Monoclinic, *P*21/*n*	Monoclinic, *P*21/*n*	Triclinic, *P*-1
Temperature (K)	150	150	150
a, *b*, *c* (Å)	12.5342(7), 65.014 (3), 21.5322(10)	11.8096(9), 21.9206 (17), 17.4680(14)	11.5081(7), 21.3715 (13), 23.6184(13)
α, β, γ (°)	90.000(0),103.097 (3), 90.000(0)	90.000(0), 93.961(1), 90.000(0)	114.089(4), 90.789 (4), 103.405(4)
V (Å^3)	17090.2(15)	4511.2(6)	5119.9(5)
Z	12	4	2
μ (mm^{-1})	0.92	3.76	3.30
Crystal shape and colour	Orange block	Red block	Brown block
Crystal size (mm)	0.58 × 0.55 × 0.35	0.36 × 0.29 × 0.16	0.47 x0.42 x 0.33
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
Diffractometer	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector
Scan method	ω and φ scans	ω and φ scans	ω and φ scans
Absorption correction	Multi-scan *SADABS*	Multi-scan *SADABS*	Multi-scan *SADABS*
θ_{max}, θ_{min} (°)	28.4, 1.0	26.4, 1.9	29.8, 1.8
T_{min}, T_{max}	0.77, 1.00	0.383, 0.548	0.3314, 0.4324
Number of measured, independent and observed [I > 2s(I)] reflections	174994, 41020, 27941	36740, 9236, 7610	89929, 26643, 22650
R_{int}	0.059	0.053	0.029
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.095, 0.082, 1.10	0.039, 0.099, 1.08	0.025, 0.059, 1.04
Number of reflections	27941	9236	26643
Number of parameters	1458	436	1037
Number of restraints	330	0	0
H atom treatment	-	Riding	Riding
$(\Delta/\sigma)_{max}$	0.009	0.003	0.004
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	2.48, −4.32	2.72, -1.89	1.18, −0.54

	U(L^D)N"$_2$(N=CPh$_2$)	**U(L^D)N"(OC{CH$_2$}SiMe$_2$N{SiMe$_3$})**	**N"$_3$UOC≡COUN"$_3$**
Chemical formula	$C_{44}H_{75}N_5OSi_4U$ 0.5(C_6H_6)	$C_{32}H_{65}N_4O_2Si_4U$	$C_{38}H_{108}N_6O_2Si_{12}U_2$·3($C_6H_6$)
M_r	1079.53	888.27	1728.77
Crystal system, space group	Monoclinic, *P*21/*n*	Triclinic, *P*-1	Triclinic, *P*-1
Temperature (K)	150	150	150
a, *b*, *c* (Å)	13.329(4), 21.293(7), 18.742 (6)	10.5064(2), 12.1604 (3), 19.8038(4)	11.0022(5), 11.7354(6), 18.0634(10)
α, β, γ (°)	90.000(0), 97.586 (19), 90.000(0)	74.810(1), 77.868(1), 86.530(1)	90.254(3), 94.779(3), 117.609(3)
V (Å^3)	5272.76(3)	2387.20(9)	2057.05(18)
Z	4	2	1
μ (mm^{-1})	3.21	3.53	4.14
Crystal shape and colour	Red block	Brown plate	Gold block
Crystal size (mm)	0.26 x 0.10 x 0.06	0.32 x 0.22 x 0.14	0.39 × 0.17 × 0.13
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
Diffractometer	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector
Scan method	ω and φ scans	ω and φ scans	ω scans
Absorption correction	Multi-scan *SADABS*	Multi-scan *SADABS*	Multi-scan *SADABS*
θ_{max}, θ_{min} (°)	26.4, 1.8	30.5, 1.7	27.5, 1.1
T_{min}, T_{max}	0.5837, 0.7454	0.3365, 0.4330	0.295, 0.615
Number of measured, independent and observed [I > 2s(I)] reflections	67958, 10820, 9337	39388, 13332, 12491	24088, 9326, 8936
R_{int}	0.067	0.039	0.026
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.042, 0.102, 1.04	0.057, 0.165, 1.57	0.030, 0.067, 1.20
Number of reflections	10820	13332	9326
Number of parameters	541	405	370
Number of restraints	0	0	0
H atom treatment	Riding	Riding	Riding
$(\Delta/\sigma)_{max}$	<0.001	0.001	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	2.89, −1.11	4.90, −1.89	2.24, −0.93

	N"$_3$UOC=C(H)OU (N{SiMe$_2$CH$_2$}{SiMe$_3$})N"$_2$: N"$_3$UOC≡COUN"$_3$	**CeBn'$_3$**	**ScBn'$_3$**
Chemical formula	$C_{57}H_{162}N_9O_3Si_{18}U_3$	$C_{27}H_{36}CeN_3$	$C_{27}H_{36}N_3Sc$
M_r	2241.67	542.71	447.55
Crystal system, space group	Monoclinic, *P*21/*c*	Monoclinic, *P*21/*c*	Monoclinic, *P*21/*c*
Temperature (K)	170	150	170
a, *b*, *c* (Å)	30.0251(6), 15.6531(3), 22.4759(4)	16.6628(4), 9.4465(2), 17.0461(4)	14.2300(2), 12.3352 (2), 13.8001(2)
α, β, γ (º)	90.000(0), 103.691(2), 90.000(0)	90.000(0), 110.332(1), 90.000(0)	90.000(0), 94.168(2), 90.000(0)
V (Å^3)	10263.2(3)	2515.97 (10)	2415.92(6)
Z	4	4	4
μ (mm^{-1})	4.97	1.83	0.32
Crystal shape and colour	Gold block	Orange plate	Orange block
Crystal size (mm)	0.22 × 0.16 × 0.14	0.45 × 0.40 × 0.17	0.14 × 0.10 × 0.07
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
Diffractometer	Xcalibur, Eos	Bruker *SMART APEX* CCD area detector	Xcalibur, Eos
Scan method	ω scans	ω and φ scans	ω scans
Absorption correction	Multi-scan SCALE3 ABSPACK	Multi-scan *SADABS*	Multi-scan SCALE3 ABSPACK
θ_{max}, θ_{min} (°)	27.5, 3.0	31.3, 2.4	29.2, 3.0
T_{min}, T_{max}	0.811, 1.000	0.556, 0.746	0.953, 1.000
Number of measured, independent and observed [I > 2s(I)] reflections	57493, 22833, 14064	60704, 7554, 6852	22280, 5797, 4035
R_{int}	0.032	0.033	0.024
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.065, 0.174, 1.09	0.025, 0.062, 1.09	0.031, 0.083, 0.91
Number of reflections	22833	7554	5797
Number of parameters	868	286	286
Number of restraints	1	0	0
H atom treatment	Mixture of constrained and independent refinement	Riding	Riding
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	8.40, −4.69	0.95, −0.74	0.30, −0.32

	Sc(L^D)Bn'$_2$	**Y(L^D)(CH_2SiMe_3)$_2$**	**Sc(L^D)(CH_2SiMe_3)$_2$**
Chemical formula	$C_{37}H_{53}N_4OSc$	$C_{54}H_{102}N_4O_2Si_4Y_2 \cdot C_7H_8$	$C_{54}H_{102}N_4O_2Sc_2Si_4$
M_r	614.79	1312.84	1041.68
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Monoclinic, *P*21/*c*
Temperature (K)	100	170	100
a, *b*, *c* (Å)	9.5340(3), 11.2810 (3), 18.2650(5)	10.3804 (4), 11.9357 (5), 16.3507 (6)	9.5128(1), 19.2311 (3), 19.6980(3)
α, β, γ (º)	104.578(2), 94.203(2), 114.173(3)	70.841 (4), 83.517 (3), 86.030 (3)	90.000(0), 97.888(1), 90.000(0)
V (Å^3)	1699.55(8)	1900.25 (13)	3569.49 (9)
Z	2	1	2
μ (mm^{-1})	2.10	1.15	2.53
Crystal shape and colour	Orange block	Colourless block	Colourless block
Crystal size (mm)	0.14 × 0.08 × 0.04	0.23 x 0.18 x 0.11	0.11 × 0.08 × 0.04
Radiation type	Cu *K*α	Mo *K*α	Cu *K*α
Diffractometer	SuperNova, Dual, Cu at zero, Atlas	Xcalibur, Eos	SuperNova, Dual, Cu at zero, Atlas
Scan method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan SCALE3 ABSPACK	Multi-scan SCALE3 ABSPACK	Multi-scan SCALE3 ABSPACK
θ_{max}, θ_{min} (°)	73.3, 2.6	29.1, 3.1	73.3, 3.2
T_{min}, T_{max}	0.757, 0.921	0.803, 1.000	0.944, 1.000
Number of measured, independent and observed [I > 2s(I)] reflections	24380, 6660, 4768	17026, 8681, 6411	23809, 6985, 5376
R_{int}	0.052	0.022	0.059
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.039, 0.097, 0.95	0.027, 0.060, 0.91	0.039, 0.091, 0.93
Number of reflections	6660	8681	6985
Number of parameters	398	385	310
Number of restraints	0	76	0
H atom treatment	Riding	Riding	Riding
$(\Delta/\sigma)_{max}$	0.001	0.002	< 0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.32, −0.33	0.30, -0.27	0.56, −0.24

	$Sc(CH_2SiMe_3)_3$ ($L^{D,Li\{thf\}}$)	**$Sc(L^D)_2CH_2SiMe_3$**	**$Sc(L^D)_2CH_2CMe_3$**
Chemical formula	$C_{35}H_{70}LiN_2O_2ScSi_3$	$C_{42}H_{69}N_4O_2ScSi$	$C_{43}H_{69}N_4O_2Sc$
M_r	687.10	-	-
Crystal system, space group	Orthorhombic, *Pbca*	Othorhombic *C*2*mm*	Tetragonal *P*41
Temperature (K)	150	170	100
a, *b*, *c* (Å)	10.1400(2), 22.3379(5), 38.2117(9)	22.9781(4), 34.2800(5), 22.9862(3)	16.1816(4), 16.1904(4), 33.4833(8)
α, β, γ (°)	90.000(0), 90.000(0), 90.000(0)	90.018(1), 91.055(1), 90.027(1)	89.958(2), 90.001(2), 90.013(2)
V (Å^3)	8655.2(3)	18102.9(5)	8772.2(4)
Z	8	-	-
μ (mm^{-1})	0.28	-	-
Crystal shape and colour	Colourless block	Colourless block	Colourless block
Crystal size (mm)	0.55 × 0.50 × 0.45	0.21 × 0.14 × 0.08	0.18 x 0.11 x 0.09
Radiation type	Mo *K*α	Mo *K*α	Cu *K*α
Diffractometer	Bruker *SMART APEX* CCD area detector	Xcalibur, Eos	SuperNova, Dual, Cu at zero, Atlas
Scan method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan *SADABS*	Multi-scan SCALE3 ABSPACK	Multi-scan SCALE3 ABSPACK
θ_{max}, θ_{min} (°)	28.9, 1.1	27.2, 3.0	75.9, 2.6
T_{min}, T_{max}	0.861, 0.884	0.972, 1.000	0.876, 1.000
Number of measured, independent and observed [I > 2s(I)] reflections	98382, 10956, 9564	-	-
R_{int}	0.064	-	-
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.079, 0.161, 1.28	-	-
Number of reflections	10956	-	-
Number of parameters	412	-	-
Number of restraints	0	-	-
H atom treatment	Riding	-	-
$(\Delta/\sigma)_{max}$	< 0.001	-	-
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.51, −0.42	-	-

	$[Ce(BH_4)_2(thf)_5]$ $[Ce(BH_4)_4(thf)_2]$	**$Sc(L^D)_2Cl$**	**$Sc(L^D)_2I$**
Chemical formula	$C_{20}H_{48}B_2CeO_5 \cdot C_8H_{32}B_4CeO_2$	$C_{38}H_{58}ClN_4O_2Sc$	$C_{38}H_{58}IN_4O_2Sc$
M_r	874.02	683.29	774.74
Crystal system, space group	Monoclinic C2/*c*	Monoclinic P*n*	Monoclinic C2/*c*
Temperature (K)	150	170	170
a, *b*, *c* (Å)	12.2372(6), 12.2516(6), 28.6898(13)	8.9058(1), 11.9061(2), 18.4358(3)	12.7783(8), 17.5588(10), 17.9912(18)
α, β, γ (º)	90.000(0), 98.122 (3), 90.000(0)	90.000(0), 91.217(1), 90.000(0)	90.000(0), 96.998(7), 90.000(0)
V (Å^3)	4258.2(4)	1954.37 (5)	4006.6 (5)
Z	4	2	4
μ (mm^{-1})	2.15	0.29	1.28
Crystal shape and colour	Colourless block	Colourless block	Colourless block
Crystal size (mm)	0.48 × 0.36 × 0.27	0.19 × 0.13 × 0.09	0.21 x 0.15 x 0.08
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
Diffractometer	Bruker *SMART APEX* CCD area detector	Xcalibur, Eos	Xcalibur, Eos
Scan method	ω and φ scans	ω scans	ω scans
Absorption correction	Multi-scan *SADABS*	Multi-scan SCALE3 ABSPACK	Multi-scan SCALE3 ABSPACK
θ_{max}, θ_{min} (°)	20.8, 2.4	29.2, 3.1	30.2, 2.9
T_{min}, T_{max}	0.599, 0.745	0.980, 1.000	0.935, 1.000
Number of measured, independent and observed [I > 2s(I)] reflections	25043, 2245, 2143	22125, 8848, 6534	25204, 5358, 3045
R_{int}	0.029	0.020	0.035
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.025, 0.072, 1.03	0.174, 0.397, 1.62	0.034, 0.078, 0.82
Number of reflections	2245	8848	5358
Number of parameters	197	427	215
Number of restraints	144	2	0
H atom treatment	Mixture of constrained and independent refinement	Riding	Riding
$(\Delta/\sigma)_{max}$	<0.001	0.011	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.29, −0.36	8.11, -0.75	0.85, -0.82

	[Sc(L^{D})(CH$_2$SiMe$_3$)(Ar^{F})]$_2$	**Sc(L^{D})$_2$Ar^{F}**
Chemical formula	$C_{58}H_{80}F_{10}N_4O2Sc_2Si_2$	$C_{44}H_{58}F_5N_4O_2Sc$
M_r	1201.35	814.90
Crystal system, space group	Monoclinic *P*21/*c*	Monoclinic, *C*12/*c*
Temperature (K)	170	100
a, *b*, *c* (Å)	18.8733(16), 15.7268(11), 27.333(2)	38.7236(16), 23.2484 (10), 20.6479(8)
α, β, γ (º)	90.000(0), 109.552(9), 90.000(0)	90.000(0), 110.141 (5), 90.000(0)
V (Å^3)	7645.1(9)	17451.8(12)
Z	10	16
μ (mm^{-1})	0.268	1.24
Crystal shape and colour	Colourless block	Colourless block
Crystal size (mm)	0.12 x 0.09 x 0.07	0.17 x 0.17 x 0.07
Radiation type	Mo *K*α	Cu *K*α
Diffractometer	Xcalibur, Eos	SuperNova, Dual, Cu at zero, Atlas
Scan method	ω scans	ω scans
Absorption correction	Multi-scan SCALE3 ABSPACK	Multi-scan SCALE3 ABSPACK
θ_{max}, θ_{min} (°)	29.3, 3.0	64.0, 2.3
T_{min}, T_{max}	0.62154, 1.0000	0.5715, 1.000
Number of measured, independent and observed [I > 2s(I)] reflections	49897, 17850, 6821	62621, 13666, 9691
R_{int}	0.089	0.059
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.128, 0.404, 1.14	0.103, 0.388, 1.59
Number of reflections	17850	13666
Number of parameters	721	1033
Number of restraints	0	0
H atom treatment	Riding	Riding
$(\Delta/\sigma)_{max}$	0.049	< 0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	1.58, −0.74	1.98, −1.14

X-ray crystallographic information files

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threshold expression of
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     C5 0.0268(12) 0.0265(13) 0.0358(14) -0.0060(11)
0.0009(10) 0.0050(10)
     C6 0.0280(13) 0.0332(14) 0.0495(17) -0.0132(12) -
0.0003(11) 0.0068(11)
     C7 0.0263(13) 0.0428(16) 0.0498(18) -0.0073(14) -
0.0061(12) 0.0020(12)
     C8 0.0283(14) 0.0346(16) 0.078(2) -0.0107(16)
0.0009(14) -0.0005(12)
     C9 0.050(2) 0.0346(19) 0.141(4) 0.011(2) 0.011(2)
0.0027(16)
     C10 0.0319(16) 0.068(2) 0.090(3) -0.031(2)
0.0005(17) -0.0075(16)
     N1 0.0236(10) 0.0313(12) 0.0368(12) -0.0034(9)
0.0008(8) 0.0022(8)
     N2 0.0241(9) 0.0201(10) 0.0279(10) 0.0005(8)
0.0030(8) 0.0024(8)
     O1 0.0355(11) 0.0422(12) 0.0622(14) 0.0011(11)
0.0026(10) -0.0013(10)
     O1W 0.115(5) 0.068(3) 0.045(3) -0.003(2) -0.016(3)
0.017(3)
     Cl1 0.0393(4) 0.0398(4) 0.0377(4) -0.0048(3)
0.0022(3) -0.0117(3)

     _geom_special_details
     ;
      All esds (except the esd in the dihedral angle
between two l.s. planes)
      are estimated using the full covariance matrix.
The cell esds are taken
      into account individually in the estimation of
esds in distances, angles
      and torsion angles; correlations between esds in
cell parameters are only
      used when they are defined by crystal symmetry.
An approximate (isotropic)
      treatment of cell esds is used for estimating esds
involving l.s. planes.
     ;

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      _geom_bond_atom_site_label_2
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C1 N1 1.305(3) . ?
C1 N2 1.317(3) . ?
C1 H3 0.9500 . ?
C21 C22 1.401(3) . ?
C21 C26 1.404(3) . ?
C21 N2 1.438(3) . ?
C22 C23 1.394(3) . ?
C22 C220 1.524(3) . ?
C23 C24 1.387(4) . ?
C23 H5 0.9500 . ?
C24 C25 1.380(4) . ?
C24 H4 0.9500 . ?
C25 C26 1.398(3) . ?
C25 H6 0.9500 . ?
C26 C260 1.512(3) . ?
C222 C220 1.529(4) . ?
C222 H19A 0.9800 . ?
C222 H19B 0.9800 . ?
C222 H19C 0.9800 . ?
C220 C221 1.529(4) . ?
C220 H17 1.0000 . ?
C221 H18A 0.9800 . ?
C221 H18B 0.9800 . ?
C221 H18C 0.9800 . ?
C261 C260 1.535(4) . ?
C261 H15A 0.9800 . ?
C261 H15B 0.9800 . ?
C261 H15C 0.9800 . ?
C260 C262 1.533(4) . ?
C260 H14 1.0000 . ?
C262 H16A 0.9800 . ?
C262 H16B 0.9800 . ?
C262 H16C 0.9800 . ?
C5 N2 1.481(3) . ?
C5 C6 1.527(3) . ?
C5 H2A 0.9900 . ?
C5 H2B 0.9900 . ?
C6 N1 1.479(3) . ?
C6 H1A 0.9900 . ?
C6 H1B 0.9900 . ?
C7 N1 1.472(3) . ?
C7 C8 1.531(4) . ?
C7 H10A 0.9900 . ?
C7 H10B 0.9900 . ?
C8 O1 1.445(4) . ?
C8 C9 1.510(5) . ?
C8 C10 1.533(4) . ?
C9 H13A 0.9800 . ?
C9 H13B 0.9800 . ?
C9 H13C 0.9800 . ?
C10 H12A 0.9800 . ?
```

```
C10 H12B 0.9800 . ?
C10 H12C 0.9800 . ?
O1 H1 0.8400 . ?
O1W H1W 0.86(2) . ?
O1W H2W 0.84(2) . ?

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N1 C1 N2 113.7(2) . . ?
N1 C1 H3 123.1 . . ?
N2 C1 H3 123.1 . . ?
C22 C21 C26 123.3(2) . . ?
C22 C21 N2 118.0(2) . . ?
C26 C21 N2 118.6(2) . . ?
C23 C22 C21 117.2(2) . . ?
C23 C22 C220 120.9(2) . . ?
C21 C22 C220 121.9(2) . . ?
C24 C23 C22 120.7(2) . . ?
C24 C23 H5 119.6 . . ?
C22 C23 H5 119.6 . . ?
C25 C24 C23 121.0(2) . . ?
C25 C24 H4 119.5 . . ?
C23 C24 H4 119.5 . . ?
C24 C25 C26 120.8(2) . . ?
C24 C25 H6 119.6 . . ?
C26 C25 H6 119.6 . . ?
C25 C26 C21 117.0(2) . . ?
C25 C26 C260 120.4(2) . . ?
C21 C26 C260 122.6(2) . . ?
C220 C222 H19A 109.5 . . ?
C220 C222 H19B 109.5 . . ?
H19A C222 H19B 109.5 . . ?
C220 C222 H19C 109.5 . . ?
H19A C222 H19C 109.5 . . ?
H19B C222 H19C 109.5 . . ?
C22 C220 C221 113.5(2) . . ?
C22 C220 C222 110.6(2) . . ?
C221 C220 C222 109.9(2) . . ?
C22 C220 H17 107.6 . . ?
C221 C220 H17 107.6 . . ?
C222 C220 H17 107.6 . . ?
C220 C221 H18A 109.5 . . ?
C220 C221 H18B 109.5 . . ?
H18A C221 H18B 109.5 . . ?
C220 C221 H18C 109.5 . . ?
H18A C221 H18C 109.5 . . ?
H18B C221 H18C 109.5 . . ?
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C260 C261 H15A 109.5 . . ?
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H15A C261 H15B 109.5 . . ?
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H15A C261 H15C 109.5 . . ?
H15B C261 H15C 109.5 . . ?
C26 C260 C262 111.0(2) . . ?
C26 C260 C261 112.2(2) . . ?
C262 C260 C261 108.6(2) . . ?
C26 C260 H14 108.3 . . ?
C262 C260 H14 108.3 . . ?
C261 C260 H14 108.3 . . ?
C260 C262 H16A 109.5 . . ?
C260 C262 H16B 109.5 . . ?
H16A C262 H16B 109.5 . . ?
C260 C262 H16C 109.5 . . ?
H16A C262 H16C 109.5 . . ?
H16B C262 H16C 109.5 . . ?
N2 C5 C6 102.86(19) . . ?
N2 C5 H2A 111.2 . . ?
C6 C5 H2A 111.2 . . ?
N2 C5 H2B 111.2 . . ?
C6 C5 H2B 111.2 . . ?
H2A C5 H2B 109.1 . . ?
N1 C6 C5 102.9(2) . . ?
N1 C6 H1A 111.2 . . ?
C5 C6 H1A 111.2 . . ?
N1 C6 H1B 111.2 . . ?
C5 C6 H1B 111.2 . . ?
H1A C6 H1B 109.1 . . ?
N1 C7 C8 114.3(3) . . ?
N1 C7 H10A 108.7 . . ?
C8 C7 H10A 108.7 . . ?
N1 C7 H10B 108.7 . . ?
C8 C7 H10B 108.7 . . ?
H10A C7 H10B 107.6 . . ?
O1 C8 C9 107.3(3) . . ?
O1 C8 C7 110.4(2) . . ?
C9 C8 C7 111.2(3) . . ?
O1 C8 C10 110.0(2) . . ?
C9 C8 C10 111.0(3) . . ?
C7 C8 C10 107.1(3) . . ?
C8 C9 H13A 109.5 . . ?
C8 C9 H13B 109.5 . . ?
H13A C9 H13B 109.5 . . ?
C8 C9 H13C 109.5 . . ?
H13A C9 H13C 109.5 . . ?
H13B C9 H13C 109.5 . . ?
C8 C10 H12A 109.5 . . ?
C8 C10 H12B 109.5 . . ?
H12A C10 H12B 109.5 . . ?
C8 C10 H12C 109.5 . . ?
H12A C10 H12C 109.5 . . ?
```

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H12B C10 H12C 109.5 . . ?
C1 N1 C7 125.3(2) . . ?
C1 N1 C6 110.1(2) . . ?
C7 N1 C6 124.6(2) . . ?
C1 N2 C21 126.9(2) . . ?
C1 N2 C5 109.77(19) . . ?
C21 N2 C5 122.40(19) . . ?
C8 O1 H1 109.5 . . ?
H1W O1W H2W 119(7) . . ?

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N2 C21 C22 C23 -176.6(2) . . . . ?
C26 C21 C22 C220 -179.2(2) . . . . ?
N2 C21 C22 C220 4.1(3) . . . . ?
C21 C22 C23 C24 0.2(4) . . . . ?
C220 C22 C23 C24 179.6(2) . . . . ?
C22 C23 C24 C25 -0.3(4) . . . . ?
C23 C24 C25 C26 0.0(4) . . . . ?
C24 C25 C26 C21 0.4(4) . . . . ?
C24 C25 C26 C260 178.5(2) . . . . ?
C22 C21 C26 C25 -0.5(4) . . . . ?
N2 C21 C26 C25 176.3(2) . . . . ?
C22 C21 C26 C260 -178.6(2) . . . . ?
N2 C21 C26 C260 -1.8(3) . . . . ?
C23 C22 C220 C221 40.2(3) . . . . ?
C21 C22 C220 C221 -140.5(2) . . . . ?
C23 C22 C220 C222 -83.8(3) . . . . ?
C21 C22 C220 C222 95.6(3) . . . . ?
C25 C26 C260 C262 -76.8(3) . . . . ?
C21 C26 C260 C262 101.2(3) . . . . ?
C25 C26 C260 C261 44.9(3) . . . . ?
C21 C26 C260 C261 -137.1(2) . . . . ?
N2 C5 C6 N1 -7.5(3) . . . . ?
N1 C7 C8 O1 59.7(3) . . . . ?
N1 C7 C8 C9 -59.3(4) . . . . ?
N1 C7 C8 C10 179.4(3) . . . . ?
N2 C1 N1 C7 176.4(2) . . . . ?
N2 C1 N1 C6 -3.9(3) . . . . ?
C8 C7 N1 C1 105.5(3) . . . . ?
C8 C7 N1 C6 -74.1(3) . . . . ?
C5 C6 N1 C1 7.3(3) . . . . ?
C5 C6 N1 C7 -173.0(2) . . . . ?
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            N1 C1 N2 C21 167.6(2) . . . . ?
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            C22 C21 N2 C1 -75.6(3) . . . . ?
            C26 C21 N2 C1 107.4(3) . . . . ?
            C22 C21 N2 C5 92.2(3) . . . . ?
            C26 C21 N2 C5 -84.7(3) . . . . ?
            C6 C5 N2 C1 5.9(3) . . . . ?
            C6 C5 N2 C21 -163.8(2) . . . . ?

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            _diffrn_reflns_theta_full              25.00
            _diffrn_measured_fraction_theta_full   1.000
            _refine_diff_density_max    0.401
            _refine_diff_density_min   -0.356
            _refine_diff_density_rms    0.062



data_po8075

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;
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 'C25 H47 N3 O Si2 Zn'
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 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Si'  'Si'   0.0817   0.0704
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Zn'  'Zn'   0.2839   1.4301
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M    P21/N
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 'x, y, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

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_cell_length_b                    11.7949(5)
_cell_length_c                    23.0602(8)
_cell_angle_alpha                 90.00
_cell_angle_beta                  101.3390(10)
_cell_angle_gamma                 90.00
_cell_volume                      2998.9(2)
_cell_formula_units_Z             4
_cell_measurement_temperature     150(2)
_cell_measurement_reflns_used     9995
_cell_measurement_theta_min       2.45
_cell_measurement_theta_max       30.45

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_exptl_crystal_colour             COLOURLESS
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_exptl_crystal_size_min           0.25
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.168
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              1136
_exptl_absorpt_coefficient_mu     0.919
_exptl_absorpt_correction_type    'MULTI-SCAN'
_exptl_absorpt_correction_T_min   0.701
_exptl_absorpt_correction_T_max   0.795
_exptl_absorpt_process_details    SADABS

_exptl_special_details
;
 INCOMPLETE DATA; Reflection count < 95% completeness
 The data collection strategy used aimed to achieve a
 complete data set to 2\? = 53 deg.  Some higher angle
 data were collected in the process and these
 have been included in the refinement.
;

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_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   'Bruker SMART APEX CCD area
detector'
_diffrn_measurement_method        'Omega scans'
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_diffrn_standards_decay_%         0
_diffrn_reflns_number             30818
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_diffrn_reflns_av_sigmaI/netI     0.0400
_diffrn_reflns_limit_h_min        -16
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_diffrn_reflns_limit_k_min        -16
_diffrn_reflns_limit_k_max        16
_diffrn_reflns_limit_l_min        -31
_diffrn_reflns_limit_l_max        32
_diffrn_reflns_theta_min          1.80
_diffrn_reflns_theta_max          30.53
_reflns_number_total              8688
_reflns_number_gt                 7357
_reflns_threshold_expression      >2sigma(I)

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_computing_cell_refinement        'SAINT (Siemens, 1995)'
_computing_data_reduction         'SAINT (Siemens, 1995)'
_computing_structure_solution     'SIR-92 (Giacovazzo, 1994)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   'enCIFer (Allen et al.,
2004)'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0351P)^2^+2.0169P] where
P=(Fo^2^+2Fc^2^)/3'
```

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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     RIDING
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          8688
_refine_ls_number_parameters      301
_refine_ls_number_restraints      0
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_refine_ls_wR_factor_gt           0.1105
_refine_ls_goodness_of_fit_ref    1.198
_refine_ls_restrained_S_all       1.198
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_refine_ls_shift/su_mean          0.000

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 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
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 _atom_site_refinement_flags
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C1 C 0.29756(18) 0.15042(18) 0.33384(9) 0.0193(4) Uani 1 1 d .
. .
C5 C 0.46963(19) 0.04381(19) 0.37471(9) 0.0237(4) Uani 1 1 d .
. .
H5A H 0.4577 -0.0283 0.3948 0.028 Uiso 1 1 calc R . .
H5B H 0.5533 0.0714 0.3894 0.028 Uiso 1 1 calc R . .
C6 C 0.44298(18) 0.02992(19) 0.30744(9) 0.0237(4) Uani 1 1 d .
. .
H6A H 0.5092 0.0617 0.2898 0.028 Uiso 1 1 calc R . .
H6B H 0.4308 -0.0507 0.2959 0.028 Uiso 1 1 calc R . .
C7 C 0.2719(2) 0.1072(2) 0.22749(9) 0.0287(5) Uani 1 1 d . . .
H7A H 0.1918 0.0694 0.2212 0.034 Uiso 1 1 calc R . .
H7B H 0.3217 0.0671 0.2030 0.034 Uiso 1 1 calc R . .
C8 C 0.2537(2) 0.2307(2) 0.20563(10) 0.0282(5) Uani 1 1 d . .
.
C9 C 0.1973(3) 0.2245(2) 0.13981(11) 0.0448(7) Uani 1 1 d . .
.
H9A H 0.1216 0.1811 0.1343 0.067 Uiso 1 1 calc R . .
H9B H 0.2538 0.1870 0.1186 0.067 Uiso 1 1 calc R . .
H9C H 0.1802 0.3013 0.1242 0.067 Uiso 1 1 calc R . .
```

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C10 C 0.3758(3) 0.2924(3) 0.21445(13) 0.0422(6) Uani 1 1 d . .
.
H10A H 0.3629 0.3708 0.2006 0.063 Uiso 1 1 calc R . .
H10B H 0.4290 0.2537 0.1918 0.063 Uiso 1 1 calc R . .
H10C H 0.4137 0.2921 0.2565 0.063 Uiso 1 1 calc R . .
C21 C 0.36780(18) 0.16886(18) 0.44111(9) 0.0207(4) Uani 1 1 d
. . .
C22 C 0.44016(19) 0.26083(18) 0.46525(9) 0.0227(4) Uani 1 1 d
. . .
C23 C 0.4278(2) 0.2979(2) 0.52122(10) 0.0293(5) Uani 1 1 d . .
.
H23 H 0.4759 0.3594 0.5392 0.035 Uiso 1 1 calc R . .
C24 C 0.3469(3) 0.2466(2) 0.55096(11) 0.0360(6) Uani 1 1 d . .
.
H24 H 0.3385 0.2743 0.5886 0.043 Uiso 1 1 calc R . .
C25 C 0.2786(2) 0.1558(2) 0.52642(10) 0.0328(5) Uani 1 1 d . .
.
H25 H 0.2239 0.1210 0.5476 0.039 Uiso 1 1 calc R . .
C26 C 0.28799(19) 0.11354(19) 0.47081(9) 0.0243(4) Uani 1 1 d
. . .
C27 C -0.0784(3) 0.1032(3) 0.25335(16) 0.0596(9) Uani 1 1 d .
. .
H27A H -0.0185 0.1183 0.2287 0.089 Uiso 1 1 calc R . .
H27B H -0.1509 0.0690 0.2291 0.089 Uiso 1 1 calc R . .
H27C H -0.0437 0.0510 0.2853 0.089 Uiso 1 1 calc R . .
C28 C -0.1828(3) 0.3331(3) 0.22163(13) 0.0531(8) Uani 1 1 d .
. .
H28A H -0.2039 0.4071 0.2362 0.080 Uiso 1 1 calc R . .
H28B H -0.2555 0.2982 0.1979 0.080 Uiso 1 1 calc R . .
H28C H -0.1216 0.3433 0.1971 0.080 Uiso 1 1 calc R . .
C29 C -0.2489(3) 0.2088(4) 0.32434(16) 0.0668(11) Uani 1 1 d .
. .
H29A H -0.2233 0.1521 0.3553 0.100 Uiso 1 1 calc R . .
H29B H -0.3183 0.1797 0.2957 0.100 Uiso 1 1 calc R . .
H29C H -0.2723 0.2787 0.3422 0.100 Uiso 1 1 calc R . .
C30 C -0.1007(3) 0.5109(2) 0.36584(13) 0.0452(7) Uani 1 1 d .
. .
H30A H -0.0738 0.5512 0.3336 0.068 Uiso 1 1 calc R . .
H30B H -0.0979 0.5624 0.3994 0.068 Uiso 1 1 calc R . .
H30C H -0.1840 0.4841 0.3523 0.068 Uiso 1 1 calc R . .
C31 C -0.0456(2) 0.3219(3) 0.45537(12) 0.0399(6) Uani 1 1 d .
. .
H31A H -0.1237 0.2835 0.4430 0.060 Uiso 1 1 calc R . .
H31B H -0.0534 0.3814 0.4840 0.060 Uiso 1 1 calc R . .
H31C H 0.0158 0.2669 0.4736 0.060 Uiso 1 1 calc R . .
C32 C 0.1577(2) 0.4417(2) 0.41744(10) 0.0311(5) Uani 1 1 d . .
.
H32A H 0.2112 0.3786 0.4331 0.047 Uiso 1 1 calc R . .
H32B H 0.1558 0.4971 0.4489 0.047 Uiso 1 1 calc R . .
H32C H 0.1882 0.4781 0.3851 0.047 Uiso 1 1 calc R . .
C220 C 0.52534(19) 0.31945(19) 0.43114(10) 0.0244(4) Uani 1 1
d . . .
H220 H 0.5603 0.2597 0.4087 0.029 Uiso 1 1 calc R . .
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C221 C 0.4578(2) 0.4041(2) 0.38591(10) 0.0299(5) Uani 1 1 d .
. .
H22A H 0.3928 0.3648 0.3588 0.045 Uiso 1 1 calc R . .
H22B H 0.5145 0.4375 0.3635 0.045 Uiso 1 1 calc R . .
H22C H 0.4227 0.4643 0.4066 0.045 Uiso 1 1 calc R . .
C222 C 0.6315(2) 0.3799(2) 0.47086(11) 0.0333(5) Uani 1 1 d .
. .
H22D H 0.6006 0.4432 0.4911 0.050 Uiso 1 1 calc R . .
H22E H 0.6874 0.4088 0.4467 0.050 Uiso 1 1 calc R . .
H22F H 0.6744 0.3264 0.5002 0.050 Uiso 1 1 calc R . .
C260 C 0.2152(2) 0.0104(2) 0.44547(10) 0.0285(5) Uani 1 1 d .
. .
H260 H 0.2405 -0.0099 0.4076 0.034 Uiso 1 1 calc R . .
C261 C 0.0790(2) 0.0338(2) 0.43142(13) 0.0406(6) Uani 1 1 d .
. .
H26A H 0.0516 0.0537 0.4679 0.061 Uiso 1 1 calc R . .
H26B H 0.0360 -0.0340 0.4140 0.061 Uiso 1 1 calc R . .
H26C H 0.0622 0.0969 0.4033 0.061 Uiso 1 1 calc R . .
C262 C 0.2432(3) -0.0910(2) 0.48713(12) 0.0403(6) Uani 1 1 d .
. .
H26D H 0.3305 -0.1064 0.4947 0.060 Uiso 1 1 calc R . .
H26E H 0.1990 -0.1576 0.4689 0.060 Uiso 1 1 calc R . .
H26F H 0.2180 -0.0739 0.5245 0.060 Uiso 1 1 calc R . .
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N3 N 0.00298(15) 0.29461(17) 0.33249(8) 0.0241(4) Uani 1 1 d .
. .
O1 O 0.17334(15) 0.28956(14) 0.23391(7) 0.0297(4) Uani 1 1 d .
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d . . .
Si2 Si 0.00151(5) 0.38686(6) 0.38925(3) 0.02437(14) Uani 1 1 d
. . .
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0.0065(8)
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0.0027(8)
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C22 0.0235(10) 0.0217(11) 0.0211(10) 0.0008(8) -0.0002(8)
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0.0023(11)
C26 0.0276(10) 0.0233(11) 0.0221(10) 0.0039(8) 0.0049(8)
0.0028(9)
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0.0100(15)
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0.0046(11)
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0.0061(7)
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0.0008(7)
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Si1 0.0203(3) 0.0393(4) 0.0371(4) -0.0058(3) 0.0026(3) -
0.0067(3)

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Si2 0.0196(3) 0.0270(3) 0.0268(3) -0.0008(2) 0.0051(2)
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0.00146(9)

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 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds involving
l.s. planes.
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C7 N1 1.462(3) . ?
C7 C8 1.541(3) . ?
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C8 C10 1.532(4) . ?
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C9 H9B 0.9800 . ?
C9 H9C 0.9800 . ?
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C21 N2 1.437(3) . ?
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C25 H25 0.9500 . ?
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H10B C10 H10C 109.5 . . ?
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Si1 C27 H27C 109.5 . . ?
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N1 C1 N2 C21 -175.19(19) . . . . ?
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Si1 N3 Si2 C32 -169.63(14) . . . . ?
Zn1 N3 Si2 C32 4.78(16) . . . . ?
Si1 N3 Si2 C31 72.99(17) . . . . ?
Zn1 N3 Si2 C31 -112.61(14) . . . . ?
Si1 N3 Si2 C30 -49.39(19) . . . . ?
Zn1 N3 Si2 C30 125.02(15) . . . . ?
C8 O1 Zn1 N3 -156.30(17) . . . . ?
C8 O1 Zn1 C1 13.56(19) . . . . ?
Si2 N3 Zn1 O1 -117.86(12) . . . . ?
Si1 N3 Zn1 O1 57.28(14) . . . . ?
Si2 N3 Zn1 C1 78.91(18) . . . . ?
Si1 N3 Zn1 C1 -105.94(14) . . . . ?
N1 C1 Zn1 O1 -30.20(17) . . . . ?
N2 C1 Zn1 O1 143.3(2) . . . . ?
N1 C1 Zn1 N3 134.92(16) . . . . ?
N2 C1 Zn1 N3 -51.6(3) . . . . ?

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 'Y'  'Y'  -2.7962   3.5667
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 'x, -y-1/2, z-1/2'

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_cell_angle_beta                  112.017(4)
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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

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P=(Fo^2^+2Fc^2^)/3'
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C1 C 0.76569(11) 0.3283(2) 0.96490(10) 0.0240(4) Uani 1 1 d .
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C5 C 0.82783(13) 0.5088(2) 0.95252(13) 0.0327(5) Uani 1 1 d .
. .
H14A H 0.8508 0.5116 0.9170 0.039 Uiso 1 1 calc R . .
H14B H 0.8511 0.5704 0.9911 0.039 Uiso 1 1 calc R . .
C6 C 0.74889(13) 0.5333(2) 0.91753(12) 0.0327(5) Uani 1 1 d .
. .
H15A H 0.7341 0.6019 0.9421 0.039 Uiso 1 1 calc R . .
H15B H 0.7350 0.5549 0.8662 0.039 Uiso 1 1 calc R . .
C21 C 0.89589(11) 0.3321(2) 1.03140(11) 0.0264(5) Uani 1 1 d .
. .
C22 C 0.91172(12) 0.3471(2) 1.10514(12) 0.0305(5) Uani 1 1 d .
. .
C23 C 0.97532(14) 0.2976(3) 1.15227(13) 0.0413(6) Uani 1 1 d .
. .
H4 H 0.9863 0.3031 1.2024 0.050 Uiso 1 1 calc R . .
C24 C 1.02274(14) 0.2408(3) 1.12770(14) 0.0484(7) Uani 1 1 d .
. .
H5 H 1.0659 0.2073 1.1608 0.058 Uiso 1 1 calc R . .
C25 C 1.00767(13) 0.2327(3) 1.05547(14) 0.0449(7) Uani 1 1 d .
. .
H6 H 1.0413 0.1951 1.0391 0.054 Uiso 1 1 calc R . .
C26 C 0.94435(12) 0.2781(2) 1.00562(12) 0.0316(5) Uani 1 1 d .
. .
C221 C 0.82537(17) 0.3270(3) 1.16629(16) 0.0554(8) Uiso 1 1 d
. . .
H13A H 0.7973 0.2671 1.1296 0.083 Uiso 1 1 calc R . .
H13B H 0.7939 0.3741 1.1841 0.083 Uiso 1 1 calc R . .
H13C H 0.8607 0.2813 1.2060 0.083 Uiso 1 1 calc R . .
C220 C 0.86268(13) 0.4172(2) 1.13404(13) 0.0335(5) Uiso 1 1 d
. . .
H11 H 0.8256 0.4604 1.0928 0.040 Uiso 1 1 calc R . .
C222 C 0.90151(16) 0.5170(3) 1.18878(15) 0.0463(7) Uani 1 1 d
. . .
H12A H 0.9372 0.4768 1.2306 0.070 Uiso 1 1 calc R . .
H12B H 0.8675 0.5626 1.2037 0.070 Uiso 1 1 calc R . .
H12C H 0.9249 0.5759 1.1673 0.070 Uiso 1 1 calc R . .
C261 C 0.94115(16) 0.1377(3) 0.90303(15) 0.0535(8) Uani 1 1 d
. . .
H10A H 0.9908 0.1125 0.9274 0.080 Uiso 1 1 calc R . .
H10B H 0.9287 0.1361 0.8510 0.080 Uiso 1 1 calc R . .
H10C H 0.9105 0.0793 0.9158 0.080 Uiso 1 1 calc R . .
C260 C 0.93092(13) 0.2704(3) 0.92630(12) 0.0368(6) Uani 1 1 d
. . .
H8 H 0.8805 0.2950 0.8991 0.044 Uiso 1 1 calc R . .
C262 C 0.97796(17) 0.3631(3) 0.90686(16) 0.0598(9) Uani 1 1 d
. . .
H9A H 0.9709 0.4477 0.9222 0.090 Uiso 1 1 calc R . .
H9B H 0.9655 0.3625 0.8548 0.090 Uiso 1 1 calc R . .
H9C H 1.0278 0.3388 0.9310 0.090 Uiso 1 1 calc R . .
C7 C 0.64114(12) 0.3976(2) 0.89784(12) 0.0317(5) Uani 1 1 d .
. .
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H16A H 0.6282 0.3269 0.8634 0.038 Uiso 1 1 calc R . .
H16B H 0.6193 0.4747 0.8711 0.038 Uiso 1 1 calc R . .
C9 C 0.52947(13) 0.3681(3) 0.91873(16) 0.0465(7) Uani 1 1 d .
. .
H19A H 0.5161 0.3041 0.8810 0.070 Uiso 1 1 calc R . .
H19B H 0.5117 0.4503 0.8976 0.070 Uiso 1 1 calc R . .
H19C H 0.5089 0.3469 0.9542 0.070 Uiso 1 1 calc R . .
C8 C 0.60984(12) 0.3730(2) 0.95509(12) 0.0307(5) Uani 1 1 d .
. .
C10 C 0.63156(15) 0.4748(3) 1.01265(14) 0.0427(6) Uani 1 1 d .
. .
H18A H 0.6106 0.4567 1.0482 0.064 Uiso 1 1 calc R . .
H18B H 0.6147 0.5567 0.9905 0.064 Uiso 1 1 calc R . .
H18C H 0.6834 0.4765 1.0362 0.064 Uiso 1 1 calc R . .
C27 C 0.84511(15) -0.0120(3) 1.02223(13) 0.0462(7) Uani 1 1 d
. . .
H25A H 0.8067 -0.0204 0.9752 0.069 Uiso 1 1 calc R . .
H25B H 0.8861 -0.0613 1.0231 0.069 Uiso 1 1 calc R . .
H25C H 0.8587 0.0766 1.0312 0.069 Uiso 1 1 calc R . .
C28 C 0.7855(2) -0.2377(3) 1.0702(2) 0.0852(13) Uani 1 1 d . .
.
H24A H 0.7720 -0.2747 1.1078 0.128 Uiso 1 1 calc R . .
H24B H 0.8247 -0.2858 1.0657 0.128 Uiso 1 1 calc R . .
H24C H 0.7448 -0.2398 1.0245 0.128 Uiso 1 1 calc R . .
C29 C 0.89474(17) -0.0727(4) 1.17730(15) 0.0786(13) Uani 1 1 d
. . .
H23A H 0.9095 0.0139 1.1920 0.118 Uiso 1 1 calc R . .
H23B H 0.9330 -0.1170 1.1686 0.118 Uiso 1 1 calc R . .
H23C H 0.8844 -0.1156 1.2154 0.118 Uiso 1 1 calc R . .
C30 C 0.64918(14) 0.1568(3) 1.14647(14) 0.0400(6) Uani 1 1 d .
. .
H20A H 0.6743 0.2359 1.1477 0.060 Uiso 1 1 calc R . .
H20B H 0.6310 0.1562 1.1852 0.060 Uiso 1 1 calc R . .
H20C H 0.6095 0.1488 1.1002 0.060 Uiso 1 1 calc R . .
C31 C 0.66268(19) -0.1255(3) 1.16155(18) 0.0554(8) Uani 1 1 d
. . .
H22A H 0.6204 -0.1329 1.1175 0.083 Uiso 1 1 calc R . .
H22B H 0.6484 -0.1229 1.2030 0.083 Uiso 1 1 calc R . .
H22C H 0.6937 -0.1981 1.1658 0.083 Uiso 1 1 calc R . .
C32 C 0.78136(16) 0.0391(3) 1.25083(12) 0.0455(7) Uani 1 1 d .
. .
H21A H 0.8043 -0.0423 1.2670 0.068 Uiso 1 1 calc R . .
H21B H 0.7593 0.0680 1.2839 0.068 Uiso 1 1 calc R . .
H21C H 0.8169 0.1005 1.2498 0.068 Uiso 1 1 calc R . .
C33 C 0.63636(16) -0.0111(3) 0.72634(13) 0.0476(7) Uani 1 1 d
. . .
H28A H 0.6077 -0.0875 0.7197 0.071 Uiso 1 1 calc R . .
H28B H 0.6625 -0.0132 0.6941 0.071 Uiso 1 1 calc R . .
H28C H 0.6053 0.0626 0.7154 0.071 Uiso 1 1 calc R . .
C34 C 0.75524(15) 0.1403(2) 0.82672(13) 0.0401(6) Uani 1 1 d .
. .
H26A H 0.7245 0.2145 0.8134 0.060 Uiso 1 1 calc R . .
H26B H 0.7803 0.1315 0.7938 0.060 Uiso 1 1 calc R . .
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H26C H 0.7898 0.1500 0.8758 0.060 Uiso 1 1 calc R . .
C35 C 0.76022(17) -0.1424(3) 0.83291(16) 0.0522(8) Uani 1 1 d
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H27A H 0.7970 -0.1415 0.8813 0.078 Uiso 1 1 calc R . .
H27B H 0.7825 -0.1391 0.7974 0.078 Uiso 1 1 calc R . .
H27C H 0.7322 -0.2196 0.8262 0.078 Uiso 1 1 calc R . .
C36 C 0.50670(14) 0.0093(3) 0.80029(15) 0.0510(7) Uani 1 1 d .
. .
H31A H 0.5075 0.1006 0.8069 0.077 Uiso 1 1 calc R . .
H31B H 0.4627 -0.0249 0.8021 0.077 Uiso 1 1 calc R . .
H31C H 0.5092 -0.0100 0.7537 0.077 Uiso 1 1 calc R . .
C37 C 0.58337(16) -0.2336(3) 0.85392(16) 0.0522(7) Uani 1 1 d
. . .
H30A H 0.5910 -0.2464 0.8091 0.078 Uiso 1 1 calc R . .
H30B H 0.5374 -0.2693 0.8493 0.078 Uiso 1 1 calc R . .
H30C H 0.6213 -0.2754 0.8933 0.078 Uiso 1 1 calc R . .
C38 C 0.56786(15) -0.0463(3) 0.95805(14) 0.0512(8) Uani 1 1 d
. . .
H29A H 0.6070 -0.0850 0.9975 0.077 Uiso 1 1 calc R . .
H29B H 0.5233 -0.0883 0.9528 0.077 Uiso 1 1 calc R . .
H29C H 0.5647 0.0430 0.9685 0.077 Uiso 1 1 calc R . .
N1 N 0.71825(10) 0.41232(18) 0.92640(9) 0.0272(4) Uani 1 1 d .
. .
N2 N 0.83012(9) 0.38091(17) 0.98183(9) 0.0246(4) Uani 1 1 d .
. .
N3 N 0.74621(10) 0.02123(17) 1.09263(9) 0.0247(4) Uani 1 1 d .
. .
N4 N 0.66331(10) 0.00761(17) 0.88458(9) 0.0266(4) Uani 1 1 d .
. .
O1 O 0.63532(8) 0.25678(15) 0.98667(8) 0.0325(4) Uani 1 1 d .
. .
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d . . .
Si2 Si 0.71153(4) 0.02230(6) 1.15842(3) 0.03164(15) Uani 1 1 d
. . .
Si3 Si 0.70048(3) -0.00210(6) 0.82115(3) 0.02940(15) Uani 1 1
d . . .
Si4 Si 0.58422(3) -0.06250(6) 0.87301(3) 0.03086(15) Uani 1 1
d . . .
Y1 Y 0.706735(11) 0.12356(2) 0.986341(10) 0.02366(7) Uani 1 1
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0.0019(9)
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0.0002(10)
C21 0.0193(11) 0.0339(12) 0.0226(10) -0.0016(9) 0.0037(8) -
0.0028(9)
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0.0043(10)
C23 0.0333(14) 0.0599(18) 0.0220(11) -0.0027(11) 0.0004(10)
0.0006(12)
C24 0.0263(13) 0.069(2) 0.0366(14) -0.0050(13) -0.0036(11)
0.0096(13)
C25 0.0233(12) 0.0646(19) 0.0410(14) -0.0122(13) 0.0054(11)
0.0057(12)
C26 0.0215(11) 0.0453(14) 0.0249(11) -0.0086(10) 0.0052(9) -
0.0057(10)
C222 0.0485(17) 0.0457(16) 0.0492(16) -0.0140(13) 0.0233(14) -
0.0124(13)
C261 0.0377(16) 0.079(2) 0.0396(15) -0.0201(14) 0.0100(12)
0.0137(15)
C260 0.0227(12) 0.0597(17) 0.0277(11) -0.0119(11) 0.0091(9) -
0.0056(11)
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0.0244(17)
C7 0.0210(11) 0.0349(13) 0.0290(11) 0.0072(10) -0.0023(9)
0.0055(9)
C9 0.0233(13) 0.0537(18) 0.0539(17) 0.0068(13) 0.0045(12)
0.0095(12)
C8 0.0204(11) 0.0334(12) 0.0335(12) 0.0050(10) 0.0045(9)
0.0080(10)
C10 0.0375(15) 0.0451(15) 0.0442(15) -0.0024(12) 0.0139(12)
0.0099(12)
C27 0.0379(15) 0.0680(19) 0.0334(13) 0.0067(13) 0.0144(12)
0.0226(14)
C28 0.109(3) 0.0355(18) 0.126(3) -0.005(2) 0.061(3) 0.015(2)
C29 0.0441(19) 0.153(4) 0.0269(14) 0.0059(19) -0.0005(13)
0.046(2)
C30 0.0381(15) 0.0469(16) 0.0382(14) -0.0007(12) 0.0179(12)
0.0018(12)
C31 0.074(2) 0.0435(17) 0.0589(19) 0.0089(14) 0.0363(18) -
0.0092(15)
C32 0.0599(19) 0.0533(17) 0.0211(12) 0.0056(11) 0.0127(12)
0.0091(14)
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0.0157(14)
C34 0.0417(15) 0.0502(16) 0.0310(13) -0.0062(11) 0.0165(11) -
0.0151(12)
C35 0.0501(18) 0.0547(19) 0.0532(18) -0.0088(14) 0.0209(15)
0.0084(14)
C36 0.0265(14) 0.066(2) 0.0490(16) 0.0112(14) 0.0005(12) -
0.0005(13)
C37 0.0434(17) 0.0425(16) 0.0622(19) -0.0015(14) 0.0100(14) -
0.0122(13)

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C38 0.0369(16) 0.080(2) 0.0388(15) -0.0041(14) 0.0161(12) -
0.0194(15)
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0.0010(8)
N2 0.0206(9) 0.0304(10) 0.0216(9) 0.0001(7) 0.0067(7) -
0.0009(8)
N3 0.0241(10) 0.0250(9) 0.0207(8) 0.0012(7) 0.0033(7)
0.0016(7)
N4 0.0203(9) 0.0316(10) 0.0224(9) -0.0002(7) 0.0015(7) -
0.0026(8)
O1 0.0240(8) 0.0347(9) 0.0367(9) 0.0096(7) 0.0090(7) 0.0065(7)
Si1 0.0320(4) 0.0365(4) 0.0222(3) 0.0030(3) 0.0028(3)
0.0130(3)
Si2 0.0377(4) 0.0311(3) 0.0273(3) 0.0039(3) 0.0134(3)
0.0008(3)
Si3 0.0267(3) 0.0364(4) 0.0211(3) -0.0039(3) 0.0045(3) -
0.0052(3)
Si4 0.0221(3) 0.0360(4) 0.0278(3) 0.0010(3) 0.0018(3) -
0.0056(3)
Y1 0.01898(11) 0.02612(11) 0.02014(10) 0.00247(8) 0.00074(7)
0.00118(9)

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;
 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds involving
l.s. planes.
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C25 C26 1.389(3) . ?
C26 C260 1.517(3) . ?
C221 C220 1.513(4) . ?
C220 C222 1.521(3) . ?
C261 C260 1.527(4) . ?
C260 C262 1.524(4) . ?
C7 N1 1.462(3) . ?
C7 C8 1.533(3) . ?
C9 C8 1.521(3) . ?
C8 O1 1.399(3) . ?
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C29 Si1 1.857(3) . ?
C30 Si2 1.867(3) . ?
C31 Si2 1.874(3) . ?
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C33 Si3 1.866(3) . ?
C34 Si3 1.859(3) . ?
C35 Si3 1.883(3) . ?
C36 Si4 1.866(3) . ?
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C38 Si4 1.870(3) . ?
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N3 Si2 1.7174(19) . ?
N3 Y1 2.2620(17) . ?
N4 Si4 1.7078(19) . ?
N4 Si3 1.7128(19) . ?
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C262 C260 C261 110.5(2) . . ?
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Y1 C1 N1 C6 175.61(14) . . . . ?
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 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

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Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
(compiled Jan  5 2010,16:28:46)
Empirical absorption correction using spherical harmonics,
 implemented in SCALE3 ABSPACK scaling algorithm.
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Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
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(compiled Jan  5 2010,16:28:46)
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are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0417P)^2^+0.0000P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     riding
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          9419
_refine_ls_number_parameters      388
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0582
_refine_ls_R_factor_gt            0.0331
_refine_ls_wR_factor_ref          0.0811
_refine_ls_wR_factor_gt           0.0787
_refine_ls_goodness_of_fit_ref    0.872
_refine_ls_restrained_S_all       0.872
_refine_ls_shift/su_max           0.001
_refine_ls_shift/su_mean          0.000

loop_
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Sc01 Sc 0.705981(16) 0.37416(3) 0.989625(15) 0.01947(8) Uani 1
1 d . . .
Si1 Si 0.69355(3) 0.49541(5) 0.82772(2) 0.02931(13) Uani 1 1 d
. . .
Si4 Si 0.72081(3) 0.48075(5) 1.15602(2) 0.02874(13) Uani 1 1 d
. . .
Si2 Si 0.58136(3) 0.55444(5) 0.87968(3) 0.03067(13) Uani 1 1 d
. . .
Si3 Si 0.81254(3) 0.57768(5) 1.08357(2) 0.02508(12) Uani 1 1 d
. . .
N2 N 0.82509(7) 0.13401(13) 0.97712(6) 0.0204(3) Uani 1 1 d .
. .
N1 N 0.71043(7) 0.10209(13) 0.92553(7) 0.0237(3) Uani 1 1 d .
. .
N4 N 0.74875(7) 0.47594(13) 1.08664(6) 0.0209(3) Uani 1 1 d .
. .
N3 N 0.66144(7) 0.48045(13) 0.89346(7) 0.0239(3) Uani 1 1 d .
. .
O1 O 0.63894(6) 0.25552(11) 0.99418(6) 0.0276(3) Uani 1 1 d .
. .
C21 C 0.89383(8) 0.17610(16) 1.02953(8) 0.0227(4) Uani 1 1 d .
. .
C22 C 0.94390(9) 0.22557(17) 1.00590(9) 0.0263(4) Uani 1 1 d .
. .
C9 C 0.60871(9) 0.13937(17) 0.96193(9) 0.0292(4) Uani 1 1 d .
. .
C26 C 0.90966(9) 0.15831(17) 1.10287(8) 0.0265(4) Uani 1 1 d .
. .
C5 C 0.76008(8) 0.18481(16) 0.96572(8) 0.0201(4) Uani 1 1 d .
. .
C6 C 0.81993(9) 0.00658(16) 0.94546(9) 0.0263(4) Uani 1 1 d .
. .
H6A H 0.8412 -0.0584 0.9833 0.032 Uiso 1 1 calc R . .
H6B H 0.8440 0.0035 0.9120 0.032 Uiso 1 1 calc R . .
C260 C 0.86060(9) 0.08835(18) 1.12972(9) 0.0313(4) Uani 1 1 d
. . .
H260 H 0.8192 0.0550 1.0867 0.038 Uiso 1 1 calc R . .
C10 C 0.63451(10) 0.03389(19) 1.01809(10) 0.0399(5) Uani 1 1 d
. . .
H10A H 0.6870 0.0304 1.0390 0.060 Uiso 1 1 calc R . .
```

```
H10B H 0.6150 -0.0472 0.9951 0.060 Uiso 1 1 calc R . .
H10C H 0.6180 0.0508 1.0562 0.060 Uiso 1 1 calc R . .
C7 C 0.73951(9) -0.01148(17) 0.90573(9) 0.0290(4) Uani 1 1 d .
. .
H7A H 0.7250 -0.0160 0.8530 0.035 Uiso 1 1 calc R . .
H7B H 0.7234 -0.0892 0.9219 0.035 Uiso 1 1 calc R . .
C262 C 0.89804(11) -0.02422(19) 1.17717(10) 0.0413(5) Uani 1 1
d . . .
H26A H 0.9163 -0.0810 1.1505 0.062 Uiso 1 1 calc R . .
H26B H 0.8638 -0.0700 1.1909 0.062 Uiso 1 1 calc R . .
H26C H 0.9380 0.0060 1.2206 0.062 Uiso 1 1 calc R . .
C220 C 0.93042(9) 0.23378(18) 0.92700(9) 0.0309(4) Uani 1 1 d
. . .
H220 H 0.8795 0.2082 0.8979 0.037 Uiso 1 1 calc R . .
C8 C 0.63242(9) 0.11567(17) 0.90051(9) 0.0288(4) Uani 1 1 d .
. .
H8A H 0.6089 0.0378 0.8745 0.035 Uiso 1 1 calc R . .
H8B H 0.6160 0.1870 0.8660 0.035 Uiso 1 1 calc R . .
C23 C 1.00953(10) 0.26647(19) 1.05811(10) 0.0379(5) Uani 1 1 d
. . .
H23 H 1.0445 0.3009 1.0436 0.045 Uiso 1 1 calc R . .
C36 C 0.79629(11) 0.4580(2) 1.24755(9) 0.0434(5) Uani 1 1 d .
. .
H36A H 0.8330 0.4031 1.2432 0.065 Uiso 1 1 calc R . .
H36B H 0.7776 0.4187 1.2800 0.065 Uiso 1 1 calc R . .
H36C H 0.8175 0.5402 1.2670 0.065 Uiso 1 1 calc R . .
C25 C 0.97559(10) 0.2042(2) 1.15215(9) 0.0389(5) Uani 1 1 d .
. .
H25 H 0.9869 0.1982 1.2022 0.047 Uiso 1 1 calc R . .
C027 C 0.52680(9) 0.1491(2) 0.93006(11) 0.0444(5) Uani 1 1 d .
. .
H02A H 0.5112 0.1700 0.9683 0.067 Uiso 1 1 calc R . .
H02B H 0.5058 0.0680 0.9082 0.067 Uiso 1 1 calc R . .
H02C H 0.5110 0.2155 0.8932 0.067 Uiso 1 1 calc R . .
C27 C 0.74688(10) 0.35359(19) 0.82602(9) 0.0379(5) Uani 1 1 d
. . .
H27A H 0.7860 0.3415 0.8736 0.057 Uiso 1 1 calc R . .
H27B H 0.7669 0.3658 0.7902 0.057 Uiso 1 1 calc R . .
H27C H 0.7158 0.2788 0.8134 0.057 Uiso 1 1 calc R . .
C24 C 1.02448(10) 0.2578(2) 1.13032(10) 0.0444(5) Uani 1 1 d .
. .
H24 H 1.0687 0.2889 1.1651 0.053 Uiso 1 1 calc R . .
C221 C 0.97908(11) 0.1409(2) 0.90989(11) 0.0498(6) Uani 1 1 d
. . .
H22A H 1.0294 0.1639 0.9378 0.075 Uiso 1 1 calc R . .
H22B H 0.9683 0.1448 0.8584 0.075 Uiso 1 1 calc R . .
H22C H 0.9706 0.0549 0.9226 0.075 Uiso 1 1 calc R . .
C34 C 0.85144(10) 0.50623(18) 1.02318(9) 0.0337(5) Uani 1 1 d
. . .
H34A H 0.8845 0.4379 1.0488 0.051 Uiso 1 1 calc R . .
H34B H 0.8775 0.5713 1.0093 0.051 Uiso 1 1 calc R . .
H34C H 0.8127 0.4722 0.9800 0.051 Uiso 1 1 calc R . .
```

```
C28 C 0.75256(12) 0.6383(2) 0.84078(11) 0.0505(6) Uani 1 1 d .
. .
H28A H 0.7241 0.7152 0.8357 0.076 Uiso 1 1 calc R . .
H28B H 0.7726 0.6382 0.8045 0.076 Uiso 1 1 calc R . .
H28C H 0.7917 0.6359 0.8890 0.076 Uiso 1 1 calc R . .
C261 C 0.83080(13) 0.1743(2) 1.17039(11) 0.0579(7) Uani 1 1 d
. . .
H26D H 0.8704 0.2088 1.2128 0.087 Uiso 1 1 calc R . .
H26E H 0.7985 0.1260 1.1857 0.087 Uiso 1 1 calc R . .
H26F H 0.8042 0.2439 1.1390 0.087 Uiso 1 1 calc R . .
C30 C 0.57910(11) 0.72572(19) 0.85502(11) 0.0493(6) Uani 1 1 d
. . .
H30A H 0.6164 0.7716 0.8945 0.074 Uiso 1 1 calc R . .
H30B H 0.5320 0.7613 0.8465 0.074 Uiso 1 1 calc R . .
H30C H 0.5877 0.7338 0.8112 0.074 Uiso 1 1 calc R . .
C29 C 0.62292(12) 0.5079(2) 0.73332(10) 0.0573(7) Uani 1 1 d .
. .
H29A H 0.5916 0.4335 0.7224 0.086 Uiso 1 1 calc R . .
H29B H 0.6459 0.5123 0.6995 0.086 Uiso 1 1 calc R . .
H29C H 0.5943 0.5845 0.7288 0.086 Uiso 1 1 calc R . .
C35 C 0.89157(10) 0.6067(2) 1.17009(9) 0.0445(5) Uani 1 1 d .
. .
H35A H 0.8761 0.6519 1.2033 0.067 Uiso 1 1 calc R . .
H35B H 0.9270 0.6579 1.1610 0.067 Uiso 1 1 calc R . .
H35C H 0.9131 0.5257 1.1914 0.067 Uiso 1 1 calc R . .
C37 C 0.65434(10) 0.35428(19) 1.14732(9) 0.0383(5) Uani 1 1 d
. . .
H37A H 0.6119 0.3655 1.1021 0.057 Uiso 1 1 calc R . .
H37B H 0.6404 0.3593 1.1879 0.057 Uiso 1 1 calc R . .
H37C H 0.6758 0.2714 1.1473 0.057 Uiso 1 1 calc R . .
C32 C 0.50112(10) 0.4772(2) 0.80842(11) 0.0518(6) Uani 1 1 d .
. .
H32A H 0.4968 0.5044 0.7608 0.078 Uiso 1 1 calc R . .
H32B H 0.4578 0.5017 0.8148 0.078 Uiso 1 1 calc R . .
H32C H 0.5067 0.3851 0.8124 0.078 Uiso 1 1 calc R . .
C38 C 0.68012(13) 0.6368(2) 1.16272(11) 0.0554(6) Uani 1 1 d .
. .
H38A H 0.7150 0.7045 1.1694 0.083 Uiso 1 1 calc R . .
H38B H 0.6668 0.6353 1.2039 0.083 Uiso 1 1 calc R . .
H38C H 0.6372 0.6521 1.1184 0.083 Uiso 1 1 calc R . .
C31 C 0.56720(10) 0.5528(2) 0.96444(10) 0.0482(6) Uani 1 1 d .
. .
H31A H 0.5631 0.4651 0.9780 0.072 Uiso 1 1 calc R . .
H31B H 0.5230 0.5987 0.9570 0.072 Uiso 1 1 calc R . .
H31C H 0.6080 0.5936 1.0030 0.072 Uiso 1 1 calc R . .
C33 C 0.77394(12) 0.73553(19) 1.04573(11) 0.0490(6) Uani 1 1 d
. . .
H33A H 0.7346 0.7241 0.9982 0.074 Uiso 1 1 calc R . .
H33B H 0.8113 0.7884 1.0413 0.074 Uiso 1 1 calc R . .
H33C H 0.7557 0.7768 1.0780 0.074 Uiso 1 1 calc R . .
C222 C 0.94021(10) 0.3694(2) 0.90469(10) 0.0427(5) Uani 1 1 d
. . .
H22D H 0.9083 0.4270 0.9155 0.064 Uiso 1 1 calc R . .
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H22E H 0.9284 0.3715 0.8529 0.064 Uiso 1 1 calc R . .
H22F H 0.9901 0.3959 0.9315 0.064 Uiso 1 1 calc R . .

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Sc01 0.01785(16) 0.01981(17) 0.01781(15) -0.00138(13)
0.00430(12) -0.00035(14)
Si1 0.0320(3) 0.0353(3) 0.0183(2) 0.0057(2) 0.0080(2)
0.0079(2)
Si4 0.0328(3) 0.0333(3) 0.0220(3) -0.0030(2) 0.0132(2)
0.0028(2)
Si2 0.0232(3) 0.0347(3) 0.0275(3) 0.0006(2) 0.0036(2)
0.0080(2)
Si3 0.0258(3) 0.0227(3) 0.0215(2) -0.0019(2) 0.00431(19) -
0.0050(2)
N2 0.0207(7) 0.0210(8) 0.0193(7) -0.0005(6) 0.0079(6)
0.0009(6)
N1 0.0211(7) 0.0225(8) 0.0248(7) -0.0050(6) 0.0067(6) -
0.0017(6)
N4 0.0223(7) 0.0210(8) 0.0168(7) -0.0018(6) 0.0054(5)
0.0001(6)
N3 0.0203(7) 0.0275(9) 0.0194(7) 0.0007(6) 0.0034(6) 0.0050(6)
O1 0.0253(6) 0.0269(7) 0.0316(6) -0.0070(5) 0.0124(5) -
0.0075(6)
C21 0.0190(9) 0.0245(10) 0.0213(9) 0.0000(7) 0.0049(7)
0.0031(7)
C22 0.0219(9) 0.0281(11) 0.0278(9) 0.0056(8) 0.0090(7)
0.0049(8)
C9 0.0227(9) 0.0298(11) 0.0338(10) -0.0057(8) 0.0101(7) -
0.0085(8)
C26 0.0255(10) 0.0288(11) 0.0221(9) 0.0035(7) 0.0064(7)
0.0060(8)
C5 0.0203(9) 0.0232(10) 0.0152(8) 0.0026(7) 0.0057(6) -
0.0012(7)
C6 0.0302(10) 0.0236(10) 0.0278(9) -0.0009(8) 0.0146(8)
0.0035(8)
C260 0.0290(10) 0.0441(12) 0.0204(9) 0.0048(8) 0.0097(7)
0.0058(9)
C10 0.0390(12) 0.0379(12) 0.0452(12) 0.0038(9) 0.0198(9) -
0.0091(10)
C7 0.0336(11) 0.0265(11) 0.0257(9) -0.0067(8) 0.0110(8) -
0.0011(8)
C262 0.0475(13) 0.0359(12) 0.0470(12) 0.0056(10) 0.0261(10)
0.0054(10)
C220 0.0235(10) 0.0408(12) 0.0305(10) 0.0021(9) 0.0133(8)
0.0008(8)
```

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C8 0.0215(9) 0.0289(11) 0.0284(9) -0.0072(8) 0.0024(7) -
0.0050(8)
C23 0.0248(10) 0.0475(13) 0.0376(11) 0.0076(9) 0.0089(8) -
0.0041(9)
C36 0.0546(13) 0.0541(14) 0.0227(10) -0.0040(9) 0.0169(9) -
0.0064(11)
C25 0.0362(11) 0.0509(14) 0.0211(9) 0.0031(9) 0.0032(8) -
0.0004(10)
C027 0.0233(10) 0.0531(15) 0.0535(13) -0.0093(11) 0.0123(9) -
0.0085(10)
C27 0.0430(12) 0.0483(13) 0.0280(10) 0.0048(9) 0.0203(9)
0.0119(10)
C24 0.0259(11) 0.0578(15) 0.0353(11) 0.0022(10) -0.0020(9) -
0.0079(10)
C221 0.0368(12) 0.0722(17) 0.0461(12) 0.0020(11) 0.0228(10)
0.0155(12)
C34 0.0302(10) 0.0395(12) 0.0323(10) -0.0016(9) 0.0136(8) -
0.0091(9)
C28 0.0643(15) 0.0476(14) 0.0457(12) 0.0142(11) 0.0288(11) -
0.0026(12)
C261 0.0785(17) 0.0594(16) 0.0539(13) 0.0260(12) 0.0453(13)
0.0381(13)
C30 0.0482(13) 0.0390(13) 0.0526(13) 0.0060(10) 0.0125(10)
0.0168(11)
C29 0.0580(15) 0.0797(18) 0.0248(10) 0.0085(11) 0.0073(10)
0.0256(13)
C35 0.0362(12) 0.0527(15) 0.0339(11) -0.0052(10) 0.0036(9) -
0.0165(10)
C37 0.0359(11) 0.0528(14) 0.0333(10) 0.0022(9) 0.0213(9)
0.0008(10)
C32 0.0261(11) 0.0625(16) 0.0511(13) -0.0101(11) -0.0003(9)
0.0070(10)
C38 0.0761(17) 0.0492(15) 0.0483(13) -0.0108(11) 0.0330(12)
0.0133(13)
C31 0.0332(11) 0.0681(17) 0.0451(12) 0.0074(11) 0.0179(10)
0.0203(11)
C33 0.0558(14) 0.0301(12) 0.0562(13) 0.0072(10) 0.0179(11) -
0.0047(11)
C222 0.0368(11) 0.0547(14) 0.0374(11) 0.0127(10) 0.0160(9) -
0.0062(10)

_geom_special_details
;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
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 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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Sc01 N4 2.0994(13) . ?
Sc01 N3 2.1127(13) . ?
Sc01 C5 2.4301(17) . ?
Sc01 Si3 3.1014(6) . ?
Sc01 Si2 3.2341(6) . ?
Si1 N3 1.7215(14) . ?
Si1 C27 1.8620(19) . ?
Si1 C29 1.8767(18) . ?
Si1 C28 1.883(2) . ?
Si4 N4 1.7265(13) . ?
Si4 C37 1.862(2) . ?
Si4 C38 1.877(2) . ?
Si4 C36 1.8854(18) . ?
Si2 N3 1.7293(14) . ?
Si2 C31 1.8622(19) . ?
Si2 C30 1.875(2) . ?
Si2 C32 1.874(2) . ?
Si3 N4 1.7104(14) . ?
Si3 C35 1.8640(17) . ?
Si3 C33 1.872(2) . ?
Si3 C34 1.8738(18) . ?
N2 C5 1.361(2) . ?
N2 C21 1.443(2) . ?
N2 C6 1.479(2) . ?
N1 C5 1.336(2) . ?
N1 C8 1.468(2) . ?
N1 C7 1.467(2) . ?
O1 C9 1.410(2) . ?
C21 C22 1.398(2) . ?
C21 C26 1.405(2) . ?
C22 C23 1.396(2) . ?
C22 C220 1.516(2) . ?
C9 C10 1.528(2) . ?
C9 C027 1.531(2) . ?
C9 C8 1.535(2) . ?
C26 C25 1.396(2) . ?
C26 C260 1.516(2) . ?
C6 C7 1.517(2) . ?
C260 C261 1.515(3) . ?
C260 C262 1.526(2) . ?
C220 C221 1.535(2) . ?
C220 C222 1.542(3) . ?
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C23 C24 1.376(2) . ?
C25 C24 1.371(3) . ?

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O1 Sc01 N4 109.01(5) . . ?
O1 Sc01 N3 110.66(5) . . ?
N4 Sc01 N3 117.01(5) . . ?
O1 Sc01 C5 82.00(5) . . ?
N4 Sc01 C5 124.20(5) . . ?
N3 Sc01 C5 108.16(5) . . ?
O1 Sc01 Si3 140.47(4) . . ?
N4 Sc01 Si3 31.52(4) . . ?
N3 Sc01 Si3 97.45(4) . . ?
C5 Sc01 Si3 115.66(4) . . ?
O1 Sc01 Si2 92.53(4) . . ?
N4 Sc01 Si2 104.80(4) . . ?
N3 Sc01 Si2 29.17(4) . . ?
C5 Sc01 Si2 129.85(4) . . ?
Si3 Sc01 Si2 99.953(16) . . ?
N3 Si1 C27 110.63(8) . . ?
N3 Si1 C29 115.10(9) . . ?
C27 Si1 C29 104.38(9) . . ?
N3 Si1 C28 112.92(8) . . ?
C27 Si1 C28 107.66(10) . . ?
C29 Si1 C28 105.53(10) . . ?
N4 Si4 C37 111.92(8) . . ?
N4 Si4 C38 112.93(8) . . ?
C37 Si4 C38 108.11(10) . . ?
N4 Si4 C36 113.19(8) . . ?
C37 Si4 C36 105.78(9) . . ?
C38 Si4 C36 104.36(10) . . ?
N3 Si2 C31 109.91(8) . . ?
N3 Si2 C30 113.49(9) . . ?
C31 Si2 C30 105.13(10) . . ?
N3 Si2 C32 113.47(8) . . ?
C31 Si2 C32 107.12(10) . . ?
C30 Si2 C32 107.21(10) . . ?
N3 Si2 Sc01 36.55(4) . . ?
C31 Si2 Sc01 74.34(6) . . ?
C30 Si2 Sc01 132.91(7) . . ?
C32 Si2 Sc01 118.05(7) . . ?
N4 Si3 C35 116.59(8) . . ?
N4 Si3 C33 112.14(9) . . ?
C35 Si3 C33 107.33(10) . . ?
N4 Si3 C34 107.71(8) . . ?
C35 Si3 C34 104.49(9) . . ?
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C33 Si3 C34 108.05(9) . . ?
N4 Si3 Sc01 39.92(4) . . ?
C35 Si3 Sc01 144.57(7) . . ?
C33 Si3 Sc01 107.08(7) . . ?
C34 Si3 Sc01 72.24(6) . . ?
C5 N2 C21 126.21(13) . . ?
C5 N2 C6 113.23(13) . . ?
C21 N2 C6 118.52(13) . . ?
C5 N1 C8 126.37(14) . . ?
C5 N1 C7 114.37(13) . . ?
C8 N1 C7 119.26(13) . . ?
Si3 N4 Si4 121.53(8) . . ?
Si3 N4 Sc01 108.56(6) . . ?
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C40, C41 and C42 are refined isotropically due to disorder
present in
this silyl methyl group that could not be modelled.
This disorder is the origin of the large non-solvent C and H
warnings.
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_refine_special_details
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are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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P=(Fo^2^+2Fc^2^)/3'
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H5A H 0.1457 -0.0751 0.5012 0.045 Uiso 1 1 calc R . .
H5B H 0.1444 -0.0240 0.5767 0.045 Uiso 1 1 calc R . .
C6 C 0.2464(2) -0.0432(4) 0.5757(2) 0.0341(9) Uani 1 1 d . . .
H6A H 0.2586 -0.0718 0.6258 0.041 Uiso 1 1 calc R . .
H6B H 0.2620 -0.1060 0.5483 0.041 Uiso 1 1 calc R . .
C7 C 0.35403(19) 0.0955(4) 0.6038(2) 0.0294(8) Uani 1 1 d . .
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H7A H 0.3753 0.0182 0.6289 0.035 Uiso 1 1 calc R . .
H7B H 0.3645 0.1625 0.6400 0.035 Uiso 1 1 calc R . .
C8 C 0.38866(19) 0.1277(4) 0.5490(2) 0.0309(8) Uani 1 1 d . .
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C9 C 0.3710(2) 0.0339(4) 0.4885(2) 0.0422(10) Uani 1 1 d . . .
H9A H 0.3200 0.0320 0.4633 0.063 Uiso 1 1 calc R . .
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H9C H 0.3944 0.0576 0.4550 0.063 Uiso 1 1 calc R . .
C10 C 0.4682(2) 0.1348(5) 0.5883(3) 0.0452(11) Uani 1 1 d . .
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H10A H 0.4911 0.1598 0.5546 0.068 Uiso 1 1 calc R . .
H10B H 0.4859 0.0533 0.6083 0.068 Uiso 1 1 calc R . .
H10C H 0.4786 0.1958 0.6270 0.068 Uiso 1 1 calc R . .
C21 C 0.10313(19) 0.1648(4) 0.46821(19) 0.0292(8) Uani 1 1 d .
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C22 C 0.0563(2) 0.2210(5) 0.4967(2) 0.0380(10) Uani 1 1 d . .
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C23 C -0.0055(2) 0.2702(5) 0.4485(3) 0.0525(13) Uani 1 1 d . .
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C24 C -0.0207(2) 0.2636(5) 0.3760(3) 0.0553(14) Uani 1 1 d . .
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C25 C 0.0253(2) 0.2068(5) 0.3493(2) 0.0451(11) Uani 1 1 d . .
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C31 C 0.2419(3) 0.3690(4) 0.6693(2) 0.0437(11) Uani 1 1 d . .
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H31B H 0.2125 0.3747 0.6990 0.065 Uiso 1 1 calc R . .
H31C H 0.2715 0.2948 0.6828 0.065 Uiso 1 1 calc R . .
C32 C 0.2409(3) 0.6482(5) 0.6761(3) 0.0508(12) Uani 1 1 d . .
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H32A H 0.2697 0.7235 0.6871 0.076 Uiso 1 1 calc R . .
H32B H 0.2161 0.6398 0.7100 0.076 Uiso 1 1 calc R . .
H32C H 0.2065 0.6536 0.6273 0.076 Uiso 1 1 calc R . .
C33 C 0.3588(2) 0.5063(5) 0.7791(2) 0.0460(11) Uani 1 1 d . .
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H33A H 0.3889 0.4328 0.7875 0.069 Uiso 1 1 calc R . .
H33B H 0.3309 0.5034 0.8103 0.069 Uiso 1 1 calc R . .
H33C H 0.3881 0.5811 0.7897 0.069 Uiso 1 1 calc R . .
C34 C 0.4178(3) 0.7452(5) 0.6484(3) 0.0605(15) Uani 1 1 d . .
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H34A H 0.3811 0.7859 0.6088 0.091 Uiso 1 1 calc R . .
H34B H 0.4638 0.7796 0.6527 0.091 Uiso 1 1 calc R . .
H34C H 0.4091 0.7594 0.6931 0.091 Uiso 1 1 calc R . .
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H35A H 0.4386 0.4656 0.5367 0.080 Uiso 1 1 calc R . .
H35B H 0.4778 0.5969 0.5488 0.080 Uiso 1 1 calc R . .
H35C H 0.3950 0.5892 0.5055 0.080 Uiso 1 1 calc R . .
C36 C 0.4927(2) 0.5052(5) 0.7035(3) 0.0526(13) Uani 1 1 d . .
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H36B H 0.5367 0.5406 0.7022 0.079 Uiso 1 1 calc R . .
H36C H 0.4929 0.4152 0.6967 0.079 Uiso 1 1 calc R . .
C37 C 0.2272(3) 0.4613(5) 0.2478(2) 0.0478(12) Uani 1 1 d . .
.
H37A H 0.1918 0.3992 0.2471 0.072 Uiso 1 1 calc R . .
H37B H 0.2516 0.4352 0.2156 0.072 Uiso 1 1 calc R . .
H37C H 0.2042 0.5414 0.2318 0.072 Uiso 1 1 calc R . .
C38 C 0.3520(2) 0.3394(4) 0.3574(2) 0.0384(9) Uani 1 1 d . . .
H38A H 0.3889 0.3459 0.4047 0.058 Uiso 1 1 calc R . .
H38B H 0.3735 0.3365 0.3205 0.058 Uiso 1 1 calc R . .
H38C H 0.3247 0.2636 0.3551 0.058 Uiso 1 1 calc R . .
C39 C 0.3463(3) 0.6179(5) 0.3396(3) 0.0555(13) Uani 1 1 d . .
.
H39A H 0.3171 0.6923 0.3334 0.083 Uiso 1 1 calc R . .
H39B H 0.3635 0.6111 0.2996 0.083 Uiso 1 1 calc R . .
H39C H 0.3864 0.6239 0.3847 0.083 Uiso 1 1 calc R . .
C220 C 0.0705(2) 0.2268(5) 0.5765(2) 0.0475(12) Uani 1 1 d . .
.
H220 H 0.1209 0.2044 0.6020 0.057 Uiso 1 1 calc R . .
C221 C 0.0250(3) 0.1316(7) 0.5971(3) 0.077(2) Uani 1 1 d . . .
H22A H -0.0247 0.1515 0.5726 0.115 Uiso 1 1 calc R . .
H22B H 0.0360 0.1339 0.6490 0.115 Uiso 1 1 calc R . .
H22C H 0.0348 0.0486 0.5830 0.115 Uiso 1 1 calc R . .
C222 C 0.0587(3) 0.3573(6) 0.6005(3) 0.072(2) Uani 1 1 d . . .
H22D H 0.0882 0.4166 0.5867 0.108 Uiso 1 1 calc R . .
```

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H22E H 0.0712 0.3585 0.6526 0.108 Uiso 1 1 calc R . .
H22F H 0.0092 0.3802 0.5775 0.108 Uiso 1 1 calc R . .
C260 C 0.1355(2) 0.0865(4) 0.3629(2) 0.0356(9) Uani 1 1 d . .
.
H260 H 0.1709 0.0398 0.4027 0.043 Uiso 1 1 calc R . .
C261 C 0.0968(3) -0.0069(4) 0.3052(2) 0.0444(11) Uani 1 1 d .
. .
H26A H 0.0734 -0.0683 0.3253 0.067 Uiso 1 1 calc R . .
H26B H 0.1305 -0.0488 0.2878 0.067 Uiso 1 1 calc R . .
H26C H 0.0616 0.0364 0.2654 0.067 Uiso 1 1 calc R . .
C262 C 0.1750(3) 0.1780(6) 0.3336(3) 0.0642(17) Uani 1 1 d . .
.
H26D H 0.1416 0.2234 0.2934 0.096 Uiso 1 1 calc R . .
H26E H 0.2084 0.1332 0.3171 0.096 Uiso 1 1 calc R . .
H26F H 0.2006 0.2366 0.3713 0.096 Uiso 1 1 calc R . .
N1 N 0.27763(16) 0.0790(3) 0.57265(17) 0.0280(7) Uani 1 1 d .
. .
N2 N 0.16717(15) 0.1110(3) 0.51576(16) 0.0262(6) Uani 1 1 d .
. .
N3 N 0.33860(16) 0.5064(3) 0.62109(16) 0.0271(6) Uani 1 1 d .
. .
N4 N 0.25384(16) 0.4855(3) 0.40517(15) 0.0268(6) Uani 1 1 d .
. .
O1 O 0.36396(14) 0.2455(3) 0.52051(14) 0.0320(6) Uani 1 1 d .
. .
Si1 Si 0.29874(6) 0.50964(10) 0.68351(5) 0.0284(2) Uani 1 1 d
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Si2 Si 0.41691(5) 0.57492(11) 0.63059(6) 0.0296(2) Uani 1 1 d
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Si3 Si 0.29271(6) 0.47701(10) 0.34176(6) 0.0314(2) Uani 1 1 d
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U1 U 0.287742(7) 0.381720(12) 0.517980(7) 0.02415(5) Uani 1 1
d . . .
Si4 Si 0.18719(7) 0.58272(14) 0.39967(6) 0.0454(3) Uani 1 1 d
. . .
C42 C 0.1062(4) 0.5694(7) 0.3173(4) 0.0774(18) Uiso 1 1 d . .
.
C41 C 0.1543(4) 0.5436(7) 0.4758(4) 0.0791(19) Uiso 1 1 d . .
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C40 C 0.2156(5) 0.7524(9) 0.4080(5) 0.110(3) Uiso 1 1 d . . .

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0.0003(14)
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0.0088(18)
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C6 0.039(2) 0.027(2) 0.037(2) 0.0022(16) 0.0136(18) -
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0.0029(14)
C8 0.0217(17) 0.036(2) 0.0321(19) 0.0036(16) 0.0053(15)
0.0067(15)
C9 0.040(2) 0.047(3) 0.041(2) -0.0042(19) 0.0146(19) 0.008(2)
C10 0.0226(19) 0.055(3) 0.052(3) 0.009(2) 0.0059(18)
0.0081(19)
C21 0.0206(17) 0.040(2) 0.0244(18) -0.0050(15) 0.0051(14) -
0.0024(15)
C22 0.0245(19) 0.060(3) 0.029(2) -0.0153(19) 0.0090(16) -
0.0061(18)
C23 0.028(2) 0.081(4) 0.045(3) -0.018(2) 0.0075(19) 0.011(2)
C24 0.030(2) 0.082(4) 0.041(3) -0.008(2) -0.004(2) 0.016(2)
C25 0.037(2) 0.065(3) 0.026(2) -0.005(2) 0.0021(17) 0.003(2)
C26 0.0263(18) 0.043(2) 0.0250(18) -0.0054(16) 0.0080(15) -
0.0046(16)
C31 0.048(3) 0.052(3) 0.036(2) -0.009(2) 0.021(2) -0.020(2)
C32 0.054(3) 0.053(3) 0.050(3) -0.004(2) 0.025(2) 0.012(2)
C33 0.047(3) 0.064(3) 0.024(2) -0.0036(19) 0.0086(18) -
0.015(2)
C34 0.052(3) 0.039(3) 0.090(4) -0.005(3) 0.024(3) -0.010(2)
C35 0.038(3) 0.079(4) 0.046(3) -0.008(3) 0.019(2) -0.021(3)
C36 0.024(2) 0.076(4) 0.049(3) 0.013(3) 0.003(2) 0.000(2)
C37 0.067(3) 0.054(3) 0.026(2) 0.0027(19) 0.019(2) 0.010(2)
C38 0.041(2) 0.040(2) 0.042(2) 0.0032(18) 0.024(2) 0.0036(19)
C39 0.072(4) 0.042(3) 0.062(3) 0.013(2) 0.037(3) -0.008(2)
C220 0.023(2) 0.091(4) 0.029(2) -0.019(2) 0.0109(17) -0.008(2)
C221 0.040(3) 0.152(7) 0.042(3) -0.017(3) 0.021(2) -0.036(4)
C222 0.038(3) 0.121(6) 0.052(3) -0.044(3) 0.009(2) 0.012(3)
C260 0.034(2) 0.050(3) 0.0251(19) -0.0078(17) 0.0135(16) -
0.0031(18)
C261 0.050(3) 0.045(3) 0.043(2) -0.013(2) 0.022(2) -0.010(2)
C262 0.075(4) 0.074(4) 0.064(3) -0.036(3) 0.050(3) -0.040(3)
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0.0017(12)
N2 0.0195(14) 0.0354(17) 0.0232(14) 0.0004(12) 0.0069(11) -
0.0035(12)
N3 0.0248(15) 0.0339(17) 0.0212(14) -0.0009(12) 0.0062(12) -
0.0043(13)
N4 0.0292(16) 0.0289(16) 0.0194(14) 0.0031(12) 0.0048(12)
0.0042(13)
O1 0.0266(14) 0.0342(15) 0.0348(14) 0.0095(12) 0.0104(11)
0.0044(11)
Si1 0.0273(5) 0.0340(6) 0.0231(5) -0.0031(4) 0.0080(4) -
0.0044(4)
Si2 0.0233(5) 0.0342(6) 0.0288(5) 0.0001(4) 0.0060(4) -
0.0042(4)
Si3 0.0397(6) 0.0292(5) 0.0282(5) 0.0048(4) 0.0154(5)
0.0024(5)
U1 0.02144(7) 0.02671(7) 0.02071(7) 0.00227(5) 0.00296(5)
0.00080(5)
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Si4 0.0479(7) 0.0606(8) 0.0212(5) 0.0018(5) 0.0041(5)
0.0314(6)

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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C1 U1 2.693(4) . ?
C5 N2 1.474(5) . ?
C5 C6 1.518(6) . ?
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C5 H5B 0.9900 . ?
C6 N1 1.472(5) . ?
C6 H6A 0.9900 . ?
C6 H6B 0.9900 . ?
C7 N1 1.466(5) . ?
C7 C8 1.535(5) . ?
C7 H7A 0.9900 . ?
C7 H7B 0.9900 . ?
C8 O1 1.410(5) . ?
C8 C9 1.517(6) . ?
C8 C10 1.531(5) . ?
C9 H9A 0.9800 . ?
C9 H9B 0.9800 . ?
C9 H9C 0.9800 . ?
C10 H10A 0.9800 . ?
C10 H10B 0.9800 . ?
C10 H10C 0.9800 . ?
C21 C26 1.405(5) . ?
C21 C22 1.406(5) . ?
C21 N2 1.436(5) . ?
C22 C23 1.391(6) . ?
C22 C220 1.516(6) . ?
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C23 C24 1.371(7) . ?
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C25 H25 0.9500 . ?
C26 C260 1.515(5) . ?
C31 Si1 1.867(4) . ?
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C33 H33A 0.9800 . ?
C33 H33B 0.9800 . ?
C33 H33C 0.9800 . ?
C34 Si2 1.869(5) . ?
C34 H34A 0.9800 . ?
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C37 Si3 1.887(5) . ?
C37 H37A 0.9800 . ?
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C262 H26F 0.9800 . ?
N3 Si2 1.704(3) . ?
N3 Si1 1.709(3) . ?
N3 U1 2.369(3) . ?
N4 Si4 1.686(3) . ?
N4 Si3 1.714(3) . ?
N4 U1 2.388(3) . ?
O1 U1 2.122(3) . ?
U1 Si4 3.3246(12) . ?
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Si4 C40 1.909(10) . ?
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N2 C5 H5A 111.3 . . ?
C6 C5 H5A 111.3 . . ?
N2 C5 H5B 111.3 . . ?
C6 C5 H5B 111.3 . . ?
H5A C5 H5B 109.2 . . ?
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C5 C6 H6A 111.3 . . ?
N1 C6 H6B 111.3 . . ?
C5 C6 H6B 111.3 . . ?
H6A C6 H6B 109.2 . . ?
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C8 C7 H7A 108.7 . . ?
N1 C7 H7B 108.7 . . ?
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H7A C7 H7B 107.6 . . ?
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O1 C8 C10 108.9(3) . . ?
C9 C8 C10 110.6(4) . . ?
O1 C8 C7 107.6(3) . . ?
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C9 C8 C7 112.2(3) . . ?
C10 C8 C7 108.2(3) . . ?
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C8 C9 H9B 109.5 . . ?
H9A C9 H9B 109.5 . . ?
C8 C9 H9C 109.5 . . ?
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H9B C9 H9C 109.5 . . ?
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C8 C10 H10B 109.5 . . ?
H10A C10 H10B 109.5 . . ?
C8 C10 H10C 109.5 . . ?
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H10B C10 H10C 109.5 . . ?
C26 C21 C22 121.8(4) . . ?
C26 C21 N2 118.6(3) . . ?
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C25 C26 C260 120.4(4) . . ?
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Si1 C31 H31A 109.5 . . ?
Si1 C31 H31B 109.5 . . ?
H31A C31 H31B 109.5 . . ?
Si1 C31 H31C 109.5 . . ?
H31A C31 H31C 109.5 . . ?
H31B C31 H31C 109.5 . . ?
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Si1 C32 H32B 109.5 . . ?
H32A C32 H32B 109.5 . . ?
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H33B C33 H33C 109.5 . . ?
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Si2 C34 H34B 109.5 . . ?
H34A C34 H34B 109.5 . . ?
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H35B C35 H35C 109.5 . . ?
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Si2 C36 H36B 109.5 . . ?
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Si2 C36 H36C 109.5 . . ?
H36A C36 H36C 109.5 . . ?
H36B C36 H36C 109.5 . . ?
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Si3 C37 H37B 109.5 . . ?
H37A C37 H37B 109.5 . . ?
Si3 C37 H37C 109.5 . . ?
H37A C37 H37C 109.5 . . ?
H37B C37 H37C 109.5 . . ?
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Si3 C38 H38B 109.5 . . ?
H38A C38 H38B 109.5 . . ?
Si3 C38 H38C 109.5 . . ?
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H38B C38 H38C 109.5 . . ?
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Si3 C39 H39B 109.5 . . ?
H39A C39 H39B 109.5 . . ?
Si3 C39 H39C 109.5 . . ?
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H39B C39 H39C 109.5 . . ?
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C220 C221 H22B 109.5 . . ?
H22A C221 H22B 109.5 . . ?
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H22B C221 H22C 109.5 . . ?
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C220 C222 H22E 109.5 . . ?
H22D C222 H22E 109.5 . . ?
C220 C222 H22F 109.5 . . ?
H22D C222 H22F 109.5 . . ?
H22E C222 H22F 109.5 . . ?
C262 C260 C26 110.9(4) . . ?
C262 C260 C261 110.0(4) . . ?
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C26 C260 H260 107.6 . . ?
C261 C260 H260 107.6 . . ?
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C260 C261 H26B 109.5 . . ?
H26A C261 H26B 109.5 . . ?
C260 C261 H26C 109.5 . . ?
H26A C261 H26C 109.5 . . ?
H26B C261 H26C 109.5 . . ?
C260 C262 H26D 109.5 . . ?
C260 C262 H26E 109.5 . . ?
H26D C262 H26E 109.5 . . ?
C260 C262 H26F 109.5 . . ?
H26D C262 H26F 109.5 . . ?
H26E C262 H26F 109.5 . . ?
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C1 N1 C6 113.9(3) . . ?
C7 N1 C6 119.9(3) . . ?
C1 N2 C21 125.6(3) . . ?
C1 N2 C5 113.5(3) . . ?
C21 N2 C5 120.6(3) . . ?
Si2 N3 Si1 125.04(18) . . ?
Si2 N3 U1 116.59(15) . . ?
Si1 N3 U1 118.09(15) . . ?
Si4 N4 Si3 123.62(18) . . ?
Si4 N4 U1 108.15(15) . . ?
Si3 N4 U1 128.03(16) . . ?
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N3 Si1 C33 115.92(19) . . ?
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N3 Si1 C32 113.8(2) . . ?
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C34 Si2 C35 107.4(3) . . ?
N4 Si3 C38 110.93(17) . . ?
N4 Si3 C39 113.3(2) . . ?
C38 Si3 C39 107.5(2) . . ?
N4 Si3 C37 113.04(19) . . ?
C38 Si3 C37 106.4(2) . . ?
C39 Si3 C37 105.2(2) . . ?
O1 U1 N3 106.28(11) . . ?
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N4 U1 C1 122.47(10) . . ?
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 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
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are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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P=(Fo^2^+2Fc^2^)/3'
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Si1 Si 0.20500(4) -0.11039(6) 0.41549(3) 0.02291(16) Uani 1 1
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O2 O 0.30119(11) 0.23935(16) 0.31022(10) 0.0348(5) Uani 1 1 d
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N3 N 0.37351(12) 0.12260(18) 0.20772(11) 0.0257(5) Uani 1 1 d
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N5 N 0.21617(11) 0.02186(17) 0.41549(10) 0.0211(5) Uani 1 1 d
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N2 N 0.07736(11) 0.29032(17) 0.28182(10) 0.0212(5) Uani 1 1 d
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C21 C 0.06795(13) 0.3187(2) 0.34901(12) 0.0215(5) Uani 1 1 d .
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N4 N 0.39381(12) -0.03634(18) 0.23712(11) 0.0242(5) Uani 1 1 d
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C31 C 0.39494(13) -0.1320(2) 0.27367(13) 0.0224(6) Uani 1 1 d
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C11 C 0.35204(13) 0.0449(2) 0.24627(12) 0.0219(5) Uani 1 1 d .
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C6 C 0.05042(14) 0.2725(2) 0.17019(13) 0.0270(6) Uani 1 1 d .
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H6A H 0.0169 0.2212 0.1531 0.032 Uiso 1 1 calc R . .
H6B H 0.0596 0.3241 0.1354 0.032 Uiso 1 1 calc R . .
C8 C 0.15449(15) 0.0415(2) 0.16184(13) 0.0278(6) Uani 1 1 d .
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C7 C 0.15064(15) 0.1600(2) 0.14725(12) 0.0249(6) Uani 1 1 d .
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H7A H 0.1968 0.1884 0.1472 0.030 Uiso 1 1 calc R . .
H7B H 0.1303 0.1700 0.1026 0.030 Uiso 1 1 calc R . .
C26 C 0.09805(14) 0.4106(2) 0.37427(14) 0.0255(6) Uani 1 1 d .
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C32 C 0.42453(14) -0.1331(2) 0.33748(14) 0.0260(6) Uani 1 1 d
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C17 C 0.34451(16) 0.2266(2) 0.20226(15) 0.0317(7) Uani 1 1 d .
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H17A H 0.2975 0.2205 0.1852 0.038 Uiso 1 1 calc R . .
H17B H 0.3697 0.2676 0.1700 0.038 Uiso 1 1 calc R . .
C1 C 0.12595(13) 0.2293(2) 0.25805(12) 0.0204(5) Uani 1 1 d .
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C222 C -0.08606(16) 0.1698(3) 0.35876(16) 0.0381(8) Uani 1 1 d
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H22A H -0.1002 0.1811 0.4038 0.057 Uiso 1 1 calc R . .
H22B H -0.1064 0.1052 0.3413 0.057 Uiso 1 1 calc R . .
H22C H -0.1006 0.2292 0.3312 0.057 Uiso 1 1 calc R . .
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C360 C 0.33971(16) -0.2262(3) 0.17487(14) 0.0348(7) Uani 1 1 d
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H360 H 0.3379 -0.1526 0.1580 0.042 Uiso 1 1 calc R . .
C37 C 0.22013(19) 0.2395(2) 0.45854(16) 0.0418(8) Uani 1 1 d .
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H37A H 0.2586 0.2538 0.4314 0.063 Uiso 1 1 calc R . .
H37B H 0.2228 0.2841 0.4977 0.063 Uiso 1 1 calc R . .
H37C H 0.1784 0.2544 0.4333 0.063 Uiso 1 1 calc R . .
C33 C 0.42378(16) -0.2262(2) 0.37262(15) 0.0338(7) Uani 1 1 d
. . .
H33 H 0.4423 -0.2281 0.4163 0.041 Uiso 1 1 calc R . .
C22 C 0.02457(14) 0.2584(2) 0.38558(13) 0.0235(6) Uani 1 1 d .
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C110 C 0.4165(2) 0.2866(4) 0.2990(2) 0.0676(13) Uani 1 1 d . .
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H11A H 0.4179 0.3320 0.3378 0.101 Uiso 1 1 calc R . .
H11B H 0.4481 0.3128 0.2671 0.101 Uiso 1 1 calc R . .
H11C H 0.4290 0.2151 0.3120 0.101 Uiso 1 1 calc R . .
C23 C 0.01268(15) 0.2900(2) 0.44992(13) 0.0285(6) Uani 1 1 d .
. .
H23 H -0.0157 0.2490 0.4762 0.034 Uiso 1 1 calc R . .
C19 C 0.3217(3) 0.3977(3) 0.2521(3) 0.0835(19) Uani 1 1 d . .
.
H19A H 0.2768 0.3953 0.2309 0.125 Uiso 1 1 calc R . .
H19B H 0.3529 0.4310 0.2225 0.125 Uiso 1 1 calc R . .
H19C H 0.3201 0.4383 0.2929 0.125 Uiso 1 1 calc R . .
C36 C 0.36879(14) -0.2235(2) 0.24469(14) 0.0268(6) Uani 1 1 d
. . .
C18 C 0.34532(18) 0.2865(2) 0.26775(17) 0.0408(8) Uani 1 1 d .
. .
C261 C 0.20804(17) 0.5086(3) 0.37239(19) 0.0467(9) Uani 1 1 d
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H26A H 0.1971 0.5497 0.4112 0.070 Uiso 1 1 calc R . .
H26B H 0.2366 0.5503 0.3442 0.070 Uiso 1 1 calc R . .
H26C H 0.2319 0.4447 0.3862 0.070 Uiso 1 1 calc R . .
C24 C 0.04173(15) 0.3799(2) 0.47541(14) 0.0296(7) Uani 1 1 d .
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H24 H 0.0329 0.4008 0.5190 0.036 Uiso 1 1 calc R . .
C5 C 0.02680(15) 0.3260(3) 0.23132(13) 0.0319(7) Uani 1 1 d .
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H5A H 0.0273 0.4033 0.2266 0.038 Uiso 1 1 calc R . .
H5B H -0.0190 0.3030 0.2420 0.038 Uiso 1 1 calc R . .
C34 C 0.39652(16) -0.3162(3) 0.34515(16) 0.0371(7) Uani 1 1 d
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H34 H 0.3958 -0.3791 0.3701 0.045 Uiso 1 1 calc R . .
C25 C 0.08314(15) 0.4390(2) 0.43851(14) 0.0307(7) Uani 1 1 d .
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H25 H 0.1023 0.5011 0.4569 0.037 Uiso 1 1 calc R . .
C35 C 0.37030(16) -0.3153(2) 0.28166(16) 0.0353(7) Uani 1 1 d
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H35 H 0.3530 -0.3783 0.2628 0.042 Uiso 1 1 calc R . .
C361 C 0.26853(17) -0.2706(3) 0.17126(17) 0.0472(9) Uani 1 1 d
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H36B H 0.2500 -0.2645 0.1262 0.071 Uiso 1 1 calc R . .
H36C H 0.2404 -0.2312 0.2010 0.071 Uiso 1 1 calc R . .
C321 C 0.41472(18) 0.0111(3) 0.41982(19) 0.0562(11) Uani 1 1 d
. . .
H32A H 0.4113 -0.0386 0.4562 0.084 Uiso 1 1 calc R . .
H32B H 0.3698 0.0260 0.4010 0.084 Uiso 1 1 calc R . .
H32C H 0.4354 0.0763 0.4360 0.084 Uiso 1 1 calc R . .
C41 C 0.22023(17) -0.1634(2) 0.33210(14) 0.0325(7) Uani 1 1 d
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H41A H 0.1864 -0.1355 0.3006 0.049 Uiso 1 1 calc R . .
H41B H 0.2172 -0.2401 0.3330 0.049 Uiso 1 1 calc R . .
H41C H 0.2651 -0.1425 0.3189 0.049 Uiso 1 1 calc R . .
C320 C 0.45763(15) -0.0361(2) 0.36740(14) 0.0307(7) Uani 1 1 d
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H320 H 0.4617 0.0171 0.3317 0.037 Uiso 1 1 calc R . .
C9 C 0.1954(2) -0.0084(3) 0.10812(15) 0.0508(10) Uani 1 1 d .
. .
H9A H 0.2405 0.0222 0.1091 0.076 Uiso 1 1 calc R . .
H9B H 0.1733 0.0047 0.0652 0.076 Uiso 1 1 calc R . .
H9C H 0.1987 -0.0842 0.1156 0.076 Uiso 1 1 calc R . .
C221 C 0.01468(18) 0.0632(3) 0.39689(17) 0.0418(8) Uani 1 1 d
. . .
H22D H 0.0636 0.0576 0.3948 0.063 Uiso 1 1 calc R . .
H22E H -0.0063 0.0005 0.3774 0.063 Uiso 1 1 calc R . .
H22F H 0.0024 0.0694 0.4429 0.063 Uiso 1 1 calc R . .
C16 C 0.43001(18) 0.0943(3) 0.16756(18) 0.0440(9) Uani 1 1 d .
. .
H16A H 0.4674 0.1449 0.1736 0.053 Uiso 1 1 calc R . .
H16B H 0.4162 0.0910 0.1204 0.053 Uiso 1 1 calc R . .
C323 C 0.52767(17) -0.0590(3) 0.39552(19) 0.0484(9) Uani 1 1 d
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H32D H 0.5250 -0.1108 0.4309 0.073 Uiso 1 1 calc R . .
H32E H 0.5478 0.0058 0.4130 0.073 Uiso 1 1 calc R . .
H32F H 0.5554 -0.0867 0.3608 0.073 Uiso 1 1 calc R . .
C10 C 0.08442(18) -0.0058(3) 0.16233(17) 0.0451(9) Uani 1 1 d
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H10A H 0.0878 -0.0814 0.1706 0.068 Uiso 1 1 calc R . .
H10B H 0.0613 0.0061 0.1197 0.068 Uiso 1 1 calc R . .
H10C H 0.0590 0.0272 0.1970 0.068 Uiso 1 1 calc R . .
C15 C 0.44957(16) -0.0125(2) 0.19368(15) 0.0346(7) Uani 1 1 d
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H15A H 0.4521 -0.0646 0.1578 0.041 Uiso 1 1 calc R . .
H15B H 0.4932 -0.0103 0.2186 0.041 Uiso 1 1 calc R . .
C362 C 0.38544(19) -0.2900(3) 0.13076(17) 0.0544(10) Uani 1 1
d . . .
H36D H 0.4308 -0.2602 0.1330 0.082 Uiso 1 1 calc R . .
H36E H 0.3676 -0.2875 0.0853 0.082 Uiso 1 1 calc R . .
H36F H 0.3871 -0.3629 0.1458 0.082 Uiso 1 1 calc R . .
C220 C -0.00964(15) 0.1605(2) 0.35877(14) 0.0285(6) Uani 1 1 d
. . .
H220 H 0.0034 0.1518 0.3122 0.034 Uiso 1 1 calc R . .
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C39 C 0.29859(19) 0.0825(3) 0.53776(16) 0.0510(10) Uani 1 1 d
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H39A H 0.3018 0.0098 0.5530 0.077 Uiso 1 1 calc R . .
H39B H 0.2963 0.1294 0.5757 0.077 Uiso 1 1 calc R . .
H39C H 0.3382 0.0999 0.5128 0.077 Uiso 1 1 calc R . .
C42 C 0.26290(19) -0.1822(3) 0.47424(17) 0.0477(9) Uani 1 1 d
. . .
H42A H 0.3095 -0.1658 0.4645 0.072 Uiso 1 1 calc R . .
H42B H 0.2554 -0.2578 0.4697 0.072 Uiso 1 1 calc R . .
H42C H 0.2541 -0.1606 0.5193 0.072 Uiso 1 1 calc R . .
C38 C 0.1507(2) 0.0811(3) 0.54067(17) 0.0487(10) Uani 1 1 d .
. .
H38A H 0.1085 0.1024 0.5184 0.073 Uiso 1 1 calc R . .
H38B H 0.1588 0.1244 0.5799 0.073 Uiso 1 1 calc R . .
H38C H 0.1479 0.0072 0.5535 0.073 Uiso 1 1 calc R . .
C262 C 0.1063(2) 0.5801(3) 0.3126(2) 0.0547(11) Uani 1 1 d . .
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H26D H 0.0949 0.6207 0.3515 0.082 Uiso 1 1 calc R . .
H26E H 0.0650 0.5614 0.2876 0.082 Uiso 1 1 calc R . .
H26F H 0.1351 0.6221 0.2850 0.082 Uiso 1 1 calc R . .
C40 C 0.11841(17) -0.1553(3) 0.43553(17) 0.0406(8) Uani 1 1 d
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H40B H 0.1188 -0.2312 0.4431 0.061 Uiso 1 1 calc R . .
H40C H 0.0871 -0.1388 0.3988 0.061 Uiso 1 1 calc R . .
C260 C 0.14358(17) 0.4793(2) 0.33433(16) 0.0369(7) Uani 1 1 d
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PGU A -1
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C3S C 0.5223(6) 1.0636(8) -0.0142(6) 0.122(4) Uani 0.50 1 d
PGU A -1
H3S H 0.4976 1.1242 -0.0276 0.147 Uiso 0.50 1 calc PR A -1
C4S C 0.5920(6) 1.0665(7) -0.0103(4) 0.129(3) Uani 0.50 1 d
PGU A -1
H4S H 0.6150 1.1291 -0.0211 0.154 Uiso 0.50 1 calc PR A -1
C5S C 0.6280(4) 0.9779(9) 0.0092(4) 0.130(3) Uani 0.50 1 d PGU
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H5S H 0.6757 0.9799 0.0119 0.157 Uiso 0.50 1 calc PR A -1
C6S C 0.5944(6) 0.8864(7) 0.0250(3) 0.125(3) Uani 0.50 1 d PGU
A -1
H6S H 0.6190 0.8258 0.0383 0.150 Uiso 0.50 1 calc PR A -1
C1S C 0.5246(6) 0.8835(7) 0.0211(4) 0.120(3) Uani 0.50 1 d PGU
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C22 0.0211(14) 0.0247(14) 0.0246(13) -0.0018(11) -0.0007(11)
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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C222 C220 1.528(4) . ?
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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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P=(Fo^2^+2Fc^2^)/3'
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Si3 Si 0.32733(6) 0.02468(3) 0.71206(5) 0.02627(18) Uani 1 1 d
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Si4 Si 0.39930(6) 0.09749(4) 0.88111(5) 0.02556(18) Uani 1 1 d
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Si1 Si 0.04480(6) 0.16801(3) 0.78428(5) 0.02551(18) Uani 1 1 d
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Si2 Si 0.10646(6) 0.28294(3) 0.73657(5) 0.02614(18) Uani 1 1 d
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O1 O 0.13282(13) 0.11970(8) 0.58836(12) 0.0233(4) Uani 1 1 d .
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C23 C 0.5354(2) 0.32625(13) 0.6179(2) 0.0318(7) Uani 1 1 d . .
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H23 H 0.5434 0.3665 0.6298 0.038 Uiso 1 1 calc R . .
C36 C 0.3555(2) 0.16311(13) 0.9260(2) 0.0343(7) Uani 1 1 d . .
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H36A H 0.3850 0.1977 0.9094 0.051 Uiso 1 1 calc R . .
H36B H 0.3797 0.1606 0.9921 0.051 Uiso 1 1 calc R . .
H36C H 0.2788 0.1654 0.8999 0.051 Uiso 1 1 calc R . .
C24 C 0.6228(2) 0.29154(15) 0.64448(19) 0.0342(7) Uani 1 1 d .
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H24 H 0.6904 0.3080 0.6732 0.041 Uiso 1 1 calc R . .
N1 N 0.16101(17) 0.19620(11) 0.46263(15) 0.0285(6) Uani 1 1 d
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N4 N 0.33117(16) 0.09095(10) 0.76457(14) 0.0221(5) Uani 1 1 d
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N3 N 0.11722(16) 0.20837(9) 0.73716(14) 0.0208(5) Uani 1 1 d .
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N2 N 0.32420(16) 0.21991(10) 0.50740(15) 0.0248(5) Uani 1 1 d
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C1 C 0.24766(19) 0.20473(12) 0.53613(18) 0.0224(6) Uani 1 1 d
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C21 C 0.4264(2) 0.24364(13) 0.55885(17) 0.0248(6) Uani 1 1 d .
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C5S C 0.1796(4) 0.0053(2) 0.2813(3) 0.0710(13) Uani 1 1 d . .
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H5S H 0.1437 -0.0163 0.3113 0.085 Uiso 1 1 calc R . .
C8 C 0.0526(2) 0.12264(13) 0.49987(18) 0.0263(6) Uani 1 1 d .
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C26 C 0.5142(2) 0.20790(13) 0.58635(19) 0.0285(6) Uani 1 1 d .
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C22 C 0.4358(2) 0.30344(13) 0.57404(18) 0.0266(6) Uani 1 1 d .
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C7 C 0.05871(19) 0.18297(13) 0.46441(19) 0.0283(7) Uani 1 1 d
. . .
H7A H 0.0051 0.1867 0.4023 0.034 Uiso 1 1 calc R . .
H7B H 0.0423 0.2115 0.5032 0.034 Uiso 1 1 calc R . .
C30 C -0.0283(2) 0.30926(14) 0.7184(3) 0.0420(8) Uani 1 1 d .
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H30A H -0.0789 0.2922 0.6628 0.063 Uiso 1 1 calc R . .
H30B H -0.0305 0.3513 0.7127 0.063 Uiso 1 1 calc R . .
H30C H -0.0461 0.2980 0.7701 0.063 Uiso 1 1 calc R . .
C220 C 0.3417(2) 0.34404(13) 0.5416(2) 0.0323(7) Uani 1 1 d .
. .
H220 H 0.2769 0.3204 0.5277 0.039 Uiso 1 1 calc R . .
C262 C 0.5597(3) 0.12475(16) 0.5072(3) 0.0549(10) Uani 1 1 d .
. .
H26A H 0.5275 0.1458 0.4500 0.082 Uiso 1 1 calc R . .
H26B H 0.5495 0.0833 0.4957 0.082 Uiso 1 1 calc R . .
H26C H 0.6348 0.1333 0.5338 0.082 Uiso 1 1 calc R . .
C260 C 0.5087(2) 0.14321(14) 0.5727(2) 0.0370(7) Uani 1 1 d .
. .
H260 H 0.4331 0.1320 0.5456 0.044 Uiso 1 1 calc R . .
C25 C 0.6126(2) 0.23306(15) 0.6296(2) 0.0346(7) Uani 1 1 d . .
.
H25 H 0.6734 0.2095 0.6489 0.042 Uiso 1 1 calc R . .
C27 C 0.0827(2) 0.09064(13) 0.7865(2) 0.0346(7) Uani 1 1 d . .
.
H27A H 0.0609 0.0762 0.7243 0.052 Uiso 1 1 calc R . .
H27B H 0.0483 0.0681 0.8193 0.052 Uiso 1 1 calc R . .
H27C H 0.1589 0.0870 0.8171 0.052 Uiso 1 1 calc R . .
C38 C 0.5433(2) 0.10452(15) 0.9108(2) 0.0360(7) Uani 1 1 d . .
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H38A H 0.5698 0.0695 0.8923 0.054 Uiso 1 1 calc R . .
H38B H 0.5788 0.1098 0.9764 0.054 Uiso 1 1 calc R . .
H38C H 0.5570 0.1379 0.8792 0.054 Uiso 1 1 calc R . .
C9 C -0.0529(2) 0.11489(14) 0.5090(2) 0.0356(7) Uani 1 1 d . .
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H9A H -0.0547 0.0773 0.5362 0.053 Uiso 1 1 calc R . .
H9B H -0.1093 0.1170 0.4489 0.053 Uiso 1 1 calc R . .
H9C H -0.0622 0.1454 0.5477 0.053 Uiso 1 1 calc R . .
C29 C 0.0676(2) 0.19162(16) 0.9020(2) 0.0396(8) Uani 1 1 d . .
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H29A H 0.1427 0.1903 0.9391 0.059 Uiso 1 1 calc R . .
H29B H 0.0301 0.1659 0.9281 0.059 Uiso 1 1 calc R . .
H29C H 0.0419 0.2311 0.9008 0.059 Uiso 1 1 calc R . .
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C37 C 0.3716(2) 0.03587(15) 0.9445(2) 0.0385(8) Uani 1 1 d . .
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H37A H 0.2957 0.0313 0.9259 0.058 Uiso 1 1 calc R . .
H37B H 0.4030 0.0437 1.0098 0.058 Uiso 1 1 calc R . .
H37C H 0.4015 0.0004 0.9311 0.058 Uiso 1 1 calc R . .
C33 C 0.3213(2) 0.03226(15) 0.5933(2) 0.0390(8) Uani 1 1 d . .
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H33A H 0.2873 0.0688 0.5677 0.058 Uiso 1 1 calc R . .
H33B H 0.2809 0.0002 0.5563 0.058 Uiso 1 1 calc R . .
H33C H 0.3924 0.0317 0.5936 0.058 Uiso 1 1 calc R . .
C10 C 0.0692(2) 0.07648(15) 0.4392(2) 0.0392(8) Uani 1 1 d . .
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H10A H 0.1358 0.0833 0.4323 0.059 Uiso 1 1 calc R . .
H10B H 0.0118 0.0778 0.3796 0.059 Uiso 1 1 calc R . .
H10C H 0.0706 0.0385 0.4666 0.059 Uiso 1 1 calc R . .
C1S C 0.1903(2) 0.03927(14) 0.1437(2) 0.0386(8) Uani 1 1 d . .
.
C4S C 0.2720(4) 0.0335(2) 0.3314(3) 0.0639(12) Uani 1 1 d . .
.
H4S H 0.3004 0.0312 0.3958 0.077 Uiso 1 1 calc R . .
C31 C 0.2001(2) 0.31500(14) 0.8445(2) 0.0390(8) Uani 1 1 d . .
.
H31A H 0.1879 0.2981 0.8960 0.058 Uiso 1 1 calc R . .
H31B H 0.1894 0.3568 0.8437 0.058 Uiso 1 1 calc R . .
H31C H 0.2721 0.3069 0.8504 0.058 Uiso 1 1 calc R . .
C5 C 0.2899(2) 0.21729(15) 0.40724(19) 0.0374(8) Uani 1 1 d .
. .
H5A H 0.3239 0.1850 0.3885 0.045 Uiso 1 1 calc R . .
H5B H 0.3056 0.2538 0.3827 0.045 Uiso 1 1 calc R . .
C221 C 0.3463(3) 0.38824(15) 0.6142(3) 0.0464(9) Uani 1 1 d .
. .
H22A H 0.3586 0.3684 0.6716 0.070 Uiso 1 1 calc R . .
H22B H 0.2797 0.4092 0.5952 0.070 Uiso 1 1 calc R . .
H22C H 0.4034 0.4155 0.6224 0.070 Uiso 1 1 calc R . .
C28 C -0.1010(2) 0.17014(14) 0.7204(2) 0.0388(8) Uani 1 1 d .
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H28A H -0.1283 0.2074 0.7303 0.058 Uiso 1 1 calc R . .
H28B H -0.1339 0.1392 0.7421 0.058 Uiso 1 1 calc R . .
H28C H -0.1169 0.1649 0.6555 0.058 Uiso 1 1 calc R . .
C35 C 0.4467(2) -0.02067(14) 0.7688(2) 0.0425(8) Uani 1 1 d .
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H35A H 0.5094 0.0017 0.7755 0.064 Uiso 1 1 calc R . .
H35B H 0.4434 -0.0549 0.7318 0.064 Uiso 1 1 calc R . .
H35C H 0.4497 -0.0326 0.8287 0.064 Uiso 1 1 calc R . .
C6 C 0.1727(2) 0.20779(17) 0.3764(2) 0.0415(8) Uani 1 1 d . .
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H6A H 0.1330 0.2425 0.3463 0.050 Uiso 1 1 calc R . .
H6B H 0.1494 0.1745 0.3346 0.050 Uiso 1 1 calc R . .
C32 C 0.1353(3) 0.31273(14) 0.6398(2) 0.0385(8) Uani 1 1 d . .
.
H32A H 0.2029 0.2980 0.6425 0.058 Uiso 1 1 calc R . .
H32B H 0.1379 0.3549 0.6436 0.058 Uiso 1 1 calc R . .
H32C H 0.0802 0.3010 0.5825 0.058 Uiso 1 1 calc R . .
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C34 C 0.2109(2) -0.01846(14) 0.7070(2) 0.0415(8) Uani 1 1 d .
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H34A H 0.2095 -0.0213 0.7679 0.062 Uiso 1 1 calc R . .
H34B H 0.2153 -0.0572 0.6842 0.062 Uiso 1 1 calc R . .
H34C H 0.1468 0.0005 0.6664 0.062 Uiso 1 1 calc R . .
C222 C 0.3339(3) 0.37560(16) 0.4550(2) 0.0470(9) Uani 1 1 d .
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H22E H 0.2727 0.4011 0.4354 0.071 Uiso 1 1 calc R . .
H22F H 0.3267 0.3474 0.4072 0.071 Uiso 1 1 calc R . .
C11S C 0.1461(3) 0.04247(18) 0.0415(3) 0.0555(10) Uani 1 1 d .
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H11B H 0.0695 0.0405 0.0188 0.083 Uiso 1 1 calc R . .
H11C H 0.1727 0.0101 0.0170 0.083 Uiso 1 1 calc R . .
C2S C 0.2810(3) 0.06694(16) 0.1941(3) 0.0494(9) Uani 1 1 d . .
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C3S C 0.3214(3) 0.06456(19) 0.2866(3) 0.0607(11) Uani 1 1 d .
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H26D H 0.6333 0.1223 0.6920 0.080 Uiso 1 1 calc R . .
H26E H 0.5529 0.0700 0.6538 0.080 Uiso 1 1 calc R . .
H26F H 0.5234 0.1229 0.7041 0.080 Uiso 1 1 calc R . .
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 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds involving
l.s. planes.
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factor wR and
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 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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P=(Fo^2^+2Fc^2^)/3'
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C6S C 0.6382(3) 0.99101(16) 0.6886(3) 0.0624(10) Uani 1 1 d .
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H6S H 0.5748 1.0102 0.6545 0.075 Uiso 1 1 calc R . .
C7 C 0.44169(19) 0.18194(11) 1.03583(17) 0.0294(6) Uani 1 1 d
. . .
H7A H 0.4948 0.1849 1.0979 0.035 Uiso 1 1 calc R . .
H7B H 0.4585 0.2113 0.9985 0.035 Uiso 1 1 calc R . .
C8 C 0.44871(18) 0.12234(11) 0.99857(16) 0.0263(5) Uani 1 1 d
. . .
C9 C 0.4323(2) 0.07507(13) 1.05734(18) 0.0399(7) Uani 1 1 d .
. .
H9A H 0.3656 0.0813 1.0646 0.060 Uiso 1 1 calc R . .
H9B H 0.4897 0.0758 1.1166 0.060 Uiso 1 1 calc R . .
H9C H 0.4310 0.0376 1.0288 0.060 Uiso 1 1 calc R . .
C10 C 0.5542(2) 0.11599(13) 0.98936(18) 0.0367(6) Uani 1 1 d .
. .
H10A H 0.5565 0.0792 0.9604 0.055 Uiso 1 1 calc R . .
H10B H 0.6103 0.1172 1.0493 0.055 Uiso 1 1 calc R . .
H10C H 0.5636 0.1476 0.9526 0.055 Uiso 1 1 calc R . .
C11S C 0.6468(3) 0.95740(17) 0.5429(2) 0.0623(10) Uani 1 1 d .
. .
H11A H 0.6737 0.9898 0.5189 0.094 Uiso 1 1 calc R . .
H11B H 0.5702 0.9592 0.5198 0.094 Uiso 1 1 calc R . .
H11C H 0.6686 0.9211 0.5240 0.094 Uiso 1 1 calc R . .
C21 C 0.07381(18) 0.24341(11) 0.94150(16) 0.0259(5) Uani 1 1 d
. . .
C22 C 0.0653(2) 0.30308(11) 0.92699(16) 0.0280(5) Uani 1 1 d .
. .
C23 C -0.0345(2) 0.32585(12) 0.88238(18) 0.0331(6) Uani 1 1 d
. . .
H23 H -0.0423 0.3660 0.8707 0.040 Uiso 1 1 calc R . .
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C24 C -0.1222(2) 0.29126(13) 0.85491(18) 0.0365(7) Uani 1 1 d
. . .
H24 H -0.1897 0.3077 0.8255 0.044 Uiso 1 1 calc R . .
C25 C -0.1120(2) 0.23290(13) 0.87015(18) 0.0352(6) Uani 1 1 d
. . .
H25 H -0.1729 0.2094 0.8509 0.042 Uiso 1 1 calc R . .
C26 C -0.0141(2) 0.20760(11) 0.91324(17) 0.0294(6) Uani 1 1 d
. . .
C27 C 0.6004(2) 0.17069(12) 0.7770(2) 0.0382(7) Uani 1 1 d . .
.
H27A H 0.6281 0.2075 0.7656 0.057 Uiso 1 1 calc R . .
H27B H 0.6327 0.1390 0.7563 0.057 Uiso 1 1 calc R . .
H27C H 0.6165 0.1665 0.8417 0.057 Uiso 1 1 calc R . .
C28 C 0.4174(2) 0.09150(11) 0.7113(2) 0.0357(6) Uani 1 1 d . .
.
H28A H 0.4402 0.0767 0.7731 0.054 Uiso 1 1 calc R . .
H28B H 0.4512 0.0695 0.6777 0.054 Uiso 1 1 calc R . .
H28C H 0.3412 0.0877 0.6818 0.054 Uiso 1 1 calc R . .
C29 C 0.4317(2) 0.19347(14) 0.59713(19) 0.0408(7) Uani 1 1 d .
. .
H29A H 0.3565 0.1929 0.5606 0.061 Uiso 1 1 calc R . .
H29B H 0.4683 0.1677 0.5703 0.061 Uiso 1 1 calc R . .
H29C H 0.4585 0.2327 0.5991 0.061 Uiso 1 1 calc R . .
C30 C 0.5301(2) 0.30975(12) 0.7827(2) 0.0421(7) Uani 1 1 d . .
.
H30A H 0.5807 0.2921 0.8373 0.063 Uiso 1 1 calc R . .
H30B H 0.5325 0.3517 0.7896 0.063 Uiso 1 1 calc R . .
H30C H 0.5476 0.2993 0.7307 0.063 Uiso 1 1 calc R . .
C31 C 0.3656(2) 0.31265(12) 0.8609(2) 0.0383(7) Uani 1 1 d . .
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H31A H 0.2966 0.2991 0.8568 0.057 Uiso 1 1 calc R . .
H31B H 0.3657 0.3548 0.8588 0.057 Uiso 1 1 calc R . .
H31C H 0.4190 0.2995 0.9178 0.057 Uiso 1 1 calc R . .
C32 C 0.3022(2) 0.31646(12) 0.6580(2) 0.0400(7) Uani 1 1 d . .
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H32A H 0.3170 0.3018 0.6067 0.060 Uiso 1 1 calc R . .
H32B H 0.3108 0.3584 0.6614 0.060 Uiso 1 1 calc R . .
H32C H 0.2301 0.3067 0.6501 0.060 Uiso 1 1 calc R . .
C33 C 0.2883(2) -0.01822(12) 0.7916(2) 0.0425(7) Uani 1 1 d .
. .
H33A H 0.2897 -0.0209 0.7310 0.064 Uiso 1 1 calc R . .
H33B H 0.2839 -0.0570 0.8141 0.064 Uiso 1 1 calc R . .
H33C H 0.3525 0.0006 0.8320 0.064 Uiso 1 1 calc R . .
C34 C 0.1786(2) 0.03259(12) 0.90579(18) 0.0388(7) Uani 1 1 d .
. .
H34A H 0.2107 0.0696 0.9304 0.058 Uiso 1 1 calc R . .
H34B H 0.2208 0.0013 0.9428 0.058 Uiso 1 1 calc R . .
H34C H 0.1077 0.0309 0.9060 0.058 Uiso 1 1 calc R . .
C35 C 0.0527(2) -0.02063(12) 0.7314(2) 0.0422(7) Uani 1 1 d .
. .
H35A H -0.0100 0.0015 0.7257 0.063 Uiso 1 1 calc R . .
H35B H 0.0568 -0.0551 0.7679 0.063 Uiso 1 1 calc R . .
H35C H 0.0490 -0.0321 0.6714 0.063 Uiso 1 1 calc R . .
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C36 C -0.04341(19) 0.10360(13) 0.58925(18) 0.0367(6) Uani 1 1
d . . .
H36A H -0.0696 0.0688 0.6084 0.055 Uiso 1 1 calc R . .
H36B H -0.0784 0.1082 0.5239 0.055 Uiso 1 1 calc R . .
H36C H -0.0579 0.1372 0.6196 0.055 Uiso 1 1 calc R . .
C37 C 0.1290(2) 0.03537(13) 0.55638(19) 0.0403(7) Uani 1 1 d .
. .
H37A H 0.2048 0.0322 0.5726 0.061 Uiso 1 1 calc R . .
H37B H 0.0947 0.0422 0.4914 0.061 Uiso 1 1 calc R . .
H37C H 0.1024 -0.0004 0.5722 0.061 Uiso 1 1 calc R . .
C38 C 0.1430(2) 0.16258(12) 0.57320(18) 0.0358(6) Uani 1 1 d .
. .
H38A H 0.1150 0.1972 0.5911 0.054 Uiso 1 1 calc R . .
H38B H 0.1165 0.1602 0.5073 0.054 Uiso 1 1 calc R . .
H38C H 0.2197 0.1646 0.5971 0.054 Uiso 1 1 calc R . .
C220 C 0.1585(2) 0.34358(12) 0.95925(19) 0.0334(6) Uani 1 1 d
. . .
H220 H 0.2234 0.3200 0.9732 0.040 Uiso 1 1 calc R . .
C221 C 0.1550(2) 0.38805(13) 0.8876(2) 0.0466(8) Uani 1 1 d .
. .
H22A H 0.1441 0.3684 0.8307 0.070 Uiso 1 1 calc R . .
H22B H 0.2213 0.4093 0.9075 0.070 Uiso 1 1 calc R . .
H22C H 0.0972 0.4150 0.8787 0.070 Uiso 1 1 calc R . .
C222 C 0.1658(2) 0.37491(14) 1.0457(2) 0.0483(8) Uani 1 1 d .
. .
H22D H 0.1019 0.3974 1.0341 0.072 Uiso 1 1 calc R . .
H22E H 0.2265 0.4007 1.0651 0.072 Uiso 1 1 calc R . .
H22F H 0.1737 0.3466 1.0932 0.072 Uiso 1 1 calc R . .
C260 C -0.0086(2) 0.14272(12) 0.9271(2) 0.0386(7) Uani 1 1 d .
. .
H260 H 0.0669 0.1315 0.9537 0.046 Uiso 1 1 calc R . .
C261 C -0.0591(3) 0.11135(14) 0.8369(2) 0.0552(9) Uani 1 1 d .
. .
H26A H -0.1327 0.1228 0.8083 0.083 Uiso 1 1 calc R . .
H26B H -0.0547 0.0697 0.8472 0.083 Uiso 1 1 calc R . .
H26C H -0.0221 0.1215 0.7973 0.083 Uiso 1 1 calc R . .
C262 C -0.0597(3) 0.12469(14) 0.9934(2) 0.0554(9) Uani 1 1 d .
. .
H26D H -0.0269 0.1458 1.0501 0.083 Uiso 1 1 calc R . .
H26E H -0.0499 0.0833 1.0051 0.083 Uiso 1 1 calc R . .
H26F H -0.1347 0.1335 0.9674 0.083 Uiso 1 1 calc R . .
N1 N 0.33864(16) 0.19455(10) 1.03749(13) 0.0295(5) Uani 1 1 d
. . .
N2 N 0.17593(15) 0.21940(9) 0.99290(13) 0.0251(4) Uani 1 1 d .
. .
N3 N 0.38300(14) 0.20903(8) 0.76215(13) 0.0210(4) Uani 1 1 d .
. .
N4 N 0.16838(15) 0.09100(8) 0.73535(13) 0.0227(4) Uani 1 1 d .
. .
O1 O 0.36837(12) 0.12009(7) 0.91047(10) 0.0235(4) Uani 1 1 d .
. .
Si1 Si 0.45451(5) 0.16883(3) 0.71416(5) 0.02554(15) Uani 1 1 d
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Si2 Si 0.39486(5) 0.28318(3) 0.76427(5) 0.02626(15) Uani 1 1 d
. . .
Si3 Si 0.17202(5) 0.02490(3) 0.78727(5) 0.02705(15) Uani 1 1 d
. . .
Si4 Si 0.10070(5) 0.09700(3) 0.61957(4) 0.02622(15) Uani 1 1 d
. . .
Cl1 Cl 0.10516(5) 0.24260(3) 0.74265(4) 0.03054(14) Uani 1 1 d
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U1 U 0.260810(6) 0.168534(3) 0.808895(5) 0.01781(3) Uani 1 1 d
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0.0105(14)
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C7 0.0188(12) 0.0395(15) 0.0242(13) -0.0054(11) 0.0017(10)
0.0014(11)
C8 0.0182(12) 0.0346(14) 0.0193(12) 0.0027(10) -0.0007(9)
0.0061(10)
C9 0.0352(16) 0.0467(17) 0.0306(15) 0.0127(13) 0.0041(12)
0.0059(13)
C10 0.0220(13) 0.0487(17) 0.0333(15) -0.0002(13) 0.0037(11)
0.0065(12)
C11S 0.056(2) 0.069(2) 0.066(2) -0.0019(19) 0.0275(19) -
0.0035(19)
C21 0.0224(12) 0.0365(14) 0.0207(12) -0.0026(10) 0.0103(10)
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C22 0.0293(14) 0.0354(15) 0.0244(13) -0.0005(11) 0.0160(11)
0.0031(11)
C23 0.0353(15) 0.0384(16) 0.0305(14) 0.0037(11) 0.0181(12)
0.0092(12)
C24 0.0234(14) 0.0551(19) 0.0299(14) 0.0001(13) 0.0089(11)
0.0120(13)
C25 0.0237(14) 0.0491(17) 0.0324(15) -0.0075(13) 0.0099(11) -
0.0032(12)
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C26 0.0268(13) 0.0377(15) 0.0260(13) -0.0068(11) 0.0124(11) -0.0006(11)
C27 0.0223(14) 0.0463(17) 0.0482(18) 0.0002(13) 0.0160(13) 0.0024(12)
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C34 0.0380(16) 0.0391(16) 0.0377(16) 0.0053(13) 0.0125(13) -0.0053(13)
C35 0.0378(16) 0.0324(15) 0.0483(18) -0.0006(13) 0.0069(14) -0.0128(13)
C36 0.0223(14) 0.0489(17) 0.0312(15) 0.0019(12) 0.0014(11) 0.0000(12)
C37 0.0335(15) 0.0517(18) 0.0340(15) -0.0173(13) 0.0107(12) -0.0072(13)
C38 0.0326(15) 0.0481(17) 0.0218(13) 0.0027(12) 0.0049(11) -0.0014(12)
C220 0.0291(14) 0.0362(15) 0.0406(16) 0.0000(12) 0.0195(12) 0.0012(12)
C221 0.0479(18) 0.0372(16) 0.065(2) 0.0101(15) 0.0331(17) 0.0034(14)
C222 0.0381(17) 0.057(2) 0.0543(19) -0.0148(16) 0.0229(15) -0.0143(15)
C260 0.0290(15) 0.0377(16) 0.0496(18) -0.0066(14) 0.0152(13) -0.0026(12)
C261 0.0464(19) 0.0497(19) 0.067(2) -0.0228(17) 0.0182(17) -0.0092(15)
C262 0.059(2) 0.0477(19) 0.067(2) 0.0060(17) 0.0316(18) -0.0031(16)
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N2 0.0209(10) 0.0357(12) 0.0190(10) -0.0007(9) 0.0078(8) 0.0033(9)
N3 0.0182(10) 0.0237(10) 0.0212(10) -0.0011(8) 0.0074(8) -0.0006(8)
N4 0.0177(10) 0.0255(11) 0.0211(10) -0.0011(8) 0.0030(8) 0.0013(8)
O1 0.0190(8) 0.0256(9) 0.0214(8) 0.0001(7) 0.0025(7) 0.0021(7)
Si1 0.0190(3) 0.0306(4) 0.0298(4) -0.0030(3) 0.0124(3) 0.0007(3)
Si2 0.0226(3) 0.0244(4) 0.0332(4) -0.0003(3) 0.0122(3) -0.0016(3)
Si3 0.0229(3) 0.0238(3) 0.0302(4) -0.0004(3) 0.0052(3) -0.0017(3)

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0.0023(3)
Cl1 0.0264(3) 0.0370(3) 0.0268(3) 0.0055(3) 0.0083(2)
0.0121(3)
U1 0.01374(5) 0.02116(5) 0.01704(5) -0.00079(3) 0.00411(3) -
0.00005(3)

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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C7 C8 1.525(3) . ?
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C8 C9 1.518(4) . ?
C8 C10 1.524(3) . ?
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C22 C220 1.518(4) . ?
C23 C24 1.379(4) . ?
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C30 Si2 1.880(3) . ?
C31 Si2 1.871(3) . ?
C32 Si2 1.868(3) . ?
C33 Si3 1.870(3) . ?
C34 Si3 1.875(3) . ?
C35 Si3 1.875(3) . ?
C36 Si4 1.866(3) . ?
C37 Si4 1.878(3) . ?
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C220 C221 1.531(4) . ?
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C260 C261 1.531(4) . ?
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N4 U1 2.2637(19) . ?
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O1 C8 C9 110.2(2) . . ?
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C21 C22 C220 123.3(2) . . ?
C24 C23 C22 121.4(3) . . ?
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C24 C25 C26 121.3(3) . . ?
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C21 C26 C260 123.6(2) . . ?
C22 C220 C221 112.3(2) . . ?
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C26 C260 C261 110.8(2) . . ?
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C1 N1 C5 114.3(2) . . ?
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C21 N2 C6 118.30(19) . . ?
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Si2 N3 U1 118.60(10) . . ?
Si1 N3 U1 122.40(10) . . ?
Si3 N4 Si4 119.22(11) . . ?
Si3 N4 U1 123.02(10) . . ?
Si4 N4 U1 117.49(10) . . ?
C8 O1 U1 144.52(14) . . ?
N3 Si1 C28 109.44(11) . . ?
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_exptl_special_details
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 Tmax/Tmin(RR) > 1.10
 SADABS corrects for all systematic errors that lead
 to disparities in the intensities of symmetry-equivalent
 data. These may include absorption by the
 mount, crystal decay, changes in the volume of the
 crystal illuminated, etc. The crystal dimensions are
 noted to be large: 0.56 x 0.38 x 0.21 as is the presence
 of heavy atoms (U)
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_computing_structure_solution     'SIR-92 (Giacovazzo, 1994)'
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2004)'

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are based
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expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
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factors based
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on F, and R-
 factors based on ALL data will be even larger.
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H7B H 0.9352 -0.2208 0.0509 0.046 Uiso 1 1 calc R . .
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H10C H 0.9008 -0.2089 0.1813 0.080 Uiso 1 1 calc R . .
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C25 C 0.74016(19) 0.0262(7) 0.0409(4) 0.0521(19) Uani 1 1 d .
. .
H25 H 0.7244 0.0638 0.0086 0.063 Uiso 1 1 calc R . .
C26 C 0.77316(16) -0.0168(6) 0.0244(3) 0.0360(14) Uani 1 1 d .
. .
C27 C 0.99621(17) 0.2397(8) 0.0388(3) 0.056(2) Uani 1 1 d . .
.
H27A H 0.9964 0.1502 0.0480 0.084 Uiso 1 1 calc R . .
H27B H 1.0184 0.2770 0.0575 0.084 Uiso 1 1 calc R . .
H27C H 0.9940 0.2530 -0.0082 0.084 Uiso 1 1 calc R . .
C28 C 0.9587(2) 0.4842(7) 0.0596(4) 0.062(2) Uani 1 1 d . . .
H28A H 0.9589 0.4986 0.0128 0.093 Uiso 1 1 calc R . .
H28B H 0.9802 0.5200 0.0819 0.093 Uiso 1 1 calc R . .
H28C H 0.9377 0.5235 0.0757 0.093 Uiso 1 1 calc R . .
C29 C 0.96472(18) 0.2937(9) 0.1657(3) 0.056(2) Uani 1 1 d . .
.
H29A H 0.9452 0.3335 0.1866 0.084 Uiso 1 1 calc R . .
H29B H 0.9873 0.3324 0.1813 0.084 Uiso 1 1 calc R . .
H29C H 0.9654 0.2049 0.1763 0.084 Uiso 1 1 calc R . .
C30 C 0.93533(19) 0.2893(8) -0.0914(3) 0.0501(19) Uani 1 1 d .
. .
H30A H 0.9487 0.3653 -0.0797 0.075 Uiso 1 1 calc R . .
H30B H 0.9235 0.2983 -0.1350 0.075 Uiso 1 1 calc R . .
H30C H 0.9517 0.2184 -0.0905 0.075 Uiso 1 1 calc R . .
C31 C 0.86830(19) 0.3917(6) -0.0433(3) 0.0459(17) Uani 1 1 d .
. .
H31A H 0.8486 0.3778 -0.0157 0.069 Uiso 1 1 calc R . .
H31B H 0.8590 0.3946 -0.0889 0.069 Uiso 1 1 calc R . .
H31C H 0.8800 0.4707 -0.0315 0.069 Uiso 1 1 calc R . .
C32 C 0.87793(19) 0.1144(6) -0.0576(3) 0.0428(16) Uani 1 1 d .
. .
H32A H 0.8952 0.0463 -0.0561 0.064 Uiso 1 1 calc R . .
H32B H 0.8671 0.1236 -0.1020 0.064 Uiso 1 1 calc R . .
H32C H 0.8594 0.0959 -0.0283 0.064 Uiso 1 1 calc R . .
C33 C 0.9245(2) 0.3274(10) 0.3334(4) 0.082(3) Uani 1 1 d . . .
H33A H 0.9452 0.3359 0.3077 0.123 Uiso 1 1 calc R . .
H33B H 0.9325 0.3021 0.3777 0.123 Uiso 1 1 calc R . .
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H33C H 0.9121 0.4073 0.3345 0.123 Uiso 1 1 calc R . .
C34 C 0.9195(3) 0.0596(9) 0.2980(4) 0.085(3) Uani 1 1 d . . .
H34A H 0.9042 -0.0098 0.2829 0.128 Uiso 1 1 calc R . .
H34B H 0.9291 0.0439 0.3427 0.128 Uiso 1 1 calc R . .
H34C H 0.9392 0.0676 0.2699 0.128 Uiso 1 1 calc R . .
C35 C 0.8573(2) 0.1854(7) 0.3524(3) 0.0490(18) Uani 1 1 d . .
.
H35A H 0.8470 0.2667 0.3614 0.074 Uiso 1 1 calc R . .
H35B H 0.8675 0.1484 0.3930 0.074 Uiso 1 1 calc R . .
H35C H 0.8387 0.1307 0.3326 0.074 Uiso 1 1 calc R . .
C36 C 0.8553(2) 0.4605(7) 0.1357(3) 0.057(2) Uani 1 1 d . . .
H36A H 0.8803 0.4872 0.1372 0.086 Uiso 1 1 calc R . .
H36B H 0.8398 0.5337 0.1336 0.086 Uiso 1 1 calc R . .
H36C H 0.8499 0.4086 0.0972 0.086 Uiso 1 1 calc R . .
C37 C 0.8009(2) 0.3163(10) 0.2051(4) 0.085(3) Uani 1 1 d . . .
H37A H 0.7964 0.2613 0.1675 0.128 Uiso 1 1 calc R . .
H37B H 0.7851 0.3887 0.2003 0.128 Uiso 1 1 calc R . .
H37C H 0.7963 0.2711 0.2447 0.128 Uiso 1 1 calc R . .
C38 C 0.8524(4) 0.4860(9) 0.2770(4) 0.114(5) Uani 1 1 d . . .
H38A H 0.8456 0.4480 0.3173 0.171 Uiso 1 1 calc R . .
H38B H 0.8369 0.5571 0.2658 0.171 Uiso 1 1 calc R . .
H38C H 0.8772 0.5144 0.2829 0.171 Uiso 1 1 calc R . .
C220 C 0.80968(19) -0.1472(8) 0.1915(3) 0.056(2) Uani 1 1 d .
. .
H220 H 0.8299 -0.1872 0.1709 0.067 Uiso 1 1 calc R . .
C221 C 0.8248(3) -0.0544(10) 0.2408(5) 0.115(5) Uani 1 1 d . .
.
H22A H 0.8054 -0.0175 0.2634 0.172 Uiso 1 1 calc R . .
H22B H 0.8373 0.0111 0.2189 0.172 Uiso 1 1 calc R . .
H22C H 0.8414 -0.0965 0.2724 0.172 Uiso 1 1 calc R . .
C222 C 0.7906(3) -0.2458(7) 0.2267(4) 0.072(3) Uani 1 1 d . .
.
H22D H 0.8066 -0.2794 0.2621 0.108 Uiso 1 1 calc R . .
H22E H 0.7832 -0.3129 0.1964 0.108 Uiso 1 1 calc R . .
H22F H 0.7696 -0.2097 0.2445 0.108 Uiso 1 1 calc R . .
C260 C 0.78349(17) -0.0028(6) -0.0442(3) 0.0353(14) Uani 1 1 d
. . .
H260 H 0.8087 -0.0313 -0.0452 0.042 Uiso 1 1 calc R . .
C261 C 0.7818(2) 0.1333(7) -0.0658(4) 0.0501(18) Uani 1 1 d .
. .
H26A H 0.7571 0.1623 -0.0677 0.075 Uiso 1 1 calc R . .
H26B H 0.7908 0.1408 -0.1088 0.075 Uiso 1 1 calc R . .
H26C H 0.7964 0.1841 -0.0347 0.075 Uiso 1 1 calc R . .
C262 C 0.76051(19) -0.0846(7) -0.0907(3) 0.0506(18) Uani 1 1 d
. . .
H26D H 0.7616 -0.1708 -0.0753 0.076 Uiso 1 1 calc R . .
H26E H 0.7693 -0.0802 -0.1341 0.076 Uiso 1 1 calc R . .
H26F H 0.7358 -0.0553 -0.0927 0.076 Uiso 1 1 calc R . .
N1 N 0.88554(13) -0.1564(4) 0.0562(3) 0.0356(12) Uani 1 1 d .
. .
N2 N 0.82937(13) -0.1210(4) 0.0586(2) 0.0264(10) Uani 1 1 d .
. .
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N3 N 0.91767(12) 0.2482(4) 0.0485(2) 0.0242(10) Uani 1 1 d . .
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N4 N 0.87679(12) 0.2432(4) 0.2178(2) 0.0255(10) Uani 1 1 d . .
.
F1 F 0.83666(8) 0.1993(3) 0.07469(16) 0.0330(8) Uani 1 1 d . .
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O1 O 0.92262(10) 0.0072(4) 0.14873(19) 0.0322(9) Uani 1 1 d .
. .
Si1 Si 0.95759(5) 0.31356(18) 0.07565(9) 0.0370(4) Uani 1 1 d
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Si2 Si 0.90098(4) 0.26241(15) -0.03156(8) 0.0287(4) Uani 1 1 d
. . .
Si3 Si 0.89326(5) 0.2054(2) 0.29511(8) 0.0421(5) Uani 1 1 d .
. .
Si4 Si 0.84798(6) 0.36899(17) 0.21011(8) 0.0420(5) Uani 1 1 d
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U001 U 0.885410(5) 0.143810(18) 0.120510(10) 0.02294(7) Uani 1
1 d . . .

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C5 0.043(4) 0.023(3) 0.040(3) -0.007(3) 0.010(3) -0.010(3)
C6 0.048(4) 0.023(3) 0.029(3) -0.004(2) 0.010(3) 0.001(3)
C7 0.030(3) 0.033(3) 0.053(4) -0.011(3) 0.016(3) 0.005(3)
C8 0.034(3) 0.029(3) 0.050(4) 0.001(3) 0.010(3) 0.014(3)
C9 0.041(4) 0.058(5) 0.073(5) -0.005(4) 0.001(4) 0.022(4)
C10 0.060(5) 0.041(4) 0.060(5) 0.014(4) 0.009(4) 0.021(4)
C21 0.028(3) 0.028(3) 0.040(3) -0.003(3) 0.013(3) -0.006(3)
C22 0.035(3) 0.047(4) 0.038(4) -0.002(3) 0.010(3) -0.005(3)
C23 0.046(4) 0.061(5) 0.051(4) -0.005(4) 0.021(4) -0.004(4)
C24 0.039(4) 0.057(5) 0.075(5) 0.002(4) 0.027(4) 0.006(4)
C25 0.039(4) 0.051(4) 0.068(5) 0.011(4) 0.013(4) 0.004(3)
C26 0.033(3) 0.029(3) 0.047(4) 0.001(3) 0.007(3) -0.003(3)
C27 0.026(4) 0.094(6) 0.048(4) -0.015(4) 0.007(3) -0.004(4)
C28 0.063(5) 0.050(5) 0.078(6) -0.021(4) 0.028(4) -0.028(4)
C29 0.034(4) 0.094(6) 0.040(4) -0.013(4) 0.004(3) -0.015(4)
C30 0.051(4) 0.065(5) 0.037(4) 0.001(3) 0.020(3) -0.008(4)
C31 0.058(5) 0.045(4) 0.035(4) 0.005(3) 0.005(3) 0.015(3)
C32 0.051(4) 0.046(4) 0.031(3) -0.011(3) -0.002(3) -0.012(3)
C33 0.057(5) 0.141(10) 0.047(5) -0.021(5) -0.005(4) -0.013(6)
C34 0.121(8) 0.101(7) 0.035(4) 0.024(5) 0.018(5) 0.074(7)
C35 0.065(5) 0.059(5) 0.024(3) -0.001(3) 0.011(3) -0.001(4)
C36 0.089(6) 0.038(4) 0.047(4) 0.010(3) 0.025(4) 0.024(4)
C37 0.054(5) 0.137(9) 0.068(6) 0.048(6) 0.029(4) 0.056(6)
C38 0.235(15) 0.059(6) 0.045(5) -0.016(4) -0.007(7) 0.062(8)
C220 0.034(4) 0.103(7) 0.033(4) 0.000(4) 0.012(3) -0.001(4)
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C221 0.168(12) 0.103(9) 0.065(6) 0.032(6) -0.039(7) -0.073(9)
C222 0.090(7) 0.044(5) 0.079(6) 0.012(4) -0.013(5) -0.006(4)
C260 0.030(3) 0.037(4) 0.038(3) 0.005(3) 0.001(3) -0.004(3)
C261 0.050(4) 0.053(5) 0.046(4) 0.013(3) -0.002(3) -0.003(4)
C262 0.047(4) 0.060(5) 0.043(4) -0.005(4) -0.008(3) -0.014(4)
N1 0.034(3) 0.021(3) 0.053(3) -0.008(2) 0.015(2) 0.004(2)
N2 0.033(3) 0.019(2) 0.028(2) -0.0018(19) 0.008(2) -0.0036(19)
N3 0.025(2) 0.020(2) 0.028(2) -0.0053(19) 0.003(2) -0.0035(19)
N4 0.025(2) 0.027(2) 0.024(2) 0.0046(19) 0.0041(19) 0.003(2)
F1 0.0294(18) 0.0356(19) 0.0336(18) 0.0001(15) 0.0000(15)
0.0054(15)
O1 0.030(2) 0.029(2) 0.038(2) -0.0035(18) 0.0074(18)
0.0080(17)
Si1 0.0285(9) 0.0477(11) 0.0360(9) -0.0106(8) 0.0098(7) -
0.0130(8)
Si2 0.0307(9) 0.0301(9) 0.0262(8) -0.0014(7) 0.0081(7) -
0.0010(7)
Si3 0.0418(11) 0.0610(13) 0.0236(9) 0.0036(8) 0.0029(8)
0.0162(9)
Si4 0.0656(13) 0.0356(10) 0.0260(9) 0.0002(7) 0.0103(8)
0.0235(9)
U001 0.02300(11) 0.02077(11) 0.02579(11) -0.00208(9)
0.00660(8) 0.00107(9)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C5 C6 1.516(8) . ?
C6 N1 1.461(7) . ?
C7 N1 1.454(8) . ?
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C7 C8 1.533(9) . ?
C8 O1 1.434(7) . ?
C8 C9 1.519(9) . ?
C8 C10 1.522(9) . ?
C21 C26 1.388(9) . ?
C21 C22 1.406(8) . ?
C21 N2 1.451(7) . ?
C22 C23 1.380(9) . ?
C22 C220 1.551(10) . ?
C23 C24 1.375(10) . ?
C24 C25 1.376(10) . ?
C25 C26 1.394(9) . ?
C26 C260 1.506(8) . ?
C27 Si1 1.871(7) . ?
C28 Si1 1.865(8) . ?
C29 Si1 1.871(7) . ?
C30 Si2 1.880(6) . ?
C31 Si2 1.861(7) . ?
C32 Si2 1.872(6) . ?
C33 Si3 1.894(9) . ?
C34 Si3 1.853(8) . ?
C35 Si3 1.879(7) . ?
C36 Si4 1.863(7) . ?
C37 Si4 1.858(9) . ?
C38 Si4 1.866(8) . ?
C220 C222 1.500(11) . ?
C220 C221 1.506(12) . ?
C260 C262 1.522(9) . ?
C260 C261 1.530(9) . ?
N3 Si1 1.715(5) . ?
N3 Si2 1.730(5) . ?
N3 U001 2.287(4) . ?
N4 Si3 1.716(5) . ?
N4 Si4 1.734(5) . ?
N4 U001 2.322(4) . ?
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O1 U001 2.082(4) . ?
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Si4 U001 3.4182(17) . ?

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N1 C6 C5 102.6(5) . . ?
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O1 C8 C9 109.0(5) . . ?
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C23 C22 C21 117.8(6) . . ?
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C21 C26 C260 123.0(5) . . ?
C25 C26 C260 119.9(6) . . ?
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C222 C220 C22 113.0(6) . . ?
C221 C220 C22 111.0(8) . . ?
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C26 C260 C261 111.2(5) . . ?
C262 C260 C261 111.1(6) . . ?
C1 N1 C7 125.9(5) . . ?
C1 N1 C6 114.0(5) . . ?
C7 N1 C6 120.1(5) . . ?
C1 N2 C21 127.0(5) . . ?
C1 N2 C5 113.4(5) . . ?
C21 N2 C5 119.3(5) . . ?
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N3 Si1 C27 112.6(3) . . ?
C28 Si1 C27 108.4(4) . . ?
N3 Si1 C29 109.5(3) . . ?
C28 Si1 C29 106.6(4) . . ?
C27 Si1 C29 107.4(3) . . ?
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C32 Si2 C30 105.7(3) . . ?
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N4 Si3 C33 113.1(4) . . ?
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C35 Si3 C33 105.8(4) . . ?
N4 Si4 C37 110.8(4) . . ?
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C37 Si4 C36 108.5(4) . . ?
N4 Si4 C38 116.0(4) . . ?
C37 Si4 C38 106.1(5) . . ?
C36 Si4 C38 104.1(4) . . ?
C37 Si4 U001 100.7(3) . . ?
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C38 Si4 U001 149.4(4) . . ?
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F1 U001 N4 94.81(14) . . ?
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C22 C21 C26 C25 2.2(9) . . . . ?
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N2 C21 C26 C260 -4.9(9) . . . . ?
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C23 C22 C220 C222 49.6(10) . . . . ?
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U001 C1 N1 C7 3.4(8) . . . . ?
N2 C1 N1 C6 -0.8(7) . . . . ?
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C8 C7 N1 C1 53.7(8) . . . . ?
C8 C7 N1 C6 -125.1(6) . . . . ?
C5 C6 N1 C1 0.8(7) . . . . ?
C5 C6 N1 C7 179.6(5) . . . . ?
N1 C1 N2 C21 174.1(5) . . . . ?
U001 C1 N2 C21 -9.6(9) . . . . ?
N1 C1 N2 C5 0.6(7) . . . . ?
U001 C1 N2 C5 176.9(4) . . . . ?
C26 C21 N2 C1 107.3(7) . . . . ?
C22 C21 N2 C1 -78.0(7) . . . . ?
C26 C21 N2 C5 -79.5(7) . . . . ?
C22 C21 N2 C5 95.2(7) . . . . ?
C6 C5 N2 C1 -0.1(6) . . . . ?
C6 C5 N2 C21 -174.2(5) . . . . ?
C9 C8 O1 U001 128.8(6) . . . . ?
C10 C8 O1 U001 -110.2(7) . . . . ?
C7 C8 O1 U001 10.5(9) . . . . ?
Si2 N3 Si1 C28 56.1(4) . . . . ?
U001 N3 Si1 C28 -122.6(3) . . . . ?
Si2 N3 Si1 C27 -66.5(4) . . . . ?
U001 N3 Si1 C27 114.9(3) . . . . ?
Si2 N3 Si1 C29 174.1(4) . . . . ?
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Si2 N3 Si1 U001 178.6(5) . . . . ?
Si1 N3 Si2 C31 -96.9(4) . . . . ?
U001 N3 Si2 C31 81.8(3) . . . . ?
Si1 N3 Si2 C32 143.5(3) . . . . ?
U001 N3 Si2 C32 -37.9(4) . . . . ?
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Si1 N3 Si2 C30 25.0(4) . . . . ?
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Si4 N4 Si3 C34 173.6(4) . . . . ?
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Si4 N4 Si3 C35 52.4(4) . . . . ?
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Si4 N4 Si3 C33 -67.6(4) . . . . ?
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Si3 N4 Si4 C37 -96.6(4) . . . . ?
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Si3 N4 Si4 C36 142.9(4) . . . . ?
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Si3 N4 Si4 U001 -177.3(4) . . . . ?
C8 O1 U001 F1 31.3(8) . . . . ?
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Si2 N3 U001 O1 121.1(3) . . . . ?
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Si1 N3 U001 N4 48.7(3) . . . . ?
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Si3 N4 U001 O1 -5.8(3) . . . . ?
Si4 N4 U001 O1 177.3(2) . . . . ?
Si3 N4 U001 F1 151.5(3) . . . . ?
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Si3 N4 U001 C1 70.7(4) . . . . ?
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Si3 N4 U001 Si1 -93.1(3) . . . . ?
Si4 N4 U001 Si1 90.0(2) . . . . ?
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N1 C1 U001 O1 -33.0(4) . . . . ?
N2 C1 U001 F1 -27.5(5) . . . . ?
N1 C1 U001 F1 148.5(5) . . . . ?
N2 C1 U001 N3 -117.0(5) . . . . ?
N1 C1 U001 N3 59.0(5) . . . . ?
N2 C1 U001 N4 60.1(6) . . . . ?
N1 C1 U001 N4 -123.9(4) . . . . ?
N2 C1 U001 Si4 22.8(6) . . . . ?
N1 C1 U001 Si4 -161.2(4) . . . . ?
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N4 Si4 U001 O1 -3.4(3) . . . . ?
C37 Si4 U001 O1 -113.6(3) . . . . ?
C36 Si4 U001 O1 139.2(3) . . . . ?
C38 Si4 U001 O1 37.7(7) . . . . ?
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C38 Si4 U001 F1 -166.0(7) . . . . ?
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C37 Si4 U001 N3 130.6(3) . . . . ?
C36 Si4 U001 N3 23.5(3) . . . . ?
C38 Si4 U001 N3 -78.1(7) . . . . ?
C37 Si4 U001 N4 -110.1(4) . . . . ?
C36 Si4 U001 N4 142.7(4) . . . . ?
C38 Si4 U001 N4 41.2(7) . . . . ?
N4 Si4 U001 C1 99.1(3) . . . . ?
C37 Si4 U001 C1 -11.0(3) . . . . ?
C36 Si4 U001 C1 -118.2(3) . . . . ?
C38 Si4 U001 C1 140.3(7) . . . . ?
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C36 Si4 U001 Si1 48.5(3) . . . . ?
C38 Si4 U001 Si1 -53.0(7) . . . . ?
N3 Si1 U001 O1 120.5(3) . . . . ?
C28 Si1 U001 O1 -163.1(4) . . . . ?
C27 Si1 U001 O1 37.0(3) . . . . ?
C29 Si1 U001 O1 -63.9(3) . . . . ?
N3 Si1 U001 F1 -38.0(3) . . . . ?
C28 Si1 U001 F1 38.4(4) . . . . ?
C27 Si1 U001 F1 -121.5(3) . . . . ?
C29 Si1 U001 F1 137.6(3) . . . . ?
C28 Si1 U001 N3 76.4(4) . . . . ?
C27 Si1 U001 N3 -83.5(4) . . . . ?
C29 Si1 U001 N3 175.6(4) . . . . ?
N3 Si1 U001 N4 -137.4(3) . . . . ?
C28 Si1 U001 N4 -61.0(4) . . . . ?
C27 Si1 U001 N4 139.1(3) . . . . ?
C29 Si1 U001 N4 38.2(3) . . . . ?
N3 Si1 U001 C1 58.1(3) . . . . ?
C28 Si1 U001 C1 134.5(4) . . . . ?
C27 Si1 U001 C1 -25.4(3) . . . . ?
C29 Si1 U001 C1 -126.3(3) . . . . ?
N3 Si1 U001 Si4 -109.5(3) . . . . ?
C28 Si1 U001 Si4 -33.2(3) . . . . ?
C27 Si1 U001 Si4 167.0(3) . . . . ?
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 'H'  'H'   0.0000   0.0000
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_symmetry_space_group_name_H-M    'P -1'

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 'x, y, z'
 '-x, -y, -z'

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_cell_length_b                    16.3315(13)
_cell_length_c                    16.4128(14)
_cell_angle_alpha                 106.924(4)
_cell_angle_beta                  94.311(4)
_cell_angle_gamma                 106.275(4)
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_cell_formula_units_Z               2
_cell_measurement_temperature       150(2)
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_exptl_crystal_F_000                952
_exptl_absorpt_coefficient_mu       2.068
_exptl_absorpt_correction_type      'MULTI-SCAN'
_exptl_absorpt_correction_T_min     0.421
_exptl_absorpt_correction_T_max     0.538
_exptl_absorpt_process_details      SADABS

_exptl_special_details
;
  HIRSHFELD TEST
 Along chemical bonds the anisotropic displacement
 parameter components are always assumed to be equal
 in magnitude. In this case, the large difference
 associated with the Y1 - I1 bond can be attributed
 to presence of heavy atoms. Here, charge deformation
 has a lesser importance with  respect to the
 total charge density present.

 Tmax/Tmin(RR) > 1.10
 SADABS corrects for all systematic errors that lead
 to disparities in the intensities of symmetry-equivalent
 data. These may include absorption by the
 mount, crystal decay, changes in the volume of the
 crystal illuminated, etc. The crystal dimensions are
 noted to be large: 0.54 x 0.44 x 0.30 as is the presence
 of some heavy atoms (Y, I)

 INCOMPLETE DATA; Reflection count < 90% completeness
 The data collection strategy used aimed to achieve a
 complete data set to 2\? = 53 deg.  Some higher angle
 data were collected in the process and these
 have been included in the refinement.
;

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_diffrn_radiation_type              MoK\a
_diffrn_radiation_source            'fine-focus sealed tube'
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_diffrn_reflns_limit_l_min        -22
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_reflns_number_gt                 10822
_reflns_threshold_expression      >2\s(I)

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_computing_cell_refinement        'SAINT (Siemens, 1995)'
_computing_data_reduction         'SAINT (Siemens, 1995)'
_computing_structure_solution     'SUPERFLIP (Palatinus L.,
Chapuis G. 2007)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   'enCIFer (Allen et al.,
2004)'

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 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0346P)^2^+0.8370P] where
P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary     difmap
_atom_sites_solution_hydrogens     geom
_refine_ls_hydrogen_treatment      RIDING
_refine_ls_extinction_method       none
_refine_ls_extinction_coef         ?
_refine_ls_number_reflns           12734
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_refine_ls_wR_factor_ref           0.0730
_refine_ls_wR_factor_gt            0.0690
_refine_ls_goodness_of_fit_ref     1.038
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_refine_ls_shift/su_max            0.007
_refine_ls_shift/su_mean           0.001

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d . . .
Y1 Y 0.658553(18) 0.197256(11) 0.241186(11) 0.01750(4) Uani 1
1 d . . .
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. . .
Si3 Si 0.51129(6) 0.30203(4) 0.39808(3) 0.02362(11) Uani 1 1 d
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Si5 Si 0.83191(6) -0.23463(3) 0.09151(3) 0.02066(10) Uani 1 1
d . . .
Si2 Si 0.95287(6) 0.38189(3) 0.28958(4) 0.02351(11) Uani 1 1 d
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Si4 Si 0.58726(6) 0.14923(4) 0.43302(3) 0.02548(11) Uani 1 1 d
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O1 O 0.76403(14) 0.10265(8) 0.21142(8) 0.0213(3) Uani 1 1 d .
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N4 N 0.59229(17) 0.21914(10) 0.37278(10) 0.0205(3) Uani 1 1 d
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N3 N 0.80380(16) 0.31655(10) 0.21103(10) 0.0207(3) Uani 1 1 d
. . .
C31 C 0.9533(3) 0.50137(14) 0.33747(16) 0.0398(5) Uani 1 1 d .
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H31A H 0.9508 0.5285 0.2916 0.060 Uiso 1 1 calc R . .
H31B H 1.0425 0.5361 0.3805 0.060 Uiso 1 1 calc R . .
H31C H 0.8667 0.5018 0.3653 0.060 Uiso 1 1 calc R . .
C30 C 1.1355(2) 0.38795(15) 0.25420(15) 0.0341(5) Uani 1 1 d .
. .
H30A H 1.1419 0.3269 0.2312 0.051 Uiso 1 1 calc R . .
H30B H 1.2144 0.4236 0.3037 0.051 Uiso 1 1 calc R . .
H30C H 1.1455 0.4166 0.2092 0.051 Uiso 1 1 calc R . .
C27 C 0.9268(2) 0.38643(17) 0.07132(15) 0.0379(5) Uani 1 1 d .
. .
H27A H 0.9836 0.4466 0.1109 0.057 Uiso 1 1 calc R . .
H27B H 0.8936 0.3910 0.0153 0.057 Uiso 1 1 calc R . .
H27C H 0.9886 0.3471 0.0635 0.057 Uiso 1 1 calc R . .
N1 N 0.69490(17) -0.09734(10) 0.15888(10) 0.0199(3) Uani 1 1 d
. . .
C9C C 0.9710(2) 0.05537(14) 0.24068(14) 0.0290(4) Uani 1 1 d .
. .
H9C1 H 1.0230 0.1170 0.2789 0.044 Uiso 1 1 calc R . .
H9C2 H 1.0416 0.0284 0.2129 0.044 Uiso 1 1 calc R . .
H9C3 H 0.9209 0.0193 0.2745 0.044 Uiso 1 1 calc R . .
N2 N 0.62755(16) -0.20651(10) 0.21342(10) 0.0198(3) Uani 1 1 d
. . .
C28 C 0.6561(3) 0.41924(14) 0.13064(14) 0.0327(5) Uani 1 1 d .
. .
H28A H 0.5645 0.3955 0.1506 0.049 Uiso 1 1 calc R . .
H28B H 0.6333 0.4275 0.0750 0.049 Uiso 1 1 calc R . .
H28C H 0.7146 0.4774 0.1731 0.049 Uiso 1 1 calc R . .
C222 C 0.2443(2) -0.36545(15) 0.20674(14) 0.0327(5) Uani 1 1 d
. . .
H22A H 0.2190 -0.4120 0.2345 0.049 Uiso 1 1 calc R . .
H22B H 0.1617 -0.3755 0.1623 0.049 Uiso 1 1 calc R . .
H22C H 0.2655 -0.3058 0.2502 0.049 Uiso 1 1 calc R . .
C35 C 0.3198(2) 0.26308(17) 0.41971(15) 0.0370(5) Uani 1 1 d .
. .
H35A H 0.2598 0.2118 0.3700 0.056 Uiso 1 1 calc R . .
H35B H 0.2777 0.3125 0.4291 0.056 Uiso 1 1 calc R . .
H35C H 0.3218 0.2445 0.4713 0.056 Uiso 1 1 calc R . .
C40 C 0.7455(2) -0.25644(14) -0.02102(13) 0.0305(4) Uani 1 1 d
. . .
H40A H 0.7495 -0.1990 -0.0297 0.046 Uiso 1 1 calc R . .
H40B H 0.6428 -0.2944 -0.0311 0.046 Uiso 1 1 calc R . .
H40C H 0.7986 -0.2874 -0.0616 0.046 Uiso 1 1 calc R . .
C261 C 1.0381(2) -0.19404(18) 0.33907(17) 0.0455(6) Uani 1 1 d
. . .
H26A H 1.0506 -0.2197 0.3851 0.068 Uiso 1 1 calc R . .
H26B H 1.1192 -0.1381 0.3499 0.068 Uiso 1 1 calc R . .
H26C H 1.0379 -0.2373 0.2833 0.068 Uiso 1 1 calc R . .
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C34 C 0.6204(3) 0.40375(15) 0.49226(15) 0.0377(5) Uani 1 1 d .
. .
H34A H 0.6231 0.3871 0.5450 0.057 Uiso 1 1 calc R . .
H34B H 0.5742 0.4512 0.4992 0.057 Uiso 1 1 calc R . .
H34C H 0.7208 0.4259 0.4817 0.057 Uiso 1 1 calc R . .
C33 C 0.4974(2) 0.34382(15) 0.30323(14) 0.0334(5) Uani 1 1 d .
. .
H33A H 0.5962 0.3697 0.2922 0.050 Uiso 1 1 calc R . .
H33B H 0.4485 0.3901 0.3162 0.050 Uiso 1 1 calc R . .
H33C H 0.4403 0.2934 0.2520 0.050 Uiso 1 1 calc R . .
C41 C 0.8147(2) -0.34421(12) 0.10827(13) 0.0270(4) Uani 1 1 d
. . .
H41A H 0.8638 -0.3779 0.0670 0.041 Uiso 1 1 calc R . .
H41B H 0.7106 -0.3792 0.0993 0.041 Uiso 1 1 calc R . .
H41C H 0.8608 -0.3335 0.1673 0.041 Uiso 1 1 calc R . .
C1 C 0.71532(19) -0.17289(11) 0.16309(11) 0.0183(3) Uani 1 1 d
. . .
C23 C 0.5144(2) -0.41268(13) 0.27537(12) 0.0248(4) Uani 1 1 d
. . .
H23 H 0.4319 -0.4653 0.2635 0.030 Uiso 1 1 calc R . .
C221 C 0.3479(2) -0.46196(14) 0.09475(13) 0.0307(4) Uani 1 1 d
. . .
H22D H 0.4345 -0.4635 0.0672 0.046 Uiso 1 1 calc R . .
H22E H 0.2645 -0.4713 0.0512 0.046 Uiso 1 1 calc R . .
H22F H 0.3240 -0.5098 0.1210 0.046 Uiso 1 1 calc R . .
C10 C 0.9359(2) 0.10624(14) 0.11262(15) 0.0325(5) Uani 1 1 d .
. .
H10A H 0.8633 0.1013 0.0648 0.049 Uiso 1 1 calc R . .
H10B H 1.0089 0.0785 0.0895 0.049 Uiso 1 1 calc R . .
H10C H 0.9851 0.1700 0.1458 0.049 Uiso 1 1 calc R . .
C220 C 0.3803(2) -0.37018(12) 0.16475(12) 0.0233(4) Uani 1 1 d
. . .
H220 H 0.4033 -0.3226 0.1364 0.028 Uiso 1 1 calc R . .
C38 C 0.7479(3) 0.10570(16) 0.42518(14) 0.0356(5) Uani 1 1 d .
. .
H38A H 0.7471 0.0732 0.3646 0.053 Uiso 1 1 calc R . .
H38B H 0.7414 0.0647 0.4590 0.053 Uiso 1 1 calc R . .
H38C H 0.8392 0.1564 0.4478 0.053 Uiso 1 1 calc R . .
C32 C 0.9569(2) 0.33323(16) 0.37969(14) 0.0333(5) Uani 1 1 d .
. .
H32A H 0.8682 0.3324 0.4055 0.050 Uiso 1 1 calc R . .
H32B H 1.0439 0.3703 0.4238 0.050 Uiso 1 1 calc R . .
H32C H 0.9607 0.2715 0.3569 0.050 Uiso 1 1 calc R . .
C24 C 0.6348(2) -0.39770(14) 0.33593(13) 0.0287(4) Uani 1 1 d
. . .
H24 H 0.6340 -0.4399 0.3655 0.034 Uiso 1 1 calc R . .
C29 C 0.6501(2) 0.23135(14) 0.02985(14) 0.0343(5) Uani 1 1 d .
. .
H29A H 0.7059 0.1886 0.0179 0.051 Uiso 1 1 calc R . .
H29B H 0.6270 0.2454 -0.0227 0.051 Uiso 1 1 calc R . .
H29C H 0.5587 0.2045 0.0484 0.051 Uiso 1 1 calc R . .
C6 C 0.5695(2) -0.08098(12) 0.20043(13) 0.0234(4) Uani 1 1 d .
. .
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H6A H 0.4807 -0.0973 0.1570 0.028 Uiso 1 1 calc R . .
H6B H 0.5935 -0.0172 0.2371 0.028 Uiso 1 1 calc R . .
C36 C 0.5971(3) 0.20547(17) 0.55196(14) 0.0403(6) Uani 1 1 d .
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H36A H 0.6852 0.2586 0.5736 0.061 Uiso 1 1 calc R . .
H36B H 0.6015 0.1630 0.5829 0.061 Uiso 1 1 calc R . .
H36C H 0.5096 0.2241 0.5612 0.061 Uiso 1 1 calc R . .
C37 C 0.4161(3) 0.04871(16) 0.39633(16) 0.0419(6) Uani 1 1 d .
. .
H37A H 0.3307 0.0685 0.4093 0.063 Uiso 1 1 calc R . .
H37B H 0.4237 0.0062 0.4267 0.063 Uiso 1 1 calc R . .
H37C H 0.4046 0.0190 0.3339 0.063 Uiso 1 1 calc R . .
C25 C 0.7557(2) -0.32208(13) 0.35373(12) 0.0265(4) Uani 1 1 d
. . .
H25 H 0.8381 -0.3134 0.3947 0.032 Uiso 1 1 calc R . .
C7 C 0.7678(2) -0.03834(11) 0.11223(11) 0.0205(4) Uani 1 1 d .
. .
H7A H 0.6925 -0.0338 0.0707 0.025 Uiso 1 1 calc R . .
H7B H 0.8337 -0.0661 0.0786 0.025 Uiso 1 1 calc R . .
C5 C 0.5494(2) -0.14320(13) 0.25416(13) 0.0259(4) Uani 1 1 d .
. .
H5A H 0.5941 -0.1097 0.3155 0.031 Uiso 1 1 calc R . .
H5B H 0.4441 -0.1753 0.2506 0.031 Uiso 1 1 calc R . .
C260 C 0.8920(2) -0.17369(14) 0.33751(14) 0.0336(5) Uani 1 1 d
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H260 H 0.8857 -0.1429 0.2935 0.040 Uiso 1 1 calc R . .
C22 C 0.5131(2) -0.35142(12) 0.23174(12) 0.0204(4) Uani 1 1 d
. . .
C21 C 0.6361(2) -0.27423(12) 0.25180(11) 0.0190(3) Uani 1 1 d
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C8 C 0.8583(2) 0.05758(12) 0.17182(12) 0.0205(4) Uani 1 1 d .
. .
C26 C 0.7591(2) -0.25828(12) 0.31264(12) 0.0234(4) Uani 1 1 d
. . .
C262 C 0.8889(3) -0.10912(18) 0.42515(18) 0.0576(8) Uani 1 1 d
. . .
H26D H 0.7946 -0.0972 0.4240 0.086 Uiso 1 1 calc R . .
H26E H 0.9690 -0.0524 0.4378 0.086 Uiso 1 1 calc R . .
H26F H 0.9010 -0.1363 0.4700 0.086 Uiso 1 1 calc R . .
C39 C 1.0274(2) -0.16301(14) 0.11766(14) 0.0304(4) Uani 1 1 d
. . .
H39A H 1.0586 -0.1388 0.1805 0.046 Uiso 1 1 calc R . .
H39B H 1.0387 -0.1131 0.0944 0.046 Uiso 1 1 calc R . .
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C26 0.0261(9) 0.0213(9) 0.0207(9) 0.0036(7) 0.0047(7)
0.0076(7)
C262 0.0621(18) 0.0337(13) 0.0512(16) -0.0107(12) -0.0067(14)
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C39 0.0236(10) 0.0277(10) 0.0399(12) 0.0091(9) 0.0123(9)
0.0085(8)

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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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Si1 N3 Y1 121.58(8) . . ?
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Si3 Y1 Si2 C31 -29.61(10) . . . . ?
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C27 Si1 N3 Y1 -145.33(11) . . . . ?
C32 Si2 N3 Si1 -179.24(11) . . . . ?
C30 Si2 N3 Si1 -62.36(14) . . . . ?
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Y1 Si2 N3 Si1 179.21(17) . . . . ?
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C30 Si2 N3 Y1 118.44(10) . . . . ?
C31 Si2 N3 Y1 -118.84(11) . . . . ?
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N4 Y1 N3 Si1 -132.01(9) . . . . ?
I1 Y1 N3 Si1 -7.60(11) . . . . ?
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O1 Y1 N3 Si2 -79.96(9) . . . . ?
N4 Y1 N3 Si2 47.22(10) . . . . ?
I1 Y1 N3 Si2 171.63(5) . . . . ?
Si3 Y1 N3 Si2 70.57(8) . . . . ?
C7 N1 C1 N2 179.44(16) . . . . ?
C6 N1 C1 N2 -7.7(2) . . . . ?
C7 N1 C1 Si5 -9.7(3) . . . . ?
C6 N1 C1 Si5 163.20(13) . . . . ?
C21 N2 C1 N1 -164.33(16) . . . . ?
C5 N2 C1 N1 -5.8(2) . . . . ?
C21 N2 C1 Si5 24.9(3) . . . . ?
C5 N2 C1 Si5 -176.53(13) . . . . ?
C41 Si5 C1 N1 -173.35(15) . . . . ?
C39 Si5 C1 N1 64.79(17) . . . . ?
C40 Si5 C1 N1 -56.84(17) . . . . ?
C41 Si5 C1 N2 -3.86(18) . . . . ?
C39 Si5 C1 N2 -125.72(16) . . . . ?
C40 Si5 C1 N2 112.65(16) . . . . ?
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C22 C23 C24 C25 -0.4(3) . . . . ?
C1 N1 C6 C5 17.2(2) . . . . ?
C7 N1 C6 C5 -169.29(15) . . . . ?
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C21 N2 C5 C6 177.25(15) . . . . ?
N1 C6 C5 N2 -18.66(18) . . . . ?
C24 C23 C22 C21 -0.7(3) . . . . ?
C24 C23 C22 C220 179.22(18) . . . . ?
C221 C220 C22 C23 -56.1(2) . . . . ?
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C222 C220 C22 C21 -112.9(2) . . . . ?
C23 C22 C21 C26 1.0(3) . . . . ?
C220 C22 C21 C26 -178.90(17) . . . . ?
C23 C22 C21 N2 -173.43(16) . . . . ?
C220 C22 C21 N2 6.6(3) . . . . ?
C1 N2 C21 C26 63.1(3) . . . . ?
C5 N2 C21 C26 -94.2(2) . . . . ?
C1 N2 C21 C22 -122.4(2) . . . . ?
C5 N2 C21 C22 80.4(2) . . . . ?
Y1 O1 C8 C9C 121.6(3) . . . . ?
Y1 O1 C8 C10 0.6(4) . . . . ?
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N1 C7 C8 C9C 55.4(2) . . . . ?
N1 C7 C8 C10 175.39(16) . . . . ?
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C24 C25 C26 C260 177.11(19) . . . . ?
C22 C21 C26 C25 -0.3(3) . . . . ?
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C262 C260 C26 C25 -74.6(3) . . . . ?
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 '-x, -y, -z'

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_exptl_special_details
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 HIRSHFELD TEST
 Along chemical bonds the anisotropic displacement
 parameter components are always assumed to be equal
 in magnitude. In this case, the large difference
 associated with the Ce1 - I1 bond can be attributed
 to presence of heavy atoms. Here, charge deformation
 has a lesser importance with  respect to the
 total charge density present.

 Tmax/Tmin(RR) > 1.10
 SADABS corrects for all systematic errors that lead
 to disparities in the intensities of symmetry-equivalent
 data. These may include absorption by the
 mount, crystal decay, changes in the volume of the
 crystal illuminated, etc. The crystal dimensions are
 noted to be large: 0.50 x 0.38 x 0.25 as is the presence
 of several heavy atoms (Ce, I)

 INCOMPLETE DATA; Reflection count < 95% completeness
 The data collection strategy used aimed to achieve a
 complete data set to 2\? = 53 deg.  Some higher angle
 data were collected in the process and these
 have been included in the refinement.

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 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

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C5 C 0.4459(3) 1.14378(18) 0.74865(19) 0.0275(6) Uani 1 1 d .
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H5B H 0.4021 1.1112 0.6870 0.033 Uiso 1 1 calc R . .
C6 C 0.4230(3) 1.08078(18) 0.80159(18) 0.0245(5) Uani 1 1 d .
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H6A H 0.3971 1.0174 0.7644 0.029 Uiso 1 1 calc R . .
H6B H 0.5110 1.0955 0.8451 0.029 Uiso 1 1 calc R . .
C7 C 0.2261(3) 1.03908(16) 0.88872(16) 0.0225(5) Uani 1 1 d .
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H7A H 0.1608 1.0668 0.9216 0.027 Uiso 1 1 calc R . .
H7B H 0.3000 1.0342 0.9309 0.027 Uiso 1 1 calc R . .
C8 C 0.1352(3) 0.94355(16) 0.82872(17) 0.0225(5) Uani 1 1 d .
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C9 C 0.0559(3) 0.89505(19) 0.8863(2) 0.0322(6) Uani 1 1 d . .
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H9A H 0.0047 0.8321 0.8523 0.048 Uiso 1 1 calc R . .
H9B H -0.0147 0.9238 0.9094 0.048 Uiso 1 1 calc R . .
H9C H 0.1269 0.8981 0.9341 0.048 Uiso 1 1 calc R . .
C10 C 0.0270(3) 0.94696(19) 0.75771(19) 0.0297(6) Uani 1 1 d .
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H10A H 0.0797 0.9828 0.7248 0.045 Uiso 1 1 calc R . .
H10B H -0.0431 0.9744 0.7838 0.045 Uiso 1 1 calc R . .
H10C H -0.0250 0.8859 0.7189 0.045 Uiso 1 1 calc R . .
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C21 C 0.3609(3) 1.27427(16) 0.74980(16) 0.0205(5) Uani 1 1 d .
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C22 C 0.2379(3) 1.25852(17) 0.68855(17) 0.0245(5) Uani 1 1 d .
. .
C23 C 0.2413(3) 1.32163(18) 0.64719(18) 0.0282(6) Uani 1 1 d .
. .
H23 H 0.1589 1.3130 0.6062 0.034 Uiso 1 1 calc R . .
C24 C 0.3620(3) 1.39693(19) 0.66438(18) 0.0300(6) Uani 1 1 d .
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H24 H 0.3629 1.4388 0.6345 0.036 Uiso 1 1 calc R . .
C25 C 0.4809(3) 1.41116(18) 0.72492(18) 0.0267(6) Uani 1 1 d .
. .
H25 H 0.5630 1.4634 0.7367 0.032 Uiso 1 1 calc R . .
C26 C 0.4838(3) 1.35084(16) 0.76925(16) 0.0213(5) Uani 1 1 d .
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C27 C 0.4080(4) 0.7964(2) 0.4444(2) 0.0454(9) Uani 1 1 d . . .
H41A H 0.4937 0.7770 0.4349 0.068 Uiso 1 1 calc R . .
H41B H 0.4050 0.8398 0.4143 0.068 Uiso 1 1 calc R . .
H41C H 0.3194 0.7442 0.4219 0.068 Uiso 1 1 calc R . .
C28 C 0.5881(4) 0.9506(2) 0.6014(2) 0.0468(9) Uani 1 1 d . . .
H40A H 0.5984 0.9801 0.6636 0.070 Uiso 1 1 calc R . .
H40B H 0.5812 0.9929 0.5707 0.070 Uiso 1 1 calc R . .
H40C H 0.6733 0.9313 0.5897 0.070 Uiso 1 1 calc R . .
C29 C 0.2585(4) 0.8930(2) 0.5734(2) 0.0382(7) Uani 1 1 d . . .
H39A H 0.1681 0.8427 0.5476 0.057 Uiso 1 1 calc R . .
H39B H 0.2659 0.9373 0.5433 0.057 Uiso 1 1 calc R . .
H39C H 0.2577 0.9211 0.6346 0.057 Uiso 1 1 calc R . .
C30 C 0.6836(3) 0.7324(2) 0.5790(2) 0.0399(7) Uani 1 1 d . . .
H38A H 0.6836 0.7508 0.5272 0.060 Uiso 1 1 calc R . .
H38B H 0.7229 0.6823 0.5704 0.060 Uiso 1 1 calc R . .
H38C H 0.7443 0.7831 0.6288 0.060 Uiso 1 1 calc R . .
C31 C 0.3822(4) 0.5946(2) 0.5060(2) 0.0386(7) Uani 1 1 d . . .
H37A H 0.2836 0.5721 0.5174 0.058 Uiso 1 1 calc R . .
H37B H 0.4288 0.5477 0.4988 0.058 Uiso 1 1 calc R . .
H37C H 0.3768 0.6108 0.4531 0.058 Uiso 1 1 calc R . .
C32 C 0.5034(3) 0.6570(2) 0.6959(2) 0.0340(7) Uani 1 1 d . . .
H36A H 0.5643 0.7071 0.7461 0.051 Uiso 1 1 calc R . .
H36B H 0.5465 0.6084 0.6839 0.051 Uiso 1 1 calc R . .
H36C H 0.4052 0.6351 0.7082 0.051 Uiso 1 1 calc R . .
C33 C 0.0439(3) 0.6646(2) 0.61958(19) 0.0342(7) Uani 1 1 d . .
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H35A H 0.0420 0.7262 0.6435 0.051 Uiso 1 1 calc R . .
H35B H -0.0416 0.6295 0.5740 0.051 Uiso 1 1 calc R . .
H35C H 0.1329 0.6655 0.5953 0.051 Uiso 1 1 calc R . .
C34 C 0.0401(4) 0.4939(2) 0.6577(2) 0.0420(8) Uani 1 1 d . . .
H33A H 0.1265 0.4942 0.6308 0.063 Uiso 1 1 calc R . .
H33B H -0.0480 0.4602 0.6137 0.063 Uiso 1 1 calc R . .
H33C H 0.0414 0.4654 0.7026 0.063 Uiso 1 1 calc R . .
C35 C -0.1397(3) 0.6065(2) 0.7405(2) 0.0351(7) Uani 1 1 d . .
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H34A H -0.1496 0.5796 0.7867 0.053 Uiso 1 1 calc R . .
H34B H -0.2176 0.5697 0.6908 0.053 Uiso 1 1 calc R . .
H34C H -0.1468 0.6672 0.7615 0.053 Uiso 1 1 calc R . .
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C36 C 0.3509(3) 0.7666(2) 0.9638(2) 0.0352(7) Uani 1 1 d . . .
H31A H 0.4392 0.7904 0.9420 0.053 Uiso 1 1 calc R . .
H31B H 0.3780 0.7560 1.0178 0.053 Uiso 1 1 calc R . .
H31C H 0.2972 0.8100 0.9744 0.053 Uiso 1 1 calc R . .
C37 C 0.3381(4) 0.5771(2) 0.8705(2) 0.0337(7) Uani 1 1 d . . .
H30A H 0.2789 0.5187 0.8291 0.051 Uiso 1 1 calc R . .
H30B H 0.3623 0.5701 0.9268 0.051 Uiso 1 1 calc R . .
H30C H 0.4281 0.5999 0.8498 0.051 Uiso 1 1 calc R . .
C38 C 0.0736(3) 0.6152(2) 0.9324(2) 0.0400(7) Uani 1 1 d . . .
H32A H 0.0121 0.6540 0.9373 0.060 Uiso 1 1 calc R . .
H32B H 0.1091 0.6151 0.9900 0.060 Uiso 1 1 calc R . .
H32C H 0.0163 0.5539 0.8963 0.060 Uiso 1 1 calc R . .
C39 C 0.2552(3) 1.25669(19) 1.02272(18) 0.0310(6) Uani 1 1 d .
. .
H27A H 0.3580 1.2929 1.0324 0.047 Uiso 1 1 calc R . .
H27B H 0.2484 1.1992 1.0317 0.047 Uiso 1 1 calc R . .
H27C H 0.2050 1.2890 1.0634 0.047 Uiso 1 1 calc R . .
C40 C 0.1874(3) 1.34527(18) 0.89372(19) 0.0282(6) Uani 1 1 d .
. .
H29A H 0.1386 1.3788 0.9343 0.042 Uiso 1 1 calc R . .
H29B H 0.1425 1.3350 0.8344 0.042 Uiso 1 1 calc R . .
H29C H 0.2910 1.3798 0.9036 0.042 Uiso 1 1 calc R . .
C41 C -0.0269(3) 1.16536(19) 0.8842(2) 0.0321(6) Uani 1 1 d .
. .
H28A H -0.0383 1.1148 0.9063 0.048 Uiso 1 1 calc R . .
H28B H -0.0592 1.1425 0.8214 0.048 Uiso 1 1 calc R . .
H28C H -0.0858 1.2017 0.9110 0.048 Uiso 1 1 calc R . .
C220 C 0.1052(3) 1.17440(19) 0.66425(19) 0.0325(6) Uani 1 1 d
. . .
H220 H 0.1119 1.1442 0.7087 0.039 Uiso 1 1 calc R . .
C221 C -0.0388(3) 1.1953(2) 0.6624(2) 0.0444(8) Uani 1 1 d . .
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H22A H -0.0376 1.2383 0.7182 0.067 Uiso 1 1 calc R . .
H22B H -0.1199 1.1398 0.6515 0.067 Uiso 1 1 calc R . .
H22C H -0.0511 1.2211 0.6164 0.067 Uiso 1 1 calc R . .
C222 C 0.1067(4) 1.1094(2) 0.5769(3) 0.0599(11) Uani 1 1 d . .
.
H22D H 0.0987 1.1373 0.5320 0.090 Uiso 1 1 calc R . .
H22E H 0.0241 1.0542 0.5634 0.090 Uiso 1 1 calc R . .
H22F H 0.1981 1.0951 0.5791 0.090 Uiso 1 1 calc R . .
C260 C 0.6162(3) 1.36966(17) 0.83622(17) 0.0237(5) Uani 1 1 d
. . .
H260 H 0.5931 1.3231 0.8657 0.028 Uiso 1 1 calc R . .
C261 C 0.6513(3) 1.46218(19) 0.90503(18) 0.0316(6) Uani 1 1 d
. . .
H26A H 0.6733 1.5089 0.8775 0.047 Uiso 1 1 calc R . .
H26B H 0.7359 1.4722 0.9480 0.047 Uiso 1 1 calc R . .
H26C H 0.5671 1.4645 0.9335 0.047 Uiso 1 1 calc R . .
C262 C 0.7500(3) 1.3635(2) 0.7945(2) 0.0326(6) Uani 1 1 d . .
.
H26D H 0.7277 1.3037 0.7519 0.049 Uiso 1 1 calc R . .
H26E H 0.8323 1.3737 0.8392 0.049 Uiso 1 1 calc R . .
H26F H 0.7753 1.4091 0.7658 0.049 Uiso 1 1 calc R . .
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N2 N 0.3691(2) 1.20720(13) 0.78895(14) 0.0209(4) Uani 1 1 d .
. .
N3 N 0.4150(2) 0.77957(14) 0.62195(14) 0.0218(4) Uani 1 1 d .
. .
N4 N 0.1869(2) 0.67584(14) 0.78754(14) 0.0221(4) Uani 1 1 d .
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O1 O 0.22984(19) 0.89862(11) 0.79068(12) 0.0227(4) Uani 1 1 d
. . .
Si1 Si 0.41898(9) 0.85047(5) 0.56337(5) 0.02762(17) Uani 1 1 d
. . .
Si2 Si 0.49246(8) 0.69631(5) 0.59931(5) 0.02454(15) Uani 1 1 d
. . .
Si3 Si 0.04121(8) 0.61239(5) 0.70745(5) 0.02493(16) Uani 1 1 d
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distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
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approximate (isotropic)
 treatment of cell esds is used for estimating esds involving
l.s. planes.
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_cell_length_c                    16.4228(4)
_cell_angle_alpha                 106.8120(10)
_cell_angle_beta                  94.5710(10)
_cell_angle_gamma                 106.3260(10)
_cell_volume                      2362.84(13)
_cell_formula_units_Z             2
_cell_measurement_temperature     150(2)
```

```
_cell_measurement_reflns_used     13204
_cell_measurement_theta_min       2.2
_cell_measurement_theta_max       30.5

_exptl_crystal_description        PLATE
_exptl_crystal_colour             'DARK RED'
_exptl_crystal_size_max           0.62
_exptl_crystal_size_mid           0.42
_exptl_crystal_size_min           0.16
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.490
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              1058
_exptl_absorpt_coefficient_mu     4.243
_exptl_absorpt_correction_type    'MULTI-SCAN'
_exptl_absorpt_correction_T_min   0.151
_exptl_absorpt_correction_T_max   0.507
_exptl_absorpt_process_details    SADABS

_exptl_special_details
;
 HIRSHFELD TEST
 Along chemical bonds the anisotropic displacement
 parameter components are always assumed to be equal
 in magnitude. In this case, the large difference
 associated with the u1 - I1 bond can be attributed
 to presence of heavy atoms. Here, charge deformation
 has a lesser importance with  respect to the
 total charge density present.

 Tmax/Tmin(RR) > 1.10
 SADABS corrects for all systematic errors that lead
 to disparities in the intensities of symmetry-equivalent
 data. These may include absorption by the
 mount, crystal decay, changes in the volume of the
 crystal illuminated, etc. The crystal dimensions are
 noted to be large: 0.62 x 0.42 x 0.16 as is the presence
 of several heavy atoms (U, I)

 INCOMPLETE DATA; Reflection count < 95% completeness
 The data collection strategy used aimed to achieve a
 complete data set to 2\? = 53 deg.  Some higher angle
 data were collected in the process and these
 have been included in the refinement.
;

_diffrn_ambient_temperature       150(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   'Bruker SMART APEX CCD area
detector'
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```
_diffrn_measurement_method        'Phi and omega scans'
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          0
_diffrn_standards_interval_count  .
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         0
_diffrn_reflns_number             39450
_diffrn_reflns_av_R_equivalents   0.0456
_diffrn_reflns_av_sigmaI/netI     0.0530
_diffrn_reflns_limit_h_min        -13
_diffrn_reflns_limit_h_max        13
_diffrn_reflns_limit_k_min        -23
_diffrn_reflns_limit_k_max        19
_diffrn_reflns_limit_l_min        -22
_diffrn_reflns_limit_l_max        22
_diffrn_reflns_theta_min          2.18
_diffrn_reflns_theta_max          30.52
_reflns_number_total              13201
_reflns_number_gt                 12222
_reflns_threshold_expression      >2sigma(I)

_computing_data_collection        'SMART (Siemens, 1993)'
_computing_cell_refinement        'SAINT (Siemens, 1995)'
_computing_data_reduction         'SAINT (Siemens, 1995)'
_computing_structure_solution     'SIR-92 (Giacovazzo, 1994)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   'enCIFer (Allen et al.,
2004)'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
```

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 'calc w=1/[\s^2^(Fo^2^)+(0.0253P)^2^+4.6253P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     RIDING
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          13201
_refine_ls_number_parameters      436
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0531
_refine_ls_R_factor_gt            0.0470
_refine_ls_wR_factor_ref          0.0981
_refine_ls_wR_factor_gt           0.0938
_refine_ls_goodness_of_fit_ref    1.213
_refine_ls_restrained_S_all       1.213
_refine_ls_shift/su_max           0.002
_refine_ls_shift/su_mean          0.000

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 _atom_site_type_symbol
 _atom_site_fract_x
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 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
C1 C 0.2819(4) 0.6733(3) 0.8374(3) 0.0188(8) Uani 1 1 d . . .
C5 C 0.4461(5) 0.6437(3) 0.7472(4) 0.0290(10) Uani 1 1 d . . .
H5A H 0.5511 0.6751 0.7515 0.035 Uiso 1 1 calc R . .
H5B H 0.4020 0.6110 0.6857 0.035 Uiso 1 1 calc R . .
C6 C 0.4241(5) 0.5810(3) 0.7997(3) 0.0256(10) Uani 1 1 d . . .
H6A H 0.3989 0.5177 0.7624 0.031 Uiso 1 1 calc R . .
H6B H 0.5121 0.5961 0.8431 0.031 Uiso 1 1 calc R . .
C7 C 0.2248(5) 0.5390(3) 0.8873(3) 0.0222(9) Uani 1 1 d . . .
H7A H 0.1587 0.5667 0.9198 0.027 Uiso 1 1 calc R . .
H7B H 0.2981 0.5343 0.9297 0.027 Uiso 1 1 calc R . .
C8 C 0.1350(5) 0.4438(3) 0.8272(3) 0.0228(9) Uani 1 1 d . . .
C9 C 0.0560(6) 0.3950(3) 0.8845(4) 0.0316(11) Uani 1 1 d . . .
H9A H 0.0038 0.3322 0.8501 0.047 Uiso 1 1 calc R . .
H9B H -0.0138 0.4241 0.9088 0.047 Uiso 1 1 calc R . .
H9C H 0.1274 0.3971 0.9316 0.047 Uiso 1 1 calc R . .
C10 C 0.0263(5) 0.4466(3) 0.7562(3) 0.0311(11) Uani 1 1 d . .
.
H10A H 0.0790 0.4817 0.7226 0.047 Uiso 1 1 calc R . .
H10B H -0.0435 0.4746 0.7824 0.047 Uiso 1 1 calc R . .
```

```
H10C H -0.0263 0.3854 0.7180 0.047 Uiso 1 1 calc R . .
C21 C 0.3621(5) 0.7747(3) 0.7493(3) 0.0199(8) Uani 1 1 d . . .
C22 C 0.2383(5) 0.7587(3) 0.6877(3) 0.0244(9) Uani 1 1 d . . .
C23 C 0.2424(5) 0.8224(3) 0.6471(3) 0.0275(10) Uani 1 1 d . .
.
H23 H 0.1603 0.8142 0.6063 0.033 Uiso 1 1 calc R . .
C24 C 0.3633(6) 0.8974(3) 0.6647(3) 0.0301(11) Uani 1 1 d . .
.
H24 H 0.3644 0.9395 0.6353 0.036 Uiso 1 1 calc R . .
C25 C 0.4825(5) 0.9116(3) 0.7250(3) 0.0264(10) Uani 1 1 d . .
.
H25 H 0.5647 0.9638 0.7368 0.032 Uiso 1 1 calc R . .
C26 C 0.4847(5) 0.8509(3) 0.7688(3) 0.0222(9) Uani 1 1 d . . .
C27 C 0.4065(8) 0.2958(4) 0.4463(4) 0.0452(15) Uani 1 1 d . .
.
H39A H 0.4932 0.2771 0.4370 0.068 Uiso 1 1 calc R . .
H39B H 0.4029 0.3388 0.4161 0.068 Uiso 1 1 calc R . .
H39C H 0.3186 0.2431 0.4238 0.068 Uiso 1 1 calc R . .
C28 C 0.5847(7) 0.4504(4) 0.6027(4) 0.0473(15) Uani 1 1 d . .
.
H41A H 0.5969 0.4785 0.6653 0.071 Uiso 1 1 calc R . .
H41B H 0.5755 0.4937 0.5738 0.071 Uiso 1 1 calc R . .
H41C H 0.6699 0.4317 0.5887 0.071 Uiso 1 1 calc R . .
C29 C 0.2552(7) 0.3916(4) 0.5735(4) 0.0410(13) Uani 1 1 d . .
.
H40A H 0.1649 0.3406 0.5513 0.062 Uiso 1 1 calc R . .
H40B H 0.2594 0.4322 0.5395 0.062 Uiso 1 1 calc R . .
H40C H 0.2570 0.4238 0.6341 0.062 Uiso 1 1 calc R . .
C30 C 0.6810(6) 0.2344(4) 0.5773(4) 0.0425(14) Uani 1 1 d . .
.
H38A H 0.6791 0.2542 0.5266 0.064 Uiso 1 1 calc R . .
H38B H 0.7214 0.1846 0.5665 0.064 Uiso 1 1 calc R . .
H38C H 0.7420 0.2843 0.6275 0.064 Uiso 1 1 calc R . .
C31 C 0.3801(6) 0.0959(4) 0.5055(4) 0.0390(13) Uani 1 1 d . .
.
H37A H 0.2801 0.0750 0.5160 0.059 Uiso 1 1 calc R . .
H37B H 0.4239 0.0478 0.4987 0.059 Uiso 1 1 calc R . .
H37C H 0.3784 0.1124 0.4527 0.059 Uiso 1 1 calc R . .
C32 C 0.5060(6) 0.1546(4) 0.6940(4) 0.0369(12) Uani 1 1 d . .
.
H36A H 0.5672 0.2042 0.7444 0.055 Uiso 1 1 calc R . .
H36B H 0.5503 0.1065 0.6799 0.055 Uiso 1 1 calc R . .
H36C H 0.4085 0.1315 0.7070 0.055 Uiso 1 1 calc R . .
C33 C 0.0417(6) 0.1628(4) 0.6187(4) 0.0364(12) Uani 1 1 d . .
.
H33A H 0.0360 0.2238 0.6413 0.055 Uiso 1 1 calc R . .
H33B H -0.0430 0.1255 0.5733 0.055 Uiso 1 1 calc R . .
H33C H 0.1315 0.1650 0.5946 0.055 Uiso 1 1 calc R . .
C34 C 0.0432(6) -0.0046(4) 0.6600(4) 0.0436(14) Uani 1 1 d . .
.
H34A H 0.1298 -0.0043 0.6330 0.065 Uiso 1 1 calc R . .
H34B H -0.0450 -0.0389 0.6163 0.065 Uiso 1 1 calc R . .
H34C H 0.0450 -0.0324 0.7053 0.065 Uiso 1 1 calc R . .
```

```
C35 C -0.1389(6) 0.1065(4) 0.7430(4) 0.0386(13) Uani 1 1 d . .
.
H35A H -0.1499 0.0767 0.7869 0.058 Uiso 1 1 calc R . .
H35B H -0.2169 0.0721 0.6928 0.058 Uiso 1 1 calc R . .
H35C H -0.1448 0.1672 0.7670 0.058 Uiso 1 1 calc R . .
C36 C 0.3512(6) 0.2665(4) 0.9659(4) 0.0355(12) Uani 1 1 d . .
.
H31A H 0.4405 0.2912 0.9451 0.053 Uiso 1 1 calc R . .
H31B H 0.3768 0.2548 1.0194 0.053 Uiso 1 1 calc R . .
H31C H 0.2972 0.3098 0.9771 0.053 Uiso 1 1 calc R . .
C37 C 0.3408(6) 0.0781(4) 0.8695(4) 0.0360(12) Uani 1 1 d . .
.
H30A H 0.2820 0.0201 0.8275 0.054 Uiso 1 1 calc R . .
H30B H 0.3643 0.0703 0.9254 0.054 Uiso 1 1 calc R . .
H30C H 0.4314 0.1015 0.8492 0.054 Uiso 1 1 calc R . .
C38 C 0.0745(6) 0.1142(4) 0.9316(4) 0.0401(13) Uani 1 1 d . .
.
H32A H 0.0143 0.1540 0.9393 0.060 Uiso 1 1 calc R . .
H32B H 0.1095 0.1110 0.9879 0.060 Uiso 1 1 calc R . .
H32C H 0.0159 0.0540 0.8935 0.060 Uiso 1 1 calc R . .
C39 C 0.1868(6) 0.8454(3) 0.8934(3) 0.0287(10) Uani 1 1 d . .
.
H29A H 0.1398 0.8793 0.9351 0.043 Uiso 1 1 calc R . .
H29B H 0.1403 0.8354 0.8346 0.043 Uiso 1 1 calc R . .
H29C H 0.2907 0.8793 0.9020 0.043 Uiso 1 1 calc R . .
C40 C -0.0285(5) 0.6651(3) 0.8830(4) 0.0333(11) Uani 1 1 d . .
.
H28A H -0.0876 0.7013 0.9104 0.050 Uiso 1 1 calc R . .
H28B H -0.0401 0.6143 0.9046 0.050 Uiso 1 1 calc R . .
H28C H -0.0608 0.6427 0.8203 0.050 Uiso 1 1 calc R . .
C41 C 0.2539(6) 0.7563(3) 1.0215(3) 0.0322(11) Uani 1 1 d . .
.
H27A H 0.3560 0.7941 1.0318 0.048 Uiso 1 1 calc R . .
H27B H 0.2497 0.6990 1.0298 0.048 Uiso 1 1 calc R . .
H27C H 0.2015 0.7869 1.0623 0.048 Uiso 1 1 calc R . .
C220 C 0.1062(6) 0.6746(4) 0.6633(4) 0.0352(12) Uani 1 1 d . .
.
H220 H 0.1131 0.6440 0.7073 0.042 Uiso 1 1 calc R . .
C221 C -0.0384(6) 0.6955(4) 0.6623(4) 0.0465(15) Uani 1 1 d .
. .
H22A H -0.0361 0.7397 0.7177 0.070 Uiso 1 1 calc R . .
H22B H -0.1193 0.6403 0.6531 0.070 Uiso 1 1 calc R . .
H22C H -0.0523 0.7198 0.6155 0.070 Uiso 1 1 calc R . .
C222 C 0.1072(8) 0.6100(4) 0.5754(5) 0.0600(19) Uani 1 1 d . .
.
H22D H 0.1003 0.6386 0.5310 0.090 Uiso 1 1 calc R . .
H22E H 0.0238 0.5551 0.5615 0.090 Uiso 1 1 calc R . .
H22F H 0.1981 0.5950 0.5771 0.090 Uiso 1 1 calc R . .
C260 C 0.6166(5) 0.8697(3) 0.8361(3) 0.0252(9) Uani 1 1 d . .
.
H260 H 0.5934 0.8229 0.8652 0.030 Uiso 1 1 calc R . .
C261 C 0.6515(6) 0.9620(4) 0.9051(3) 0.0336(11) Uani 1 1 d . .
.
```

```
H26D H 0.6738 1.0088 0.8778 0.050 Uiso 1 1 calc R . .
H26E H 0.7360 0.9718 0.9480 0.050 Uiso 1 1 calc R . .
H26F H 0.5670 0.9643 0.9337 0.050 Uiso 1 1 calc R . .
C262 C 0.7503(5) 0.8638(4) 0.7938(4) 0.0336(11) Uani 1 1 d . .
.
H26A H 0.7281 0.8041 0.7510 0.050 Uiso 1 1 calc R . .
H26B H 0.8330 0.8741 0.8381 0.050 Uiso 1 1 calc R . .
H26C H 0.7753 0.9095 0.7652 0.050 Uiso 1 1 calc R . .
N1 N 0.3000(4) 0.5978(2) 0.8414(2) 0.0209(7) Uani 1 1 d . . .
N2 N 0.3695(4) 0.7074(2) 0.7877(2) 0.0206(7) Uani 1 1 d . . .
N3 N 0.1890(4) 0.1780(2) 0.7881(3) 0.0230(8) Uani 1 1 d . . .
N4 N 0.4123(4) 0.2792(3) 0.6241(3) 0.0250(8) Uani 1 1 d . . .
O1 O 0.2298(3) 0.3991(2) 0.7887(2) 0.0239(7) Uani 1 1 d . . .
Si1 Si 0.41574(16) 0.34980(10) 0.56479(9) 0.0285(3) Uani 1 1 d
. . .
Si2 Si 0.49059(14) 0.19601(9) 0.59912(9) 0.0258(3) Uani 1 1 d
. . .
Si3 Si 0.04285(14) 0.11338(9) 0.70875(9) 0.0254(3) Uani 1 1 d
. . .
Si4 Si 0.23480(14) 0.15946(9) 0.88215(9) 0.0237(3) Uani 1 1 d
. . .
Si5 Si 0.16738(14) 0.73558(8) 0.90931(9) 0.0221(3) Uani 1 1 d
. . .
I1 I 0.64731(3) 0.43546(2) 0.87116(2) 0.03240(8) Uani 1 1 d .
. .
U1 U 0.347253(17) 0.304314(10) 0.762455(11) 0.01856(5) Uani 1
1 d . . .

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C1 0.0177(19) 0.0164(19) 0.019(2) 0.0030(16) 0.0024(16)
0.0031(16)
C5 0.031(2) 0.022(2) 0.039(3) 0.012(2) 0.019(2) 0.011(2)
C6 0.023(2) 0.023(2) 0.034(3) 0.010(2) 0.0111(19) 0.0082(18)
C7 0.027(2) 0.019(2) 0.023(2) 0.0080(18) 0.0107(18) 0.0083(18)
C8 0.021(2) 0.0150(19) 0.032(3) 0.0075(18) 0.0060(18)
0.0046(16)
C9 0.029(2) 0.026(2) 0.044(3) 0.015(2) 0.017(2) 0.009(2)
C10 0.025(2) 0.030(3) 0.033(3) 0.003(2) -0.003(2) 0.011(2)
C21 0.019(2) 0.0158(19) 0.025(2) 0.0056(17) 0.0077(17)
0.0062(16)
C22 0.026(2) 0.022(2) 0.021(2) 0.0014(18) 0.0043(18)
0.0078(18)
C23 0.027(2) 0.033(3) 0.024(2) 0.009(2) 0.0036(19) 0.012(2)
C24 0.040(3) 0.027(2) 0.033(3) 0.017(2) 0.012(2) 0.018(2)
C25 0.030(2) 0.021(2) 0.030(3) 0.0104(19) 0.011(2) 0.0066(19)
```

```
C26 0.025(2) 0.019(2) 0.023(2) 0.0059(18) 0.0096(17)
0.0075(17)
C27 0.062(4) 0.053(4) 0.032(3) 0.018(3) 0.017(3) 0.029(3)
C28 0.047(3) 0.037(3) 0.053(4) 0.017(3) 0.011(3) 0.004(3)
C29 0.055(4) 0.047(3) 0.031(3) 0.016(3) 0.011(3) 0.027(3)
C30 0.029(3) 0.057(4) 0.048(4) 0.019(3) 0.015(2) 0.018(3)
C31 0.039(3) 0.029(3) 0.042(3) -0.003(2) 0.006(2) 0.014(2)
C32 0.036(3) 0.042(3) 0.047(3) 0.023(3) 0.015(2) 0.024(3)
C33 0.027(3) 0.047(3) 0.031(3) 0.011(2) -0.003(2) 0.009(2)
C34 0.036(3) 0.031(3) 0.056(4) 0.005(3) 0.000(3) 0.011(2)
C35 0.023(2) 0.041(3) 0.051(4) 0.016(3) 0.010(2) 0.008(2)
C36 0.036(3) 0.035(3) 0.033(3) 0.011(2) 0.002(2) 0.011(2)
C37 0.047(3) 0.033(3) 0.038(3) 0.017(2) 0.012(2) 0.022(2)
C38 0.030(3) 0.052(4) 0.044(3) 0.023(3) 0.017(2) 0.012(3)
C39 0.033(3) 0.022(2) 0.035(3) 0.011(2) 0.010(2) 0.012(2)
C40 0.027(2) 0.024(2) 0.043(3) 0.005(2) 0.012(2) 0.005(2)
C41 0.040(3) 0.028(2) 0.028(3) 0.003(2) 0.010(2) 0.015(2)
C220 0.031(3) 0.030(3) 0.034(3) 0.007(2) -0.003(2) 0.000(2)
C221 0.024(3) 0.054(4) 0.052(4) 0.013(3) -0.001(2) 0.004(3)
C222 0.058(4) 0.035(3) 0.061(5) -0.010(3) -0.003(3) 0.005(3)
C260 0.025(2) 0.024(2) 0.027(2) 0.0099(19) 0.0076(18)
0.0056(18)
C261 0.030(3) 0.033(3) 0.030(3) 0.003(2) 0.003(2) 0.006(2)
C262 0.025(2) 0.032(3) 0.039(3) 0.007(2) 0.006(2) 0.007(2)
N1 0.0249(18) 0.0165(17) 0.0224(19) 0.0054(15) 0.0086(15)
0.0080(15)
N2 0.0219(18) 0.0167(17) 0.024(2) 0.0065(15) 0.0087(15)
0.0065(14)
N3 0.0192(18) 0.0198(18) 0.029(2) 0.0070(16) 0.0063(15)
0.0052(15)
N4 0.026(2) 0.0246(19) 0.024(2) 0.0065(16) 0.0032(16)
0.0094(16)
O1 0.0254(16) 0.0159(14) 0.0304(18) 0.0061(13) 0.0066(13)
0.0075(12)
Si1 0.0367(7) 0.0298(7) 0.0239(7) 0.0116(6) 0.0090(6)
0.0140(6)
Si2 0.0229(6) 0.0271(7) 0.0284(7) 0.0071(6) 0.0069(5)
0.0111(5)
Si3 0.0192(6) 0.0201(6) 0.0348(8) 0.0073(5) 0.0031(5)
0.0053(5)
Si4 0.0234(6) 0.0214(6) 0.0281(7) 0.0093(5) 0.0086(5)
0.0077(5)
Si5 0.0224(6) 0.0178(6) 0.0256(7) 0.0047(5) 0.0086(5)
0.0068(5)
I1 0.02226(15) 0.03603(18) 0.03441(19) 0.01283(15) -
0.00126(13) 0.00273(13)
U1 0.01775(8) 0.01608(8) 0.02213(9) 0.00601(6) 0.00534(6)
0.00553(6)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two
l.s. planes)
```

```
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds involving
l.s. planes.
;

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C1 N1 1.319(5) . ?
C1 N2 1.344(6) . ?
C1 Si5 1.955(4) . ?
C5 N2 1.482(6) . ?
C5 C6 1.504(7) . ?
C6 N1 1.483(6) . ?
C7 N1 1.464(6) . ?
C7 C8 1.543(6) . ?
C8 O1 1.408(5) . ?
C8 C9 1.523(7) . ?
C8 C10 1.528(6) . ?
C21 C26 1.397(6) . ?
C21 C22 1.416(6) . ?
C21 N2 1.438(6) . ?
C22 C23 1.387(7) . ?
C22 C220 1.520(7) . ?
C23 C24 1.378(7) . ?
C24 C25 1.378(7) . ?
C25 C26 1.390(6) . ?
C26 C260 1.519(6) . ?
C27 Si1 1.874(6) . ?
C28 Si1 1.876(6) . ?
C29 Si1 1.868(6) . ?
C30 Si2 1.874(6) . ?
C31 Si2 1.871(5) . ?
C32 Si2 1.883(5) . ?
C33 Si3 1.882(6) . ?
C34 Si3 1.871(6) . ?
C35 Si3 1.874(5) . ?
C36 Si4 1.869(5) . ?
C37 Si4 1.878(5) . ?
C38 Si4 1.878(5) . ?
C39 Si5 1.855(5) . ?
C40 Si5 1.864(5) . ?
C41 Si5 1.856(5) . ?
```

```
C220 C222 1.526(9) . ?
C220 C221 1.534(8) . ?
C260 C262 1.532(7) . ?
C260 C261 1.534(7) . ?
N3 Si3 1.701(4) . ?
N3 Si4 1.706(4) . ?
N3 U1 2.377(4) . ?
N4 Si2 1.708(4) . ?
N4 Si1 1.711(4) . ?
N4 U1 2.359(4) . ?
O1 U1 2.142(3) . ?
Si2 U1 3.3924(13) . ?
I1 U1 3.1155(4) . ?

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N1 C1 Si5 123.6(3) . . ?
N2 C1 Si5 124.9(3) . . ?
N2 C5 C6 102.9(4) . . ?
N1 C6 C5 102.0(4) . . ?
N1 C7 C8 113.6(4) . . ?
O1 C8 C9 109.5(4) . . ?
O1 C8 C10 109.0(4) . . ?
C9 C8 C10 110.9(4) . . ?
O1 C8 C7 109.6(4) . . ?
C9 C8 C7 106.3(4) . . ?
C10 C8 C7 111.5(4) . . ?
C26 C21 C22 122.1(4) . . ?
C26 C21 N2 117.9(4) . . ?
C22 C21 N2 119.8(4) . . ?
C23 C22 C21 117.3(4) . . ?
C23 C22 C220 119.8(4) . . ?
C21 C22 C220 122.8(4) . . ?
C24 C23 C22 121.3(4) . . ?
C23 C24 C25 120.3(4) . . ?
C24 C25 C26 121.3(5) . . ?
C25 C26 C21 117.7(4) . . ?
C25 C26 C260 119.9(4) . . ?
C21 C26 C260 122.5(4) . . ?
C22 C220 C222 110.3(5) . . ?
C22 C220 C221 112.5(5) . . ?
C222 C220 C221 109.8(5) . . ?
C26 C260 C262 110.9(4) . . ?
C26 C260 C261 111.3(4) . . ?
C262 C260 C261 109.9(4) . . ?
C1 N1 C7 128.2(4) . . ?
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C1 N1 C6 111.0(4) . . ?
C7 N1 C6 120.5(3) . . ?
C1 N2 C21 129.2(4) . . ?
C1 N2 C5 109.8(4) . . ?
C21 N2 C5 117.6(4) . . ?
Si3 N3 Si4 126.5(2) . . ?
Si3 N3 U1 116.0(2) . . ?
Si4 N3 U1 117.40(19) . . ?
Si2 N4 Si1 122.7(2) . . ?
Si2 N4 U1 112.1(2) . . ?
Si1 N4 U1 124.0(2) . . ?
C8 O1 U1 158.6(3) . . ?
N4 Si1 C29 110.7(2) . . ?
N4 Si1 C27 114.0(2) . . ?
C29 Si1 C27 105.5(3) . . ?
N4 Si1 C28 111.9(3) . . ?
C29 Si1 C28 107.5(3) . . ?
C27 Si1 C28 107.0(3) . . ?
N4 Si2 C31 113.2(2) . . ?
N4 Si2 C30 113.5(3) . . ?
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N4 Si2 C32 109.1(2) . . ?
C31 Si2 C32 106.2(3) . . ?
C30 Si2 C32 105.8(3) . . ?
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C30 Si2 U1 126.9(2) . . ?
C32 Si2 U1 69.00(17) . . ?
N3 Si3 C34 113.3(2) . . ?
N3 Si3 C35 114.5(2) . . ?
C34 Si3 C35 106.9(3) . . ?
N3 Si3 C33 109.8(2) . . ?
C34 Si3 C33 107.1(3) . . ?
C35 Si3 C33 104.6(3) . . ?
N3 Si4 C36 110.5(2) . . ?
N3 Si4 C37 113.1(2) . . ?
C36 Si4 C37 106.8(3) . . ?
N3 Si4 C38 114.3(2) . . ?
C36 Si4 C38 105.8(3) . . ?
C37 Si4 C38 105.8(3) . . ?
C39 Si5 C41 108.6(2) . . ?
C39 Si5 C40 110.4(2) . . ?
C41 Si5 C40 113.1(3) . . ?
C39 Si5 C1 110.2(2) . . ?
C41 Si5 C1 104.1(2) . . ?
C40 Si5 C1 110.3(2) . . ?
O1 U1 N4 112.10(13) . . ?
O1 U1 N3 102.85(12) . . ?
N4 U1 N3 116.39(14) . . ?
O1 U1 I1 96.73(9) . . ?
N4 U1 I1 98.54(10) . . ?
N3 U1 I1 128.58(9) . . ?
O1 U1 Si2 139.71(9) . . ?
N4 U1 Si2 27.81(9) . . ?
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I1 U1 Si2 95.18(2) . . ?

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N1 C7 C8 O1 66.0(5) . . . . ?
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N1 C7 C8 C10 -54.7(5) . . . . ?
C26 C21 C22 C23 -0.4(7) . . . . ?
N2 C21 C22 C23 -174.4(4) . . . . ?
C26 C21 C22 C220 177.7(4) . . . . ?
N2 C21 C22 C220 3.7(7) . . . . ?
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C22 C23 C24 C25 -1.3(8) . . . . ?
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C21 C22 C220 C222 -103.9(6) . . . . ?
C23 C22 C220 C221 -48.8(7) . . . . ?
C21 C22 C220 C221 133.1(5) . . . . ?
C25 C26 C260 C262 -68.0(6) . . . . ?
C21 C26 C260 C262 112.9(5) . . . . ?
C25 C26 C260 C261 54.7(6) . . . . ?
C21 C26 C260 C261 -124.4(5) . . . . ?
N2 C1 N1 C7 -179.0(4) . . . . ?
Si5 C1 N1 C7 10.3(6) . . . . ?
N2 C1 N1 C6 7.4(5) . . . . ?
Si5 C1 N1 C6 -163.3(3) . . . . ?
C8 C7 N1 C1 117.9(5) . . . . ?
C8 C7 N1 C6 -69.1(5) . . . . ?
C5 C6 N1 C1 -16.7(5) . . . . ?
C5 C6 N1 C7 169.2(4) . . . . ?
N1 C1 N2 C21 163.6(4) . . . . ?
Si5 C1 N2 C21 -25.8(6) . . . . ?
N1 C1 N2 C5 5.6(5) . . . . ?
Si5 C1 N2 C5 176.2(3) . . . . ?
C26 C21 N2 C1 123.3(5) . . . . ?
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C6 C5 N2 C1 -15.6(5) . . . . ?
C6 C5 N2 C21 -176.5(4) . . . . ?
C9 C8 O1 U1 -6.9(10) . . . . ?
C10 C8 O1 U1 -128.4(7) . . . . ?
C7 C8 O1 U1 109.3(7) . . . . ?
Si2 N4 Si1 C29 152.7(3) . . . . ?
U1 N4 Si1 C29 -41.0(3) . . . . ?
Si2 N4 Si1 C27 34.0(4) . . . . ?
U1 N4 Si1 C27 -159.7(3) . . . . ?
Si2 N4 Si1 C28 -87.5(3) . . . . ?
U1 N4 Si1 C28 78.8(3) . . . . ?
Si1 N4 Si2 C31 -76.5(4) . . . . ?
U1 N4 Si2 C31 115.7(3) . . . . ?
Si1 N4 Si2 C30 47.7(4) . . . . ?
U1 N4 Si2 C30 -120.0(3) . . . . ?
Si1 N4 Si2 C32 165.4(3) . . . . ?
U1 N4 Si2 C32 -2.3(3) . . . . ?
Si1 N4 Si2 U1 167.8(4) . . . . ?
Si4 N3 Si3 C34 -60.2(4) . . . . ?
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Si3 N3 Si4 C38 -37.7(4) . . . . ?
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N1 C1 Si5 C39 173.3(4) . . . . ?
N2 C1 Si5 C39 3.9(4) . . . . ?
N1 C1 Si5 C41 57.0(4) . . . . ?
N2 C1 Si5 C41 -112.4(4) . . . . ?
N1 C1 Si5 C40 -64.6(4) . . . . ?
N2 C1 Si5 C40 126.0(4) . . . . ?
C8 O1 U1 N4 156.5(8) . . . . ?
C8 O1 U1 N3 30.7(8) . . . . ?
C8 O1 U1 I1 -101.4(8) . . . . ?
C8 O1 U1 Si2 152.4(7) . . . . ?
Si2 N4 U1 O1 -174.22(18) . . . . ?
Si1 N4 U1 O1 18.2(3) . . . . ?
Si2 N4 U1 N3 -56.2(2) . . . . ?
Si1 N4 U1 N3 136.2(2) . . . . ?
Si2 N4 U1 I1 84.89(19) . . . . ?
Si1 N4 U1 I1 -82.7(2) . . . . ?
Si1 N4 U1 Si2 -167.6(4) . . . . ?
Si3 N3 U1 O1 77.6(2) . . . . ?
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Si3 N3 U1 I1 -172.77(12) . . . . ?
Si4 N3 U1 I1 5.7(3) . . . . ?
Si3 N3 U1 Si2 -68.48(19) . . . . ?
Si4 N3 U1 Si2 110.00(19) . . . . ?
N4 Si2 U1 O1 8.3(3) . . . . ?
C31 Si2 U1 O1 -78.2(3) . . . . ?
C30 Si2 U1 O1 91.5(3) . . . . ?
C32 Si2 U1 O1 -174.0(2) . . . . ?
C31 Si2 U1 N4 -86.5(3) . . . . ?
C30 Si2 U1 N4 83.2(3) . . . . ?
C32 Si2 U1 N4 177.7(3) . . . . ?
N4 Si2 U1 N3 131.0(2) . . . . ?
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C32 Si2 U1 N3 -51.3(2) . . . . ?
N4 Si2 U1 I1 -98.5(2) . . . . ?
C31 Si2 U1 I1 175.0(2) . . . . ?
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C32 Si2 U1 I1 79.2(2) . . . . ?

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data_po8085a

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;
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4(C6 H6)'
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 'C92 H172 Ce2 N14 O2 Si10'
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 'Ce'  'Ce'  -0.2486   2.6331
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_symmetry_space_group_name_H-M    P-1

loop_
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 'x, y, z'
 '-x, -y, -z'

_cell_length_a                    13.7100(6)
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_cell_length_c                    14.9982(7)
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_cell_angle_beta                  81.333(2)
_cell_angle_gamma                 72.347(2)
_cell_volume                      2899.0(2)
_cell_formula_units_Z             1
_cell_measurement_temperature     150(2)
_cell_measurement_reflns_used     16821
_cell_measurement_theta_min       1.4
_cell_measurement_theta_max       30.51

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_exptl_crystal_size_mid           0.33
_exptl_crystal_size_min           0.31
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.184
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_exptl_crystal_F_000              1094
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_exptl_absorpt_correction_T_min   0.6213
_exptl_absorpt_correction_T_max   0.7461
_exptl_absorpt_process_details    SADABS

_exptl_special_details
;
 INCOMPLETE DATA; Reflection count < 95% completeness
 The data collection strategy used aimed to achieve a
 complete data set to 2\? = 53 deg.  Some higher angle
 data were collected in the process and these
 have been included in the refinement.
```

```
;

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detector'
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_diffrn_reflns_limit_k_max        20
_diffrn_reflns_limit_l_min        -21
_diffrn_reflns_limit_l_max        20
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_reflns_number_gt                 14932
_reflns_threshold_expression      >2sigma(I)

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_computing_cell_refinement        'SAINT (Siemens, 1995)'
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_computing_structure_solution     'SIR-92 (Giacovazzo, 1994)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   'enCIFer (Allen et al.,
2004)'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
```

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 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0338P)^2^+2.7744P] where
P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
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 _atom_site_disorder_group
C1 C 0.3584(2) 0.23424(18) 1.26555(17) 0.0235(5) Uani 1 1 d .
. .
C5 C 0.3758(3) 0.3589(2) 1.1743(2) 0.0417(8) Uani 1 1 d . . .
H5A H 0.4379 0.3523 1.1286 0.050 Uiso 1 1 calc R . .
H5B H 0.3429 0.4261 1.1903 0.050 Uiso 1 1 calc R . .
C6 C 0.3002(2) 0.3165(2) 1.1403(2) 0.0324(6) Uani 1 1 d . . .
H6A H 0.2301 0.3622 1.1452 0.039 Uiso 1 1 calc R . .
H6B H 0.3237 0.2948 1.0768 0.039 Uiso 1 1 calc R . .
C7 C 0.2365(2) 0.1770(2) 1.19069(18) 0.0270(5) Uani 1 1 d . .
.
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H7A H 0.1633 0.2163 1.1975 0.032 Uiso 1 1 calc R . .
H7B H 0.2433 0.1305 1.2396 0.032 Uiso 1 1 calc R . .
C8 C 0.2643(2) 0.12431(19) 1.09894(18) 0.0269(5) Uani 1 1 d .
. .
C9 C 0.2100(3) 0.0480(2) 1.1085(2) 0.0379(7) Uani 1 1 d . . .
H9A H 0.1362 0.0763 1.1304 0.057 Uiso 1 1 calc R . .
H9B H 0.2409 0.0011 1.1514 0.057 Uiso 1 1 calc R . .
H9C H 0.2183 0.0177 1.0496 0.057 Uiso 1 1 calc R . .
C10 C 0.3815(2) 0.0791(2) 1.0747(2) 0.0375(7) Uani 1 1 d . . .
H10A H 0.3962 0.0431 1.0182 0.056 Uiso 1 1 calc R . .
H10B H 0.4073 0.0371 1.1231 0.056 Uiso 1 1 calc R . .
H10C H 0.4158 0.1281 1.0674 0.056 Uiso 1 1 calc R . .
C21 C 0.4840(2) 0.31285(19) 1.29942(18) 0.0261(5) Uani 1 1 d .
. .
C22 C 0.4598(2) 0.3814(2) 1.36747(19) 0.0289(6) Uani 1 1 d . .
.
C23 C 0.5416(3) 0.3888(2) 1.4088(2) 0.0366(7) Uani 1 1 d . . .
H23 H 0.5279 0.4337 1.4560 0.044 Uiso 1 1 calc R . .
C24 C 0.6413(3) 0.3330(2) 1.3833(2) 0.0385(7) Uani 1 1 d . . .
H24 H 0.6953 0.3392 1.4132 0.046 Uiso 1 1 calc R . .
C25 C 0.6630(2) 0.2681(2) 1.3144(2) 0.0350(7) Uani 1 1 d . . .
H25 H 0.7325 0.2306 1.2964 0.042 Uiso 1 1 calc R . .
C26 C 0.5852(2) 0.2563(2) 1.2705(2) 0.0307(6) Uani 1 1 d . . .
C27 C 0.2489(3) 0.5151(2) 0.9934(2) 0.0434(8) Uani 1 1 d . . .
H27A H 0.1785 0.5103 1.0002 0.065 Uiso 1 1 calc R . .
H27B H 0.2464 0.5811 0.9879 0.065 Uiso 1 1 calc R . .
H27C H 0.2809 0.4886 1.0463 0.065 Uiso 1 1 calc R . .
C28 C 0.2843(4) 0.5211(3) 0.7908(3) 0.0611(12) Uani 1 1 d . .
.
H28A H 0.3293 0.4927 0.7354 0.092 Uiso 1 1 calc R . .
H28B H 0.2883 0.5846 0.7987 0.092 Uiso 1 1 calc R . .
H28C H 0.2127 0.5241 0.7865 0.092 Uiso 1 1 calc R . .
C29 C 0.4637(3) 0.4496(3) 0.8931(3) 0.0648(12) Uani 1 1 d . .
.
H29A H 0.4884 0.4161 0.9465 0.097 Uiso 1 1 calc R . .
H29B H 0.4648 0.5146 0.8962 0.097 Uiso 1 1 calc R . .
H29C H 0.5087 0.4188 0.8387 0.097 Uiso 1 1 calc R . .
C30 C 0.3532(3) 0.1489(2) 0.8150(2) 0.0414(8) Uani 1 1 d . . .
H30A H 0.3400 0.1237 0.8751 0.062 Uiso 1 1 calc R . .
H30B H 0.4031 0.0996 0.7756 0.062 Uiso 1 1 calc R . .
H30C H 0.2882 0.1712 0.7897 0.062 Uiso 1 1 calc R . .
C31 C 0.4491(3) 0.2811(3) 0.7047(2) 0.0477(9) Uani 1 1 d . . .
H31A H 0.3879 0.3085 0.6751 0.072 Uiso 1 1 calc R . .
H31B H 0.4938 0.2246 0.6714 0.072 Uiso 1 1 calc R . .
H31C H 0.4872 0.3268 0.7056 0.072 Uiso 1 1 calc R . .
C32 C 0.5301(3) 0.1992(3) 0.8734(3) 0.0540(10) Uani 1 1 d . .
.
H32A H 0.5634 0.2481 0.8773 0.081 Uiso 1 1 calc R . .
H32B H 0.5771 0.1475 0.8350 0.081 Uiso 1 1 calc R . .
H32C H 0.5139 0.1760 0.9339 0.081 Uiso 1 1 calc R . .
C33 C -0.0383(3) 0.2069(2) 1.0308(2) 0.0355(7) Uani 1 1 d . .
.
H33A H 0.0296 0.1946 1.0503 0.053 Uiso 1 1 calc R . .
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H33B H -0.0739 0.1643 1.0615 0.053 Uiso 1 1 calc R . .
H33C H -0.0796 0.2719 1.0458 0.053 Uiso 1 1 calc R . .
C34 C -0.1556(3) 0.2197(3) 0.8758(2) 0.0449(8) Uani 1 1 d . .
.
H34A H -0.1923 0.2852 0.8931 0.067 Uiso 1 1 calc R . .
H34B H -0.1928 0.1790 0.9081 0.067 Uiso 1 1 calc R . .
H34C H -0.1518 0.2116 0.8107 0.067 Uiso 1 1 calc R . .
C35 C 0.0387(3) 0.0588(2) 0.8826(3) 0.0504(9) Uani 1 1 d . . .
H35A H 0.0493 0.0466 0.8175 0.076 Uiso 1 1 calc R . .
H35B H -0.0074 0.0250 0.9133 0.076 Uiso 1 1 calc R . .
H35C H 0.1055 0.0373 0.9049 0.076 Uiso 1 1 calc R . .
C36 C -0.0773(3) 0.3891(3) 0.7364(2) 0.0480(9) Uani 1 1 d . .
.
H36A H -0.1369 0.3649 0.7445 0.072 Uiso 1 1 calc R . .
H36B H -0.0715 0.4177 0.6769 0.072 Uiso 1 1 calc R . .
H36C H -0.0867 0.4362 0.7834 0.072 Uiso 1 1 calc R . .
C37 C 0.1548(3) 0.3340(3) 0.6955(2) 0.0421(8) Uani 1 1 d . . .
H37A H 0.1645 0.3774 0.7384 0.063 Uiso 1 1 calc R . .
H37B H 0.1394 0.3667 0.6392 0.063 Uiso 1 1 calc R . .
H37C H 0.2182 0.2810 0.6830 0.063 Uiso 1 1 calc R . .
C38 C 0.0512(3) 0.1918(3) 0.6658(2) 0.0459(8) Uani 1 1 d . . .
H38A H 0.1140 0.1397 0.6699 0.069 Uiso 1 1 calc R . .
H38B H 0.0527 0.2148 0.6038 0.069 Uiso 1 1 calc R . .
H38C H -0.0097 0.1702 0.6824 0.069 Uiso 1 1 calc R . .
C40 C 0.4532(3) 0.1625(3) 1.4444(2) 0.0419(8) Uani 1 1 d . . .
H40A H 0.4493 0.1219 1.4966 0.063 Uiso 1 1 calc R . .
H40B H 0.4364 0.2275 1.4652 0.063 Uiso 1 1 calc R . .
H40C H 0.5233 0.1426 1.4106 0.063 Uiso 1 1 calc R . .
C41 C 0.2251(3) 0.2009(2) 1.4302(2) 0.0400(7) Uani 1 1 d . . .
H41A H 0.1762 0.1951 1.3910 0.060 Uiso 1 1 calc R . .
H41B H 0.2114 0.2671 1.4458 0.060 Uiso 1 1 calc R . .
H41C H 0.2169 0.1654 1.4854 0.060 Uiso 1 1 calc R . .
C42 C 0.3954(3) 0.0295(2) 1.3325(2) 0.0376(7) Uani 1 1 d . . .
H42A H 0.4100 -0.0117 1.3841 0.056 Uiso 1 1 calc R . .
H42B H 0.4572 0.0157 1.2866 0.056 Uiso 1 1 calc R . .
H42C H 0.3382 0.0189 1.3068 0.056 Uiso 1 1 calc R . .
C220 C 0.3509(2) 0.4458(2) 1.3957(2) 0.0369(7) Uani 1 1 d . .
.
H220 H 0.3035 0.4256 1.3618 0.044 Uiso 1 1 calc R . .
C221 C 0.3138(3) 0.4399(3) 1.4968(3) 0.0491(9) Uani 1 1 d . .
.
H22E H 0.3142 0.3755 1.5114 0.074 Uiso 1 1 calc R . .
H22D H 0.2433 0.4824 1.5120 0.074 Uiso 1 1 calc R . .
H22F H 0.3601 0.4580 1.5315 0.074 Uiso 1 1 calc R . .
C222 C 0.3446(3) 0.5470(2) 1.3696(3) 0.0447(8) Uani 1 1 d . .
.
H22B H 0.3937 0.5672 1.3990 0.067 Uiso 1 1 calc R . .
H22C H 0.2743 0.5881 1.3890 0.067 Uiso 1 1 calc R . .
H22A H 0.3619 0.5504 1.3040 0.067 Uiso 1 1 calc R . .
C260 C 0.6129(3) 0.1861(3) 1.1928(3) 0.0472(9) Uani 1 1 d . .
.
H260 H 0.5468 0.1810 1.1763 0.057 Uiso 1 1 calc R . .
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C261 C 0.6763(4) 0.0883(3) 1.2190(4) 0.0757(15) Uani 1 1 d . .
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H26D H 0.7444 0.0899 1.2299 0.114 Uiso 1 1 calc R . .
H26E H 0.6849 0.0436 1.1698 0.114 Uiso 1 1 calc R . .
H26F H 0.6400 0.0687 1.2738 0.114 Uiso 1 1 calc R . .
C262 C 0.6703(4) 0.2209(4) 1.1097(3) 0.0763(15) Uani 1 1 d . .
.
H26A H 0.6285 0.2834 1.0941 0.114 Uiso 1 1 calc R . .
H26B H 0.6820 0.1775 1.0589 0.114 Uiso 1 1 calc R . .
H26C H 0.7370 0.2240 1.1232 0.114 Uiso 1 1 calc R . .
C900 C 0.8295(2) 0.0800(2) 0.65798(17) 0.0607(11) Uani 1 1 d G
. .
H900 H 0.8534 0.0756 0.7147 0.073 Uiso 1 1 calc R . .
C901 C 0.7453(2) 0.15480(18) 0.64128(17) 0.0594(11) Uani 1 1 d
G . .
H901 H 0.7118 0.2015 0.6866 0.071 Uiso 1 1 calc R . .
C902 C 0.71029(19) 0.16121(19) 0.5583(2) 0.0629(12) Uani 1 1 d
G . .
H902 H 0.6528 0.2123 0.5469 0.076 Uiso 1 1 calc R . .
C903 C 0.7594(2) 0.0928(2) 0.49210(15) 0.0690(14) Uani 1 1 d G
. .
H903 H 0.7354 0.0972 0.4354 0.083 Uiso 1 1 calc R . .
C904 C 0.8435(2) 0.0181(2) 0.5088(2) 0.0731(15) Uani 1 1 d G .
.
H904 H 0.8771 -0.0286 0.4635 0.088 Uiso 1 1 calc R . .
C905 C 0.87855(18) 0.01167(17) 0.5917(2) 0.0689(13) Uani 1 1 d
G . .
H905 H 0.9361 -0.0394 0.6031 0.083 Uiso 1 1 calc R . .
C906 C 0.9595(2) 0.2973(2) 0.28910(14) 0.0623(12) Uani 1 1 d G
. .
H906 H 0.9650 0.2844 0.2266 0.075 Uiso 1 1 calc R . .
C907 C 0.9339(2) 0.2353(2) 0.3526(2) 0.0705(13) Uani 1 1 d G .
.
H907 H 0.9219 0.1801 0.3336 0.085 Uiso 1 1 calc R . .
C908 C 0.9258(2) 0.2541(2) 0.4441(2) 0.0765(16) Uani 1 1 d G .
.
H908 H 0.9083 0.2118 0.4875 0.092 Uiso 1 1 calc R . .
C909 C 0.9433(2) 0.3349(3) 0.47198(13) 0.0792(17) Uani 1 1 d G
. .
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C910 C 0.9689(3) 0.3968(2) 0.4084(2) 0.0800(16) Uani 1 1 d G .
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H910 H 0.9809 0.4520 0.4275 0.096 Uiso 1 1 calc R . .
C911 C 0.9770(2) 0.3780(2) 0.31699(17) 0.0695(13) Uani 1 1 d G
. .
H911 H 0.9945 0.4204 0.2736 0.083 Uiso 1 1 calc R . .
N1 N 0.30144(18) 0.23684(16) 1.20128(15) 0.0269(5) Uani 1 1 d
. . .
N2 N 0.40258(18) 0.30283(16) 1.25477(15) 0.0263(5) Uani 1 1 d
. . .
N3 N 0.31629(19) 0.33797(16) 0.88515(16) 0.0280(5) Uani 1 1 d
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N4 N 0.05426(18) 0.25147(17) 0.85222(15) 0.0288(5) Uani 1 1 d
. . .
N5 N 0.0616(2) 0.38606(17) 1.08685(16) 0.0323(5) Uani 1 1 d .
. .
N6 N 0.00098(18) 0.46135(16) 1.09601(14) 0.0249(4) Uani 1 1 d
. . .
N7 N 0.0592(2) 0.46484(18) 0.89193(17) 0.0385(6) Uani 1 1 d .
. .
O1 O 0.22757(15) 0.18727(13) 1.03200(13) 0.0271(4) Uani 1 1 d
. . .
Si1 Si 0.32731(8) 0.44846(6) 0.88936(6) 0.0364(2) Uani 1 1 d .
. .
Si2 Si 0.40734(7) 0.24944(6) 0.82351(6) 0.03315(18) Uani 1 1 d
. . .
Si3 Si -0.02075(6) 0.18757(6) 0.90568(6) 0.03055(17) Uani 1 1
d . . .
Si4 Si 0.04452(7) 0.28957(6) 0.74479(5) 0.03276(18) Uani 1 1 d
. . .
Si5 Si 0.35926(6) 0.15368(6) 1.37038(5) 0.02639(15) Uani 1 1 d
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Ce1 Ce 0.159817(11) 0.299999(10) 0.941884(9) 0.02213(5) Uani 1
1 d . . .

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0.0094(10)
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0.0300(17)
C6 0.0377(16) 0.0333(15) 0.0335(14) 0.0111(12) -0.0160(12) -
0.0175(13)
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0.0148(11)
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0.0069(11)
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0.0191(14)
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0.0005(13)
C21 0.0274(14) 0.0275(13) 0.0283(13) 0.0038(10) -0.0068(10) -
0.0147(11)
C22 0.0294(14) 0.0267(14) 0.0337(14) -0.0006(11) -0.0080(11) -
0.0114(11)
C23 0.0404(17) 0.0357(16) 0.0395(16) -0.0040(13) -0.0143(13) -
0.0154(14)
C24 0.0354(17) 0.0379(17) 0.0509(19) 0.0061(14) -0.0197(14) -
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C25 0.0245(14) 0.0312(15) 0.0515(18) 0.0012(13) -0.0044(13) -
0.0122(12)
C26 0.0284(14) 0.0289(14) 0.0380(15) -0.0008(11) -0.0008(11) -
0.0151(12)
C27 0.065(2) 0.0253(15) 0.0440(18) -0.0013(13) -0.0121(16) -
0.0171(15)
C28 0.111(4) 0.037(2) 0.043(2) 0.0125(15) -0.012(2) -0.035(2)
C29 0.067(3) 0.066(3) 0.079(3) -0.009(2) -0.002(2) -0.049(2)
C30 0.0417(18) 0.0287(16) 0.0484(18) -0.0096(13) 0.0089(15) -
0.0092(13)
C31 0.0425(19) 0.056(2) 0.0431(18) -0.0012(16) 0.0085(15) -
0.0192(17)
C32 0.0350(19) 0.050(2) 0.072(3) 0.0155(19) -0.0078(18) -
0.0085(16)
C33 0.0360(16) 0.0386(17) 0.0332(15) 0.0051(12) -0.0042(12) -
0.0143(13)
C34 0.0354(18) 0.064(2) 0.0415(18) -0.0054(16) -0.0038(14) -
0.0242(17)
C35 0.058(2) 0.0349(18) 0.057(2) -0.0043(16) 0.0048(18) -
0.0184(17)
C36 0.044(2) 0.060(2) 0.0387(17) 0.0074(16) -0.0152(15) -
0.0106(17)
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0.0244(17)
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0.0281(18)
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0.0129(14)
C42 0.0420(18) 0.0285(15) 0.0431(17) 0.0075(13) -0.0077(14) -
0.0120(13)
C220 0.0302(15) 0.0368(17) 0.0436(17) -0.0074(13) -0.0069(13)
-0.0087(13)
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0.0121(16)
C222 0.045(2) 0.0345(18) 0.052(2) -0.0011(15) -0.0138(16) -
0.0040(15)
C260 0.0382(18) 0.049(2) 0.056(2) -0.0231(17) 0.0113(15) -
0.0216(16)
C261 0.066(3) 0.042(2) 0.113(4) -0.029(2) 0.010(3) -0.014(2)
C262 0.075(3) 0.097(4) 0.055(2) -0.026(2) 0.027(2) -0.040(3)
C900 0.066(3) 0.075(3) 0.061(2) 0.015(2) -0.018(2) -0.049(3)
C901 0.066(3) 0.052(2) 0.063(3) -0.0045(19) 0.014(2) -0.032(2)
C902 0.046(2) 0.062(3) 0.075(3) 0.024(2) 0.002(2) -0.016(2)
C903 0.074(3) 0.106(4) 0.047(2) 0.015(2) -0.010(2) -0.059(3)
C904 0.073(3) 0.062(3) 0.086(3) -0.030(3) 0.029(3) -0.039(3)
C905 0.044(2) 0.046(2) 0.116(4) 0.016(3) -0.009(3) -0.0167(19)
C906 0.044(2) 0.083(3) 0.044(2) 0.007(2) -0.0067(17) 0.003(2)
C907 0.034(2) 0.080(3) 0.096(4) 0.015(3) -0.024(2) -0.010(2)
C908 0.032(2) 0.119(5) 0.063(3) 0.043(3) -0.0035(19) -0.006(2)
C909 0.062(3) 0.103(4) 0.036(2) 0.008(2) 0.0008(19) 0.024(3)
C910 0.099(4) 0.059(3) 0.057(3) 0.000(2) -0.014(3) 0.014(3)
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C911 0.080(3) 0.066(3) 0.046(2) 0.016(2) -0.004(2) -0.003(2)
N1 0.0308(12) 0.0276(12) 0.0271(11) 0.0055(9) -0.0097(9) -
0.0139(10)
N2 0.0299(12) 0.0273(12) 0.0277(11) 0.0054(9) -0.0107(9) -
0.0148(10)
N3 0.0304(12) 0.0227(11) 0.0334(12) 0.0011(9) -0.0042(10) -
0.0118(9)
N4 0.0291(12) 0.0335(13) 0.0260(11) 0.0012(9) -0.0043(9) -
0.0128(10)
N5 0.0374(14) 0.0243(12) 0.0282(11) -0.0007(9) -0.0021(10)
0.0001(10)
N6 0.0296(12) 0.0238(11) 0.0213(10) 0.0017(8) -0.0046(9) -
0.0077(9)
N7 0.0467(16) 0.0276(13) 0.0318(13) 0.0002(10) -0.0049(11)
0.0022(11)
O1 0.0308(10) 0.0224(9) 0.0285(9) 0.0023(7) -0.0086(8) -
0.0069(8)
Si1 0.0523(5) 0.0279(4) 0.0360(4) 0.0031(3) -0.0066(4) -
0.0226(4)
Si2 0.0284(4) 0.0295(4) 0.0402(4) 0.0003(3) 0.0004(3) -
0.0094(3)
Si3 0.0294(4) 0.0325(4) 0.0321(4) -0.0028(3) -0.0016(3) -
0.0139(3)
Si4 0.0345(4) 0.0416(5) 0.0259(4) 0.0009(3) -0.0073(3) -
0.0156(4)
Si5 0.0273(4) 0.0269(4) 0.0265(3) 0.0045(3) -0.0043(3) -
0.0107(3)
Ce1 0.02400(8) 0.02010(7) 0.02182(7) -0.00033(5) -0.00464(5) -
0.00529(5)

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 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds involving
l.s. planes.
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C7 N1 1.468(3) . ?
C7 C8 1.546(4) . ?
C8 O1 1.398(3) . ?
C8 C10 1.533(4) . ?
C8 C9 1.535(4) . ?
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C21 C22 1.401(4) . ?
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C22 C23 1.394(4) . ?
C22 C220 1.516(4) . ?
C23 C24 1.371(5) . ?
C24 C25 1.378(5) . ?
C25 C26 1.391(4) . ?
C26 C260 1.520(4) . ?
C27 Si1 1.878(4) . ?
C28 Si1 1.868(4) . ?
C29 Si1 1.884(4) . ?
C30 Si2 1.884(3) . ?
C31 Si2 1.879(4) . ?
C32 Si2 1.880(4) . ?
C33 Si3 1.876(3) . ?
C34 Si3 1.883(3) . ?
C35 Si3 1.872(4) . ?
C36 Si4 1.888(4) . ?
C37 Si4 1.875(3) . ?
C38 Si4 1.884(3) . ?
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 SADABS PROBLEMS

SADABS corrects for all systematic errors that lead to
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intensities of symmetry-equivalent data. These may include
absorption by the
mount, crystal decay, changes in the volume of the crystal
illuminated, etc.
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expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0374P)^2^+2.5708P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     RIDING
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
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_refine_ls_R_factor_all          0.0473
_refine_ls_R_factor_gt           0.0403
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_refine_ls_wR_factor_gt          0.0861
_refine_ls_goodness_of_fit_ref   1.163
_refine_ls_restrained_S_all      1.163
_refine_ls_shift/su_max          0.000
_refine_ls_shift/su_mean         0.000

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 _atom_site_symmetry_multiplicity
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 _atom_site_refinement_flags
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C1 C 0.1654(4) 0.5587(3) 0.61545(19) 0.0175(6) Uani 1 1 d . .
.
C5 C 0.3199(4) 0.6483(3) 0.7010(2) 0.0265(8) Uani 1 1 d . . .
H5A H 0.2930 0.6764 0.7515 0.032 Uiso 1 1 calc R . .
H5B H 0.4040 0.6884 0.6817 0.032 Uiso 1 1 calc R . .
C6 C 0.3509(5) 0.5297(4) 0.7043(3) 0.0329(10) Uani 1 1 d . . .
H6A H 0.4536 0.5148 0.6935 0.039 Uiso 1 1 calc R . .
H6B H 0.3261 0.4999 0.7547 0.039 Uiso 1 1 calc R . .
C7 C 0.2452(4) 0.3713(3) 0.6352(2) 0.0248(8) Uani 1 1 d . . .
H7A H 0.1498 0.3482 0.6541 0.030 Uiso 1 1 calc R . .
H7B H 0.3196 0.3366 0.6672 0.030 Uiso 1 1 calc R . .
C8 C 0.2624(4) 0.3323(3) 0.5531(2) 0.0237(8) Uani 1 1 d . . .
C9 C 0.4086(5) 0.3613(4) 0.5213(3) 0.0349(10) Uani 1 1 d . . .
H9A H 0.4143 0.3382 0.4682 0.052 Uiso 1 1 calc R . .
H9B H 0.4841 0.3258 0.5510 0.052 Uiso 1 1 calc R . .
H9C H 0.4220 0.4386 0.5241 0.052 Uiso 1 1 calc R . .
C10 C 0.2338(5) 0.2124(3) 0.5514(3) 0.0365(10) Uani 1 1 d . .
.
H10A H 0.1377 0.1980 0.5719 0.055 Uiso 1 1 calc R . .
H10B H 0.3065 0.1758 0.5824 0.055 Uiso 1 1 calc R . .
H10C H 0.2389 0.1867 0.4989 0.055 Uiso 1 1 calc R . .
C21 C 0.1123(4) 0.7489(3) 0.6371(2) 0.0216(7) Uani 1 1 d . . .
C22 C 0.1738(4) 0.8365(3) 0.6011(2) 0.0234(7) Uani 1 1 d . . .
C23 C 0.0926(5) 0.9300(3) 0.5952(2) 0.0293(9) Uani 1 1 d . . .
H23 H 0.1325 0.9902 0.5703 0.035 Uiso 1 1 calc R . .
C24 C -0.0439(5) 0.9360(3) 0.6251(2) 0.0319(9) Uani 1 1 d . .
.
H24 H -0.0972 1.0004 0.6213 0.038 Uiso 1 1 calc R . .
C25 C -0.1036(5) 0.8483(3) 0.6605(2) 0.0293(9) Uani 1 1 d . .
.
```

```
H25 H -0.1981 0.8535 0.6809 0.035 Uiso 1 1 calc R . .
C26 C -0.0290(4) 0.7525(3) 0.6672(2) 0.0227(7) Uani 1 1 d . .
.
C220 C 0.3256(5) 0.8355(3) 0.5685(2) 0.0284(8) Uani 1 1 d . .
.
H220 H 0.3578 0.7597 0.5653 0.034 Uiso 1 1 calc R . .
C221 C 0.3344(6) 0.8834(4) 0.4890(3) 0.0380(10) Uani 1 1 d . .
.
H22A H 0.2653 0.8474 0.4555 0.057 Uiso 1 1 calc R . .
H22B H 0.4322 0.8740 0.4691 0.057 Uiso 1 1 calc R . .
H22C H 0.3115 0.9595 0.4914 0.057 Uiso 1 1 calc R . .
C222 C 0.4300(5) 0.8945(4) 0.6221(3) 0.0401(11) Uani 1 1 d . .
.
H22D H 0.4047 0.9702 0.6236 0.060 Uiso 1 1 calc R . .
H22E H 0.5289 0.8865 0.6035 0.060 Uiso 1 1 calc R . .
H22F H 0.4229 0.8644 0.6734 0.060 Uiso 1 1 calc R . .
C260 C -0.0966(4) 0.6578(3) 0.7071(2) 0.0263(8) Uani 1 1 d . .
.
H260 H -0.0627 0.5919 0.6808 0.032 Uiso 1 1 calc R . .
C261 C -0.2614(5) 0.6581(4) 0.7042(3) 0.0403(11) Uani 1 1 d .
. .
H26A H -0.2982 0.7163 0.7357 0.061 Uiso 1 1 calc R . .
H26B H -0.2980 0.5901 0.7235 0.061 Uiso 1 1 calc R . .
H26C H -0.2936 0.6680 0.6516 0.061 Uiso 1 1 calc R . .
C262 C -0.0458(5) 0.6517(4) 0.7900(2) 0.0361(10) Uani 1 1 d .
. .
H26D H 0.0595 0.6463 0.7915 0.054 Uiso 1 1 calc R . .
H26E H -0.0882 0.5890 0.8143 0.054 Uiso 1 1 calc R . .
H26F H -0.0763 0.7160 0.8170 0.054 Uiso 1 1 calc R . .
N1 N 0.2571(4) 0.4862(2) 0.64468(19) 0.0227(7) Uani 1 1 d . .
.
N2 N 0.1963(3) 0.6534(2) 0.64685(17) 0.0192(6) Uani 1 1 d . .
.
O1 O 0.1539(3) 0.3832(2) 0.50833(15) 0.0242(5) Uani 1 1 d . .
.
I1 I 0.18350(3) 0.62466(2) 0.385430(17) 0.03798(9) Uani 1 1 d
. . .
U1 U 0.0000 0.5000 0.5000 0.01955(6) Uani 1 2 d S . .

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 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
C1 0.0158(16) 0.0172(17) 0.0195(15) 0.0006(13) -0.0025(12) -
0.0002(13)
C5 0.0257(19) 0.027(2) 0.0266(18) -0.0068(15) -0.0119(15)
0.0023(15)
C6 0.035(2) 0.027(2) 0.036(2) -0.0039(18) -0.0216(18)
0.0010(17)
```

```
C7 0.030(2) 0.0180(17) 0.0263(18) 0.0061(15) -0.0098(15)
0.0009(15)
C8 0.0260(19) 0.0142(16) 0.0309(19) 0.0000(15) -0.0112(15)
0.0032(14)
C9 0.026(2) 0.035(2) 0.044(2) -0.003(2) -0.0012(17) 0.0079(18)
C10 0.046(3) 0.0159(19) 0.048(3) -0.0001(18) -0.016(2)
0.0062(18)
C21 0.0253(18) 0.0193(17) 0.0202(16) -0.0050(14) -0.0027(13)
0.0026(14)
C22 0.0259(19) 0.0206(18) 0.0236(17) -0.0048(14) -0.0028(14)
0.0015(15)
C23 0.041(2) 0.0183(18) 0.0287(19) 0.0000(15) -0.0051(17)
0.0038(17)
C24 0.037(2) 0.026(2) 0.033(2) -0.0040(17) -0.0075(17)
0.0128(18)
C25 0.026(2) 0.031(2) 0.031(2) -0.0085(17) -0.0027(15)
0.0094(16)
C26 0.0217(17) 0.0268(19) 0.0196(16) -0.0041(15) -0.0050(13)
0.0021(15)
C220 0.034(2) 0.0170(18) 0.034(2) -0.0026(16) 0.0060(16) -
0.0016(16)
C221 0.053(3) 0.025(2) 0.036(2) 0.0008(18) 0.011(2) -0.002(2)
C222 0.034(2) 0.033(2) 0.053(3) -0.004(2) 0.001(2) -0.0084(19)
C260 0.0233(19) 0.0256(19) 0.0300(19) -0.0053(16) 0.0033(15) -
0.0018(15)
C261 0.026(2) 0.054(3) 0.041(2) -0.004(2) 0.0001(18) -0.006(2)
C262 0.032(2) 0.045(3) 0.032(2) 0.0076(19) -0.0009(17) -
0.0001(19)
N1 0.0256(17) 0.0155(15) 0.0268(16) 0.0000(12) -0.0098(13)
0.0015(12)
N2 0.0188(14) 0.0184(15) 0.0205(14) -0.0020(11) -0.0047(11)
0.0009(11)
O1 0.0265(14) 0.0200(13) 0.0262(13) -0.0017(11) -0.0072(10)
0.0040(11)
I1 0.03609(16) 0.03452(16) 0.04335(17) 0.00610(13) 0.00161(12)
-0.01294(12)
U1 0.02013(10) 0.01674(10) 0.02171(10) -0.00003(7) -0.00765(6)
0.00096(7)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds involving
l.s. planes.
```

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C1 N1 1.346(5) . ?
C1 U1 2.647(3) . ?
C5 N2 1.489(5) . ?
C5 C6 1.518(6) . ?
C6 N1 1.466(5) . ?
C7 N1 1.457(5) . ?
C7 C8 1.536(6) . ?
C8 O1 1.426(4) . ?
C8 C9 1.513(6) . ?
C8 C10 1.530(5) . ?
C21 C22 1.393(5) . ?
C21 C26 1.416(5) . ?
C21 N2 1.440(5) . ?
C22 C23 1.399(5) . ?
C22 C220 1.521(6) . ?
C23 C24 1.375(6) . ?
C24 C25 1.383(6) . ?
C25 C26 1.393(5) . ?
C26 C260 1.519(6) . ?
C220 C221 1.526(6) . ?
C220 C222 1.540(6) . ?
C260 C261 1.529(6) . ?
C260 C262 1.532(6) . ?
O1 U1 2.053(3) . ?
I1 U1 3.0727(3) . ?
U1 O1 2.053(3) 3_566 ?
U1 C1 2.647(3) 3_566 ?
U1 I1 3.0727(3) 3_566 ?

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N2 C1 N1 108.0(3) . . ?
N2 C1 U1 133.3(2) . . ?
N1 C1 U1 117.9(2) . . ?
N2 C5 C6 102.3(3) . . ?
N1 C6 C5 103.1(3) . . ?
N1 C7 C8 114.5(3) . . ?
O1 C8 C9 108.7(3) . . ?
```

```
O1 C8 C10 108.0(3) . . ?
C9 C8 C10 112.7(4) . . ?
O1 C8 C7 107.5(3) . . ?
C9 C8 C7 111.6(3) . . ?
C10 C8 C7 108.2(3) . . ?
C22 C21 C26 121.7(4) . . ?
C22 C21 N2 119.3(3) . . ?
C26 C21 N2 118.9(3) . . ?
C21 C22 C23 118.4(4) . . ?
C21 C22 C220 123.1(3) . . ?
C23 C22 C220 118.5(4) . . ?
C24 C23 C22 121.0(4) . . ?
C23 C24 C25 119.9(4) . . ?
C24 C25 C26 121.7(4) . . ?
C25 C26 C21 117.2(4) . . ?
C25 C26 C260 120.6(4) . . ?
C21 C26 C260 122.2(3) . . ?
C22 C220 C221 113.3(4) . . ?
C22 C220 C222 110.3(3) . . ?
C221 C220 C222 109.6(4) . . ?
C26 C260 C261 113.4(4) . . ?
C26 C260 C262 110.7(3) . . ?
C261 C260 C262 109.7(3) . . ?
C1 N1 C7 125.3(3) . . ?
C1 N1 C6 113.2(3) . . ?
C7 N1 C6 119.7(3) . . ?
C1 N2 C21 125.0(3) . . ?
C1 N2 C5 112.8(3) . . ?
C21 N2 C5 121.8(3) . . ?
C8 O1 U1 148.1(2) . . ?
O1 U1 O1 180.000(1) . 3_566 ?
O1 U1 C1 75.12(10) . . ?
O1 U1 C1 104.88(10) 3_566 . ?
O1 U1 C1 104.88(10) . 3_566 ?
O1 U1 C1 75.12(10) 3_566 3_566 ?
C1 U1 C1 180.0 . 3_566 ?
O1 U1 I1 91.40(8) . . ?
O1 U1 I1 88.60(8) 3_566 . ?
C1 U1 I1 92.34(8) . . ?
C1 U1 I1 87.66(8) 3_566 . ?
O1 U1 I1 88.60(8) . 3_566 ?
O1 U1 I1 91.40(8) 3_566 3_566 ?
C1 U1 I1 87.66(8) . 3_566 ?
C1 U1 I1 92.34(8) 3_566 3_566 ?
I1 U1 I1 180.000(10) . 3_566 ?

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N2 C5 C6 N1 7.8(4) . . . . ?
N1 C7 C8 O1 -58.6(4) . . . . ?
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N1 C7 C8 C10 -175.0(3) . . . . ?
C26 C21 C22 C23 0.3(5) . . . . ?
N2 C21 C22 C23 -177.1(3) . . . . ?
C26 C21 C22 C220 179.6(3) . . . . ?
N2 C21 C22 C220 2.2(5) . . . . ?
C21 C22 C23 C24 0.7(6) . . . . ?
C220 C22 C23 C24 -178.6(4) . . . . ?
C22 C23 C24 C25 -0.9(6) . . . . ?
C23 C24 C25 C26 0.0(6) . . . . ?
C24 C25 C26 C21 1.0(6) . . . . ?
C24 C25 C26 C260 179.4(4) . . . . ?
C22 C21 C26 C25 -1.1(5) . . . . ?
N2 C21 C26 C25 176.3(3) . . . . ?
C22 C21 C26 C260 -179.5(3) . . . . ?
N2 C21 C26 C260 -2.1(5) . . . . ?
C21 C22 C220 C221 134.2(4) . . . . ?
C23 C22 C220 C221 -46.5(5) . . . . ?
C21 C22 C220 C222 -102.5(4) . . . . ?
C23 C22 C220 C222 76.8(5) . . . . ?
C25 C26 C260 C261 27.0(5) . . . . ?
C21 C26 C260 C261 -154.7(4) . . . . ?
C25 C26 C260 C262 -96.7(4) . . . . ?
C21 C26 C260 C262 81.6(4) . . . . ?
N2 C1 N1 C7 169.4(4) . . . . ?
U1 C1 N1 C7 -19.8(5) . . . . ?
N2 C1 N1 C6 4.7(5) . . . . ?
U1 C1 N1 C6 175.6(3) . . . . ?
C8 C7 N1 C1 64.8(5) . . . . ?
C8 C7 N1 C6 -131.5(4) . . . . ?
C5 C6 N1 C1 -8.2(5) . . . . ?
C5 C6 N1 C7 -173.8(4) . . . . ?
N1 C1 N2 C21 -172.5(3) . . . . ?
U1 C1 N2 C21 18.6(5) . . . . ?
N1 C1 N2 C5 1.1(4) . . . . ?
U1 C1 N2 C5 -167.8(3) . . . . ?
C22 C21 N2 C1 -116.5(4) . . . . ?
C26 C21 N2 C1 66.0(5) . . . . ?
C22 C21 N2 C5 70.4(5) . . . . ?
C26 C21 N2 C5 -107.1(4) . . . . ?
C6 C5 N2 C1 -5.9(4) . . . . ?
C6 C5 N2 C21 167.9(4) . . . . ?
C9 C8 O1 U1 -107.9(5) . . . . ?
C10 C8 O1 U1 129.6(4) . . . . ?
C7 C8 O1 U1 13.0(6) . . . . ?
C8 O1 U1 C1 17.6(5) . . . . ?
C8 O1 U1 C1 -162.4(5) . . . 3_566 ?
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C8 O1 U1 I1 109.7(5) . . . . ?
C8 O1 U1 I1 -70.3(5) . . . 3_566 ?
N2 C1 U1 O1 154.1(4) . . . . ?
N1 C1 U1 O1 -14.0(3) . . . . ?
N2 C1 U1 O1 -25.9(4) . . . 3_566 ?
N1 C1 U1 O1 166.0(3) . . . 3_566 ?
N2 C1 U1 I1 63.2(3) . . . . ?
N1 C1 U1 I1 -104.8(3) . . . . ?
N2 C1 U1 I1 -116.8(3) . . . 3_566 ?
N1 C1 U1 I1 75.2(3) . . . 3_566 ?

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_audit_creation_method CRYSTALS_ver_12.87

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#looking for refcif

_publ_contact_author_name         'Simon Parsons'
_publ_contact_author_email        'S.Parsons@ed.ac.uk'

_publ_section_exptl_refinement
;
H atoms placed geometrically after each cycle

The three molecules were restarined to have similar bond
distances
and angles.

The peak shapes were rather broad and tended to run into
eachother, limiting the
quality of the data set. There is a lot of quite high thermal
motion. Clearly this
is not a very precise structure, but it's the best we can get,
and it does
establish chemical connectivity.

Disordered solvent regions were treated using the squeeze
procedure. Details are
given below.
```

Checkcif output:

213_ALERT_2_A Atom C129 has ADP max/min Ratio ..... 7.50 prola
220_ALERT_2_A Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.65 Ratio
220_ALERT_2_A Large Non-Solvent C Ueq(max)/Ueq(min) ... 6.19 Ratio
220_ALERT_2_A Large Non-Solvent C Ueq(max)/Ueq(min) ... 5.22 Ratio
222_ALERT_3_A Large Non-Solvent H Ueq(max)/Ueq(min) ... 5.21 Ratio
222_ALERT_3_B Large Non-Solvent H Ueq(max)/Ueq(min) ... 4.47 Ratio
241_ALERT_2_B Check High Ueq as Compared to Neighbors for C344
241_ALERT_2_B Check High Ueq as Compared to Neighbors for C346
242_ALERT_2_B Check Low Ueq as Compared to Neighbors for Si4
242_ALERT_2_B Check Low Ueq as Compared to Neighbors for Si11
242_ALERT_2_B Check Low Ueq as Compared to Neighbors for Si14
242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C339
242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C345
242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C960
213_ALERT_2_C Atom C34 has ADP max/min Ratio ..... 3.10 prola
213_ALERT_2_C Atom C128 has ADP max/min Ratio ..... 3.20 prola
213_ALERT_2_C Atom C344 has ADP max/min Ratio ..... 3.20 prola
213_ALERT_2_C Atom C962 has ADP max/min Ratio ..... 3.50 prola
222_ALERT_3_C Large Non-Solvent H Ueq(max)/Ueq(min) ... 3.70 Ratio
241_ALERT_2_C Check High Ueq as Compared to Neighbors for C47
241_ALERT_2_C Check High Ueq as Compared to Neighbors for C105
241_ALERT_2_C Check High Ueq as Compared to Neighbors for C348
242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Si2
242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Si3
242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C220

242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C260
242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C620
242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Si31
242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Si34

See comments above about thermal motion. The Si atoms tend to have lower
displacement parameters because they are piviot atoms on librating groups.

602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure !

Squueze used. See below.

919_ALERT_3_B Reflection(s) # Likely Affected by the Beamstop 9
910_ALERT_3_C Missing # of FCF Reflections Below Th(Min) 1
911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 760
913_ALERT_3_C Missing # of Very Strong Reflections in FCF 2
912_ALERT_4_C Missing # of FCF Reflections Above STh/L= 0.600 9884
951_ALERT_1_C Reported and Calculated Kmax Values Differ by .. 2

Completeness statistics:

Resolution & Completeness Statistics (Cumulative and Friedel Pairs Averaged)

Theta	sin(th)/Lambda	Complete	Expected	Measured	Missing
20.82	0.500	0.996	17924	17855	69
23.01	0.550	0.997	23823	23751	72
25.24	0.600	0.975	30907	30146	761

342_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang ... 9

```
See comments above.

360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C341   -   C342   ...
1.41 Ang.

Librational shortening.

860_ALERT_3_G Note: Number of Least-Squares Restraints .......
330

See above.

Lots of A, B and C alerts like this:

721_ALERT_1_A Bond    Calc    14.50000, Rep     0.95000 Dev...
13.55 Ang.
              C32  -H323    1.555   1.555
722_ALERT_1_A Angle   Calc      126.00, Rep      109.40 Dev...
16.60 Deg.
              SI2  -C32  -H323    1.555   1.555   1.555
722_ALERT_1_A Angle   Calc      121.00, Rep      109.50 Dev...
11.50 Deg.
              H321 -C32  -H323    1.555   1.555   1.555
722_ALERT_1_A Angle   Calc       38.00, Rep      109.50 Dev...
71.50 Deg.
              H322 -C32  -H323    1.555   1.555   1.555
732_ALERT_1_B Angle   Calc    106.0(4), Rep   105.99(9) ......
4.44 su-Ra
              C36  -SI4  -C37     1.555   1.555   1.555
732_ALERT_1_B Angle   Calc    111.5(4), Rep   111.51(8) ......
5.00 su-Ra
732_ALERT_1_C Angle   Calc    110.0(2), Rep   110.00(8) ......
2.50 su-Ra
              N3   -SI1  -C27     1.555   1.555   1.555
732_ALERT_1_C Angle   Calc    112.7(2), Rep   112.65(9) ......
2.22 su-Ra
              N3   -SI1  -C28     1.555   1.555   1.555
732_ALERT_1_C Angle   Calc    105.7(3), Rep   105.72(9) ......
3.33 su-Ra
              C27  -SI1  -C28     1.555   1.555   1.555
732_ALERT_1_C Angle   Calc    115.4(2), Rep   115.38(9) ......
2.22 su-Ra
              N3   -SI1  -C29     1.555   1.555   1.555
...[others deleted]


The use of restraints in the refinement mean that off diagonal
terms in the
variance-covariance matrix are significant, and the diagonal
approximation
used in Platon/Checkcif can be badly in error.
```

```
125_ALERT_4_C No _symmetry_space_group_name_Hall Given .......
?
234_ALERT_4_C Large Hirshfeld Difference C143   --  C144    ..
0.16 Ang.
234_ALERT_4_C Large Hirshfeld Difference C339   --  C340    ..
0.17 Ang.
234_ALERT_4_C Large Hirshfeld Difference C339   --  C348    ..
0.16 Ang.
234_ALERT_4_C Large Hirshfeld Difference C343   --  C344    ..
0.19 Ang.
234_ALERT_4_C Large Hirshfeld Difference C344   --  C345    ..
0.22 Ang.
234_ALERT_4_C Large Hirshfeld Difference C345   --  C347    ..
0.16 Ang.
234_ALERT_4_C Large Hirshfeld Difference C960   --  C961    ..
0.15 Ang.

No action taken.


128_ALERT_4_G Non-standard setting of Space-group P21/c   ....
P21/n
720_ALERT_4_G Number of Unusual/Non-Standard Labels .........
169
760_ALERT_1_G CIF Contains no Torsion Angles ................
?
795_ALERT_4_G C-Atom in CIF Coordinate List out of Sequence ..
C261

No action taken.

929_ALERT_4_G No Interpretable (SHELX) Weight Parameters found
?

These are given below.



;

#end of refcif
_cell_length_a                    12.5342(7)
_cell_length_b                    65.014(3)
_cell_length_c                    21.5322(10)
_cell_angle_alpha                 90
_cell_angle_beta                  103.097(3)
_cell_angle_gamma                 90
_cell_volume                      17090.2(15)

_symmetry_cell_setting            'Monoclinic'
_symmetry_space_group_name_H-M    'P 1 21/n 1 '
_symmetry_space_group_name_Hall   ?
```

```
loop_
 _symmetry_equiv_pos_as_xyz
 'x,y,z'
 '-x,-y,-z'
 '-x+1/2,y+1/2,-z+1/2'
 'x+1/2,-y+1/2,z+1/2'

loop_
_atom_type_symbol
_atom_type_scat_dispersion_real
_atom_type_scat_dispersion_imag
_atom_type_scat_Cromer_Mann_a1
_atom_type_scat_Cromer_Mann_b1
_atom_type_scat_Cromer_Mann_a2
_atom_type_scat_Cromer_Mann_b2
_atom_type_scat_Cromer_Mann_a3
_atom_type_scat_Cromer_Mann_b3
_atom_type_scat_Cromer_Mann_a4
_atom_type_scat_Cromer_Mann_b4
_atom_type_scat_Cromer_Mann_c
_atom_type_scat_source
 C       0.0033   0.0016   2.3100  20.8439   1.0200  10.2075
1.5886   0.5687
   0.8650  51.6512   0.2156 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 H       0.0000   0.0000   0.4930  10.5109   0.3229  26.1257
0.1402   3.1424
   0.0408  57.7998   0.0030 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 N       0.0061   0.0033  12.2126   0.0057   3.1322   9.8933
2.0125  28.9975
   1.1663   0.5826 -11.5290 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 O       0.0106   0.0060   3.0485  13.2771   2.2868   5.7011
1.5463   0.3239
   0.8670  32.9089   0.2508 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 Si      0.0817   0.0704   6.2915   2.4386   3.0353  32.3337
1.9891   0.6785
   1.5410  81.6937   1.1407 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 Ce     -0.2486   2.6331  21.1671   2.8122  19.7695   0.2268
11.8513  17.6083
   3.3305 127.1130   1.8626 'International Tables Vol C
4.2.6.8 and 6.1.1.4'


_cell_formula_units_Z                    12

# Given Formula = C51 H95 Ce1 N10 O1 Si4
# Dc =      1.30 Fooo =   5964.00 Mu =      9.28 M =   3350.54
# Found Formula = C41 H80 Ce1 N7 O1 Si4
# Dc =      1.10 FOOO =   5964.00 Mu =      9.15 M =   2818.79
```

```
_chemical_formula_sum             'C41 H80 Ce1 N7 O1 Si4'
_chemical_formula_moiety          'C41 H80 Ce1 N7 O1 Si4'
_chemical_compound_source               ?
_chemical_formula_weight           939.60


_cell_measurement_reflns_used         9235
_cell_measurement_theta_min              2
_cell_measurement_theta_max             28
_cell_measurement_temperature           150

_exptl_crystal_description        'block'
_exptl_crystal_colour             'orange'
_exptl_crystal_size_min           0.35
_exptl_crystal_size_mid           0.55
_exptl_crystal_size_max           0.58

_exptl_crystal_density_diffrn     1.095
_exptl_crystal_density_meas       ?
_exptl_crystal_density_method     'not measured'
# Non-dispersive F(000):
_exptl_crystal_F_000              5964
_exptl_absorpt_coefficient_mu     0.915

# Sheldrick geometric approximatio 1.00 1.00
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_process_details    'SADABS (Siemens, 1996)'
_exptl_absorpt_correction_T_min   0.77
_exptl_absorpt_correction_T_max   1.00
_diffrn_measurement_device        'Bruker Kappa Apex2'
_diffrn_measurement_device_type   'Area'
_diffrn_radiation_monochromator   'graphite'
_diffrn_radiation_type            'Mo K\a'
_diffrn_radiation_wavelength           0.71073
_diffrn_measurement_method        '\f & \w scans'

# If a reference occurs more than once, delete the author
# and date from subsequent references.
_computing_data_collection        'Apex2 (Bruker AXS, 2006)'
_computing_cell_refinement        'Apex2 (Bruker AXS, 2006)'
_computing_data_reduction         'Apex2 (Bruker AXS, 2006)'
_computing_structure_solution     'SHELXS 86 (Sheldrick,
1986)'
_computing_structure_refinement   'CRYSTALS (Betteridge et
al., 2003)'
_computing_publication_material   'CRYSTALS (Betteridge et
al., 2003)'
_computing_molecular_graphics     'CAMERON (Watkin et al.,
1996)'

_diffrn_standards_interval_time   .
_diffrn_standards_interval_count  .
```

```
_diffrn_standards_number          0
_diffrn_standards_decay_%         ?

_diffrn_ambient_temperature        150
_diffrn_reflns_number             174994
_reflns_number_total              41020
_diffrn_reflns_av_R_equivalents   0.059
# Number of reflections with Friedels Law is 41020
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 30155


_diffrn_reflns_theta_min          1.020
_diffrn_reflns_theta_max          28.397
_diffrn_measured_fraction_theta_max 0.956

_diffrn_reflns_theta_full         27.261
_diffrn_measured_fraction_theta_full 0.996


_diffrn_reflns_limit_h_min        -16
_diffrn_reflns_limit_h_max        16
_diffrn_reflns_limit_k_min        0
_diffrn_reflns_limit_k_max        85
_diffrn_reflns_limit_l_min        0
_diffrn_reflns_limit_l_max        28
_reflns_limit_h_min               -16
_reflns_limit_h_max               16
_reflns_limit_k_min               0
_reflns_limit_k_max               85
_reflns_limit_l_min               0
_reflns_limit_l_max               28

_oxford_diffrn_Wilson_B_factor    0.00
_oxford_diffrn_Wilson_scale       0.00

_atom_sites_solution_primary      direct
#heavy,direct,difmap,geom
# _atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens    geom

_refine_diff_density_min          -4.32
_refine_diff_density_max          2.48


loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
```

```
   1 -0.006  0.000  0.000       402       171 ' '
   2  0.034  0.164  0.479       450       185 ' '
   3 -0.033  0.336 -0.021       450       187 ' '
   4  0.042  0.359  0.572        35         6 ' '
   5  0.001  0.500  0.500       403       168 ' '
   6  0.014  0.664  0.021       450       174 ' '
   7 -0.042  0.641  0.428        35         5 ' '
   8 -0.007  0.836  0.521       450       182 ' '
   9  0.177  0.692  0.583         9         1 ' '
  10  0.220  0.458  0.139        15         2 ' '
  11  0.280  0.958  0.361        15         2 ' '
  12  0.323  0.192  0.917         9         1 ' '
  13  0.458  0.859  0.928        35         7 ' '
  14  0.542  0.141  0.072        35         4 ' '
  15  0.677  0.807  0.083         9         1 ' '
  16  0.720  0.042  0.639        15         3 ' '
  17  0.780  0.542  0.861        15         3 ' '
  18  0.823  0.307  0.417         9         1 ' '
_platon_squeeze_details
;
;



# The current dictionary definitions do not cover the
# situation where the reflections used for refinement were
# selected by a user-defined sigma threshold


# The values actually used during refinement
_oxford_reflns_threshold_expression_ref     I>2.0\s(I)
_refine_ls_number_reflns          27941
_refine_ls_number_restraints      330
_refine_ls_number_parameters      1459
_oxford_refine_ls_R_factor_ref    0.0951
_refine_ls_wR_factor_ref          0.0820
_refine_ls_goodness_of_fit_ref    1.1032
_refine_ls_shift/su_max           0.008943


# The values computed from all data
_oxford_reflns_number_all         30078
_refine_ls_R_factor_all           0.1000
_refine_ls_wR_factor_all          0.0825

# The values computed with a 2 sigma cutoff - a la SHELX
_reflns_threshold_expression      I>2.0\s(I)
_reflns_number_gt                 27941
_refine_ls_R_factor_gt            0.0951
_refine_ls_wR_factor_gt           0.0820
```

```
# choose from: rm (reference molecule of known chirality),
# ad (anomolous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'


_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     none           # none,
undef, noref, refall,
                                                 # refxyz,
refU, constr or mixed
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
;
 Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince,
1982)
 [weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~]*T~n-
1~(x)]
 where A~i~ are the Chebychev coefficients listed below and x=
Fcalc/Fmax
 Method = Robust Weighting (Prince, 1982)
 W = [weight] * [1-(deltaF/6*sigmaF)^2^]^2^
 A~i~ are:
 75.9 36.2 56.1 39.2 14.1
;
# Insert your own references if required - in alphabetical
order
_publ_section_references
;
Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

Siemens Industrial Automation, Inc (1996).
SADABS: Area-Detector Absorption Correction;: Madison, WI.

Sheldrick, G. M. (2008). Acta Cryst A64, 112-122.

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON,
Chemical
Crystallography Laboratory, Oxford, UK.

Bruker Analytical X-ray Systems, Inc., 2006. <i>Apex2</i>,
Version 2 User Manual, M86-E01078, Madison, WI.
;
```

```
# Uequiv = arithmetic mean of Ui i.e. Ueqiv = (U1+U2+U3)/3

# Replace last . with number of unfound hydrogen atomsattached
to an atom.

# ..._refinement_flags_...
# . no refinement constraints           S special position
constraint on site
# G rigid group refinement of site      R riding atom
# D distance or angle restraint on site T thermal displacement
constraints
# U Uiso or Uij restraint (rigid bond)  P partial occupancy
constraint


loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_occupancy
_atom_site_adp_type
_atom_site_refinement_flags_posn
_atom_site_refinement_flags_adp
_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
_oxford_atom_site_special_shape
_atom_site_attached_hydrogens
Ce1 Ce 0.28494(3) 0.263792(5) 0.651431(15) 0.0228 1.0000 Uani
D . . . . . .
Si1 Si 0.12642(16) 0.22300(3) 0.68659(10) 0.0432 1.0000 Uani D
. . . . . .
Si2 Si 0.37194(15) 0.21461(3) 0.71224(9) 0.0369 1.0000 Uani D
. . . . . .
Si3 Si 0.14386(15) 0.25540(3) 0.49028(8) 0.0458 1.0000 Uani D
. . . . . .
Si4 Si 0.14143(15) 0.29890(3) 0.54220(9) 0.0420 1.0000 Uani D
. . . . . .
O1 O 0.22712(17) 0.27956(4) 0.72555(15) 0.0307 1.0000 Uani D .
. . . . .
N1 N 0.4411(3) 0.29822(5) 0.80609(15) 0.0320 1.0000 Uani D . .
. . . .
N2 N 0.5743(3) 0.31168(5) 0.76682(15) 0.0280 1.0000 Uani D . .
. . . .
N3 N 0.25540(14) 0.22979(3) 0.68597(12) 0.0332 1.0000 Uani D .
. . . . .
N4 N 0.17909(19) 0.27368(3) 0.54841(10) 0.0321 1.0000 Uani D .
. . . . .
```

```
N5 N 0.4606(2) 0.28439(4) 0.70976(11) 0.0230 1.0000 Uani D . .
. . . .
N6 N 0.5213(3) 0.28537(6) 0.66412(17) 0.0220 1.0000 Uani D . .
. . . .
N7 N 0.4786(2) 0.27381(4) 0.61797(11) 0.0236 1.0000 Uani D . .
. . . .
C1 C 0.4922(3) 0.29784(6) 0.75729(15) 0.0252 1.0000 Uani D . .
. . . .
C5 C 0.5798(4) 0.32325(9) 0.8263(3) 0.0379 1.0000 Uani D . . .
. . .
C6 C 0.4906(5) 0.31342(9) 0.8545(2) 0.0360 1.0000 Uani D . . .
. . .
C7 C 0.3652(4) 0.28274(5) 0.82072(15) 0.0265 1.0000 Uani D . .
. . . .
C8 C 0.2436(2) 0.28566(5) 0.78867(15) 0.0287 1.0000 Uani D . .
. . . .
C9 C 0.2082(4) 0.30793(9) 0.7916(2) 0.0463 1.0000 Uani D . . .
. . .
C10 C 0.1798(4) 0.27159(10) 0.8244(2) 0.0504 1.0000 Uani D . .
. . . .
C21 C 0.6606(3) 0.31476(5) 0.73419(17) 0.0257 1.0000 Uani D .
. . . . .
C22 C 0.7541(3) 0.30209(7) 0.7482(2) 0.0377 1.0000 Uani D . .
. . . .
C23 C 0.8384(4) 0.30643(9) 0.7183(3) 0.0397 1.0000 Uani D . .
. . . .
C24 C 0.8316(4) 0.32251(9) 0.6760(3) 0.0441 1.0000 Uani D . .
. . . .
C25 C 0.7388(4) 0.33464(8) 0.6618(3) 0.0405 1.0000 Uani D . .
. . . .
C26 C 0.6523(3) 0.33100(7) 0.6913(2) 0.0346 1.0000 Uani D . .
. . . .
C27 C 0.0328(4) 0.24519(8) 0.6624(3) 0.0447 1.0000 Uani D . .
. . . .
C28 C 0.0726(4) 0.20185(10) 0.6279(4) 0.0712 1.0000 Uani D . .
. . . .
C29 C 0.1047(4) 0.21362(10) 0.7655(3) 0.0827 1.0000 Uani D . .
. . . .
C30 C 0.3856(4) 0.20276(10) 0.7928(3) 0.0819 1.0000 Uani D . .
. . . .
C31 C 0.3840(4) 0.19336(9) 0.6547(3) 0.0639 1.0000 Uani D . .
. . . .
C32 C 0.4966(5) 0.23099(8) 0.7183(3) 0.0530 1.0000 Uani D . .
. . . .
C33 C 0.2296(5) 0.23204(10) 0.5132(2) 0.0591 1.0000 Uani D . .
. . . .
C34 C -0.0038(5) 0.24714(10) 0.4757(3) 0.0897 1.0000 Uani D .
. . . . .
C35 C 0.1646(5) 0.26269(8) 0.4091(3) 0.0667 1.0000 Uani D . .
. . . .
C36 C -0.0016(6) 0.30340(8) 0.5510(4) 0.1178 1.0000 Uani D . .
. . . .
```

```
C37 C 0.1512(7) 0.31169(8) 0.4654(3) 0.0962 1.0000 Uani D . .
. . . .
C38 C 0.2336(6) 0.31407(7) 0.6055(3) 0.0664 1.0000 Uani D . .
. . . .
C39 C 0.5341(2) 0.27408(4) 0.56456(14) 0.0274 1.0000 Uani D .
. . . . .
C40 C 0.6401(4) 0.28669(7) 0.57630(17) 0.0391 1.0000 Uani D .
. . . . .
C41 C 0.6878(3) 0.28579(7) 0.5165(2) 0.0511 1.0000 Uani D . .
. . . .
C42 C 0.6052(5) 0.29448(7) 0.4603(2) 0.0468 1.0000 Uani D . .
. . . .
C43 C 0.5018(3) 0.28164(6) 0.44763(17) 0.0384 1.0000 Uani D .
. . . . .
C44 C 0.5266(4) 0.25914(8) 0.43512(19) 0.0476 1.0000 Uani D .
. . . . .
C45 C 0.6086(4) 0.25060(6) 0.4925(2) 0.0521 1.0000 Uani D . .
. . . .
C46 C 0.5595(4) 0.25151(6) 0.5517(2) 0.0484 1.0000 Uani D . .
. . . .
C47 C 0.7134(3) 0.26319(10) 0.5040(3) 0.0671 1.0000 Uani D . .
. . . .
C48 C 0.4528(3) 0.28279(6) 0.5065(2) 0.0378 1.0000 Uani D . .
. . . .
C220 C 0.7648(3) 0.28475(8) 0.7963(2) 0.0428 1.0000 Uani D . .
. . . .
C221 C 0.7890(7) 0.26458(11) 0.7681(4) 0.0653 1.0000 Uani D .
. . . . .
C222 C 0.8528(7) 0.29037(13) 0.8575(3) 0.0747 1.0000 Uani D .
. . . . .
C260 C 0.5525(4) 0.34499(7) 0.6753(2) 0.0375 1.0000 Uani D . .
. . . .
C262 C 0.5808(6) 0.36709(11) 0.6980(4) 0.0669 1.0000 Uani D .
. . . . .
C261 C 0.4985(6) 0.34466(11) 0.6046(3) 0.0595 1.0000 Uani D .
. . . . .
Ce12 Ce 0.36714(3) 0.599592(5) 0.694236(15) 0.0216 1.0000 Uani
D . . . . . .
Si11 Si 0.39601(16) 0.54979(3) 0.75686(10) 0.0439 1.0000 Uani
D . . . . . .
Si12 Si 0.16363(15) 0.56607(3) 0.72263(8) 0.0385 1.0000 Uani D
. . . . . .
Si13 Si 0.23682(12) 0.59351(3) 0.53039(7) 0.0322 1.0000 Uani D
. . . . . .
Si14 Si 0.24598(15) 0.63671(3) 0.58326(8) 0.0367 1.0000 Uani D
. . . . . .
O101 O 0.31751(17) 0.61780(4) 0.76598(14) 0.0279 1.0000 Uani D
. . . . . .
N101 N 0.5347(3) 0.63334(5) 0.84660(15) 0.0305 1.0000 Uani D .
. . . . .
N102 N 0.6754(3) 0.64349(5) 0.80755(15) 0.0261 1.0000 Uani D .
. . . . .
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```
N103 N 0.30176(14) 0.56789(3) 0.72722(12) 0.0309 1.0000 Uani D
. . . . . .
N104 N 0.27696(18) 0.61120(3) 0.58859(9) 0.0252 1.0000 Uani D
. . . . . .
N105 N 0.5545(2) 0.61584(4) 0.75697(11) 0.0203 1.0000 Uani D .
. . . . .
N106 N 0.6211(2) 0.61397(6) 0.71301(17) 0.0235 1.0000 Uani D .
. . . . .
N107 N 0.5745(2) 0.60265(4) 0.66781(11) 0.0245 1.0000 Uani D .
. . . . .
C101 C 0.5900(3) 0.62996(5) 0.80152(14) 0.0236 1.0000 Uani D .
. . . . .
C105 C 0.6789(5) 0.65740(9) 0.8615(3) 0.0543 1.0000 Uani D . .
. . . .
C106 C 0.5883(4) 0.64939(8) 0.8918(2) 0.0347 1.0000 Uani D . .
. . . .
C107 C 0.4542(4) 0.61986(5) 0.86386(15) 0.0280 1.0000 Uani D .
. . . . .
C108 C 0.3336(2) 0.62383(5) 0.83042(15) 0.0307 1.0000 Uani D .
. . . . .
C109 C 0.3034(4) 0.64624(10) 0.8337(2) 0.0484 1.0000 Uani D .
. . . . .
C110 C 0.2648(4) 0.61031(10) 0.8648(2) 0.0501 1.0000 Uani D .
. . . . .
C121 C 0.7661(3) 0.64395(5) 0.77755(17) 0.0308 1.0000 Uani D .
. . . . .
C122 C 0.8553(3) 0.63076(7) 0.7990(2) 0.0330 1.0000 Uani D . .
. . . .
C123 C 0.9472(4) 0.63346(9) 0.7744(3) 0.0391 1.0000 Uani D . .
. . . .
C124 C 0.9510(4) 0.64827(11) 0.7293(3) 0.0482 1.0000 Uani D .
. . . . .
C125 C 0.8629(4) 0.66102(9) 0.7082(3) 0.0425 1.0000 Uani D . .
. . . .
C126 C 0.7697(3) 0.65931(7) 0.7331(2) 0.0379 1.0000 Uani D . .
. . . .
C127 C 0.5353(5) 0.56018(7) 0.7577(3) 0.0454 1.0000 Uani D . .
. . . .
C128 C 0.4004(4) 0.54162(11) 0.8409(4) 0.1263 1.0000 Uani D .
. . . . .
C129 C 0.3812(5) 0.52613(10) 0.7065(4) 0.1463 1.0000 Uani D .
. . . . .
C130 C 0.1242(3) 0.55918(8) 0.7993(3) 0.0506 1.0000 Uani D . .
. . . .
C131 C 0.0944(4) 0.54619(9) 0.6625(3) 0.0588 1.0000 Uani D . .
. . . .
C132 C 0.0959(3) 0.59091(9) 0.6953(2) 0.0397 1.0000 Uani D . .
. . . .
C133 C 0.0834(5) 0.58973(8) 0.5066(2) 0.0490 1.0000 Uani D . .
. . . .
C134 C 0.2995(4) 0.56795(9) 0.55789(19) 0.0419 1.0000 Uani D .
. . . . .
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C135 C 0.2787(4) 0.59874(7) 0.4533(3) 0.0509 1.0000 Uani D . .
. . . .
C136 C 0.2629(7) 0.64943(8) 0.5083(3) 0.0749 1.0000 Uani D . .
. . . .
C137 C 0.1033(6) 0.64248(7) 0.5899(4) 0.1035 1.0000 Uani D . .
. . . .
C138 C 0.3398(6) 0.65093(8) 0.6487(3) 0.0868 1.0000 Uani D . .
. . . .
C139 C 0.6373(2) 0.59940(4) 0.61792(13) 0.0244 1.0000 Uani D .
. . . . .
C140 C 0.7524(3) 0.60899(6) 0.63244(16) 0.0324 1.0000 Uani D .
. . . . .
C141 C 0.8071(3) 0.60443(7) 0.57686(18) 0.0408 1.0000 Uani D .
. . . . .
C142 C 0.7380(5) 0.61355(7) 0.5158(2) 0.0491 1.0000 Uani D . .
. . . .
C143 C 0.6251(3) 0.60368(7) 0.50087(16) 0.0428 1.0000 Uani D .
. . . . .
C144 C 0.6335(4) 0.58040(9) 0.4942(2) 0.0562 1.0000 Uani D . .
. . . .
C145 C 0.7021(3) 0.57147(6) 0.55619(19) 0.0405 1.0000 Uani D .
. . . . .
C146 C 0.6468(3) 0.57592(6) 0.61062(18) 0.0286 1.0000 Uani D .
. . . . .
C147 C 0.8162(3) 0.58101(9) 0.5704(2) 0.0493 1.0000 Uani D . .
. . . .
C148 C 0.5700(3) 0.60849(6) 0.5560(2) 0.0348 1.0000 Uani D . .
. . . .
C620 C 0.8521(4) 0.61402(8) 0.8479(2) 0.0457 1.0000 Uani D . .
. . . .
C621 C 0.8613(8) 0.59292(11) 0.8207(4) 0.0704 1.0000 Uani D .
. . . . .
C622 C 0.9429(8) 0.61804(14) 0.9096(3) 0.0866 1.0000 Uani D .
. . . . .
C660 C 0.6734(4) 0.67344(7) 0.7076(2) 0.0494 1.0000 Uani D . .
. . . .
C661 C 0.6228(7) 0.66945(11) 0.6377(4) 0.0785 1.0000 Uani D .
. . . . .
C662 C 0.7054(7) 0.69614(10) 0.7183(4) 0.0630 1.0000 Uani D .
. . . . .
Ce13 Ce 1.16560(3) 0.432583(5) 0.824962(15) 0.0225 1.0000 Uani
. . . . . .
Si31 Si 1.04132(14) 0.38493(3) 0.76725(9) 0.0308 1.0000 Uani .
. . . . . .
Si32 Si 1.27587(14) 0.39100(3) 0.75844(9) 0.0322 1.0000 Uani .
. . . . . .
Si33 Si 1.33633(14) 0.42183(3) 0.97894(8) 0.0321 1.0000 Uani .
. . . . . .
Si34 Si 1.32753(15) 0.46577(3) 0.93537(10) 0.0358 1.0000 Uani
. . . . . .
O301 O 1.2094(3) 0.44996(7) 0.7493(2) 0.0311 1.0000 Uani . . .
. . . .
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N301 N 0.9671(4) 0.45162(8) 0.6527(2) 0.0288 1.0000 Uani . . .
. . . .
N302 N 0.8318(4) 0.46589(8) 0.6873(2) 0.0270 1.0000 Uani . . .
. . . .
N303 N 1.1609(4) 0.39842(8) 0.7810(2) 0.0277 1.0000 Uani . . .
. . . .
N304 N 1.2852(4) 0.44071(8) 0.9255(2) 0.0291 1.0000 Uani . . .
. . . .
N305 N 0.9762(4) 0.44771(7) 0.7608(2) 0.0255 1.0000 Uani . . .
. . . .
N306 N 0.9256(4) 0.45243(7) 0.8090(2) 0.0238 1.0000 Uani . . .
. . . .
N307 N 0.9837(4) 0.44582(7) 0.8610(2) 0.0222 1.0000 Uani . . .
. . . .
C301 C 0.9252(5) 0.45494(8) 0.7040(3) 0.0222 1.0000 Uani . . .
. . . .
C305 C 0.8021(6) 0.46840(12) 0.6173(3) 0.0407 1.0000 Uani . .
. . . . .
C306 C 0.9067(6) 0.46334(11) 0.5979(3) 0.0357 1.0000 Uani . .
. . . . .
C307 C 1.0760(5) 0.44343(10) 0.6522(3) 0.0314 1.0000 Uani . .
. . . . .
C308 C 1.1777(5) 0.45663(10) 0.6856(3) 0.0305 1.0000 Uani . .
. . . . .
C309 C 1.1552(7) 0.47937(12) 0.6838(4) 0.0472 1.0000 Uani . .
. . . . .
C310 C 1.2701(6) 0.45154(13) 0.6522(3) 0.0456 1.0000 Uani . .
. . . . .
C321 C 0.7521(5) 0.47137(9) 0.7234(3) 0.0285 1.0000 Uani . . .
. . . .
C322 C 0.6741(5) 0.45711(10) 0.7318(3) 0.0316 1.0000 Uani . .
. . . . .
C323 C 0.5943(5) 0.46310(11) 0.7624(3) 0.0349 1.0000 Uani . .
. . . . .
C324 C 0.5906(7) 0.48303(12) 0.7843(4) 0.0451 1.0000 Uani . .
. . . . .
C325 C 0.6703(7) 0.49704(11) 0.7769(4) 0.0461 1.0000 Uani . .
. . . . .
C326 C 0.7514(6) 0.49166(10) 0.7449(3) 0.0352 1.0000 Uani . .
. . . . .
C327 C 0.9673(6) 0.39032(13) 0.8327(4) 0.0528 1.0000 Uani . .
. . . . .
C328 C 0.9430(7) 0.39210(16) 0.6914(5) 0.0645 1.0000 Uani . .
. . . . .
C329 C 1.0561(6) 0.35609(13) 0.7667(5) 0.0585 1.0000 Uani . .
. . . . .
C330 C 1.2558(8) 0.38826(14) 0.6696(4) 0.0567 1.0000 Uani . .
. . . . .
C331 C 1.3351(7) 0.36591(12) 0.7933(4) 0.0527 1.0000 Uani . .
. . . . .
C332 C 1.3877(5) 0.41025(11) 0.7866(3) 0.0364 1.0000 Uani . .
. . . . .
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C333 C 1.2686(8) 0.39663(13) 0.9508(4) 0.0597 1.0000 Uani . .
. . . . .
C334 C 1.3116(7) 0.42544(14) 1.0606(4) 0.0527 1.0000 Uani . .
. . . . .
C335 C 1.4875(6) 0.41824(13) 0.9879(4) 0.0479 1.0000 Uani . .
. . . . .
C336 C 1.4718(8) 0.46958(17) 0.9249(7) 0.0883 1.0000 Uani . .
. . . . .
C337 C 1.3260(8) 0.47690(13) 1.0157(4) 0.0602 1.0000 Uani . .
. . . . .
C338 C 1.2341(7) 0.48249(11) 0.8742(4) 0.0467 1.0000 Uani . .
. . . . .
C339 C 0.9371(5) 0.45034(9) 0.9177(3) 0.0234 1.0000 Uani . . .
. . . .
C340 C 1.0213(7) 0.46515(15) 0.9602(4) 0.0569 1.0000 Uani . .
. . . . .
C341 C 0.9833(7) 0.46889(17) 1.0268(5) 0.0677 1.0000 Uani . .
. . . . .
C342 C 0.9797(8) 0.4494(2) 1.0545(5) 0.0803 1.0000 Uani . . .
. . . .
C343 C 0.8971(13) 0.43481(16) 1.0190(4) 0.0896 1.0000 Uani . .
. . . . .
C344 C 0.7843(9) 0.44403(19) 0.9954(9) 0.1157 1.0000 Uani . .
. . . . .
C345 C 0.7853(6) 0.46547(14) 0.9699(4) 0.0516 1.0000 Uani . .
. . . . .
C346 C 0.8253(7) 0.46014(18) 0.9045(4) 0.0698 1.0000 Uani . .
. . . . .
C347 C 0.8769(7) 0.47838(15) 1.0039(5) 0.0623 1.0000 Uani . .
. . . . .
C348 C 0.9445(10) 0.43056(16) 0.9565(5) 0.0770 1.0000 Uani . .
. . . . .
C920 C 0.6740(5) 0.43505(11) 0.7066(4) 0.0384 1.0000 Uani . .
. . . . .
C921 C 0.6947(6) 0.41969(12) 0.7621(4) 0.0527 1.0000 Uani . .
. . . . .
C922 C 0.5674(6) 0.43007(14) 0.6591(4) 0.0543 1.0000 Uani . .
. . . . .
C960 C 0.8382(7) 0.50772(11) 0.7360(4) 0.0468 1.0000 Uani . .
. . . . .
C961 C 0.9271(12) 0.5098(2) 0.7947(6) 0.1123 1.0000 Uani . . .
. . . .
C962 C 0.7873(10) 0.52715(17) 0.7085(9) 0.1160 1.0000 Uani . .
. . . . .
H51 H 0.5650 0.3374 0.8177 0.0454 1.0000 Uiso . . . . . .
H52 H 0.6496 0.3218 0.8544 0.0454 1.0000 Uiso . . . . . .
H61 H 0.4382 0.3234 0.8603 0.0431 1.0000 Uiso . . . . . .
H62 H 0.5212 0.3069 0.8941 0.0431 1.0000 Uiso . . . . . .
H71 H 0.3718 0.2828 0.8656 0.0318 1.0000 Uiso . . . . . .
H72 H 0.3873 0.2697 0.8080 0.0318 1.0000 Uiso . . . . . .
H91 H 0.2195 0.3121 0.8349 0.0557 1.0000 Uiso . . . . . .
H92 H 0.2502 0.3164 0.7702 0.0557 1.0000 Uiso . . . . . .
H93 H 0.1328 0.3092 0.7715 0.0557 1.0000 Uiso . . . . . .
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H101 H 0.1915 0.2759 0.8676 0.0607 1.0000 Uiso . . . . . .
H102 H 0.1038 0.2723 0.8050 0.0607 1.0000 Uiso . . . . . .
H103 H 0.2043 0.2578 0.8227 0.0607 1.0000 Uiso . . . . . .
H23 H 0.9023 0.2981 0.7272 0.0476 1.0000 Uiso . . . . . .
H24 H 0.8910 0.3253 0.6566 0.0529 1.0000 Uiso . . . . . .
H25 H 0.7339 0.3455 0.6318 0.0485 1.0000 Uiso . . . . . .
H271 H -0.0399 0.2412 0.6629 0.0537 1.0000 Uiso . . . . . .
H272 H 0.0547 0.2562 0.6914 0.0537 1.0000 Uiso . . . . . .
H273 H 0.0358 0.2494 0.6206 0.0537 1.0000 Uiso . . . . . .
H281 H -0.0003 0.1986 0.6301 0.0858 1.0000 Uiso . . . . . .
H282 H 0.0736 0.2063 0.5860 0.0858 1.0000 Uiso . . . . . .
H283 H 0.1176 0.1900 0.6381 0.0858 1.0000 Uiso . . . . . .
H291 H 0.0298 0.2102 0.7613 0.0993 1.0000 Uiso . . . . . .
H292 H 0.1246 0.2242 0.7965 0.0993 1.0000 Uiso . . . . . .
H293 H 0.1489 0.2018 0.7785 0.0993 1.0000 Uiso . . . . . .
H301 H 0.4510 0.1948 0.8031 0.0979 1.0000 Uiso . . . . . .
H302 H 0.3886 0.2133 0.8237 0.0979 1.0000 Uiso . . . . . .
H303 H 0.3244 0.1941 0.7926 0.0979 1.0000 Uiso . . . . . .
H311 H 0.4484 0.1856 0.6711 0.0766 1.0000 Uiso . . . . . .
H312 H 0.3880 0.1991 0.6147 0.0766 1.0000 Uiso . . . . . .
H313 H 0.3218 0.1846 0.6492 0.0766 1.0000 Uiso . . . . . .
H321 H 0.5603 0.2228 0.7325 0.0634 1.0000 Uiso . . . . . .
H322 H 0.4957 0.2418 0.7477 0.0634 1.0000 Uiso . . . . . .
H323 H 0.4969 0.2366 0.6776 0.0634 1.0000 Uiso . . . . . .
H331 H 0.2100 0.2219 0.4808 0.0710 1.0000 Uiso . . . . . .
H332 H 0.3047 0.2355 0.5182 0.0710 1.0000 Uiso . . . . . .
H333 H 0.2180 0.2268 0.5523 0.0710 1.0000 Uiso . . . . . .
H341 H -0.0180 0.2370 0.4430 0.1077 1.0000 Uiso . . . . . .
H342 H -0.0500 0.2587 0.4629 0.1077 1.0000 Uiso . . . . . .
H343 H -0.0179 0.2415 0.5138 0.1077 1.0000 Uiso . . . . . .
H351 H 0.1428 0.2516 0.3804 0.0801 1.0000 Uiso . . . . . .
H352 H 0.1217 0.2745 0.3940 0.0801 1.0000 Uiso . . . . . .
H353 H 0.2397 0.2657 0.4120 0.0801 1.0000 Uiso . . . . . .
H361 H -0.0177 0.3177 0.5472 0.1421 1.0000 Uiso . . . . . .
H362 H -0.0083 0.2987 0.5918 0.1421 1.0000 Uiso . . . . . .
H363 H -0.0514 0.2961 0.5188 0.1421 1.0000 Uiso . . . . . .
H371 H 0.1289 0.3257 0.4659 0.1148 1.0000 Uiso . . . . . .
H372 H 0.2249 0.3111 0.4608 0.1148 1.0000 Uiso . . . . . .
H373 H 0.1050 0.3048 0.4306 0.1148 1.0000 Uiso . . . . . .
H381 H 0.2122 0.3281 0.6018 0.0795 1.0000 Uiso . . . . . .
H382 H 0.2286 0.3090 0.6461 0.0795 1.0000 Uiso . . . . . .
H383 H 0.3069 0.3128 0.6009 0.0795 1.0000 Uiso . . . . . .
H401 H 0.6249 0.3006 0.5851 0.0469 1.0000 Uiso . . . . . .
H402 H 0.6916 0.2811 0.6117 0.0469 1.0000 Uiso . . . . . .
H411 H 0.7533 0.2937 0.5234 0.0612 1.0000 Uiso . . . . . .
H421 H 0.5879 0.3082 0.4694 0.0563 1.0000 Uiso . . . . . .
H422 H 0.6354 0.2944 0.4236 0.0563 1.0000 Uiso . . . . . .
H431 H 0.4508 0.2870 0.4118 0.0460 1.0000 Uiso . . . . . .
H441 H 0.5567 0.2583 0.3984 0.0572 1.0000 Uiso . . . . . .
H442 H 0.4609 0.2513 0.4282 0.0572 1.0000 Uiso . . . . . .
H451 H 0.6246 0.2367 0.4844 0.0623 1.0000 Uiso . . . . . .
H461 H 0.6104 0.2461 0.5875 0.0582 1.0000 Uiso . . . . . .
H462 H 0.4938 0.2436 0.5444 0.0582 1.0000 Uiso . . . . . .
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H471 H 0.7640 0.2579 0.5401 0.0806 1.0000 Uiso . . . . . .
H472 H 0.7440 0.2624 0.4677 0.0806 1.0000 Uiso . . . . . .
H481 H 0.4374 0.2967 0.5144 0.0454 1.0000 Uiso . . . . . .
H482 H 0.3870 0.2750 0.4992 0.0454 1.0000 Uiso . . . . . .
H2201 H 0.6965 0.2834 0.8080 0.0514 1.0000 Uiso . . . . . .
H2211 H 0.7953 0.2541 0.7993 0.0784 1.0000 Uiso . . . . . .
H2212 H 0.8559 0.2656 0.7545 0.0784 1.0000 Uiso . . . . . .
H2213 H 0.7314 0.2613 0.7326 0.0784 1.0000 Uiso . . . . . .
H2221 H 0.8590 0.2794 0.8874 0.0895 1.0000 Uiso . . . . . .
H2222 H 0.8313 0.3026 0.8757 0.0895 1.0000 Uiso . . . . . .
H2223 H 0.9213 0.2925 0.8468 0.0895 1.0000 Uiso . . . . . .
H2601 H 0.5006 0.3399 0.6975 0.0451 1.0000 Uiso . . . . . .
H2621 H 0.5170 0.3754 0.6872 0.0801 1.0000 Uiso . . . . . .
H2622 H 0.6081 0.3672 0.7429 0.0801 1.0000 Uiso . . . . . .
H2623 H 0.6351 0.3724 0.6778 0.0801 1.0000 Uiso . . . . . .
H2611 H 0.4366 0.3535 0.5966 0.0715 1.0000 Uiso . . . . . .
H2612 H 0.5492 0.3491 0.5809 0.0715 1.0000 Uiso . . . . . .
H2613 H 0.4754 0.3310 0.5923 0.0715 1.0000 Uiso . . . . . .
H1051 H 0.6648 0.6712 0.8473 0.0650 1.0000 Uiso . . . . . .
H1052 H 0.7481 0.6567 0.8908 0.0650 1.0000 Uiso . . . . . .
H1061 H 0.5382 0.6600 0.8955 0.0416 1.0000 Uiso . . . . . .
H1062 H 0.6178 0.6437 0.9327 0.0416 1.0000 Uiso . . . . . .
H1071 H 0.4604 0.6212 0.9085 0.0336 1.0000 Uiso . . . . . .
H1072 H 0.4716 0.6062 0.8543 0.0336 1.0000 Uiso . . . . . .
H1091 H 0.3142 0.6503 0.8771 0.0581 1.0000 Uiso . . . . . .
H1092 H 0.3484 0.6544 0.8133 0.0581 1.0000 Uiso . . . . . .
H1093 H 0.2288 0.6481 0.8129 0.0581 1.0000 Uiso . . . . . .
H1101 H 0.2762 0.6145 0.9080 0.0601 1.0000 Uiso . . . . . .
H1102 H 0.1895 0.6117 0.8446 0.0601 1.0000 Uiso . . . . . .
H1103 H 0.2862 0.5963 0.8629 0.0601 1.0000 Uiso . . . . . .
H123 H 1.0091 0.6249 0.7891 0.0470 1.0000 Uiso . . . . . .
H124 H 1.0147 0.6497 0.7128 0.0577 1.0000 Uiso . . . . . .
H125 H 0.8654 0.6710 0.6764 0.0509 1.0000 Uiso . . . . . .
H1271 H 0.5889 0.5501 0.7744 0.0545 1.0000 Uiso . . . . . .
H1272 H 0.5480 0.5721 0.7838 0.0545 1.0000 Uiso . . . . . .
H1273 H 0.5398 0.5636 0.7155 0.0545 1.0000 Uiso . . . . . .
H1281 H 0.4554 0.5314 0.8535 0.1514 1.0000 Uiso . . . . . .
H1282 H 0.4165 0.5531 0.8684 0.1514 1.0000 Uiso . . . . . .
H1283 H 0.3313 0.5361 0.8433 0.1514 1.0000 Uiso . . . . . .
H1291 H 0.4359 0.5164 0.7251 0.1751 1.0000 Uiso . . . . . .
H1292 H 0.3895 0.5296 0.6649 0.1751 1.0000 Uiso . . . . . .
H1293 H 0.3108 0.5203 0.7036 0.1751 1.0000 Uiso . . . . . .
H1301 H 0.0467 0.5585 0.7923 0.0607 1.0000 Uiso . . . . . .
H1302 H 0.1513 0.5694 0.8306 0.0607 1.0000 Uiso . . . . . .
H1303 H 0.1547 0.5462 0.8138 0.0607 1.0000 Uiso . . . . . .
H1311 H 0.0184 0.5458 0.6618 0.0705 1.0000 Uiso . . . . . .
H1312 H 0.1043 0.5498 0.6215 0.0705 1.0000 Uiso . . . . . .
H1313 H 0.1259 0.5331 0.6743 0.0705 1.0000 Uiso . . . . . .
H1321 H 0.0195 0.5898 0.6929 0.0477 1.0000 Uiso . . . . . .
H1322 H 0.1258 0.6015 0.7246 0.0477 1.0000 Uiso . . . . . .
H1323 H 0.1077 0.5942 0.6544 0.0477 1.0000 Uiso . . . . . .
H1331 H 0.0664 0.5796 0.4739 0.0587 1.0000 Uiso . . . . . .
H1332 H 0.0491 0.6024 0.4913 0.0587 1.0000 Uiso . . . . . .
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H1342 H 0.3770 0.5691 0.5675 0.0503 1.0000 Uiso . . . . . .
H1343 H 0.2762 0.5638 0.5950 0.0503 1.0000 Uiso . . . . . .
H1351 H 0.2525 0.5880 0.4238 0.0610 1.0000 Uiso . . . . . .
H1352 H 0.2483 0.6115 0.4362 0.0610 1.0000 Uiso . . . . . .
H1353 H 0.3563 0.5994 0.4610 0.0610 1.0000 Uiso . . . . . .
H1361 H 0.2440 0.6636 0.5092 0.0901 1.0000 Uiso . . . . . .
H1362 H 0.3369 0.6483 0.5049 0.0901 1.0000 Uiso . . . . . .
H1363 H 0.2164 0.6430 0.4726 0.0901 1.0000 Uiso . . . . . .
H1371 H 0.0911 0.6569 0.5867 0.1244 1.0000 Uiso . . . . . .
H1372 H 0.0932 0.6378 0.6301 0.1244 1.0000 Uiso . . . . . .
H1373 H 0.0529 0.6357 0.5567 0.1244 1.0000 Uiso . . . . . .
H1381 H 0.3222 0.6652 0.6455 0.1042 1.0000 Uiso . . . . . .
H1382 H 0.3315 0.6458 0.6887 0.1042 1.0000 Uiso . . . . . .
H1383 H 0.4133 0.6490 0.6452 0.1042 1.0000 Uiso . . . . . .
H1401 H 0.7468 0.6234 0.6375 0.0389 1.0000 Uiso . . . . . .
H1402 H 0.7951 0.6032 0.6706 0.0389 1.0000 Uiso . . . . . .
H1411 H 0.8782 0.6104 0.5854 0.0489 1.0000 Uiso . . . . . .
H1421 H 0.7307 0.6280 0.5210 0.0589 1.0000 Uiso . . . . . .
H1422 H 0.7727 0.6111 0.4816 0.0589 1.0000 Uiso . . . . . .
H1431 H 0.5826 0.6093 0.4624 0.0514 1.0000 Uiso . . . . . .
H1441 H 0.6675 0.5773 0.4601 0.0673 1.0000 Uiso . . . . . .
H1442 H 0.5623 0.5745 0.4858 0.0673 1.0000 Uiso . . . . . .
H1451 H 0.7083 0.5570 0.5516 0.0486 1.0000 Uiso . . . . . .
H1461 H 0.6891 0.5702 0.6491 0.0344 1.0000 Uiso . . . . . .
H1462 H 0.5757 0.5699 0.6016 0.0344 1.0000 Uiso . . . . . .
H1471 H 0.8582 0.5755 0.6092 0.0592 1.0000 Uiso . . . . . .
H1472 H 0.8509 0.5779 0.5367 0.0592 1.0000 Uiso . . . . . .
H1481 H 0.5650 0.6230 0.5603 0.0418 1.0000 Uiso . . . . . .
H1482 H 0.4986 0.6027 0.5470 0.0418 1.0000 Uiso . . . . . .
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H6211 H 0.8589 0.5828 0.8523 0.0844 1.0000 Uiso . . . . . .
H6212 H 0.9285 0.5918 0.8076 0.0844 1.0000 Uiso . . . . . .
H6213 H 0.8020 0.5908 0.7850 0.0844 1.0000 Uiso . . . . . .
H6221 H 0.9404 0.6075 0.9399 0.1036 1.0000 Uiso . . . . . .
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H6223 H 1.0127 0.6180 0.8993 0.1036 1.0000 Uiso . . . . . .
H6601 H 0.6190 0.6706 0.7308 0.0592 1.0000 Uiso . . . . . .
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H6613 H 0.5973 0.6557 0.6325 0.0946 1.0000 Uiso . . . . . .
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H3072 H 1.0824 0.4304 0.6727 0.0376 1.0000 Uiso . . . . . .
H3091 H 1.1339 0.4838 0.6408 0.0565 1.0000 Uiso . . . . . .
H3092 H 1.2196 0.4865 0.7047 0.0565 1.0000 Uiso . . . . . .
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H325 H 0.6697 0.5105 0.7939 0.0553 1.0000 Uiso . . . . . .
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H3272 H 0.9519 0.4046 0.8336 0.0634 1.0000 Uiso . . . . . .
H3273 H 1.0122 0.3863 0.8726 0.0634 1.0000 Uiso . . . . . .
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H3313 H 1.2826 0.3553 0.7807 0.0632 1.0000 Uiso . . . . . .
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H3323 H 1.3652 0.4233 0.7685 0.0437 1.0000 Uiso . . . . . .
H3331 H 1.2973 0.3861 0.9807 0.0715 1.0000 Uiso . . . . . .
H3332 H 1.1919 0.3978 0.9471 0.0715 1.0000 Uiso . . . . . .
H3333 H 1.2825 0.3932 0.9105 0.0715 1.0000 Uiso . . . . . .
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H3342 H 1.3444 0.4379 1.0782 0.0634 1.0000 Uiso . . . . . .
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H3363 H 1.4758 0.4654 0.8832 0.1058 1.0000 Uiso . . . . . .
H3371 H 1.3503 0.4908 1.0176 0.0724 1.0000 Uiso . . . . . .
H3372 H 1.3732 0.4691 1.0480 0.0724 1.0000 Uiso . . . . . .
H3373 H 1.2535 0.4764 1.0222 0.0724 1.0000 Uiso . . . . . .
H3381 H 1.2577 0.4964 0.8797 0.0560 1.0000 Uiso . . . . . .
H3382 H 1.1612 0.4814 0.8796 0.0560 1.0000 Uiso . . . . . .
H3383 H 1.2366 0.4780 0.8325 0.0560 1.0000 Uiso . . . . . .
H3401 H 1.0225 0.4779 0.9388 0.0683 1.0000 Uiso . . . . . .
H3402 H 1.0922 0.4592 0.9687 0.0683 1.0000 Uiso . . . . . .
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H3421 H 0.9647 0.4514 1.0956 0.0938 1.0000 Uiso . . . . . .
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H3431 H 0.8951 0.4226 1.0427 0.1079 1.0000 Uiso . . . . . .
H3441 H 0.7487 0.4443 1.0301 0.1392 1.0000 Uiso . . . . . .
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H3451 H 0.7161 0.4721 0.9627 0.0619 1.0000 Uiso . . . . . .
H3461 H 0.8276 0.4726 0.8815 0.0838 1.0000 Uiso . . . . . .
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H3472 H 0.8862 0.4891 0.9757 0.0745 1.0000 Uiso . . . . . .
H3481 H 1.0188 0.4262 0.9689 0.0924 1.0000 Uiso . . . . . .
H3482 H 0.9023 0.4201 0.9316 0.0924 1.0000 Uiso . . . . . .
H9201 H 0.7323 0.4338 0.6853 0.0461 1.0000 Uiso . . . . . .
H9211 H 0.6944 0.4061 0.7458 0.0632 1.0000 Uiso . . . . . .
H9212 H 0.7637 0.4225 0.7897 0.0632 1.0000 Uiso . . . . . .
H9213 H 0.6386 0.4210 0.7850 0.0632 1.0000 Uiso . . . . . .
H9221 H 0.5699 0.4163 0.6444 0.0652 1.0000 Uiso . . . . . .
H9222 H 0.5580 0.4392 0.6239 0.0652 1.0000 Uiso . . . . . .
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H9612 H 0.8967 0.5141 0.8291 0.1347 1.0000 Uiso . . . . . .
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H9621 H 0.8427 0.5366 0.7036 0.1390 1.0000 Uiso . . . . . .
H9622 H 0.7456 0.5329 0.7359 0.1390 1.0000 Uiso . . . . . .
H9623 H 0.7405 0.5244 0.6679 0.1390 1.0000 Uiso . . . . . .
loop_
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_atom_site_aniso_U_12
Ce1 0.02513(17) 0.02166(17) 0.02160(16) -0.00313(12)
0.00504(13) -0.00688(12)
Si1 0.0445(11) 0.0297(10) 0.0585(13) 0.0028(9) 0.0182(10) -
0.0126(8)
Si2 0.0423(10) 0.0242(9) 0.0417(10) 0.0085(8) 0.0041(8) -
0.0019(8)
Si3 0.0331(10) 0.0739(15) 0.0294(10) -0.0143(10) 0.0048(8) -
0.0114(10)
Si4 0.0320(10) 0.0527(12) 0.0430(11) 0.0118(9) 0.0121(8)
0.0093(9)
O1 0.029(2) 0.028(2) 0.038(2) -0.0064(18) 0.0125(19) -
0.0083(18)
N1 0.035(3) 0.035(3) 0.028(3) -0.012(2) 0.012(2) -0.006(2)
N2 0.026(3) 0.032(3) 0.025(3) -0.006(2) 0.004(2) -0.008(2)
N3 0.036(3) 0.025(3) 0.039(3) -0.002(2) 0.009(2) -0.002(2)
N4 0.024(3) 0.046(3) 0.027(3) -0.004(2) 0.007(2) -0.005(2)
N5 0.025(2) 0.029(3) 0.016(2) -0.0037(19) 0.0071(19) -0.001(2)
N6 0.028(2) 0.019(2) 0.018(2) -0.0019(18) 0.0045(19) -
0.0012(19)
N7 0.027(2) 0.023(2) 0.023(2) -0.0024(19) 0.010(2) 0.0001(19)
C1 0.026(3) 0.027(3) 0.023(3) 0.005(2) 0.005(2) 0.001(2)
C5 0.039(4) 0.042(4) 0.035(4) -0.014(3) 0.012(3) -0.010(3)
C6 0.041(4) 0.041(4) 0.030(3) -0.016(3) 0.014(3) -0.009(3)
C7 0.035(3) 0.029(3) 0.018(3) -0.003(2) 0.011(2) -0.007(3)
C8 0.026(3) 0.031(3) 0.030(3) -0.009(3) 0.009(3) -0.006(2)
C9 0.040(4) 0.036(4) 0.059(5) -0.023(3) 0.004(3) 0.012(3)
```

C10 0.046(4) 0.071(5) 0.043(4) -0.010(4) 0.027(4) -0.020(4)
C21 0.025(3) 0.026(3) 0.026(3) -0.005(2) 0.005(2) -0.011(2)
C22 0.030(3) 0.044(4) 0.036(4) -0.005(3) 0.002(3) -0.002(3)
C23 0.023(3) 0.059(5) 0.035(4) -0.007(3) 0.002(3) 0.000(3)
C24 0.035(4) 0.054(5) 0.048(4) -0.015(4) 0.019(3) -0.014(3)
C25 0.041(4) 0.041(4) 0.041(4) -0.001(3) 0.011(3) -0.016(3)
C26 0.037(4) 0.032(3) 0.037(4) -0.006(3) 0.012(3) -0.011(3)
C27 0.036(4) 0.046(4) 0.051(4) -0.009(3) 0.007(3) -0.003(3)
C28 0.047(5) 0.043(5) 0.121(9) -0.016(5) 0.013(5) -0.007(4)
C29 0.078(7) 0.084(8) 0.094(8) 0.029(6) 0.037(6) -0.016(6)
C30 0.094(8) 0.092(8) 0.064(6) 0.040(6) 0.026(6) 0.025(6)
C31 0.052(5) 0.030(4) 0.107(8) -0.031(4) 0.013(5) 0.011(3)
C32 0.043(4) 0.046(4) 0.064(5) 0.002(4) -0.001(4) 0.009(3)
C33 0.093(7) 0.051(5) 0.038(4) -0.017(4) 0.022(4) -0.015(5)
C34 0.041(5) 0.181(13) 0.044(5) -0.039(6) 0.002(4) -0.039(6)
C35 0.052(5) 0.109(8) 0.041(5) -0.021(5) 0.013(4) 0.009(5)
C36 0.052(6) 0.115(11) 0.205(17) 0.018(11) 0.068(9) 0.021(6)
C37 0.130(11) 0.105(9) 0.063(7) 0.045(6) 0.041(7) 0.039(8)
C38 0.093(7) 0.033(4) 0.062(6) 0.004(4) -0.006(5) 0.002(4)
C39 0.035(3) 0.024(3) 0.026(3) -0.007(2) 0.012(3) 0.001(2)
C40 0.031(3) 0.057(5) 0.028(3) 0.002(3) 0.006(3) -0.012(3)
C41 0.035(4) 0.084(6) 0.034(4) -0.012(4) 0.008(3) -0.003(4)
C42 0.049(4) 0.053(5) 0.042(4) 0.002(3) 0.020(4) -0.011(4)
C43 0.039(4) 0.042(4) 0.033(4) 0.009(3) 0.007(3) 0.002(3)
C44 0.055(5) 0.058(5) 0.032(4) -0.011(3) 0.014(3) -0.004(4)
C45 0.086(6) 0.032(4) 0.042(4) 0.001(3) 0.023(4) 0.021(4)
C46 0.068(5) 0.039(4) 0.046(4) 0.002(3) 0.028(4) 0.016(4)
C47 0.037(4) 0.110(8) 0.062(5) 0.027(5) 0.028(4) 0.033(5)
C48 0.037(4) 0.044(4) 0.031(3) -0.007(3) 0.006(3) 0.004(3)
C220 0.037(4) 0.052(4) 0.039(4) 0.013(3) 0.009(3) 0.013(3)
C221 0.072(6) 0.055(6) 0.070(6) 0.011(4) 0.017(5) 0.002(4)
C222 0.078(7) 0.098(8) 0.042(5) 0.018(5) 0.000(5) 0.019(6)
C260 0.038(4) 0.029(3) 0.051(4) 0.001(3) 0.022(3) -0.001(3)
C262 0.078(6) 0.036(4) 0.093(7) -0.012(4) 0.034(6) 0.002(4)
C261 0.066(6) 0.056(5) 0.052(5) 0.008(4) 0.005(4) 0.009(4)
Ce12 0.02162(16) 0.02336(17) 0.01818(16) -0.00401(12)
0.00121(12) -0.00315(12)
Si11 0.0464(11) 0.0286(10) 0.0466(12) 0.0081(8) -0.0108(9) -
0.0067(8)
Si12 0.0394(10) 0.0435(11) 0.0331(9) -0.0030(8) 0.0092(8) -
0.0158(9)
Si13 0.0229(8) 0.0508(11) 0.0211(8) -0.0061(8) 0.0011(7)
0.0017(8)
Si14 0.0452(11) 0.0339(10) 0.0334(10) 0.0097(8) 0.0137(8)
0.0026(8)
O101 0.027(2) 0.036(2) 0.021(2) -0.0096(17) 0.0049(17)
0.0005(18)
N101 0.028(3) 0.038(3) 0.025(3) -0.014(2) 0.004(2) -0.005(2)
N102 0.022(2) 0.031(3) 0.025(2) -0.010(2) 0.006(2) -0.006(2)
N103 0.036(3) 0.025(3) 0.029(3) -0.002(2) 0.002(2) -0.010(2)
N104 0.026(2) 0.030(3) 0.019(2) -0.001(2) 0.004(2) 0.000(2)
N105 0.020(2) 0.018(2) 0.021(2) -0.0080(18) 0.0015(18)
0.0010(18)

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N106 0.025(2) 0.025(2) 0.019(2) -0.0047(19) 0.0022(19)
0.003(2)
N107 0.021(2) 0.031(3) 0.021(2) -0.005(2) 0.0031(19) -0.006(2)
C101 0.022(3) 0.023(3) 0.021(3) -0.003(2) -0.005(2) -0.002(2)
C105 0.043(4) 0.064(5) 0.055(5) -0.041(4) 0.009(4) -0.008(4)
C106 0.040(4) 0.032(3) 0.028(3) -0.009(3) 0.001(3) -0.001(3)
C107 0.028(3) 0.036(3) 0.021(3) 0.000(2) 0.007(2) 0.000(3)
C108 0.019(3) 0.045(4) 0.027(3) -0.009(3) 0.002(2) 0.000(3)
C109 0.041(4) 0.046(4) 0.052(4) -0.025(4) -0.001(3) 0.007(3)
C110 0.039(4) 0.076(6) 0.036(4) -0.010(4) 0.009(3) -0.011(4)
C121 0.025(3) 0.038(4) 0.027(3) -0.010(3) 0.000(2) -0.010(3)
C122 0.028(3) 0.037(4) 0.034(3) -0.009(3) 0.007(3) -0.005(3)
C123 0.034(4) 0.045(4) 0.035(4) -0.007(3) 0.001(3) 0.001(3)
C124 0.037(4) 0.070(5) 0.041(4) -0.007(4) 0.015(3) -0.016(4)
C125 0.041(4) 0.041(4) 0.046(4) 0.002(3) 0.010(3) -0.017(3)
C126 0.037(4) 0.029(3) 0.043(4) -0.002(3) 0.000(3) -0.005(3)
C127 0.038(4) 0.040(4) 0.063(5) 0.011(4) 0.020(4) 0.008(3)
C128 0.051(6) 0.226(17) 0.096(9) 0.113(11) 0.004(6) -0.014(8)
C129 0.120(10) 0.044(6) 0.207(16) -0.039(8) -0.104(11)
0.062(7)
C130 0.054(5) 0.056(5) 0.046(4) 0.007(4) 0.021(4) -0.011(4)
C131 0.062(5) 0.050(5) 0.060(5) -0.012(4) 0.006(4) -0.025(4)
C132 0.026(3) 0.056(4) 0.034(4) 0.001(3) -0.001(3) -0.002(3)
C133 0.024(3) 0.085(6) 0.036(4) -0.020(4) 0.004(3) -0.003(3)
C134 0.036(4) 0.056(5) 0.032(3) -0.024(3) 0.006(3) 0.001(3)
C135 0.042(4) 0.088(6) 0.021(3) -0.007(4) 0.005(3) 0.013(4)
C136 0.109(8) 0.068(6) 0.052(5) 0.020(5) 0.026(6) -0.006(6)
C137 0.103(9) 0.052(6) 0.187(14) 0.018(7) 0.098(10) 0.033(6)
C138 0.147(11) 0.049(6) 0.052(6) -0.003(4) -0.004(6) -0.001(6)
C139 0.023(3) 0.029(3) 0.019(3) -0.004(2) 0.000(2) 0.001(2)
C140 0.026(3) 0.049(4) 0.024(3) -0.008(3) 0.011(3) -0.012(3)
C141 0.032(3) 0.066(5) 0.028(3) -0.009(3) 0.014(3) -0.014(3)
C142 0.057(5) 0.068(5) 0.030(4) -0.005(3) 0.023(3) -0.015(4)
C143 0.046(4) 0.065(5) 0.016(3) -0.004(3) 0.003(3) -0.013(4)
C144 0.028(4) 0.100(7) 0.040(4) -0.046(4) 0.006(3) -0.007(4)
C145 0.034(3) 0.038(4) 0.050(4) -0.022(3) 0.008(3) 0.001(3)
C146 0.025(3) 0.031(3) 0.028(3) -0.003(2) 0.002(2) 0.003(2)
C147 0.033(4) 0.083(6) 0.033(4) -0.012(4) 0.009(3) 0.006(4)
C148 0.030(3) 0.048(4) 0.024(3) -0.001(3) 0.002(3) -0.009(3)
C620 0.041(4) 0.064(5) 0.033(4) 0.006(3) 0.012(3) 0.017(4)
C621 0.097(8) 0.059(6) 0.059(6) 0.016(5) 0.026(5) 0.024(5)
C622 0.096(8) 0.128(10) 0.027(4) 0.031(5) -0.006(5) 0.011(7)
C660 0.053(5) 0.029(4) 0.065(5) 0.009(4) 0.011(4) -0.002(3)
C661 0.070(6) 0.041(5) 0.103(8) 0.014(5) -0.027(6) 0.001(4)
C662 0.085(7) 0.027(4) 0.069(6) 0.002(4) 0.001(5) 0.005(4)
Ce13 0.02089(16) 0.02422(17) 0.02223(16) -0.00037(13)
0.00426(12) 0.00236(13)
Si31 0.0248(8) 0.0256(8) 0.037(1) -0.0038(7) -0.0025(7) -
0.0008(7)
Si32 0.0298(9) 0.0328(9) 0.0338(9) -0.0029(7) 0.0069(7)
0.0064(7)
Si33 0.0287(9) 0.0448(11) 0.0225(8) 0.0010(7) 0.0052(7)
0.0020(8)
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Si34 0.0262(9) 0.0340(10) 0.0463(11) -0.0108(8) 0.0065(8) -
0.0044(7)
O301 0.029(2) 0.038(2) 0.027(2) 0.0012(18) 0.0065(18) -
0.0039(18)
N301 0.025(3) 0.038(3) 0.022(2) 0.003(2) 0.004(2) 0.002(2)
N302 0.028(3) 0.035(3) 0.017(2) 0.002(2) 0.003(2) 0.002(2)
N303 0.025(2) 0.027(3) 0.030(3) -0.003(2) 0.004(2) 0.002(2)
N304 0.021(2) 0.037(3) 0.030(3) 0.005(2) 0.007(2) 0.002(2)
N305 0.026(2) 0.022(2) 0.029(3) -0.006(2) 0.006(2) 0.0007(19)
N306 0.024(2) 0.024(2) 0.023(2) -0.001(2) 0.002(2) -0.0021(19)
N307 0.020(2) 0.020(2) 0.027(3) -0.0031(19) 0.005(2)
0.0016(18)
C301 0.023(3) 0.019(3) 0.023(3) -0.001(2) 0.002(2) -0.001(2)
C305 0.039(4) 0.055(4) 0.025(3) 0.007(3) 0.001(3) 0.010(3)
C306 0.038(4) 0.052(4) 0.015(3) 0.006(3) 0.003(3) 0.008(3)
C307 0.035(3) 0.036(3) 0.026(3) -0.001(3) 0.014(3) 0.003(3)
C308 0.027(3) 0.041(4) 0.025(3) 0.009(3) 0.011(3) 0.002(3)
C309 0.055(5) 0.047(4) 0.038(4) 0.009(3) 0.009(3) -0.009(4)
C310 0.038(4) 0.067(5) 0.036(4) 0.008(4) 0.016(3) 0.002(4)
C321 0.025(3) 0.027(3) 0.029(3) -0.002(2) -0.002(2) 0.010(2)
C322 0.027(3) 0.040(4) 0.024(3) 0.005(3) -0.001(2) 0.005(3)
C323 0.023(3) 0.046(4) 0.034(3) 0.006(3) 0.004(3) 0.003(3)
C324 0.052(4) 0.041(4) 0.043(4) 0.007(3) 0.012(3) 0.019(3)
C325 0.057(5) 0.032(4) 0.046(4) 0.000(3) 0.004(4) 0.014(3)
C326 0.040(4) 0.031(3) 0.029(3) 0.008(3) -0.005(3) 0.000(3)
C327 0.030(4) 0.052(5) 0.076(6) -0.002(4) 0.012(4) -0.008(3)
C328 0.039(4) 0.081(7) 0.063(6) 0.000(5) -0.009(4) -0.024(4)
C329 0.038(4) 0.041(4) 0.098(7) -0.017(4) 0.020(4) -0.004(3)
C330 0.067(5) 0.060(5) 0.047(5) -0.006(4) 0.020(4) 0.012(4)
C331 0.045(4) 0.035(4) 0.078(6) 0.001(4) 0.011(4) 0.017(3)
C332 0.025(3) 0.036(4) 0.050(4) 0.002(3) 0.011(3) -0.001(3)
C333 0.081(6) 0.045(5) 0.042(4) 0.013(4) -0.009(4) -0.011(4)
C334 0.056(5) 0.071(6) 0.034(4) -0.002(4) 0.015(4) -0.002(4)
C335 0.036(4) 0.064(5) 0.044(4) 0.012(4) 0.010(3) 0.014(4)
C336 0.053(6) 0.065(6) 0.153(12) 0.003(7) 0.036(7) -0.026(5)
C337 0.082(6) 0.043(4) 0.038(4) -0.015(3) -0.022(4) 0.021(4)
C338 0.065(5) 0.028(4) 0.047(4) -0.007(3) 0.013(4) -0.002(3)
C339 0.024(3) 0.027(3) 0.019(3) -0.002(2) 0.006(2) -0.001(2)
C340 0.057(5) 0.066(6) 0.049(5) -0.005(4) 0.015(4) -0.008(4)
C341 0.041(5) 0.094(8) 0.056(5) -0.018(5) -0.012(4) 0.014(5)
C342 0.055(6) 0.135(11) 0.062(6) 0.037(7) 0.038(5) 0.022(6)
C343 0.183(13) 0.055(6) 0.039(5) 0.008(4) 0.041(7) 0.030(7)
C344 0.063(7) 0.073(8) 0.240(18) -0.034(9) 0.095(10) -0.020(6)
C345 0.041(4) 0.064(5) 0.044(4) -0.004(4) -0.003(3) -0.005(4)
C346 0.049(5) 0.114(9) 0.043(5) -0.017(5) 0.004(4) 0.022(5)
C347 0.053(5) 0.067(6) 0.068(6) 0.008(5) 0.016(4) -0.002(4)
C348 0.125(9) 0.060(6) 0.064(6) 0.010(5) 0.058(6) 0.019(6)
C920 0.023(3) 0.044(4) 0.049(4) -0.016(3) 0.008(3) 0.000(3)
C921 0.041(4) 0.033(4) 0.076(6) -0.006(4) -0.005(4) -0.005(3)
C922 0.038(4) 0.071(6) 0.048(5) -0.017(4) -0.002(4) -0.010(4)
C960 0.051(4) 0.029(4) 0.056(5) 0.007(3) 0.003(4) -0.005(3)
C961 0.132(11) 0.095(9) 0.091(8) 0.018(7) -0.015(8) -0.083(9)
C962 0.092(8) 0.054(6) 0.217(16) 0.080(9) 0.066(10) 0.021(6)
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Ce1 . N5 . 2.639(3)    yes
Ce1 . N7 . 2.762(3)    yes
Si1 . N3 . 1.679(2)    yes
Si1 . C27 . 1.858(6)    yes
Si1 . C28 . 1.886(7)    yes
Si1 . C29 . 1.883(7)    yes
Si2 . N3 . 1.747(2)    yes
Si2 . C30 . 1.870(7)    yes
Si2 . C31 . 1.885(6)    yes
Si2 . C32 . 1.871(7)    yes
Si3 . N4 . 1.710(3)    yes
Si3 . C33 . 1.861(7)    yes
Si3 . C34 . 1.884(7)    yes
Si3 . C35 . 1.885(7)    yes
Si4 . N4 . 1.703(3)    yes
Si4 . C36 . 1.868(7)    yes
Si4 . C37 . 1.880(7)    yes
Si4 . C38 . 1.858(7)    yes
O1 . C8 . 1.386(4)    yes
N1 . C1 . 1.349(4)    yes
N1 . C6 . 1.467(4)    yes
N1 . C7 . 1.467(5)    yes
N2 . C1 . 1.348(4)    yes
N2 . C5 . 1.473(5)    yes
N2 . C21 . 1.431(4)    yes
N5 . N6 . 1.374(4)    yes
N5 . C1 . 1.336(4)    yes
N6 . N7 . 1.264(3)    yes
N7 . C39 . 1.473(4)    yes
C5 . C6 . 1.527(5)    yes
C5 . H51 . 0.950    no
C5 . H52 . 0.950    no
C6 . H61 . 0.950    no
C6 . H62 . 0.950    no
C7 . C8 . 1.536(5)    yes
C7 . H71 . 0.950    no
C7 . H72 . 0.950    no
C8 . C9 . 1.520(6)    yes
C8 . C10 . 1.532(6)    yes
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C9 . H91 . 0.950    no
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C10 . H102 . 0.950    no
C10 . H103 . 0.951    no
C21 . C22 . 1.408(4)    yes
C21 . C26 . 1.391(4)    yes
C22 . C23 . 1.385(5)    yes
C22 . C220 . 1.517(5)    yes
C23 . C24 . 1.376(6)    yes
C23 . H23 . 0.950    no
C24 . C25 . 1.380(6)    yes
C24 . H24 . 0.950    no
C25 . C26 . 1.396(5)    yes
C25 . H25 . 0.950    no
C26 . C260 . 1.522(5)    yes
C27 . H271 . 0.950    no
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C39 . C40 . 1.533(5)    yes
C39 . C46 . 1.540(5)    yes
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C40 . H401 . 0.950    no
C40 . H402 . 0.951    no
C41 . C42 . 1.513(5)    yes
C41 . C47 . 1.541(6)    yes
C41 . H411 . 0.951    no
C42 . C43 . 1.514(5)    yes
C42 . H421 . 0.951    no
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C43 . C44 . 1.532(5)    yes
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C43 . H431 . 0.950    no
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C44 . H441 . 0.951    no
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C45 . C46 . 1.536(5)    yes
C45 . C47 . 1.519(6)    yes
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C47 . H472 . 0.948    no
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C220 . C222 . 1.558(7)    yes
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C260 . C262 . 1.533(7)    yes
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C260 . H2601 . 0.949    no
C262 . H2621 . 0.950    no
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C262 . H2623 . 0.950    no
C261 . H2611 . 0.950    no
C261 . H2612 . 0.949    no
C261 . H2613 . 0.951    no
Ce12 . O101 . 2.147(3)    yes
Ce12 . N103 . 2.3848(19)    yes
Ce12 . N104 . 2.4200(18)    yes
Ce12 . N105 . 2.649(3)    yes
Ce12 . N107 . 2.790(3)    yes
Si11 . N103 . 1.687(3)    yes
Si11 . C127 . 1.868(6)    yes
Si11 . C128 . 1.875(7)    yes
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Si11 . C129 . 1.867(7)    yes
Si12 . N103 . 1.716(2)    yes
Si12 . C130 . 1.882(6)    yes
Si12 . C131 . 1.895(6)    yes
Si12 . C132 . 1.857(6)    yes
Si13 . N104 . 1.691(2)    yes
Si13 . C133 . 1.891(6)    yes
Si13 . C134 . 1.876(6)    yes
Si13 . C135 . 1.882(6)    yes
Si14 . N104 . 1.701(2)    yes
Si14 . C136 . 1.869(7)    yes
Si14 . C137 . 1.864(7)    yes
Si14 . C138 . 1.863(7)    yes
O101 . C108 . 1.412(4)    yes
N101 . C101 . 1.332(4)    yes
N101 . C106 . 1.480(5)    yes
N101 . C107 . 1.447(5)    yes
N102 . C101 . 1.369(4)    yes
N102 . C105 . 1.465(5)    yes
N102 . C121 . 1.429(4)    yes
N105 . N106 . 1.402(4)    yes
N105 . C101 . 1.329(4)    yes
N106 . N107 . 1.254(3)    yes
N107 . C139 . 1.484(4)    yes
C105 . C106 . 1.525(5)    yes
C105 . H1051 . 0.949    no
C105 . H1052 . 0.950    no
C106 . H1061 . 0.950    no
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C107 . C108 . 1.543(5)    yes
C107 . H1071 . 0.950    no
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C108 . C109 . 1.511(6)    yes
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C121 . C126 . 1.391(5)    yes
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C122 . C620 . 1.521(5)    yes
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C141 . C142 . 1.521(5)    yes
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C148 . H1481 . 0.949    no
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C620 . C622 . 1.563(7)    yes
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C662 . H6623 . 0.950    no
Ce13 . O301 . 2.153(4)    yes
Ce13 . N303 . 2.410(5)    yes
Ce13 . N304 . 2.397(5)    yes
Ce13 . N305 . 2.651(5)    yes
Ce13 . N307 . 2.711(5)    yes
Si31 . N303 . 1.704(5)    yes
Si31 . C327 . 1.888(9)    yes
Si31 . C328 . 1.868(9)    yes
Si31 . C329 . 1.884(8)    yes
Si32 . N303 . 1.692(5)    yes
Si32 . C330 . 1.881(8)    yes
Si32 . C331 . 1.877(8)    yes
Si32 . C332 . 1.874(7)    yes
Si33 . N304 . 1.705(5)    yes
Si33 . C333 . 1.881(9)    yes
Si33 . C334 . 1.869(8)    yes
Si33 . C335 . 1.875(7)    yes
Si34 . N304 . 1.712(6)    yes
Si34 . C336 . 1.889(10)    yes
Si34 . C337 . 1.879(8)    yes
Si34 . C338 . 1.895(8)    yes
O301 . C308 . 1.409(7)    yes
N301 . C301 . 1.344(8)    yes
N301 . C306 . 1.463(8)    yes
N301 . C307 . 1.467(8)    yes
N302 . C301 . 1.348(7)    yes
N302 . C305 . 1.478(8)    yes
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N302 . C321 . 1.442(8)    yes
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N307 . C339 . 1.496(7)    yes
C305 . C306 . 1.501(10)    yes
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C305 . H3052 . 0.950    no
C306 . H3061 . 0.950    no
C306 . H3062 . 0.950    no
C307 . C308 . 1.569(9)    yes
C307 . H3071 . 0.950    no
C307 . H3072 . 0.950    no
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C308 . C310 . 1.531(9)    yes
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C310 . H3103 . 0.950    no
C321 . C322 . 1.389(9)    yes
C321 . C326 . 1.399(9)    yes
C322 . C323 . 1.373(9)    yes
C322 . C920 . 1.533(9)    yes
C323 . C324 . 1.383(10)    yes
C323 . H323 . 0.950    no
C324 . C325 . 1.387(12)    yes
C324 . H324 . 0.950    no
C325 . C326 . 1.394(11)    yes
C325 . H325 . 0.950    no
C326 . C960 . 1.552(10)    yes
C327 . H3271 . 0.950    no
C327 . H3272 . 0.950    no
C327 . H3273 . 0.950    no
C328 . H3281 . 0.950    no
C328 . H3282 . 0.950    no
C328 . H3283 . 0.950    no
C329 . H3291 . 0.950    no
C329 . H3292 . 0.950    no
C329 . H3293 . 0.951    no
C330 . H3301 . 0.950    no
C330 . H3302 . 0.950    no
C330 . H3303 . 0.950    no
C331 . H3311 . 0.949    no
C331 . H3312 . 0.950    no
C331 . H3313 . 0.950    no
C332 . H3321 . 0.950    no
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C333 . H3331 . 0.950    no
C333 . H3332 . 0.950    no
C333 . H3333 . 0.950    no
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C334 . H3341 . 0.950    no
C334 . H3342 . 0.950    no
C334 . H3343 . 0.950    no
C335 . H3351 . 0.950    no
C335 . H3352 . 0.950    no
C335 . H3353 . 0.950    no
C336 . H3361 . 0.950    no
C336 . H3362 . 0.951    no
C336 . H3363 . 0.950    no
C337 . H3371 . 0.950    no
C337 . H3372 . 0.950    no
C337 . H3373 . 0.951    no
C338 . H3381 . 0.950    no
C338 . H3382 . 0.950    no
C338 . H3383 . 0.951    no
C339 . C340 . 1.562(10)    yes
C339 . C346 . 1.506(10)    yes
C339 . C348 . 1.525(11)    yes
C340 . C341 . 1.629(13)    yes
C340 . H3401 . 0.950    no
C340 . H3402 . 0.949    no
C341 . C342 . 1.407(16)    yes
C341 . C347 . 1.451(12)    yes
C341 . H3411 . 0.949    no
C342 . C343 . 1.482(18)    yes
C342 . H3421 . 0.954    no
C342 . H3422 . 0.951    no
C343 . C344 . 1.514(19)    yes
C343 . C348 . 1.612(13)    yes
C343 . H3431 . 0.947    no
C344 . C345 . 1.499(16)    yes
C344 . H3441 . 0.952    no
C344 . H3442 . 0.949    no
C345 . C346 . 1.637(12)    yes
C345 . C347 . 1.475(12)    yes
C345 . H3451 . 0.950    no
C346 . H3461 . 0.951    no
C346 . H3462 . 0.949    no
C347 . H3471 . 0.950    no
C347 . H3472 . 0.950    no
C348 . H3481 . 0.951    no
C348 . H3482 . 0.951    no
C920 . C921 . 1.532(11)    yes
C920 . C922 . 1.523(9)    yes
C920 . H9201 . 0.950    no
C921 . H9211 . 0.950    no
C921 . H9212 . 0.950    no
C921 . H9213 . 0.950    no
C922 . H9221 . 0.951    no
C922 . H9222 . 0.949    no
C922 . H9223 . 0.950    no
C960 . C961 . 1.489(14)    yes
C960 . C962 . 1.478(12)    yes
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C960 . H9601 . 0.950    no
C961 . H9611 . 0.951    no
C961 . H9612 . 0.948    no
C961 . H9613 . 0.951    no
C962 . H9621 . 0.949    no
C962 . H9622 . 0.949    no
C962 . H9623 . 0.952    no
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O1 . Ce1 . N3 . 96.19(7)    yes
O1 . Ce1 . N4 . 110.40(7)    yes
N3 . Ce1 . N4 . 116.34(6)    yes
O1 . Ce1 . N5 . 77.91(6)    yes
N3 . Ce1 . N5 . 119.55(6)    yes
N4 . Ce1 . N5 . 122.05(6)    yes
O1 . Ce1 . N7 . 122.94(6)    yes
N3 . Ce1 . N7 . 120.47(6)    yes
N4 . Ce1 . N7 . 91.73(7)    yes
N5 . Ce1 . N7 . 46.90(5)    yes
N3 . Si1 . C27 . 110.00(8)    yes
N3 . Si1 . C28 . 112.65(9)    yes
C27 . Si1 . C28 . 105.72(9)    yes
N3 . Si1 . C29 . 115.38(9)    yes
C27 . Si1 . C29 . 107.05(9)    yes
C28 . Si1 . C29 . 105.43(9)    yes
N3 . Si2 . C30 . 115.29(9)    yes
N3 . Si2 . C31 . 112.75(9)    yes
C30 . Si2 . C31 . 107.70(9)    yes
N3 . Si2 . C32 . 108.94(9)    yes
C30 . Si2 . C32 . 105.70(9)    yes
C31 . Si2 . C32 . 105.83(9)    yes
N4 . Si3 . C33 . 109.61(9)    yes
N4 . Si3 . C34 . 113.64(9)    yes
C33 . Si3 . C34 . 107.33(9)    yes
N4 . Si3 . C35 . 115.92(9)    yes
C33 . Si3 . C35 . 104.93(9)    yes
C34 . Si3 . C35 . 104.73(9)    yes
N4 . Si4 . C36 . 113.45(9)    yes
N4 . Si4 . C37 . 114.99(9)    yes
C36 . Si4 . C37 . 105.99(9)    yes
N4 . Si4 . C38 . 109.77(9)    yes
C36 . Si4 . C38 . 107.11(9)    yes
C37 . Si4 . C38 . 104.91(9)    yes
Ce1 . O1 . C8 . 149.50(9)    yes
C1 . N1 . C6 . 111.51(8)    yes
C1 . N1 . C7 . 126.86(9)    yes
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C6 . N1 . C7 . 119.98(9)    yes
C1 . N2 . C5 . 110.89(7)    yes
C1 . N2 . C21 . 130.93(8)    yes
C5 . N2 . C21 . 117.64(8)    yes
Ce1 . N3 . Si2 . 116.52(7)    yes
Ce1 . N3 . Si1 . 117.61(7)    yes
Si2 . N3 . Si1 . 125.79(8)    yes
Ce1 . N4 . Si3 . 119.16(7)    yes
Ce1 . N4 . Si4 . 114.57(7)    yes
Si3 . N4 . Si4 . 126.21(8)    yes
Ce1 . N5 . N6 . 102.74(8)    yes
Ce1 . N5 . C1 . 140.07(9)    yes
N6 . N5 . C1 . 113.71(8)    yes
N5 . N6 . N7 . 109.29(7)    yes
Ce1 . N7 . N6 . 100.13(7)    yes
Ce1 . N7 . C39 . 143.63(7)    yes
N6 . N7 . C39 . 114.57(8)    yes
N1 . C1 . N2 . 110.49(7)    yes
N1 . C1 . N5 . 119.91(7)    yes
N2 . C1 . N5 . 129.56(7)    yes
N2 . C5 . C6 . 103.75(8)    yes
N2 . C5 . H51 . 110.9    no
C6 . C5 . H51 . 110.9    no
N2 . C5 . H52 . 110.9    no
C6 . C5 . H52 . 110.9    no
H51 . C5 . H52 . 109.5    no
C5 . C6 . N1 . 103.25(8)    yes
C5 . C6 . H61 . 111.0    no
N1 . C6 . H61 . 111.0    no
C5 . C6 . H62 . 111.0    no
N1 . C6 . H62 . 111.0    no
H61 . C6 . H62 . 109.5    no
N1 . C7 . C8 . 116.41(10)    yes
N1 . C7 . H71 . 107.7    no
C8 . C7 . H71 . 107.7    no
N1 . C7 . H72 . 107.7    no
C8 . C7 . H72 . 107.8    no
H71 . C7 . H72 . 109.5    no
C7 . C8 . O1 . 108.53(9)    yes
C7 . C8 . C9 . 111.62(9)    yes
O1 . C8 . C9 . 109.45(9)    yes
C7 . C8 . C10 . 106.20(9)    yes
O1 . C8 . C10 . 110.05(9)    yes
C9 . C8 . C10 . 110.91(9)    yes
C8 . C9 . H91 . 109.4    no
C8 . C9 . H92 . 109.4    no
H91 . C9 . H92 . 109.5    no
C8 . C9 . H93 . 109.5    no
H91 . C9 . H93 . 109.5    no
H92 . C9 . H93 . 109.5    no
C8 . C10 . H101 . 109.5    no
C8 . C10 . H102 . 109.5    no
H101 . C10 . H102 . 109.5    no
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C8 . C10 . H103 . 109.5    no
H101 . C10 . H103 . 109.5    no
H102 . C10 . H103 . 109.4    no
N2 . C21 . C22 . 119.87(8)    yes
N2 . C21 . C26 . 118.75(8)    yes
C22 . C21 . C26 . 121.30(7)    yes
C21 . C22 . C23 . 117.85(7)    yes
C21 . C22 . C220 . 121.43(8)    yes
C23 . C22 . C220 . 120.67(8)    yes
C22 . C23 . C24 . 121.52(9)    yes
C22 . C23 . H23 . 119.2    no
C24 . C23 . H23 . 119.3    no
C23 . C24 . C25 . 120.20(9)    yes
C23 . C24 . H24 . 119.8    no
C25 . C24 . H24 . 120.0    no
C24 . C25 . C26 . 120.32(9)    yes
C24 . C25 . H25 . 119.8    no
C26 . C25 . H25 . 119.9    no
C25 . C26 . C21 . 118.79(7)    yes
C25 . C26 . C260 . 118.64(8)    yes
C21 . C26 . C260 . 122.57(8)    yes
Si1 . C27 . H271 . 109.4    no
Si1 . C27 . H272 . 109.4    no
H271 . C27 . H272 . 109.5    no
Si1 . C27 . H273 . 109.4    no
H271 . C27 . H273 . 109.5    no
H272 . C27 . H273 . 109.5    no
Si1 . C28 . H281 . 109.5    no
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Si1 . C28 . H283 . 109.4    no
H281 . C28 . H283 . 109.4    no
H282 . C28 . H283 . 109.5    no
Si1 . C29 . H291 . 109.4    no
Si1 . C29 . H292 . 109.4    no
H291 . C29 . H292 . 109.5    no
Si1 . C29 . H293 . 109.5    no
H291 . C29 . H293 . 109.6    no
H292 . C29 . H293 . 109.5    no
Si2 . C30 . H301 . 109.5    no
Si2 . C30 . H302 . 109.5    no
H301 . C30 . H302 . 109.4    no
Si2 . C30 . H303 . 109.5    no
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Si2 . C31 . H311 . 109.5    no
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Si2 . C31 . H313 . 109.5    no
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Si2 . C32 . H321 . 109.4    no
Si2 . C32 . H322 . 109.5    no
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H321 . C32 . H322 . 109.5    no
Si2 . C32 . H323 . 109.4    no
H321 . C32 . H323 . 109.5    no
H322 . C32 . H323 . 109.5    no
Si3 . C33 . H331 . 109.5    no
Si3 . C33 . H332 . 109.5    no
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Si3 . C33 . H333 . 109.5    no
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Si3 . C34 . H341 . 109.4    no
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Si3 . C34 . H343 . 109.5    no
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Si3 . C35 . H351 . 109.5    no
Si3 . C35 . H352 . 109.4    no
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Si3 . C35 . H353 . 109.5    no
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Si4 . C36 . H362 . 109.3    no
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Si4 . C37 . H371 . 109.4    no
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H371 . C37 . H372 . 109.3    no
Si4 . C37 . H373 . 109.6    no
H371 . C37 . H373 . 109.5    no
H372 . C37 . H373 . 109.5    no
Si4 . C38 . H381 . 109.4    no
Si4 . C38 . H382 . 109.5    no
H381 . C38 . H382 . 109.5    no
Si4 . C38 . H383 . 109.5    no
H381 . C38 . H383 . 109.5    no
H382 . C38 . H383 . 109.6    no
N7 . C39 . C40 . 115.01(8)    yes
N7 . C39 . C46 . 106.41(9)    yes
C40 . C39 . C46 . 109.47(9)    yes
N7 . C39 . C48 . 107.22(9)    yes
C40 . C39 . C48 . 109.18(9)    yes
C46 . C39 . C48 . 109.40(9)    yes
C39 . C40 . C41 . 109.14(9)    yes
C39 . C40 . H401 . 109.6    no
C41 . C40 . H401 . 109.7    no
C39 . C40 . H402 . 109.5    no
C41 . C40 . H402 . 109.5    no
H401 . C40 . H402 . 109.4    no
C40 . C41 . C42 . 109.31(9)    yes
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C40 . C41 . C47 . 108.52(9)    yes
C42 . C41 . C47 . 110.40(9)    yes
C40 . C41 . H411 . 109.6    no
C42 . C41 . H411 . 109.4    no
C47 . C41 . H411 . 109.6    no
C41 . C42 . C43 . 109.90(9)    yes
C41 . C42 . H421 . 109.4    no
C43 . C42 . H421 . 109.3    no
C41 . C42 . H422 . 109.4    no
C43 . C42 . H422 . 109.4    no
H421 . C42 . H422 . 109.4    no
C42 . C43 . C44 . 111.01(9)    yes
C42 . C43 . C48 . 108.16(9)    yes
C44 . C43 . C48 . 109.16(9)    yes
C42 . C43 . H431 . 109.5    no
C44 . C43 . H431 . 109.5    no
C48 . C43 . H431 . 109.5    no
C43 . C44 . C45 . 109.40(9)    yes
C43 . C44 . H441 . 109.4    no
C45 . C44 . H441 . 109.5    no
C43 . C44 . H442 . 109.5    no
C45 . C44 . H442 . 109.6    no
H441 . C44 . H442 . 109.4    no
C44 . C45 . C46 . 109.61(9)    yes
C44 . C45 . C47 . 109.61(9)    yes
C46 . C45 . C47 . 109.75(9)    yes
C44 . C45 . H451 . 109.2    no
C46 . C45 . H451 . 109.3    no
C47 . C45 . H451 . 109.3    no
C39 . C46 . C45 . 108.88(9)    yes
C39 . C46 . H461 . 109.7    no
C45 . C46 . H461 . 109.7    no
C39 . C46 . H462 . 109.6    no
C45 . C46 . H462 . 109.7    no
H461 . C46 . H462 . 109.3    no
C41 . C47 . C45 . 109.63(9)    yes
C41 . C47 . H471 . 109.4    no
C45 . C47 . H471 . 109.3    no
C41 . C47 . H472 . 109.6    no
C45 . C47 . H472 . 109.4    no
H471 . C47 . H472 . 109.6    no
C43 . C48 . C39 . 109.88(9)    yes
C43 . C48 . H481 . 109.3    no
C39 . C48 . H481 . 109.4    no
C43 . C48 . H482 . 109.4    no
C39 . C48 . H482 . 109.4    no
H481 . C48 . H482 . 109.5    no
C22 . C220 . C221 . 111.48(10)    yes
C22 . C220 . C222 . 109.86(10)    yes
C221 . C220 . C222 . 112.17(10)    yes
C22 . C220 . H2201 . 107.7    no
C221 . C220 . H2201 . 107.7    no
C222 . C220 . H2201 . 107.8    no
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C220 . C221 . H2211 . 109.5    no
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H2211 . C221 . H2213 . 109.5    no
H2212 . C221 . H2213 . 109.5    no
C220 . C222 . H2221 . 109.4    no
C220 . C222 . H2222 . 109.4    no
H2221 . C222 . H2222 . 109.4    no
C220 . C222 . H2223 . 109.5    no
H2221 . C222 . H2223 . 109.5    no
H2222 . C222 . H2223 . 109.5    no
C26 . C260 . C262 . 111.61(10)    yes
C26 . C260 . C261 . 112.07(10)    yes
C262 . C260 . C261 . 110.53(10)    yes
C26 . C260 . H2601 . 107.5    no
C262 . C260 . H2601 . 107.5    no
C261 . C260 . H2601 . 107.5    no
C260 . C262 . H2621 . 109.5    no
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H2611 . C261 . H2612 . 109.6    no
C260 . C261 . H2613 . 109.4    no
H2611 . C261 . H2613 . 109.4    no
H2612 . C261 . H2613 . 109.5    no
O101 . Ce12 . N103 . 95.00(7)    yes
O101 . Ce12 . N104 . 110.77(6)    yes
N103 . Ce12 . N104 . 115.51(6)    yes
O101 . Ce12 . N105 . 77.35(6)    yes
N103 . Ce12 . N105 . 121.17(6)    yes
N104 . Ce12 . N105 . 121.75(6)    yes
O101 . Ce12 . N107 . 122.85(6)    yes
N103 . Ce12 . N107 . 121.41(6)    yes
N104 . Ce12 . N107 . 92.54(6)    yes
N105 . Ce12 . N107 . 46.90(5)    yes
N103 . Si11 . C127 . 108.92(9)    yes
N103 . Si11 . C128 . 115.32(9)    yes
C127 . Si11 . C128 . 105.68(9)    yes
N103 . Si11 . C129 . 112.71(9)    yes
C127 . Si11 . C129 . 105.85(9)    yes
C128 . Si11 . C129 . 107.72(9)    yes
N103 . Si12 . C130 . 115.35(9)    yes
N103 . Si12 . C131 . 112.75(9)    yes
C130 . Si12 . C131 . 105.42(9)    yes
N103 . Si12 . C132 . 109.95(8)    yes
C130 . Si12 . C132 . 107.05(9)    yes
C131 . Si12 . C132 . 105.72(9)    yes
N104 . Si13 . C133 . 113.75(8)    yes
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N104 . Si13 . C134 . 109.61(8)    yes
C133 . Si13 . C134 . 107.35(9)    yes
N104 . Si13 . C135 . 115.78(9)    yes
C133 . Si13 . C135 . 104.72(9)    yes
C134 . Si13 . C135 . 104.96(9)    yes
N104 . Si14 . C136 . 114.90(9)    yes
N104 . Si14 . C137 . 113.54(9)    yes
C136 . Si14 . C137 . 105.98(9)    yes
N104 . Si14 . C138 . 109.72(9)    yes
C136 . Si14 . C138 . 104.96(9)    yes
C137 . Si14 . C138 . 107.13(9)    yes
Ce12 . O101 . C108 . 149.35(8)    yes
C101 . N101 . C106 . 111.26(8)    yes
C101 . N101 . C107 . 126.51(9)    yes
C106 . N101 . C107 . 119.76(9)    yes
C101 . N102 . C105 . 110.74(7)    yes
C101 . N102 . C121 . 130.94(8)    yes
C105 . N102 . C121 . 117.50(9)    yes
Ce12 . N103 . Si12 . 116.92(7)    yes
Ce12 . N103 . Si11 . 117.20(7)    yes
Si12 . N103 . Si11 . 125.78(8)    yes
Ce12 . N104 . Si14 . 114.73(7)    yes
Ce12 . N104 . Si13 . 118.78(7)    yes
Si14 . N104 . Si13 . 126.02(8)    yes
Ce12 . N105 . N106 . 102.44(8)    yes
Ce12 . N105 . C101 . 139.17(9)    yes
N106 . N105 . C101 . 113.21(8)    yes
N105 . N106 . N107 . 109.37(7)    yes
Ce12 . N107 . N106 . 100.08(7)    yes
Ce12 . N107 . C139 . 143.99(7)    yes
N106 . N107 . C139 . 114.55(7)    yes
N102 . C101 . N101 . 110.44(7)    yes
N102 . C101 . N105 . 129.72(8)    yes
N101 . C101 . N105 . 119.69(7)    yes
N102 . C105 . C106 . 103.75(9)    yes
N102 . C105 . H1051 . 110.9    no
C106 . C105 . H1051 . 110.9    no
N102 . C105 . H1052 . 110.8    no
C106 . C105 . H1052 . 110.8    no
H1051 . C105 . H1052 . 109.5    no
C105 . C106 . N101 . 103.27(9)    yes
C105 . C106 . H1061 . 111.0    no
N101 . C106 . H1061 . 111.0    no
C105 . C106 . H1062 . 111.0    no
N101 . C106 . H1062 . 111.0    no
H1061 . C106 . H1062 . 109.4    no
N101 . C107 . C108 . 116.48(10)    yes
N101 . C107 . H1071 . 107.7    no
C108 . C107 . H1071 . 107.7    no
N101 . C107 . H1072 . 107.7    no
C108 . C107 . H1072 . 107.7    no
H1071 . C107 . H1072 . 109.5    no
C107 . C108 . O101 . 108.58(9)    yes
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C107 . C108 . C109 . 111.62(9)    yes
O101 . C108 . C109 . 109.42(9)    yes
C107 . C108 . C110 . 106.12(9)    yes
O101 . C108 . C110 . 110.15(9)    yes
C109 . C108 . C110 . 110.88(9)    yes
C108 . C109 . H1091 . 109.5    no
C108 . C109 . H1092 . 109.4    no
H1091 . C109 . H1092 . 109.4    no
C108 . C109 . H1093 . 109.5    no
H1091 . C109 . H1093 . 109.5    no
H1092 . C109 . H1093 . 109.5    no
C108 . C110 . H1101 . 109.5    no
C108 . C110 . H1102 . 109.4    no
H1101 . C110 . H1102 . 109.5    no
C108 . C110 . H1103 . 109.4    no
H1101 . C110 . H1103 . 109.5    no
H1102 . C110 . H1103 . 109.4    no
N102 . C121 . C122 . 119.70(8)    yes
N102 . C121 . C126 . 118.59(8)    yes
C122 . C121 . C126 . 121.21(7)    yes
C121 . C122 . C123 . 117.90(7)    yes
C121 . C122 . C620 . 121.41(8)    yes
C123 . C122 . C620 . 120.68(8)    yes
C122 . C123 . C124 . 121.54(9)    yes
C122 . C123 . H123 . 119.2    no
C124 . C123 . H123 . 119.3    no
C123 . C124 . C125 . 120.20(9)    yes
C123 . C124 . H124 . 119.9    no
C125 . C124 . H124 . 120.0    no
C124 . C125 . C126 . 120.30(9)    yes
C124 . C125 . H125 . 119.8    no
C126 . C125 . H125 . 119.9    no
C125 . C126 . C121 . 118.80(8)    yes
C125 . C126 . C660 . 118.61(8)    yes
C121 . C126 . C660 . 122.48(8)    yes
Si11 . C127 . H1271 . 109.5    no
Si11 . C127 . H1272 . 109.4    no
H1271 . C127 . H1272 . 109.4    no
Si11 . C127 . H1273 . 109.5    no
H1271 . C127 . H1273 . 109.5    no
H1272 . C127 . H1273 . 109.5    no
Si11 . C128 . H1281 . 109.4    no
Si11 . C128 . H1282 . 109.6    no
H1281 . C128 . H1282 . 109.6    no
Si11 . C128 . H1283 . 109.4    no
H1281 . C128 . H1283 . 109.3    no
H1282 . C128 . H1283 . 109.5    no
Si11 . C129 . H1291 . 109.5    no
Si11 . C129 . H1292 . 109.4    no
H1291 . C129 . H1292 . 109.3    no
Si11 . C129 . H1293 . 109.6    no
H1291 . C129 . H1293 . 109.5    no
H1292 . C129 . H1293 . 109.4    no
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Si12 . C130 . H1301 . 109.4    no
Si12 . C130 . H1302 . 109.4    no
H1301 . C130 . H1302 . 109.5    no
Si12 . C130 . H1303 . 109.4    no
H1301 . C130 . H1303 . 109.5    no
H1302 . C130 . H1303 . 109.5    no
Si12 . C131 . H1311 . 109.5    no
Si12 . C131 . H1312 . 109.5    no
H1311 . C131 . H1312 . 109.6    no
Si12 . C131 . H1313 . 109.4    no
H1311 . C131 . H1313 . 109.5    no
H1312 . C131 . H1313 . 109.5    no
Si12 . C132 . H1321 . 109.5    no
Si12 . C132 . H1322 . 109.4    no
H1321 . C132 . H1322 . 109.4    no
Si12 . C132 . H1323 . 109.5    no
H1321 . C132 . H1323 . 109.5    no
H1322 . C132 . H1323 . 109.5    no
Si13 . C133 . H1331 . 109.5    no
Si13 . C133 . H1332 . 109.5    no
H1331 . C133 . H1332 . 109.4    no
Si13 . C133 . H1333 . 109.5    no
H1331 . C133 . H1333 . 109.5    no
H1332 . C133 . H1333 . 109.5    no
Si13 . C134 . H1341 . 109.5    no
Si13 . C134 . H1342 . 109.5    no
H1341 . C134 . H1342 . 109.5    no
Si13 . C134 . H1343 . 109.4    no
H1341 . C134 . H1343 . 109.4    no
H1342 . C134 . H1343 . 109.5    no
Si13 . C135 . H1351 . 109.5    no
Si13 . C135 . H1352 . 109.5    no
H1351 . C135 . H1352 . 109.4    no
Si13 . C135 . H1353 . 109.5    no
H1351 . C135 . H1353 . 109.5    no
H1352 . C135 . H1353 . 109.5    no
Si14 . C136 . H1361 . 109.4    no
Si14 . C136 . H1362 . 109.5    no
H1361 . C136 . H1362 . 109.3    no
Si14 . C136 . H1363 . 109.6    no
H1361 . C136 . H1363 . 109.5    no
H1362 . C136 . H1363 . 109.6    no
Si14 . C137 . H1371 . 109.5    no
Si14 . C137 . H1372 . 109.3    no
H1371 . C137 . H1372 . 109.3    no
Si14 . C137 . H1373 . 109.6    no
H1371 . C137 . H1373 . 109.7    no
H1372 . C137 . H1373 . 109.4    no
Si14 . C138 . H1381 . 109.4    no
Si14 . C138 . H1382 . 109.5    no
H1381 . C138 . H1382 . 109.4    no
Si14 . C138 . H1383 . 109.5    no
H1381 . C138 . H1383 . 109.5    no
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H1382 . C138 . H1383 . 109.5    no
N107 . C139 . C140 . 114.98(8)    yes
N107 . C139 . C146 . 106.31(9)    yes
C140 . C139 . C146 . 109.40(9)    yes
N107 . C139 . C148 . 107.35(8)    yes
C140 . C139 . C148 . 109.14(9)    yes
C146 . C139 . C148 . 109.53(9)    yes
C139 . C140 . C141 . 109.10(9)    yes
C139 . C140 . H1401 . 109.6    no
C141 . C140 . H1401 . 109.7    no
C139 . C140 . H1402 . 109.5    no
C141 . C140 . H1402 . 109.5    no
H1401 . C140 . H1402 . 109.4    no
C140 . C141 . C142 . 109.30(9)    yes
C140 . C141 . C147 . 108.51(9)    yes
C142 . C141 . C147 . 110.33(9)    yes
C140 . C141 . H1411 . 109.6    no
C142 . C141 . H1411 . 109.4    no
C147 . C141 . H1411 . 109.6    no
C141 . C142 . C143 . 109.81(9)    yes
C141 . C142 . H1421 . 109.4    no
C143 . C142 . H1421 . 109.3    no
C141 . C142 . H1422 . 109.5    no
C143 . C142 . H1422 . 109.4    no
H1421 . C142 . H1422 . 109.4    no
C142 . C143 . C144 . 110.95(9)    yes
C142 . C143 . C148 . 108.14(9)    yes
C144 . C143 . C148 . 109.09(9)    yes
C142 . C143 . H1431 . 109.6    no
C144 . C143 . H1431 . 109.5    no
C148 . C143 . H1431 . 109.5    no
C143 . C144 . C145 . 109.41(9)    yes
C143 . C144 . H1441 . 109.4    no
C145 . C144 . H1441 . 109.5    no
C143 . C144 . H1442 . 109.5    no
C145 . C144 . H1442 . 109.5    no
H1441 . C144 . H1442 . 109.5    no
C144 . C145 . C146 . 109.60(9)    yes
C144 . C145 . C147 . 109.71(9)    yes
C146 . C145 . C147 . 109.84(9)    yes
C144 . C145 . H1451 . 109.2    no
C146 . C145 . H1451 . 109.3    no
C147 . C145 . H1451 . 109.2    no
C139 . C146 . C145 . 109.05(9)    yes
C139 . C146 . H1461 . 109.6    no
C145 . C146 . H1461 . 109.6    no
C139 . C146 . H1462 . 109.6    no
C145 . C146 . H1462 . 109.6    no
H1461 . C146 . H1462 . 109.3    no
C141 . C147 . C145 . 109.62(9)    yes
C141 . C147 . H1471 . 109.4    no
C145 . C147 . H1471 . 109.3    no
C141 . C147 . H1472 . 109.5    no
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C145 . C147 . H1472 . 109.4    no
H1471 . C147 . H1472 . 109.6    no
C143 . C148 . C139 . 109.87(9)    yes
C143 . C148 . H1481 . 109.3    no
C139 . C148 . H1481 . 109.4    no
C143 . C148 . H1482 . 109.3    no
C139 . C148 . H1482 . 109.4    no
H1481 . C148 . H1482 . 109.5    no
C122 . C620 . C621 . 111.48(10)    yes
C122 . C620 . C622 . 109.90(10)    yes
C621 . C620 . C622 . 112.18(10)    yes
C122 . C620 . H6201 . 107.7    no
C621 . C620 . H6201 . 107.7    no
C622 . C620 . H6201 . 107.7    no
C620 . C621 . H6211 . 109.4    no
C620 . C621 . H6212 . 109.5    no
H6211 . C621 . H6212 . 109.6    no
C620 . C621 . H6213 . 109.4    no
H6211 . C621 . H6213 . 109.4    no
H6212 . C621 . H6213 . 109.5    no
C620 . C622 . H6221 . 109.4    no
C620 . C622 . H6222 . 109.5    no
H6221 . C622 . H6222 . 109.5    no
C620 . C622 . H6223 . 109.5    no
H6221 . C622 . H6223 . 109.4    no
H6222 . C622 . H6223 . 109.5    no
C126 . C660 . C661 . 112.06(10)    yes
C126 . C660 . C662 . 111.66(10)    yes
C661 . C660 . C662 . 110.55(10)    yes
C126 . C660 . H6601 . 107.5    no
C661 . C660 . H6601 . 107.4    no
C662 . C660 . H6601 . 107.4    no
C660 . C661 . H6611 . 109.4    no
C660 . C661 . H6612 . 109.5    no
H6611 . C661 . H6612 . 109.5    no
C660 . C661 . H6613 . 109.4    no
H6611 . C661 . H6613 . 109.4    no
H6612 . C661 . H6613 . 109.5    no
C660 . C662 . H6621 . 109.5    no
C660 . C662 . H6622 . 109.4    no
H6621 . C662 . H6622 . 109.5    no
C660 . C662 . H6623 . 109.5    no
H6621 . C662 . H6623 . 109.5    no
H6622 . C662 . H6623 . 109.5    no
O301 . Ce13 . N303 . 100.01(17)    yes
O301 . Ce13 . N304 . 110.69(16)    yes
N303 . Ce13 . N304 . 120.86(17)    yes
O301 . Ce13 . N305 . 76.27(16)    yes
N303 . Ce13 . N305 . 101.40(15)    yes
N304 . Ce13 . N305 . 133.80(16)    yes
O301 . Ce13 . N307 . 115.18(15)    yes
N303 . Ce13 . N307 . 117.26(15)    yes
N304 . Ce13 . N307 . 93.76(15)    yes
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N305 . Ce13 . N307 . 47.11(15)    yes
N303 . Si31 . C327 . 109.7(3)    yes
N303 . Si31 . C328 . 113.8(3)    yes
C327 . Si31 . C328 . 105.5(4)    yes
N303 . Si31 . C329 . 115.4(3)    yes
C327 . Si31 . C329 . 104.8(4)    yes
C328 . Si31 . C329 . 106.8(4)    yes
N303 . Si32 . C330 . 113.1(3)    yes
N303 . Si32 . C331 . 114.7(3)    yes
C330 . Si32 . C331 . 105.9(4)    yes
N303 . Si32 . C332 . 109.9(3)    yes
C330 . Si32 . C332 . 108.1(4)    yes
C331 . Si32 . C332 . 104.6(3)    yes
N304 . Si33 . C333 . 109.7(3)    yes
N304 . Si33 . C334 . 115.3(3)    yes
C333 . Si33 . C334 . 104.7(4)    yes
N304 . Si33 . C335 . 112.1(3)    yes
C333 . Si33 . C335 . 107.2(4)    yes
C334 . Si33 . C335 . 107.3(4)    yes
N304 . Si34 . C336 . 112.9(4)    yes
N304 . Si34 . C337 . 114.4(4)    yes
C336 . Si34 . C337 . 105.6(5)    yes
N304 . Si34 . C338 . 109.6(3)    yes
C336 . Si34 . C338 . 107.4(5)    yes
C337 . Si34 . C338 . 106.6(3)    yes
Ce13 . O301 . C308 . 146.6(4)    yes
C301 . N301 . C306 . 110.6(5)    yes
C301 . N301 . C307 . 127.0(5)    yes
C306 . N301 . C307 . 119.7(5)    yes
C301 . N302 . C305 . 109.5(5)    yes
C301 . N302 . C321 . 130.7(5)    yes
C305 . N302 . C321 . 118.5(5)    yes
Ce13 . N303 . Si31 . 119.0(3)    yes
Ce13 . N303 . Si32 . 115.4(3)    yes
Si31 . N303 . Si32 . 125.2(3)    yes
Ce13 . N304 . Si34 . 115.8(3)    yes
Ce13 . N304 . Si33 . 120.9(3)    yes
Si34 . N304 . Si33 . 122.9(3)    yes
Ce13 . N305 . N306 . 101.6(3)    yes
Ce13 . N305 . C301 . 142.9(4)    yes
N306 . N305 . C301 . 114.2(5)    yes
N305 . N306 . N307 . 108.9(5)    yes
Ce13 . N307 . N306 . 101.9(3)    yes
Ce13 . N307 . C339 . 143.6(3)    yes
N306 . N307 . C339 . 113.8(4)    yes
N302 . C301 . N301 . 110.1(5)    yes
N302 . C301 . N305 . 129.7(5)    yes
N301 . C301 . N305 . 120.2(5)    yes
N302 . C305 . C306 . 103.1(5)    yes
N302 . C305 . H3051 . 111.0    no
C306 . C305 . H3051 . 111.1    no
N302 . C305 . H3052 . 111.0    no
C306 . C305 . H3052 . 111.1    no
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H3051 . C305 . H3052 . 109.5    no
C305 . C306 . N301 . 102.4(5)    yes
C305 . C306 . H3061 . 111.2    no
N301 . C306 . H3061 . 111.2    no
C305 . C306 . H3062 . 111.2    no
N301 . C306 . H3062 . 111.2    no
H3061 . C306 . H3062 . 109.5    no
N301 . C307 . C308 . 117.3(5)    yes
N301 . C307 . H3071 . 107.5    no
C308 . C307 . H3071 . 107.5    no
N301 . C307 . H3072 . 107.5    no
C308 . C307 . H3072 . 107.5    no
H3071 . C307 . H3072 . 109.5    no
C307 . C308 . O301 . 107.4(5)    yes
C307 . C308 . C309 . 113.4(5)    yes
O301 . C308 . C309 . 109.7(5)    yes
C307 . C308 . C310 . 106.8(5)    yes
O301 . C308 . C310 . 108.4(5)    yes
C309 . C308 . C310 . 111.0(6)    yes
C308 . C309 . H3091 . 109.4    no
C308 . C309 . H3092 . 109.5    no
H3091 . C309 . H3092 . 109.5    no
C308 . C309 . H3093 . 109.4    no
H3091 . C309 . H3093 . 109.5    no
H3092 . C309 . H3093 . 109.5    no
C308 . C310 . H3101 . 109.5    no
C308 . C310 . H3102 . 109.5    no
H3101 . C310 . H3102 . 109.5    no
C308 . C310 . H3103 . 109.5    no
H3101 . C310 . H3103 . 109.5    no
H3102 . C310 . H3103 . 109.5    no
N302 . C321 . C322 . 119.9(5)    yes
N302 . C321 . C326 . 118.0(6)    yes
C322 . C321 . C326 . 121.9(6)    yes
C321 . C322 . C323 . 118.9(6)    yes
C321 . C322 . C920 . 121.5(6)    yes
C323 . C322 . C920 . 119.5(6)    yes
C322 . C323 . C324 . 120.9(7)    yes
C322 . C323 . H323 . 119.5    no
C324 . C323 . H323 . 119.5    no
C323 . C324 . C325 . 119.7(7)    yes
C323 . C324 . H324 . 120.2    no
C325 . C324 . H324 . 120.1    no
C324 . C325 . C326 . 121.0(7)    yes
C324 . C325 . H325 . 119.5    no
C326 . C325 . H325 . 119.5    no
C321 . C326 . C325 . 117.4(6)    yes
C321 . C326 . C960 . 122.4(7)    yes
C325 . C326 . C960 . 120.2(7)    yes
Si31 . C327 . H3271 . 109.4    no
Si31 . C327 . H3272 . 109.4    no
H3271 . C327 . H3272 . 109.5    no
Si31 . C327 . H3273 . 109.5    no
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H3271 . C327 . H3273 . 109.5    no
H3272 . C327 . H3273 . 109.5    no
Si31 . C328 . H3281 . 109.5    no
Si31 . C328 . H3282 . 109.5    no
H3281 . C328 . H3282 . 109.5    no
Si31 . C328 . H3283 . 109.5    no
H3281 . C328 . H3283 . 109.4    no
H3282 . C328 . H3283 . 109.5    no
Si31 . C329 . H3291 . 109.5    no
Si31 . C329 . H3292 . 109.5    no
H3291 . C329 . H3292 . 109.5    no
Si31 . C329 . H3293 . 109.4    no
H3291 . C329 . H3293 . 109.4    no
H3292 . C329 . H3293 . 109.5    no
Si32 . C330 . H3301 . 109.5    no
Si32 . C330 . H3302 . 109.5    no
H3301 . C330 . H3302 . 109.5    no
Si32 . C330 . H3303 . 109.5    no
H3301 . C330 . H3303 . 109.5    no
H3302 . C330 . H3303 . 109.5    no
Si32 . C331 . H3311 . 109.5    no
Si32 . C331 . H3312 . 109.4    no
H3311 . C331 . H3312 . 109.5    no
Si32 . C331 . H3313 . 109.4    no
H3311 . C331 . H3313 . 109.5    no
H3312 . C331 . H3313 . 109.4    no
Si32 . C332 . H3321 . 109.5    no
Si32 . C332 . H3322 . 109.5    no
H3321 . C332 . H3322 . 109.5    no
Si32 . C332 . H3323 . 109.5    no
H3321 . C332 . H3323 . 109.5    no
H3322 . C332 . H3323 . 109.5    no
Si33 . C333 . H3331 . 109.5    no
Si33 . C333 . H3332 . 109.5    no
H3331 . C333 . H3332 . 109.4    no
Si33 . C333 . H3333 . 109.5    no
H3331 . C333 . H3333 . 109.5    no
H3332 . C333 . H3333 . 109.5    no
Si33 . C334 . H3341 . 109.4    no
Si33 . C334 . H3342 . 109.4    no
H3341 . C334 . H3342 . 109.5    no
Si33 . C334 . H3343 . 109.4    no
H3341 . C334 . H3343 . 109.5    no
H3342 . C334 . H3343 . 109.5    no
Si33 . C335 . H3351 . 109.5    no
Si33 . C335 . H3352 . 109.5    no
H3351 . C335 . H3352 . 109.5    no
Si33 . C335 . H3353 . 109.5    no
H3351 . C335 . H3353 . 109.5    no
H3352 . C335 . H3353 . 109.5    no
Si34 . C336 . H3361 . 109.5    no
Si34 . C336 . H3362 . 109.5    no
H3361 . C336 . H3362 . 109.4    no
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Si34 . C336 . H3363 . 109.5    no
H3361 . C336 . H3363 . 109.5    no
H3362 . C336 . H3363 . 109.4    no
Si34 . C337 . H3371 . 109.5    no
Si34 . C337 . H3372 . 109.5    no
H3371 . C337 . H3372 . 109.5    no
Si34 . C337 . H3373 . 109.4    no
H3371 . C337 . H3373 . 109.4    no
H3372 . C337 . H3373 . 109.4    no
Si34 . C338 . H3381 . 109.5    no
Si34 . C338 . H3382 . 109.5    no
H3381 . C338 . H3382 . 109.5    no
Si34 . C338 . H3383 . 109.4    no
H3381 . C338 . H3383 . 109.4    no
H3382 . C338 . H3383 . 109.5    no
N307 . C339 . C340 . 105.2(5)    yes
N307 . C339 . C346 . 116.6(5)    yes
C340 . C339 . C346 . 109.0(6)    yes
N307 . C339 . C348 . 107.1(5)    yes
C340 . C339 . C348 . 104.4(7)    yes
C346 . C339 . C348 . 113.5(7)    yes
C339 . C340 . C341 . 108.3(6)    yes
C339 . C340 . H3401 . 109.8    no
C341 . C340 . H3401 . 109.6    no
C339 . C340 . H3402 . 109.8    no
C341 . C340 . H3402 . 109.8    no
H3401 . C340 . H3402 . 109.5    no
C340 . C341 . C342 . 106.5(8)    yes
C340 . C341 . C347 . 101.2(7)    yes
C342 . C341 . C347 . 114.3(9)    yes
C340 . C341 . H3411 . 111.5    no
C342 . C341 . H3411 . 111.2    no
C347 . C341 . H3411 . 111.5    no
C341 . C342 . C343 . 116.3(9)    yes
C341 . C342 . H3421 . 107.6    no
C343 . C342 . H3421 . 107.8    no
C341 . C342 . H3422 . 107.8    no
C343 . C342 . H3422 . 108.2    no
H3421 . C342 . H3422 . 109.1    no
C342 . C343 . C344 . 114.2(9)    yes
C342 . C343 . C348 . 101.2(11)    yes
C344 . C343 . C348 . 106.4(10)    yes
C342 . C343 . H3431 . 110.9    no
C344 . C343 . H3431 . 112.1    no
C348 . C343 . H3431 . 111.5    no
C343 . C344 . C345 . 113.9(8)    yes
C343 . C344 . H3441 . 108.1    no
C345 . C344 . H3441 . 108.5    no
C343 . C344 . H3442 . 108.2    no
C345 . C344 . H3442 . 108.7    no
H3441 . C344 . H3442 . 109.4    no
C344 . C345 . C346 . 98.5(9)    yes
C344 . C345 . C347 . 114.7(9)    yes
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C346 . C345 . C347 . 101.0(7)    yes
C344 . C345 . H3451 . 113.6    no
C346 . C345 . H3451 . 113.7    no
C347 . C345 . H3451 . 113.6    no
C339 . C346 . C345 . 112.4(6)    yes
C339 . C346 . H3461 . 108.8    no
C345 . C346 . H3461 . 108.7    no
C339 . C346 . H3462 . 108.9    no
C345 . C346 . H3462 . 108.8    no
H3461 . C346 . H3462 . 109.4    no
C345 . C347 . C341 . 118.6(9)    yes
C345 . C347 . H3471 . 107.2    no
C341 . C347 . H3471 . 107.2    no
C345 . C347 . H3472 . 107.2    no
C341 . C347 . H3472 . 107.0    no
H3471 . C347 . H3472 . 109.5    no
C339 . C348 . C343 . 108.9(7)    yes
C339 . C348 . H3481 . 109.7    no
C343 . C348 . H3481 . 109.9    no
C339 . C348 . H3482 . 109.7    no
C343 . C348 . H3482 . 109.3    no
H3481 . C348 . H3482 . 109.3    no
C322 . C920 . C921 . 110.4(6)    yes
C322 . C920 . C922 . 111.5(6)    yes
C921 . C920 . C922 . 110.6(6)    yes
C322 . C920 . H9201 . 108.1    no
C921 . C920 . H9201 . 108.0    no
C922 . C920 . H9201 . 108.1    no
C920 . C921 . H9211 . 109.5    no
C920 . C921 . H9212 . 109.5    no
H9211 . C921 . H9212 . 109.5    no
C920 . C921 . H9213 . 109.4    no
H9211 . C921 . H9213 . 109.5    no
H9212 . C921 . H9213 . 109.4    no
C920 . C922 . H9221 . 109.4    no
C920 . C922 . H9222 . 109.5    no
H9221 . C922 . H9222 . 109.4    no
C920 . C922 . H9223 . 109.5    no
H9221 . C922 . H9223 . 109.4    no
H9222 . C922 . H9223 . 109.6    no
C326 . C960 . C961 . 111.5(7)    yes
C326 . C960 . C962 . 111.9(7)    yes
C961 . C960 . C962 . 115.8(10)    yes
C326 . C960 . H9601 . 105.6    no
C961 . C960 . H9601 . 105.6    no
C962 . C960 . H9601 . 105.6    no
C960 . C961 . H9611 . 109.4    no
C960 . C961 . H9612 . 109.5    no
H9611 . C961 . H9612 . 109.6    no
C960 . C961 . H9613 . 109.4    no
H9611 . C961 . H9613 . 109.4    no
H9612 . C961 . H9613 . 109.6    no
C960 . C962 . H9621 . 109.5    no
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C960 . C962 . H9622 . 109.5    no
H9621 . C962 . H9622 . 109.7    no
C960 . C962 . H9623 . 109.3    no
H9621 . C962 . H9623 . 109.4    no
H9622 . C962 . H9623 . 109.4    no



data_po9003

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 'C34 H74 N5 O Si5 U'
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 'H'  'H'   0.0000   0.0000
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 'Si'  'Si'   0.0817   0.0704
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 'U'  'U'  -9.6767   9.6646
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 'x, y, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

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_cell_length_b                    21.9206(17)
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_cell_length_c                     17.4680(14)
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_cell_angle_gamma                  90.00
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_exptl_crystal_F_000               1932
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_exptl_absorpt_process_details     SADABS

_exptl_special_details
;
 Tmax/Tmin(RR) > 1.10
 SADABS corrects for all systematic errors that lead
 to disparities in the intensities of symmetry-equivalent
 data. These may include absorption by the
 mount, crystal decay, changes in the volume of the
 crystal illuminated, etc. The presence of heavy atoms (U, Si)
 is noted.

 Large Non-Solvent    C     Ueq(max)/Ueq(min) ...3.80  Ratio
reported
 is a a consequence of disorder within the SiMe3 groups
present
 within the structure.

 Check Low       Ueq as Compared to Neighbors for C260
;

_diffrn_ambient_temperature        150(2)
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DETECTOR'
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_diffrn_reflns_number             36740
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_diffrn_reflns_av_sigmaI/netI     0.0469
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_diffrn_reflns_limit_k_min        -27
_diffrn_reflns_limit_k_max        25
_diffrn_reflns_limit_l_min        -21
_diffrn_reflns_limit_l_max        21
_diffrn_reflns_theta_min          1.86
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_reflns_number_total              9236
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_computing_cell_refinement        'SAINT (Siemans, 1995)'
_computing_data_reduction         'SAINT (Siemans, 1995)'
_computing_structure_solution     'SIR-92 (Giacovazzo, 1994)'
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1997)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0513P)^2^+2.8517P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
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_refine_ls_wR_factor_ref          0.0987
_refine_ls_wR_factor_gt           0.0922
_refine_ls_goodness_of_fit_ref    1.082
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C1 C 0.4615(3) 0.2176(2) 0.5283(3) 0.0241(9) Uani 1 1 d . . .
C5 C 0.5664(6) 0.1502(3) 0.4551(3) 0.0519(16) Uani 1 1 d . . .
H5A H 0.5532 0.1067 0.4420 0.062 Uiso 1 1 calc R . .
H5B H 0.6485 0.1592 0.4547 0.062 Uiso 1 1 calc R . .
C6 C 0.4976(4) 0.1914(2) 0.4006(3) 0.0350(11) Uani 1 1 d . . .
H6A H 0.5463 0.2131 0.3657 0.042 Uiso 1 1 calc R . .
H6B H 0.4383 0.1684 0.3700 0.042 Uiso 1 1 calc R . .
C7 C 0.3944(4) 0.2902(2) 0.4255(3) 0.0332(11) Uani 1 1 d . . .
H7A H 0.3182 0.2939 0.4454 0.040 Uiso 1 1 calc R . .
H7B H 0.3843 0.2878 0.3688 0.040 Uiso 1 1 calc R . .
C8 C 0.4633(4) 0.3466(2) 0.4479(3) 0.0356(12) Uani 1 1 d . . .
C9 C 0.4067(6) 0.4028(3) 0.4109(3) 0.0594(18) Uani 1 1 d . . .
H9A H 0.3303 0.4074 0.4287 0.089 Uiso 1 1 calc R . .
H9B H 0.4015 0.3981 0.3549 0.089 Uiso 1 1 calc R . .
H9C H 0.4518 0.4391 0.4251 0.089 Uiso 1 1 calc R . .
C10 C 0.5856(4) 0.3420(3) 0.4263(3) 0.0460(14) Uani 1 1 d . .
.
H10A H 0.6273 0.3787 0.4438 0.069 Uiso 1 1 calc R . .
H10B H 0.5869 0.3385 0.3704 0.069 Uiso 1 1 calc R . .
H10C H 0.6214 0.3059 0.4507 0.069 Uiso 1 1 calc R . .
C21 C 0.5356(4) 0.1200(2) 0.5903(3) 0.0267(10) Uani 1 1 d . .
.
```

```
C22 C 0.6419(4) 0.1125(2) 0.6300(3) 0.0288(10) Uani 1 1 d . .
.
C23 C 0.6536(4) 0.0662(2) 0.6849(3) 0.0371(12) Uani 1 1 d . .
.
H23 H 0.7247 0.0604 0.7129 0.045 Uiso 1 1 calc R . .
C24 C 0.5637(4) 0.0288(3) 0.6992(3) 0.0429(14) Uani 1 1 d . .
.
H24 H 0.5723 -0.0013 0.7384 0.051 Uiso 1 1 calc R . .
C25 C 0.4608(4) 0.0348(2) 0.6570(3) 0.0417(13) Uani 1 1 d . .
.
H25 H 0.4013 0.0068 0.6649 0.050 Uiso 1 1 calc R . .
C26 C 0.4430(4) 0.0810(2) 0.6031(3) 0.0316(11) Uani 1 1 d . .
.
C27 C 0.3168(4) 0.4101(3) 0.7911(3) 0.0401(13) Uani 1 1 d . .
.
H27A H 0.2816 0.4450 0.7638 0.060 Uiso 1 1 calc R . .
H27B H 0.2982 0.4111 0.8449 0.060 Uiso 1 1 calc R . .
H27C H 0.2882 0.3722 0.7672 0.060 Uiso 1 1 calc R . .
C28 C 0.5133(5) 0.4967(3) 0.7809(4) 0.0573(17) Uani 1 1 d . .
.
H28A H 0.5960 0.5010 0.7836 0.086 Uiso 1 1 calc R . .
H28B H 0.4829 0.5186 0.8240 0.086 Uiso 1 1 calc R . .
H28C H 0.4809 0.5139 0.7325 0.086 Uiso 1 1 calc R . .
C29 C 0.5415(5) 0.3865(4) 0.8803(3) 0.067(2) Uani 1 1 d . . .
H29A H 0.5348 0.3420 0.8831 0.101 Uiso 1 1 calc R . .
H29B H 0.5027 0.4052 0.9222 0.101 Uiso 1 1 calc R . .
H29C H 0.6218 0.3981 0.8847 0.101 Uiso 1 1 calc R . .
C30 C 0.6894(4) 0.4389(3) 0.6203(4) 0.0470(14) Uani 1 1 d . .
.
H30A H 0.6352 0.4397 0.5753 0.070 Uiso 1 1 calc R . .
H30B H 0.7664 0.4335 0.6038 0.070 Uiso 1 1 calc R . .
H30C H 0.6851 0.4774 0.6485 0.070 Uiso 1 1 calc R . .
C31 C 0.6807(4) 0.3007(3) 0.6342(4) 0.0446(14) Uani 1 1 d . .
.
H31A H 0.6483 0.2672 0.6628 0.067 Uiso 1 1 calc R . .
H31B H 0.7625 0.2944 0.6321 0.067 Uiso 1 1 calc R . .
H31C H 0.6447 0.3018 0.5820 0.067 Uiso 1 1 calc R . .
C32 C 0.7630(4) 0.3760(3) 0.7673(4) 0.0522(16) Uani 1 1 d . .
.
H32A H 0.7545 0.4136 0.7968 0.078 Uiso 1 1 calc R . .
H32B H 0.8393 0.3745 0.7486 0.078 Uiso 1 1 calc R . .
H32C H 0.7517 0.3406 0.8002 0.078 Uiso 1 1 calc R . .
C33 C 0.0828(4) 0.4499(3) 0.6486(3) 0.0421(13) Uani 1 1 d . .
.
H33A H 0.0079 0.4322 0.6347 0.063 Uiso 1 1 calc R . .
H33B H 0.0782 0.4944 0.6448 0.063 Uiso 1 1 calc R . .
H33C H 0.1074 0.4383 0.7013 0.063 Uiso 1 1 calc R . .
C34 C 0.1175(4) 0.4332(3) 0.4822(3) 0.0444(13) Uani 1 1 d . .
.
H34A H 0.1514 0.4059 0.4457 0.067 Uiso 1 1 calc R . .
H34B H 0.1285 0.4757 0.4667 0.067 Uiso 1 1 calc R . .
H34C H 0.0361 0.4246 0.4827 0.067 Uiso 1 1 calc R . .
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C35 C 0.3149(4) 0.4720(2) 0.5910(3) 0.0374(12) Uani 1 1 d . .
.
H35A H 0.3543 0.4663 0.6417 0.056 Uiso 1 1 calc R . .
H35B H 0.2904 0.5145 0.5851 0.056 Uiso 1 1 calc R . .
H35C H 0.3664 0.4619 0.5512 0.056 Uiso 1 1 calc R . .
C36 C 0.0811(4) 0.2828(3) 0.7093(3) 0.0444(14) Uani 1 1 d . .
.
H36A H 0.1469 0.2664 0.7399 0.067 Uiso 1 1 calc R . .
H36B H 0.0173 0.2544 0.7111 0.067 Uiso 1 1 calc R . .
H36C H 0.0600 0.3223 0.7302 0.067 Uiso 1 1 calc R . .
C37 C 0.1621(5) 0.2178(3) 0.5698(4) 0.0546(17) Uani 1 1 d . .
.
H37A H 0.1721 0.2214 0.5148 0.082 Uiso 1 1 calc R . .
H37B H 0.1035 0.1873 0.5781 0.082 Uiso 1 1 calc R . .
H37C H 0.2339 0.2053 0.5967 0.082 Uiso 1 1 calc R . .
C38 C -0.0185(4) 0.3113(3) 0.5516(3) 0.0412(13) Uani 1 1 d . .
.
H38A H -0.0527 0.3474 0.5738 0.062 Uiso 1 1 calc R . .
H38B H -0.0707 0.2767 0.5535 0.062 Uiso 1 1 calc R . .
H38C H -0.0035 0.3197 0.4981 0.062 Uiso 1 1 calc R . .
C39 C 0.3301(4) 0.2584(3) 0.8715(3) 0.0412(13) Uani 1 1 d . .
.
H39A H 0.3708 0.2969 0.8813 0.062 Uiso 1 1 calc R . .
H39B H 0.3333 0.2340 0.9185 0.062 Uiso 1 1 calc R . .
H39C H 0.2507 0.2670 0.8550 0.062 Uiso 1 1 calc R . .
C40 C 0.3276(7) 0.1392(3) 0.7903(4) 0.083(3) Uani 1 1 d . . .
H40A H 0.2474 0.1440 0.7729 0.124 Uiso 1 1 calc R . .
H40B H 0.3333 0.1207 0.8415 0.124 Uiso 1 1 calc R . .
H40C H 0.3650 0.1129 0.7545 0.124 Uiso 1 1 calc R . .
C41 C 0.5533(5) 0.2053(4) 0.8198(4) 0.078(3) Uani 1 1 d . . .
H41A H 0.5857 0.1785 0.7821 0.117 Uiso 1 1 calc R . .
H41B H 0.5647 0.1871 0.8710 0.117 Uiso 1 1 calc R . .
H41C H 0.5909 0.2452 0.8195 0.117 Uiso 1 1 calc R . .
C220 C 0.7465(4) 0.1480(2) 0.6115(3) 0.0341(11) Uani 1 1 d . .
.
H220 H 0.7211 0.1859 0.5834 0.041 Uiso 1 1 calc R . .
C221 C 0.8192(5) 0.1669(3) 0.6833(4) 0.0484(15) Uani 1 1 d . .
.
H22A H 0.7712 0.1864 0.7197 0.073 Uiso 1 1 calc R . .
H22B H 0.8779 0.1956 0.6691 0.073 Uiso 1 1 calc R . .
H22C H 0.8554 0.1307 0.7071 0.073 Uiso 1 1 calc R . .
C222 C 0.8218(4) 0.1116(3) 0.5598(4) 0.0483(15) Uani 1 1 d . .
.
H22D H 0.8482 0.0743 0.5864 0.072 Uiso 1 1 calc R . .
H22E H 0.8874 0.1364 0.5481 0.072 Uiso 1 1 calc R . .
H22F H 0.7781 0.1008 0.5121 0.072 Uiso 1 1 calc R . .
C260 C 0.3343(4) 0.0820(2) 0.5518(3) 0.0357(12) Uani 1 1 d . .
.
H260 H 0.3243 0.1243 0.5311 0.043 Uiso 1 1 calc R . .
C261 C 0.2303(5) 0.0667(4) 0.5931(5) 0.078(3) Uani 1 1 d . . .
H26A H 0.2304 0.0230 0.6053 0.117 Uiso 1 1 calc R . .
H26B H 0.1621 0.0766 0.5603 0.117 Uiso 1 1 calc R . .
H26C H 0.2306 0.0903 0.6407 0.117 Uiso 1 1 calc R . .
```

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C262 C 0.3434(6) 0.0387(4) 0.4827(5) 0.092(3) Uani 1 1 d . . .
H26D H 0.4085 0.0506 0.4541 0.138 Uiso 1 1 calc R . .
H26E H 0.2737 0.0414 0.4489 0.138 Uiso 1 1 calc R . .
H26F H 0.3537 -0.0033 0.5011 0.138 Uiso 1 1 calc R . .
N1 N 0.4475(3) 0.23388(18) 0.4549(2) 0.0271(8) Uani 1 1 d . .
.
N2 N 0.5229(3) 0.16536(18) 0.5305(2) 0.0256(8) Uani 1 1 d . .
.
N3 N 0.5162(3) 0.37423(19) 0.7078(2) 0.0314(9) Uani 1 1 d . .
.
N4 N 0.2255(3) 0.34542(18) 0.6007(2) 0.0247(8) Uani 1 1 d . .
.
N5 N 0.3815(3) 0.25248(19) 0.7071(2) 0.0303(9) Uani 1 1 d . .
.
O1 O 0.4619(3) 0.35120(15) 0.52979(18) 0.0306(7) Uani 1 1 d .
. .
Si1 Si 0.47485(11) 0.41390(8) 0.78611(9) 0.0388(4) Uani 1 1 d
. . .
Si2 Si 0.65474(10) 0.37480(7) 0.68353(9) 0.0345(3) Uani 1 1 d
. . .
Si3 Si 0.18785(11) 0.42060(6) 0.58125(8) 0.0300(3) Uani 1 1 d
. . .
Si4 Si 0.11791(10) 0.29263(7) 0.60744(8) 0.0278(3) Uani 1 1 d
. . .
Si5 Si 0.39763(12) 0.21524(8) 0.79442(9) 0.0390(4) Uani 1 1 d
. . .
U1 U 0.407138(12) 0.310246(8) 0.627275(9) 0.02315(7) Uani 1 1
d . . .

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C5 0.089(4) 0.036(3) 0.032(3) 0.002(3) 0.012(3) 0.022(3)
C6 0.046(3) 0.033(3) 0.026(3) -0.004(2) 0.004(2) 0.001(2)
C7 0.037(2) 0.036(3) 0.026(3) 0.007(2) 0.004(2) 0.011(2)
C8 0.055(3) 0.022(3) 0.031(3) 0.010(2) 0.016(2) 0.009(2)
C9 0.094(5) 0.042(4) 0.044(4) 0.018(3) 0.021(3) 0.026(3)
C10 0.058(3) 0.036(3) 0.048(3) 0.001(3) 0.030(3) -0.005(3)
C21 0.037(2) 0.017(2) 0.026(2) -0.001(2) 0.0058(19) 0.0039(18)
C22 0.035(2) 0.021(3) 0.030(3) 0.002(2) 0.0056(19) 0.0059(19)
C23 0.037(2) 0.036(3) 0.039(3) 0.008(3) 0.007(2) 0.009(2)
C24 0.046(3) 0.035(3) 0.050(3) 0.019(3) 0.017(2) 0.019(2)
C25 0.046(3) 0.019(3) 0.063(4) 0.014(3) 0.021(3) 0.006(2)
C26 0.032(2) 0.024(3) 0.039(3) 0.001(2) 0.005(2) 0.0052(19)
C27 0.040(3) 0.041(3) 0.040(3) -0.009(3) 0.006(2) -0.006(2)
C28 0.059(4) 0.048(4) 0.067(4) -0.024(3) 0.013(3) -0.020(3)
C29 0.049(3) 0.112(7) 0.039(4) 0.009(4) -0.004(3) -0.024(4)
```

```
C30 0.041(3) 0.033(3) 0.067(4) 0.014(3) 0.009(3) -0.003(2)
C31 0.035(3) 0.040(3) 0.060(4) 0.007(3) 0.009(2) 0.009(2)
C32 0.032(3) 0.052(4) 0.072(4) 0.009(3) -0.006(3) -0.004(2)
C33 0.039(3) 0.040(3) 0.047(3) -0.007(3) 0.003(2) 0.013(2)
C34 0.049(3) 0.034(3) 0.049(3) 0.012(3) -0.003(2) 0.005(2)
C35 0.043(3) 0.021(3) 0.048(3) 0.001(2) 0.002(2) -0.001(2)
C36 0.037(3) 0.060(4) 0.037(3) 0.009(3) 0.003(2) -0.015(3)
C37 0.043(3) 0.033(3) 0.087(5) -0.020(3) 0.002(3) -0.004(2)
C38 0.026(2) 0.053(4) 0.044(3) 0.000(3) -0.002(2) -0.006(2)
C39 0.038(3) 0.054(4) 0.032(3) 0.002(3) 0.007(2) 0.003(2)
C40 0.144(7) 0.030(4) 0.082(5) 0.013(4) 0.071(5) 0.010(4)
C41 0.057(4) 0.130(7) 0.049(4) 0.040(4) 0.019(3) 0.052(4)
C220 0.034(2) 0.026(3) 0.042(3) 0.001(2) 0.002(2) 0.002(2)
C221 0.045(3) 0.037(3) 0.061(4) 0.003(3) -0.009(3) 0.000(3)
C222 0.043(3) 0.043(4) 0.061(4) 0.003(3) 0.018(3) 0.002(2)
C260 0.033(2) 0.019(3) 0.055(3) 0.005(2) 0.002(2) 0.0033(19)
C261 0.032(3) 0.074(5) 0.128(7) 0.064(5) 0.002(3) 0.000(3)
C262 0.071(4) 0.071(5) 0.128(7) -0.058(5) -0.043(5) 0.030(4)
N1 0.0340(19) 0.025(2) 0.022(2) 0.0005(17) 0.0026(15)
0.0002(16)
N2 0.0347(19) 0.0173(19) 0.025(2) 0.0013(17) 0.0055(16)
0.0013(16)
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0.0023(16)
N4 0.0268(17) 0.022(2) 0.026(2) 0.0017(17) 0.0044(15) -
0.0007(15)
N5 0.0345(19) 0.030(2) 0.027(2) 0.0048(19) 0.0033(16)
0.0023(17)
O1 0.0378(17) 0.0237(18) 0.0319(18) 0.0081(15) 0.0134(14)
0.0051(14)
Si1 0.0349(7) 0.0459(10) 0.0354(8) -0.0066(7) 0.0014(6) -
0.0122(6)
Si2 0.0248(6) 0.0256(8) 0.0528(9) 0.0092(7) 0.0015(6) -
0.0012(5)
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0.0064(5)
Si4 0.0258(6) 0.0299(7) 0.0277(7) -0.0016(6) 0.0023(5) -
0.0024(5)
Si5 0.0453(8) 0.0404(9) 0.0330(8) 0.0141(7) 0.0149(6)
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0.00190(6)

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;
 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
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 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds involving
l.s. planes.
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C220 C222 1.535(7) . ?
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N3 Si1 1.720(4) . ?
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_exptl_absorpt_correction_type     'multi-scan'
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_exptl_absorpt_correction_T_max    0.4324
_exptl_absorpt_process_details     SADABS

_exptl_special_details
;
A alert - Large Non-Solvent C Ueq(max)/Ueq(min) = 5.03 Ratio

Large thermal ellipsoid associated with C31, part of
an SiMe3 group. The thermal rotation about the Si atom
is not unusual and results in a large ADP for C31.
Modelling the disorder was not successful

This test expects that all carbon atoms in a structure
to have approximately the same thermal motion and calculates
the ratio of the lowest C Ueq with the highest C Ueq.
The environment of the C atom is not really accounted for.

Hence this alert is a result of comparing the thermal
parameters
of an SiMe3 carbon which is free to rotate with those of
a more rigidly held carbon, such as those in the phenyl ring.
;

_diffrn_ambient_temperature        150(2)
_diffrn_radiation_wavelength       0.71073
_diffrn_radiation_type             MoK\a
_diffrn_radiation_source           'fine-focus sealed tube'
_diffrn_radiation_monochromator    graphite
_diffrn_measurement_device_type    'Bruker SMART APEX CCD area
detector'
_diffrn_measurement_method         'omega and phi scans'
_diffrn_detector_area_resol_mean   ?
_diffrn_standards_number           ?
_diffrn_standards_interval_count   ?
_diffrn_standards_interval_time    ?
_diffrn_standards_decay_%          ?
_diffrn_reflns_number              89929
_diffrn_reflns_av_R_equivalents    0.0291
_diffrn_reflns_av_sigmaI/netI      0.0303
_diffrn_reflns_limit_h_min         -15
_diffrn_reflns_limit_h_max         15
_diffrn_reflns_limit_k_min         -24
_diffrn_reflns_limit_k_max         29
_diffrn_reflns_limit_l_min         -32
_diffrn_reflns_limit_l_max         32
_diffrn_reflns_theta_min           1.75
_diffrn_reflns_theta_max           29.80
_reflns_number_total               26643
_reflns_number_gt                  22650
```

```
_reflns_threshold_expression      >2\s(I)

_computing_data_collection        'SMART (Siemens, 1993)'
_computing_cell_refinement        'SAINT (Siemens, 1995)'
_computing_data_reduction         'SAINT (Siemens, 1995)'
_computing_structure_solution     'SIR-92 (Giacovazzo, 1994)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
2008)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   'enCIFer (Allen et al.,
2004)'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0282P)^2^+2.4725P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     riding
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          26643
_refine_ls_number_parameters      1037
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0338
_refine_ls_R_factor_gt            0.0247
_refine_ls_wR_factor_ref          0.0594
_refine_ls_wR_factor_gt           0.0560
_refine_ls_goodness_of_fit_ref    1.041
_refine_ls_restrained_S_all       1.041
_refine_ls_shift/su_max           0.004
_refine_ls_shift/su_mean          0.000
```

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loop_
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
C1 C 0.0133(2) 0.33710(12) 0.78134(10) 0.0200(4) Uani 1 1 d .
. .
C5 C -0.1242(2) 0.37011(15) 0.73011(12) 0.0319(6) Uani 1 1 d .
. .
H5A H -0.2088 0.3428 0.7250 0.038 Uiso 1 1 calc R . .
H5B H -0.1144 0.3904 0.6990 0.038 Uiso 1 1 calc R . .
C6 C -0.0852(2) 0.42711(14) 0.79586(12) 0.0313(6) Uani 1 1 d .
. .
H6A H -0.0308 0.4707 0.7963 0.038 Uiso 1 1 calc R . .
H6B H -0.1552 0.4391 0.8177 0.038 Uiso 1 1 calc R . .
C7 C 0.0132(2) 0.42549(13) 0.89056(11) 0.0259(5) Uani 1 1 d .
. .
H7A H -0.0161 0.3901 0.9076 0.031 Uiso 1 1 calc R . .
H7B H -0.0267 0.4643 0.9097 0.031 Uiso 1 1 calc R . .
C8 C 0.1484(2) 0.45573(12) 0.90956(11) 0.0245(5) Uani 1 1 d .
. .
C9 C 0.1749(3) 0.49626(14) 0.98060(12) 0.0350(6) Uani 1 1 d .
. .
H9A H 0.1348 0.4658 1.0001 0.052 Uiso 1 1 calc R . .
H9B H 0.1449 0.5388 0.9943 0.052 Uiso 1 1 calc R . .
H9C H 0.2619 0.5101 0.9930 0.052 Uiso 1 1 calc R . .
C10 C 0.2030(3) 0.50413(14) 0.87889(13) 0.0361(6) Uani 1 1 d .
. .
H10A H 0.2896 0.5231 0.8928 0.054 Uiso 1 1 calc R . .
H10B H 0.1648 0.5434 0.8907 0.054 Uiso 1 1 calc R . .
H10C H 0.1899 0.4771 0.8334 0.054 Uiso 1 1 calc R . .
C11 C 0.4029(2) 0.24458(12) 0.24978(10) 0.0197(4) Uani 1 1 d .
. .
C15 C 0.2706(2) 0.24793(14) 0.17393(11) 0.0286(5) Uani 1 1 d .
. .
H15A H 0.2085 0.2030 0.1500 0.034 Uiso 1 1 calc R . .
H15B H 0.2825 0.2769 0.1497 0.034 Uiso 1 1 calc R . .
C16 C 0.2372(2) 0.28799(14) 0.23767(11) 0.0275(5) Uani 1 1 d .
. .
H16A H 0.2588 0.3398 0.2497 0.033 Uiso 1 1 calc R . .
H16B H 0.1503 0.2716 0.2398 0.033 Uiso 1 1 calc R . .
C17 C 0.2865(2) 0.28624(14) 0.34123(11) 0.0262(5) Uani 1 1 d .
. .
H17A H 0.2762 0.2429 0.3484 0.031 Uiso 1 1 calc R . .
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H17B H 0.2096 0.3001 0.3469 0.031 Uiso 1 1 calc R . .
C18 C 0.3849(2) 0.34562(13) 0.39035(11) 0.0280(5) Uani 1 1 d .
. .
C19 C 0.3452(3) 0.36156(17) 0.45515(12) 0.0412(7) Uani 1 1 d .
. .
H19A H 0.3270 0.3181 0.4617 0.062 Uiso 1 1 calc R . .
H19B H 0.2731 0.3793 0.4583 0.062 Uiso 1 1 calc R . .
H19C H 0.4100 0.3976 0.4870 0.062 Uiso 1 1 calc R . .
C21 C -0.0298(2) 0.27511(13) 0.66318(11) 0.0223(5) Uani 1 1 d
. . .
C22 C 0.0697(2) 0.29155(13) 0.63336(11) 0.0249(5) Uani 1 1 d .
. .
C23 C 0.0737(3) 0.24464(15) 0.57230(12) 0.0338(6) Uani 1 1 d .
. .
H23 H 0.1412 0.2543 0.5517 0.041 Uiso 1 1 calc R . .
C24 C -0.0185(3) 0.18431(15) 0.54109(12) 0.0379(7) Uani 1 1 d
. . .
H24 H -0.0134 0.1523 0.4997 0.046 Uiso 1 1 calc R . .
C25 C -0.1174(3) 0.17059(14) 0.57000(12) 0.0354(6) Uani 1 1 d
. . .
H25 H -0.1813 0.1295 0.5477 0.043 Uiso 1 1 calc R . .
C26 C -0.1269(2) 0.21538(13) 0.63142(12) 0.0275(5) Uani 1 1 d
. . .
C27 C 0.5458(3) 0.30532(17) 0.95679(14) 0.0426(7) Uani 1 1 d .
. .
H27A H 0.6173 0.3316 0.9462 0.064 Uiso 1 1 calc R . .
H27B H 0.5694 0.2752 0.9744 0.064 Uiso 1 1 calc R . .
H27C H 0.5080 0.3389 0.9875 0.064 Uiso 1 1 calc R . .
C28 C 0.3176(3) 0.18571(15) 0.90267(15) 0.0426(7) Uani 1 1 d .
. .
H28A H 0.2765 0.2128 0.9367 0.064 Uiso 1 1 calc R . .
H28B H 0.3551 0.1560 0.9155 0.064 Uiso 1 1 calc R . .
H28C H 0.2591 0.1554 0.8655 0.064 Uiso 1 1 calc R . .
C29 C 0.5221(3) 0.19205(19) 0.82620(16) 0.0560(9) Uani 1 1 d .
. .
H29A H 0.4794 0.1728 0.7840 0.084 Uiso 1 1 calc R . .
H29B H 0.5289 0.1529 0.8364 0.084 Uiso 1 1 calc R . .
H29C H 0.6027 0.2212 0.8280 0.084 Uiso 1 1 calc R . .
C30 C 0.5071(3) 0.45196(19) 0.91355(19) 0.0702(12) Uani 1 1 d
. . .
H30A H 0.4347 0.4661 0.9294 0.105 Uiso 1 1 calc R . .
H30B H 0.5561 0.4880 0.9020 0.105 Uiso 1 1 calc R . .
H30C H 0.5538 0.4474 0.9460 0.105 Uiso 1 1 calc R . .
C31 C 0.6040(3) 0.3454(3) 0.8101(3) 0.0950(18) Uani 1 1 d . .
.
H31A H 0.6578 0.3439 0.8418 0.142 Uiso 1 1 calc R . .
H31B H 0.6441 0.3826 0.7976 0.142 Uiso 1 1 calc R . .
H31C H 0.5837 0.2994 0.7736 0.142 Uiso 1 1 calc R . .
C32 C 0.3797(3) 0.37743(18) 0.78198(14) 0.0442(7) Uani 1 1 d .
. .
H32A H 0.3504 0.3317 0.7456 0.066 Uiso 1 1 calc R . .
H32B H 0.4338 0.4110 0.7695 0.066 Uiso 1 1 calc R . .
H32C H 0.3113 0.3961 0.7986 0.066 Uiso 1 1 calc R . .
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C33 C 0.0863(3) 0.23316(16) 1.02256(13) 0.0374(6) Uani 1 1 d .
. .
H33A H 0.0021 0.2078 1.0196 0.056 Uiso 1 1 calc R . .
H33B H 0.1205 0.2590 1.0666 0.056 Uiso 1 1 calc R . .
H33C H 0.1322 0.1990 1.0003 0.056 Uiso 1 1 calc R . .
C34 C 0.2514(2) 0.35625(14) 1.01032(12) 0.0309(5) Uani 1 1 d .
. .
H34A H 0.3043 0.3318 1.0210 0.046 Uiso 1 1 calc R . .
H34B H 0.2526 0.4004 1.0467 0.046 Uiso 1 1 calc R . .
H34C H 0.2795 0.3673 0.9756 0.046 Uiso 1 1 calc R . .
C35 C -0.0114(3) 0.35261(15) 1.02745(12) 0.0343(6) Uani 1 1 d
. . .
H35A H -0.0316 0.3772 1.0031 0.052 Uiso 1 1 calc R . .
H35B H 0.0276 0.3876 1.0691 0.052 Uiso 1 1 calc R . .
H35C H -0.0851 0.3216 1.0314 0.052 Uiso 1 1 calc R . .
C36 C -0.1936(2) 0.18947(17) 0.92510(14) 0.0386(7) Uani 1 1 d
. . .
H36A H -0.1650 0.1873 0.9634 0.058 Uiso 1 1 calc R . .
H36B H -0.2627 0.1488 0.9026 0.058 Uiso 1 1 calc R . .
H36C H -0.2180 0.2336 0.9359 0.058 Uiso 1 1 calc R . .
C37 C -0.0331(3) 0.09994(14) 0.85334(14) 0.0364(6) Uani 1 1 d
. . .
H37A H 0.0239 0.0934 0.8223 0.055 Uiso 1 1 calc R . .
H37B H -0.1070 0.0614 0.8360 0.055 Uiso 1 1 calc R . .
H37C H 0.0029 0.0994 0.8909 0.055 Uiso 1 1 calc R . .
C38 C -0.1385(2) 0.18837(15) 0.80262(12) 0.0311(6) Uani 1 1 d
. . .
H38A H -0.1614 0.2330 0.8141 0.047 Uiso 1 1 calc R . .
H38B H -0.2102 0.1484 0.7841 0.047 Uiso 1 1 calc R . .
H38C H -0.0802 0.1845 0.7723 0.047 Uiso 1 1 calc R . .
C39 C 0.1689(2) 0.14323(11) 0.70482(10) 0.0189(4) Uani 1 1 d .
. .
C40 C 0.2127(2) 0.09054(13) 0.72286(11) 0.0275(5) Uani 1 1 d .
. .
H40A H 0.1520 0.0714 0.7450 0.033 Uiso 1 1 calc R . .
H40B H 0.2888 0.1152 0.7515 0.033 Uiso 1 1 calc R . .
C41 C 0.2331(3) 0.02930(14) 0.66410(12) 0.0326(6) Uani 1 1 d .
. .
H41 H 0.2620 -0.0045 0.6765 0.039 Uiso 1 1 calc R . .
C42 C 0.3267(3) 0.05828(15) 0.63026(13) 0.0369(6) Uani 1 1 d .
. .
H42A H 0.3407 0.0187 0.5928 0.044 Uiso 1 1 calc R . .
H42B H 0.4037 0.0833 0.6581 0.044 Uiso 1 1 calc R . .
C43 C 0.2823(3) 0.10970(16) 0.61084(13) 0.0376(6) Uani 1 1 d .
. .
H43 H 0.3438 0.1288 0.5885 0.045 Uiso 1 1 calc R . .
C44 C 0.2626(2) 0.17112(13) 0.66955(12) 0.0292(5) Uani 1 1 d .
. .
H44A H 0.3397 0.1967 0.6972 0.035 Uiso 1 1 calc R . .
H44B H 0.2350 0.2050 0.6574 0.035 Uiso 1 1 calc R . .
C45 C 0.1147(3) -0.00954(14) 0.62107(14) 0.0404(7) Uani 1 1 d
. . .
H45A H 0.0538 -0.0290 0.6429 0.048 Uiso 1 1 calc R . .
```

```
H45B H 0.1267 -0.0496 0.5834 0.048 Uiso 1 1 calc R . .
C46 C 0.0707(3) 0.04235(15) 0.60212(12) 0.0381(7) Uani 1 1 d .
. .
H46 H -0.0069 0.0171 0.5739 0.046 Uiso 1 1 calc R . .
C47 C 0.0512(2) 0.10365(13) 0.66097(11) 0.0283(5) Uani 1 1 d .
. .
H47A H 0.0213 0.1369 0.6489 0.034 Uiso 1 1 calc R . .
H47B H -0.0103 0.0847 0.6829 0.034 Uiso 1 1 calc R . .
C48 C 0.1646(3) 0.07124(17) 0.56812(12) 0.0447(8) Uani 1 1 d .
. .
H48A H 0.1769 0.0317 0.5301 0.054 Uiso 1 1 calc R . .
H48B H 0.1363 0.1044 0.5552 0.054 Uiso 1 1 calc R . .
C71 C 0.4547(2) 0.20757(13) 0.13835(10) 0.0221(5) Uani 1 1 d .
. .
C72 C 0.5593(2) 0.25441(13) 0.13355(11) 0.0255(5) Uani 1 1 d .
. .
C73 C 0.6183(2) 0.22952(15) 0.08115(12) 0.0325(6) Uani 1 1 d .
. .
H73 H 0.6896 0.2599 0.0775 0.039 Uiso 1 1 calc R . .
C74 C 0.5767(2) 0.16223(15) 0.03442(12) 0.0353(6) Uani 1 1 d .
. .
H74 H 0.6187 0.1466 -0.0010 0.042 Uiso 1 1 calc R . .
C75 C 0.4740(2) 0.11769(15) 0.03913(11) 0.0317(6) Uani 1 1 d .
. .
H75 H 0.4454 0.0713 0.0065 0.038 Uiso 1 1 calc R . .
C76 C 0.4103(2) 0.13873(13) 0.09075(10) 0.0237(5) Uani 1 1 d .
. .
C77 C 0.8608(3) 0.32479(15) 0.52234(12) 0.0373(6) Uani 1 1 d .
. .
H77A H 0.9137 0.3713 0.5301 0.056 Uiso 1 1 calc R . .
H77B H 0.9001 0.3021 0.5428 0.056 Uiso 1 1 calc R . .
H77C H 0.7848 0.3308 0.5392 0.056 Uiso 1 1 calc R . .
C78 C 0.7523(3) 0.17427(14) 0.42165(12) 0.0335(6) Uani 1 1 d .
. .
H78A H 0.7166 0.1742 0.4591 0.050 Uiso 1 1 calc R . .
H78B H 0.8108 0.1457 0.4122 0.050 Uiso 1 1 calc R . .
H78C H 0.6888 0.1541 0.3863 0.050 Uiso 1 1 calc R . .
C79 C 0.9821(2) 0.26526(18) 0.40853(15) 0.0490(8) Uani 1 1 d .
. .
H79A H 0.9753 0.2506 0.3633 0.073 Uiso 1 1 calc R . .
H79B H 1.0130 0.2314 0.4185 0.073 Uiso 1 1 calc R . .
H79C H 1.0375 0.3127 0.4296 0.073 Uiso 1 1 calc R . .
C80 C 0.7320(3) 0.44766(15) 0.48202(14) 0.0439(7) Uani 1 1 d .
. .
H80A H 0.6454 0.4291 0.4811 0.066 Uiso 1 1 calc R . .
H80B H 0.7476 0.4948 0.4822 0.066 Uiso 1 1 calc R . .
H80C H 0.7748 0.4511 0.5198 0.066 Uiso 1 1 calc R . .
C81 C 0.7234(3) 0.39204(18) 0.34035(15) 0.0489(8) Uani 1 1 d .
. .
H81A H 0.7467 0.3577 0.3029 0.073 Uiso 1 1 calc R . .
H81B H 0.7554 0.4400 0.3432 0.073 Uiso 1 1 calc R . .
H81C H 0.6355 0.3812 0.3378 0.073 Uiso 1 1 calc R . .
```

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C82 C 0.9524(3) 0.42421(19) 0.41869(15) 0.0544(9) Uani 1 1 d .
. .
H82A H 0.9912 0.4247 0.4561 0.082 Uiso 1 1 calc R . .
H82B H 0.9688 0.4728 0.4221 0.082 Uiso 1 1 calc R . .
H82C H 0.9844 0.3949 0.3817 0.082 Uiso 1 1 calc R . .
C83 C 0.4534(3) 0.09619(15) 0.45867(13) 0.0416(7) Uani 1 1 d .
. .
H83A H 0.3949 0.0511 0.4329 0.062 Uiso 1 1 calc R . .
H83B H 0.4470 0.1076 0.5029 0.062 Uiso 1 1 calc R . .
H83C H 0.5348 0.0921 0.4497 0.062 Uiso 1 1 calc R . .
C84 C 0.2645(3) 0.17117(17) 0.45844(15) 0.0476(8) Uani 1 1 d .
. .
H84A H 0.2363 0.2008 0.4416 0.071 Uiso 1 1 calc R . .
H84B H 0.2634 0.1912 0.5038 0.071 Uiso 1 1 calc R . .
H84C H 0.2115 0.1229 0.4394 0.071 Uiso 1 1 calc R . .
C85 C 0.5198(3) 0.25546(14) 0.49861(11) 0.0335(6) Uani 1 1 d .
. .
H85A H 0.6029 0.2519 0.5012 0.050 Uiso 1 1 calc R . .
H85B H 0.4913 0.2669 0.5397 0.050 Uiso 1 1 calc R . .
H85C H 0.5166 0.2929 0.4853 0.050 Uiso 1 1 calc R . .
C86 C 0.2220(2) 0.03036(14) 0.32133(13) 0.0335(6) Uani 1 1 d .
. .
H86A H 0.2319 0.0235 0.3595 0.050 Uiso 1 1 calc R . .
H86B H 0.1879 -0.0157 0.2860 0.050 Uiso 1 1 calc R . .
H86C H 0.1676 0.0609 0.3266 0.050 Uiso 1 1 calc R . .
C87 C 0.4665(2) 0.00900(14) 0.28788(13) 0.0337(6) Uani 1 1 d .
. .
H87A H 0.5405 0.0268 0.2730 0.051 Uiso 1 1 calc R . .
H87B H 0.4218 -0.0371 0.2555 0.051 Uiso 1 1 calc R . .
H87C H 0.4870 0.0036 0.3258 0.051 Uiso 1 1 calc R . .
C88 C 0.3356(2) 0.08149(14) 0.23257(12) 0.0337(6) Uani 1 1 d .
. .
H88A H 0.2783 0.1106 0.2394 0.050 Uiso 1 1 calc R . .
H88B H 0.3000 0.0342 0.1991 0.050 Uiso 1 1 calc R . .
H88C H 0.4094 0.1040 0.2206 0.050 Uiso 1 1 calc R . .
C89 C 0.7258(2) 0.14674(12) 0.22612(10) 0.0205(4) Uani 1 1 d .
. .
C90 C 0.8204(2) 0.20332(13) 0.21544(12) 0.0271(5) Uani 1 1 d .
. .
H90A H 0.8659 0.2393 0.2560 0.032 Uiso 1 1 calc R . .
H90B H 0.7800 0.2276 0.1965 0.032 Uiso 1 1 calc R . .
C91 C 0.9079(2) 0.16833(15) 0.17174(12) 0.0319(6) Uani 1 1 d .
. .
H91 H 0.9690 0.2055 0.1650 0.038 Uiso 1 1 calc R . .
C92 C 0.8370(3) 0.11355(18) 0.10894(12) 0.0416(7) Uani 1 1 d .
. .
H92A H 0.7965 0.1372 0.0894 0.050 Uiso 1 1 calc R . .
H92B H 0.8925 0.0912 0.0805 0.050 Uiso 1 1 calc R . .
C93 C 0.7442(3) 0.05745(16) 0.11942(12) 0.0395(7) Uani 1 1 d .
. .
H93 H 0.6980 0.0216 0.0784 0.047 Uiso 1 1 calc R . .
C94 C 0.6567(2) 0.09165(14) 0.16296(11) 0.0288(5) Uani 1 1 d .
. .
```

```
H94A H 0.6143 0.1148 0.1437 0.035 Uiso 1 1 calc R . .
H94B H 0.5958 0.0546 0.1691 0.035 Uiso 1 1 calc R . .
C95 C 0.9716(2) 0.13188(15) 0.20130(13) 0.0337(6) Uani 1 1 d .
. .
H95A H 1.0283 0.1098 0.1736 0.040 Uiso 1 1 calc R . .
H95B H 1.0181 0.1673 0.2418 0.040 Uiso 1 1 calc R . .
C96 C 0.8781(2) 0.07517(14) 0.21144(13) 0.0321(6) Uani 1 1 d .
. .
H96 H 0.9195 0.0511 0.2308 0.038 Uiso 1 1 calc R . .
C97 C 0.7913(2) 0.10991(13) 0.25505(12) 0.0265(5) Uani 1 1 d .
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H97A H 0.7317 0.0733 0.2624 0.032 Uiso 1 1 calc R . .
H97B H 0.8369 0.1452 0.2958 0.032 Uiso 1 1 calc R . .
C98 C 0.8072(3) 0.02039(15) 0.14890(15) 0.0437(7) Uani 1 1 d .
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H98A H 0.7467 -0.0166 0.1554 0.052 Uiso 1 1 calc R . .
H98B H 0.8624 -0.0028 0.1207 0.052 Uiso 1 1 calc R . .
C110 C 0.4139(3) 0.41218(14) 0.37881(14) 0.0397(7) Uani 1 1 d
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H11A H 0.4787 0.4485 0.4104 0.060 Uiso 1 1 calc R . .
H11B H 0.3421 0.4300 0.3814 0.060 Uiso 1 1 calc R . .
H11C H 0.4395 0.4009 0.3372 0.060 Uiso 1 1 calc R . .
C220 C 0.1691(2) 0.36009(15) 0.66456(13) 0.0336(6) Uani 1 1 d
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H220 H 0.1846 0.3700 0.7096 0.040 Uiso 1 1 calc R . .
C221 C 0.1305(3) 0.42300(17) 0.66192(19) 0.0589(10) Uani 1 1 d
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H22D H 0.1128 0.4142 0.6182 0.088 Uiso 1 1 calc R . .
H22E H 0.1957 0.4664 0.6828 0.088 Uiso 1 1 calc R . .
H22F H 0.0584 0.4286 0.6830 0.088 Uiso 1 1 calc R . .
C222 C 0.2877(3) 0.3563(2) 0.63659(14) 0.0493(8) Uani 1 1 d .
. .
H22A H 0.3120 0.3154 0.6368 0.074 Uiso 1 1 calc R . .
H22B H 0.3500 0.3999 0.6615 0.074 Uiso 1 1 calc R . .
H22C H 0.2770 0.3512 0.5935 0.074 Uiso 1 1 calc R . .
C260 C -0.2414(2) 0.19912(15) 0.65921(13) 0.0339(6) Uani 1 1 d
. . .
H260 H -0.2270 0.2299 0.7052 0.041 Uiso 1 1 calc R . .
C261 C -0.3439(3) 0.21629(18) 0.63041(16) 0.0468(8) Uani 1 1 d
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H26A H -0.3201 0.2662 0.6372 0.070 Uiso 1 1 calc R . .
H26B H -0.4166 0.2079 0.6503 0.070 Uiso 1 1 calc R . .
H26C H -0.3604 0.1858 0.5855 0.070 Uiso 1 1 calc R . .
C262 C -0.2807(3) 0.12154(16) 0.64929(16) 0.0492(8) Uani 1 1 d
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H26D H -0.3080 0.0911 0.6049 0.074 Uiso 1 1 calc R . .
H26E H -0.3466 0.1155 0.6739 0.074 Uiso 1 1 calc R . .
H26F H -0.2125 0.1084 0.6627 0.074 Uiso 1 1 calc R . .
C720 C 0.6013(2) 0.33128(15) 0.18166(13) 0.0352(6) Uani 1 1 d
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H720 H 0.5845 0.3330 0.2236 0.042 Uiso 1 1 calc R . .
C721 C 0.5322(3) 0.37728(17) 0.1671(2) 0.0621(10) Uani 1 1 d .
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H72E H 0.5648 0.4271 0.1965 0.093 Uiso 1 1 calc R . .
H72F H 0.4468 0.3619 0.1711 0.093 Uiso 1 1 calc R . .
C722 C 0.7360(2) 0.36357(15) 0.18495(13) 0.0375(6) Uani 1 1 d
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H72A H 0.7817 0.3335 0.1921 0.056 Uiso 1 1 calc R . .
H72B H 0.7597 0.4112 0.2193 0.056 Uiso 1 1 calc R . .
H72C H 0.7529 0.3667 0.1455 0.056 Uiso 1 1 calc R . .
C760 C 0.2958(2) 0.08599(13) 0.09073(11) 0.0265(5) Uani 1 1 d
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C761 C 0.1934(2) 0.07884(15) 0.04411(12) 0.0345(6) Uani 1 1 d
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H76B H 0.1207 0.0450 0.0453 0.052 Uiso 1 1 calc R . .
H76C H 0.2173 0.0617 0.0019 0.052 Uiso 1 1 calc R . .
C762 C 0.3154(3) 0.01263(14) 0.07477(12) 0.0341(6) Uani 1 1 d
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H76E H 0.2445 -0.0173 0.0822 0.051 Uiso 1 1 calc R . .
H76F H 0.3863 0.0174 0.1011 0.051 Uiso 1 1 calc R . .
C50 C 0.7342(2) 0.49296(15) 0.70423(14) 0.0360(6) Uani 1 1 d .
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C55 C 0.7137(3) 0.52440(17) 0.76604(15) 0.0432(7) Uani 1 1 d .
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H55 H 0.6378 0.5086 0.7778 0.052 Uiso 1 1 calc R . .
C54 C 0.8023(3) 0.57862(17) 0.81104(14) 0.0446(8) Uani 1 1 d .
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H54 H 0.7867 0.5995 0.8532 0.054 Uiso 1 1 calc R . .
C53 C 0.9124(3) 0.60201(17) 0.79462(14) 0.0427(7) Uani 1 1 d .
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H53 H 0.9732 0.6392 0.8252 0.051 Uiso 1 1 calc R . .
C52 C 0.9340(3) 0.57106(17) 0.73319(14) 0.0406(7) Uani 1 1 d .
. .
H52 H 1.0102 0.5867 0.7215 0.049 Uiso 1 1 calc R . .
C51 C 0.8455(3) 0.51752(16) 0.68875(14) 0.0378(6) Uani 1 1 d .
. .
H51 H 0.8613 0.4971 0.6466 0.045 Uiso 1 1 calc R . .
C56 C 0.6388(3) 0.43353(18) 0.65555(17) 0.0547(9) Uani 1 1 d .
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H56A H 0.5710 0.4516 0.6495 0.082 Uiso 1 1 calc R . .
H56B H 0.6107 0.3958 0.6695 0.082 Uiso 1 1 calc R . .
H56C H 0.6725 0.4145 0.6160 0.082 Uiso 1 1 calc R . .
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N2 N -0.03909(17) 0.32555(10) 0.72498(9) 0.0219(4) Uani 1 1 d
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N4 N 0.05788(17) 0.25775(10) 0.90648(9) 0.0213(4) Uani 1 1 d .
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N8 N 0.74358(17) 0.29935(10) 0.39934(9) 0.0226(4) Uani 1 1 d .
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N9 N 0.44299(17) 0.15556(10) 0.36435(8) 0.0205(4) Uani 1 1 d .
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Si4 Si -0.06935(6) 0.18700(4) 0.87396(3) 0.02391(13) Uani 1 1
d . . .
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Si6 Si 0.78594(7) 0.38652(4) 0.41132(3) 0.03103(16) Uani 1 1 d
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Si7 Si 0.42132(7) 0.16862(4) 0.44041(3) 0.02833(15) Uani 1 1 d
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Si8 Si 0.37191(6) 0.07309(3) 0.30578(3) 0.02165(13) Uani 1 1 d
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U1 U 0.170142(7) 0.287686(4) 0.836268(3) 0.01614(2) Uani 1 1 d
. . .
U2 U 0.564138(7) 0.235612(4) 0.334317(3) 0.01603(2) Uani 1 1 d
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O2 O 0.48804(14) 0.31861(8) 0.38547(7) 0.0235(3) Uani 1 1 d .
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0.0046(3)
Si5 0.0223(3) 0.0313(4) 0.0253(3) 0.0060(3) -0.0016(3)
0.0103(3)
Si6 0.0343(4) 0.0250(4) 0.0262(3) 0.0111(3) -0.0036(3) -
0.0063(3)
Si7 0.0348(4) 0.0267(4) 0.0219(3) 0.0096(3) 0.0109(3)
0.0059(3)
Si8 0.0227(3) 0.0182(3) 0.0228(3) 0.0095(3) 0.0026(2)
0.0016(2)
U1 0.01633(4) 0.01538(4) 0.01706(4) 0.00633(3) 0.00297(3)
0.00571(3)
U2 0.01632(4) 0.01529(4) 0.01663(4) 0.00663(3) 0.00211(3)
0.00463(3)
O1 0.0264(8) 0.0165(8) 0.0239(8) 0.0059(7) 0.0048(6) 0.0079(6)
O2 0.0252(8) 0.0215(8) 0.0238(8) 0.0068(7) 0.0020(6) 0.0114(7)

_geom_special_details
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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C1 U1 2.828(2) . ?
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C5 H5A 0.9900 . ?
C5 H5B 0.9900 . ?
C6 N1 1.470(3) . ?
C6 H6A 0.9900 . ?
C6 H6B 0.9900 . ?
C7 N1 1.452(3) . ?
C7 C8 1.522(3) . ?
C7 H7A 0.9900 . ?
C7 H7B 0.9900 . ?
C8 O1 1.422(3) . ?
C8 C10 1.521(3) . ?
C8 C9 1.528(3) . ?
C9 H9A 0.9800 . ?
C9 H9B 0.9800 . ?
C9 H9C 0.9800 . ?
C10 H10A 0.9800 . ?
C10 H10B 0.9800 . ?
C10 H10C 0.9800 . ?
C11 N6 1.349(3) . ?
C11 N7 1.360(3) . ?
C11 U2 2.800(2) . ?
C15 N7 1.488(3) . ?
C15 C16 1.505(3) . ?
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C16 N6 1.470(3) . ?
C16 H16A 0.9900 . ?
C16 H16B 0.9900 . ?
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C17 N6 1.460(3) . ?
C17 C18 1.528(3) . ?
C17 H17A 0.9900 . ?
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C18 O2 1.423(3) . ?
C18 C110 1.519(4) . ?
C18 C19 1.527(4) . ?
C19 H19A 0.9800 . ?
C19 H19B 0.9800 . ?
C19 H19C 0.9800 . ?
C21 C22 1.403(3) . ?
C21 C26 1.405(3) . ?
C21 N2 1.441(3) . ?
C22 C23 1.389(3) . ?
C22 C220 1.521(4) . ?
C23 C24 1.378(4) . ?
C23 H23 0.9500 . ?
C24 C25 1.371(4) . ?
C24 H24 0.9500 . ?
C25 C26 1.397(4) . ?
C25 H25 0.9500 . ?
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C27 Si1 1.883(3) . ?
C27 H27A 0.9800 . ?
C27 H27B 0.9800 . ?
C27 H27C 0.9800 . ?
C28 Si1 1.865(3) . ?
C28 H28A 0.9800 . ?
C28 H28B 0.9800 . ?
C28 H28C 0.9800 . ?
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C34 H34A 0.9800 . ?
C34 H34B 0.9800 . ?
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C36 H36C 0.9800 . ?
C37 Si4 1.871(3) . ?
C37 H37A 0.9800 . ?
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C41 H41 1.0000 . ?
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C47 H47B 0.9900 . ?
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C261 H26B 0.9800 . ?
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C262 H26E 0.9800 . ?
C262 H26F 0.9800 . ?
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C720 H720 1.0000 . ?
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C721 H72E 0.9800 . ?
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N4 Si4 1.736(2) . ?
N4 U1 2.3174(19) . ?
N5 U1 1.9296(18) . ?
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N8 Si5 1.720(2) . ?
N8 U2 2.3193(19) . ?
N9 Si8 1.732(2) . ?
N9 Si7 1.7328(19) . ?
N9 U2 2.2992(18) . ?
N10 U2 1.9320(19) . ?
Si2 U1 3.3578(8) . ?
Si4 U1 3.4496(7) . ?
Si6 U2 3.3899(7) . ?
Si8 U2 3.4492(7) . ?
U1 O1 2.0855(15) . ?
U2 O2 2.0911(15) . ?

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H5A C5 H5B 109.3 . . ?
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N1 C6 H6B 111.5 . . ?
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H6A C6 H6B 109.4 . . ?
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O1 C8 C9 109.1(2) . . ?
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C7 C8 C9 109.8(2) . . ?
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C8 C9 H9B 109.5 . . ?
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H9A C9 H9C 109.5 . . ?
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C8 C10 H10A 109.5 . . ?
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H10A C10 H10B 109.5 . . ?
C8 C10 H10C 109.5 . . ?
H10A C10 H10C 109.5 . . ?
H10B C10 H10C 109.5 . . ?
N6 C11 N7 105.82(19) . . ?
N6 C11 U2 112.37(14) . . ?
N7 C11 U2 141.76(16) . . ?
N7 C15 C16 102.24(18) . . ?
N7 C15 H15A 111.3 . . ?
C16 C15 H15A 111.3 . . ?
N7 C15 H15B 111.3 . . ?
C16 C15 H15B 111.3 . . ?
H15A C15 H15B 109.2 . . ?
N6 C16 C15 101.33(18) . . ?
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N6 C16 H16B 111.5 . . ?
C15 C16 H16B 111.5 . . ?
H16A C16 H16B 109.3 . . ?
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C18 C17 H17A 108.7 . . ?
N6 C17 H17B 108.7 . . ?
C18 C17 H17B 108.7 . . ?
H17A C17 H17B 107.6 . . ?
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H19A C19 H19B 109.5 . . ?
C18 C19 H19C 109.5 . . ?
H19A C19 H19C 109.5 . . ?
H19B C19 H19C 109.5 . . ?
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C25 C26 C260 119.0(2) . . ?
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Si1 C27 H27B 109.5 . . ?
H27A C27 H27B 109.5 . . ?
Si1 C27 H27C 109.5 . . ?
H27A C27 H27C 109.5 . . ?
H27B C27 H27C 109.5 . . ?
Si1 C28 H28A 109.5 . . ?
Si1 C28 H28B 109.5 . . ?
H28A C28 H28B 109.5 . . ?
Si1 C28 H28C 109.5 . . ?
H28A C28 H28C 109.5 . . ?
H28B C28 H28C 109.5 . . ?
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H29A C29 H29B 109.5 . . ?
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Si2 C30 H30B 109.5 . . ?
H30A C30 H30B 109.5 . . ?
Si2 C30 H30C 109.5 . . ?
H30A C30 H30C 109.5 . . ?
H30B C30 H30C 109.5 . . ?
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Si2 C31 H31B 109.5 . . ?
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Si3 C35 H35B 109.5 . . ?
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Si3 C35 H35C 109.5 . . ?
H35A C35 H35C 109.5 . . ?
H35B C35 H35C 109.5 . . ?
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Si4 C36 H36B 109.5 . . ?
H36A C36 H36B 109.5 . . ?
Si4 C36 H36C 109.5 . . ?
H36A C36 H36C 109.5 . . ?
H36B C36 H36C 109.5 . . ?
Si4 C37 H37A 109.5 . . ?
Si4 C37 H37B 109.5 . . ?
H37A C37 H37B 109.5 . . ?
Si4 C37 H37C 109.5 . . ?
H37A C37 H37C 109.5 . . ?
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C76 C71 N7 119.8(2) . . ?
C72 C71 N7 118.8(2) . . ?
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C76 C75 H75 119.1 . . ?
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C75 C76 C760 117.6(2) . . ?
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Si5 C77 H77B 109.5 . . ?
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Si5 C77 H77C 109.5 . . ?
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H77B C77 H77C 109.5 . . ?
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Si5 C78 H78B 109.5 . . ?
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Si5 C78 H78C 109.5 . . ?
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H78B C78 H78C 109.5 . . ?
Si5 C79 H79A 109.5 . . ?
Si5 C79 H79B 109.5 . . ?
H79A C79 H79B 109.5 . . ?
Si5 C79 H79C 109.5 . . ?
H79A C79 H79C 109.5 . . ?
H79B C79 H79C 109.5 . . ?
Si6 C80 H80A 109.5 . . ?
Si6 C80 H80B 109.5 . . ?
H80A C80 H80B 109.5 . . ?
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H80A C80 H80C 109.5 . . ?
H80B C80 H80C 109.5 . . ?
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Si6 C81 H81B 109.5 . . ?
H81A C81 H81B 109.5 . . ?
Si6 C81 H81C 109.5 . . ?
H81A C81 H81C 109.5 . . ?
H81B C81 H81C 109.5 . . ?
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Si6 C82 H82B 109.5 . . ?
H82A C82 H82B 109.5 . . ?
Si6 C82 H82C 109.5 . . ?
H82A C82 H82C 109.5 . . ?
H82B C82 H82C 109.5 . . ?
Si7 C83 H83A 109.5 . . ?
Si7 C83 H83B 109.5 . . ?
H83A C83 H83B 109.5 . . ?
Si7 C83 H83C 109.5 . . ?
H83A C83 H83C 109.5 . . ?
H83B C83 H83C 109.5 . . ?
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Si7 C84 H84B 109.5 . . ?
H84A C84 H84B 109.5 . . ?
Si7 C84 H84C 109.5 . . ?
H84A C84 H84C 109.5 . . ?
H84B C84 H84C 109.5 . . ?
Si7 C85 H85A 109.5 . . ?
Si7 C85 H85B 109.5 . . ?
H85A C85 H85B 109.5 . . ?
Si7 C85 H85C 109.5 . . ?
H85A C85 H85C 109.5 . . ?
H85B C85 H85C 109.5 . . ?
Si8 C86 H86A 109.5 . . ?
Si8 C86 H86B 109.5 . . ?
H86A C86 H86B 109.5 . . ?
Si8 C86 H86C 109.5 . . ?
H86A C86 H86C 109.5 . . ?
H86B C86 H86C 109.5 . . ?
Si8 C87 H87A 109.5 . . ?
Si8 C87 H87B 109.5 . . ?
H87A C87 H87B 109.5 . . ?
Si8 C87 H87C 109.5 . . ?
H87A C87 H87C 109.5 . . ?
H87B C87 H87C 109.5 . . ?
Si8 C88 H88A 109.5 . . ?
Si8 C88 H88B 109.5 . . ?
H88A C88 H88B 109.5 . . ?
Si8 C88 H88C 109.5 . . ?
H88A C88 H88C 109.5 . . ?
H88B C88 H88C 109.5 . . ?
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N10 C89 C97 111.13(18) . . ?
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H22B C222 H22C 109.5 . . ?
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H26E C262 H26F 109.5 . . ?
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C722 C720 H720 108.3 . . ?
C721 C720 H720 108.3 . . ?
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N3 U1 Si4 126.85(5) . . ?
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N10 U2 N9 105.50(7) . . ?
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N10 U2 N8 93.18(7) . . ?
O2 U2 N8 88.92(7) . . ?
N9 U2 N8 114.06(7) . . ?
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N1 C7 C8 C9 174.2(2) . . . . ?
N7 C15 C16 N6 -18.7(2) . . . . ?
N6 C17 C18 O2 -66.3(3) . . . . ?
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N2 C21 C26 C260 -2.0(3) . . . . ?
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C44 C39 C40 C41 -58.2(3) . . . . ?
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C39 C40 C41 C45 -60.6(3) . . . . ?
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C41 C42 C43 C48 -59.6(3) . . . . ?
C41 C42 C43 C44 60.2(3) . . . . ?
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C95 C91 C92 C93 60.3(3) . . . . ?
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_diffrn_reflns_av_sigmaI/netI     0.0462
_diffrn_reflns_limit_h_min        -16
_diffrn_reflns_limit_h_max        16
_diffrn_reflns_limit_k_min        -26
_diffrn_reflns_limit_k_max        25
_diffrn_reflns_limit_l_min        -23
_diffrn_reflns_limit_l_max        23
_diffrn_reflns_theta_min          1.77
_diffrn_reflns_theta_max          26.44
_reflns_number_total              10820
_reflns_number_gt                 9337
_reflns_threshold_expression      >2\s(I)

_computing_data_collection        'SMART (Siemens, 1993)'
_computing_cell_refinement        'SAINT (Siemens, 1995)'
_computing_data_reduction         'SAINT (Siemens, 1995)'
_computing_structure_solution
;
'SUPERFLIP (Palatinus, L. & Chapuis, G., 2007)'
J. Appl. Cryst. 40, 786-790
;
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
2008)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   'enCIFer (Allen et al.,
2004)'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
```

```
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0470P)^2^+13.5573P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     ridin
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          10820
_refine_ls_number_parameters      541
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0520
_refine_ls_R_factor_gt            0.0425
_refine_ls_wR_factor_ref          0.1015
_refine_ls_wR_factor_gt           0.0968
_refine_ls_goodness_of_fit_ref    1.067
_refine_ls_restrained_S_all       1.067
_refine_ls_shift/su_max           0.001
_refine_ls_shift/su_mean          0.000

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 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
U1 U 0.790822(12) 0.695959(8) 0.028273(8) 0.01516(6) Uani 1 1
d . . .
Si4 Si 0.55856(10) 0.77479(7) 0.01113(7) 0.0205(3) Uani 1 1 d
. . .
Si1 Si 0.86871(10) 0.68149(6) 0.21156(7) 0.0209(3) Uani 1 1 d
. . .
Si2 Si 0.96973(10) 0.59225(6) 0.12100(7) 0.0208(3) Uani 1 1 d
. . .
Si3 Si 0.54824(10) 0.64297(7) 0.06223(8) 0.0241(3) Uani 1 1 d
. . .
N5 N 0.8629(3) 0.78805(18) 0.0591(2) 0.0183(8) Uani 1 1 d . .
.
O1 O 0.7754(2) 0.61209(15) -0.03279(17) 0.0213(7) Uani 1 1 d .
. .
N3 N 0.8852(3) 0.65240(18) 0.1274(2) 0.0186(8) Uani 1 1 d . .
.
N4 N 0.6182(3) 0.70424(18) 0.0335(2) 0.0196(8) Uani 1 1 d . .
.
```

```
N1 N 0.7407(3) 0.69686(19) -0.1572(2) 0.0219(9) Uani 1 1 d . .
.
C31 C 1.0166(4) 0.5937(3) 0.0316(3) 0.0298(12) Uani 1 1 d . .
.
H31A H 0.9592 0.5896 -0.0066 0.045 Uiso 1 1 calc R . .
H31B H 1.0636 0.5587 0.0285 0.045 Uiso 1 1 calc R . .
H31C H 1.0516 0.6335 0.0259 0.045 Uiso 1 1 calc R . .
C35 C 0.4728(4) 0.6666(3) 0.1354(3) 0.0386(14) Uani 1 1 d . .
.
H35A H 0.5186 0.6818 0.1770 0.058 Uiso 1 1 calc R . .
H35B H 0.4349 0.6303 0.1497 0.058 Uiso 1 1 calc R . .
H35C H 0.4255 0.7001 0.1178 0.058 Uiso 1 1 calc R . .
C34 C 0.4520(4) 0.6097(3) -0.0103(3) 0.0384(14) Uani 1 1 d . .
.
H34A H 0.3868 0.6307 -0.0091 0.058 Uiso 1 1 calc R . .
H34B H 0.4444 0.5645 -0.0023 0.058 Uiso 1 1 calc R . .
H34C H 0.4746 0.6165 -0.0574 0.058 Uiso 1 1 calc R . .
N2 N 0.8632(3) 0.7636(2) -0.1482(2) 0.0213(9) Uani 1 1 d . . .
C33 C 0.6334(4) 0.5773(2) 0.0998(3) 0.0303(12) Uani 1 1 d . .
.
H33A H 0.6718 0.5616 0.0625 0.045 Uiso 1 1 calc R . .
H33B H 0.5924 0.5432 0.1160 0.045 Uiso 1 1 calc R . .
H33C H 0.6803 0.5929 0.1407 0.045 Uiso 1 1 calc R . .
C6 C 0.7489(4) 0.7113(3) -0.2328(2) 0.0270(12) Uani 1 1 d . .
.
H6A H 0.6820 0.7208 -0.2603 0.032 Uiso 1 1 calc R . .
H6B H 0.7810 0.6765 -0.2565 0.032 Uiso 1 1 calc R . .
C29 C 0.9800(4) 0.7290(3) 0.2534(3) 0.0288(12) Uani 1 1 d . .
.
H29A H 1.0337 0.7007 0.2748 0.043 Uiso 1 1 calc R . .
H29B H 0.9589 0.7563 0.2909 0.043 Uiso 1 1 calc R . .
H29C H 1.0054 0.7548 0.2164 0.043 Uiso 1 1 calc R . .
C39 C 0.9219(4) 0.8280(2) 0.0929(3) 0.0213(10) Uani 1 1 d . .
.
C5 C 0.8163(4) 0.7692(3) -0.2247(3) 0.0290(12) Uani 1 1 d . .
.
H5A H 0.8680 0.7679 -0.2580 0.035 Uiso 1 1 calc R . .
H5B H 0.7763 0.8082 -0.2330 0.035 Uiso 1 1 calc R . .
C30 C 1.0876(4) 0.5995(3) 0.1880(3) 0.0348(13) Uani 1 1 d . .
.
H30A H 1.1202 0.6400 0.1814 0.052 Uiso 1 1 calc R . .
H30B H 1.1343 0.5653 0.1805 0.052 Uiso 1 1 calc R . .
H30C H 1.0695 0.5970 0.2369 0.052 Uiso 1 1 calc R . .
C23 C 1.0397(4) 0.8985(3) -0.1090(3) 0.0335(13) Uani 1 1 d . .
.
H23 H 1.0376 0.9429 -0.1048 0.040 Uiso 1 1 calc R . .
C38 C 0.5438(4) 0.8235(3) 0.0924(3) 0.0286(12) Uani 1 1 d . .
.
H38A H 0.4949 0.8034 0.1199 0.043 Uiso 1 1 calc R . .
H38B H 0.5196 0.8655 0.0772 0.043 Uiso 1 1 calc R . .
H38C H 0.6094 0.8271 0.1228 0.043 Uiso 1 1 calc R . .
C262 C 1.0368(4) 0.6763(3) -0.2080(3) 0.0320(12) Uani 1 1 d .
. .
```

```
H26A H 0.9680 0.6884 -0.2284 0.048 Uiso 1 1 calc R . .
H26B H 1.0443 0.6307 -0.2113 0.048 Uiso 1 1 calc R . .
H26C H 1.0858 0.6970 -0.2348 0.048 Uiso 1 1 calc R . .
C36 C 0.4284(4) 0.7672(3) -0.0400(3) 0.0283(12) Uani 1 1 d . .
.
H36A H 0.4316 0.7427 -0.0838 0.042 Uiso 1 1 calc R . .
H36B H 0.4013 0.8091 -0.0529 0.042 Uiso 1 1 calc R . .
H36C H 0.3840 0.7459 -0.0099 0.042 Uiso 1 1 calc R . .
C9 C 0.8260(4) 0.5689(3) -0.1416(3) 0.0327(13) Uani 1 1 d . .
.
H9A H 0.8716 0.6046 -0.1451 0.049 Uiso 1 1 calc R . .
H9B H 0.7997 0.5543 -0.1900 0.049 Uiso 1 1 calc R . .
H9C H 0.8632 0.5348 -0.1148 0.049 Uiso 1 1 calc R . .
C37 C 0.6323(4) 0.8208(2) -0.0493(3) 0.0274(11) Uani 1 1 d . .
.
H37A H 0.7029 0.8242 -0.0271 0.041 Uiso 1 1 calc R . .
H37B H 0.6030 0.8628 -0.0568 0.041 Uiso 1 1 calc R . .
H37C H 0.6297 0.7993 -0.0958 0.041 Uiso 1 1 calc R . .
C40 C 0.8850(4) 0.8748(2) 0.1433(3) 0.0237(11) Uani 1 1 d . .
.
C1 C 0.8121(3) 0.7245(2) -0.1103(2) 0.0192(10) Uani 1 1 d . .
.
C28 C 0.8485(4) 0.6185(3) 0.2774(3) 0.0334(13) Uani 1 1 d . .
.
H28A H 0.7874 0.5946 0.2596 0.050 Uiso 1 1 calc R . .
H28B H 0.8406 0.6375 0.3239 0.050 Uiso 1 1 calc R . .
H28C H 0.9070 0.5902 0.2832 0.050 Uiso 1 1 calc R . .
C10 C 0.6685(4) 0.5337(3) -0.0953(3) 0.0328(13) Uani 1 1 d . .
.
H10A H 0.7060 0.5007 -0.0666 0.049 Uiso 1 1 calc R . .
H10B H 0.6436 0.5173 -0.1432 0.049 Uiso 1 1 calc R . .
H10C H 0.6110 0.5472 -0.0714 0.049 Uiso 1 1 calc R . .
C48 C 1.1878(4) 0.7724(3) 0.0801(3) 0.0313(12) Uani 1 1 d . .
.
H48 H 1.2220 0.7338 0.0757 0.038 Uiso 1 1 calc R . .
C261 C 1.1575(4) 0.6698(3) -0.0955(3) 0.0331(13) Uani 1 1 d .
. .
H26D H 1.2108 0.6840 -0.1231 0.050 Uiso 1 1 calc R . .
H26E H 1.1545 0.6238 -0.0962 0.050 Uiso 1 1 calc R . .
H26F H 1.1726 0.6844 -0.0456 0.050 Uiso 1 1 calc R . .
C222 C 0.8357(5) 0.9432(3) -0.1927(3) 0.0392(14) Uani 1 1 d .
. .
H22A H 0.8885 0.9755 -0.1872 0.059 Uiso 1 1 calc R . .
H22B H 0.7690 0.9632 -0.1968 0.059 Uiso 1 1 calc R . .
H22C H 0.8411 0.9185 -0.2362 0.059 Uiso 1 1 calc R . .
C26 C 1.0489(4) 0.7671(2) -0.1204(2) 0.0231(11) Uani 1 1 d . .
.
C260 C 1.0561(4) 0.6964(2) -0.1289(3) 0.0263(11) Uani 1 1 d .
. .
H260 H 1.0024 0.6769 -0.1036 0.032 Uiso 1 1 calc R . .
C27 C 0.7565(4) 0.7339(3) 0.2066(3) 0.0286(12) Uani 1 1 d . .
.
H27A H 0.7662 0.7701 0.1759 0.043 Uiso 1 1 calc R . .
```

```
H27B H 0.7482 0.7486 0.2550 0.043 Uiso 1 1 calc R . .
H27C H 0.6959 0.7107 0.1863 0.043 Uiso 1 1 calc R . .
C41 C 0.7877(4) 0.8993(3) 0.1296(3) 0.0295(12) Uani 1 1 d . .
.
H41 H 0.7466 0.8894 0.0857 0.035 Uiso 1 1 calc R . .
C25 C 1.1350(4) 0.8039(3) -0.1080(3) 0.0309(12) Uani 1 1 d . .
.
H25 H 1.1993 0.7839 -0.1025 0.037 Uiso 1 1 calc R . .
C42 C 0.7499(5) 0.9380(3) 0.1795(3) 0.0439(16) Uani 1 1 d . .
.
H42 H 0.6828 0.9538 0.1698 0.053 Uiso 1 1 calc R . .
C47 C 1.0847(4) 0.7730(3) 0.0818(3) 0.0268(11) Uani 1 1 d . .
.
H47 H 1.0480 0.7346 0.0782 0.032 Uiso 1 1 calc R . .
C8 C 0.7381(4) 0.5894(2) -0.1024(3) 0.0229(10) Uani 1 1 d . .
.
C21 C 0.9550(4) 0.7991(2) -0.1264(3) 0.0234(11) Uani 1 1 d . .
.
C46 C 1.0340(4) 0.8290(2) 0.0886(3) 0.0220(10) Uani 1 1 d . .
.
C24 C 1.1308(4) 0.8685(3) -0.1032(3) 0.0350(13) Uani 1 1 d . .
.
H24 H 1.1917 0.8922 -0.0959 0.042 Uiso 1 1 calc R . .
C2S C 0.5896(7) 0.0287(4) 0.9910(5) 0.069(2) Uani 1 1 d . . .
H2S H 0.6526 0.0482 0.9868 0.082 Uiso 1 1 calc R . .
C32 C 0.9114(4) 0.5135(2) 0.1318(3) 0.0353(13) Uani 1 1 d . .
.
H32A H 0.8922 0.5099 0.1803 0.053 Uiso 1 1 calc R . .
H32B H 0.9603 0.4805 0.1244 0.053 Uiso 1 1 calc R . .
H32C H 0.8510 0.5088 0.0961 0.053 Uiso 1 1 calc R . .
C49 C 1.2414(4) 0.8282(3) 0.0849(3) 0.0358(14) Uani 1 1 d . .
.
H49 H 1.3126 0.8277 0.0845 0.043 Uiso 1 1 calc R . .
C51 C 1.0888(4) 0.8844(3) 0.0924(3) 0.0346(13) Uani 1 1 d . .
.
H51 H 1.0552 0.9233 0.0968 0.042 Uiso 1 1 calc R . .
C7 C 0.6780(4) 0.6436(2) -0.1413(3) 0.0232(11) Uani 1 1 d . .
.
H7A H 0.6410 0.6277 -0.1870 0.028 Uiso 1 1 calc R . .
H7B H 0.6272 0.6584 -0.1111 0.028 Uiso 1 1 calc R . .
C1S C 0.5559(7) 0.0262(4) 1.0583(4) 0.063(2) Uani 1 1 d . . .
H1S H 0.5954 0.0454 1.0982 0.076 Uiso 1 1 calc R . .
C220 C 0.8491(4) 0.8997(3) -0.1268(3) 0.0307(12) Uani 1 1 d .
. .
H220 H 0.7930 0.8682 -0.1327 0.037 Uiso 1 1 calc R . .
C221 C 0.8411(5) 0.9373(3) -0.0580(3) 0.0367(13) Uani 1 1 d .
. .
H22D H 0.8462 0.9087 -0.0167 0.055 Uiso 1 1 calc R . .
H22E H 0.7759 0.9592 -0.0626 0.055 Uiso 1 1 calc R . .
H22F H 0.8962 0.9681 -0.0507 0.055 Uiso 1 1 calc R . .
C22 C 0.9490(4) 0.8643(2) -0.1210(3) 0.0268(11) Uani 1 1 d . .
.
```

```
C50 C 1.1924(4) 0.8834(3) 0.0900(3) 0.0431(15) Uani 1 1 d . .
.
H50 H 1.2293 0.9217 0.0919 0.052 Uiso 1 1 calc R . .
C44 C 0.9055(5) 0.9301(3) 0.2570(3) 0.0462(17) Uani 1 1 d . .
.
H44 H 0.9458 0.9401 0.3013 0.055 Uiso 1 1 calc R . .
C45 C 0.9439(4) 0.8923(3) 0.2077(3) 0.0345(13) Uani 1 1 d . .
.
H45 H 1.0117 0.8777 0.2176 0.041 Uiso 1 1 calc R . .
C43 C 0.8087(5) 0.9537(3) 0.2425(4) 0.0494(18) Uani 1 1 d . .
.
H43 H 0.7829 0.9807 0.2760 0.059 Uiso 1 1 calc R . .
C3S C 0.5350(7) 0.0039(3) 0.9313(4) 0.063(2) Uani 1 1 d . . .
H3S H 0.5570 0.0068 0.8852 0.076 Uiso 1 1 calc R . .

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U1 0.01363(10) 0.01861(10) 0.01307(9) -0.00038(7) 0.00114(6)
0.00017(7)
Si4 0.0157(6) 0.0282(7) 0.0176(6) 0.0011(5) 0.0015(5)
0.0042(5)
Si1 0.0226(7) 0.0244(7) 0.0153(6) 0.0006(5) 0.0013(5)
0.0033(5)
Si2 0.0201(7) 0.0226(7) 0.0197(6) 0.0019(5) 0.0022(5)
0.0038(5)
Si3 0.0188(7) 0.0290(8) 0.0253(7) 0.0023(6) 0.0058(6) -
0.0028(6)
N5 0.018(2) 0.019(2) 0.0171(19) -0.0003(15) 0.0003(16) -
0.0008(16)
O1 0.0217(17) 0.0225(18) 0.0187(16) -0.0045(13) -0.0014(14) -
0.0023(14)
N3 0.018(2) 0.022(2) 0.0160(19) -0.0009(16) 0.0002(15) -
0.0001(16)
N4 0.015(2) 0.024(2) 0.020(2) -0.0016(16) 0.0040(16)
0.0013(16)
N1 0.019(2) 0.028(2) 0.019(2) 0.0001(17) 0.0024(16) -
0.0032(17)
C31 0.029(3) 0.036(3) 0.025(3) 0.000(2) 0.005(2) 0.008(2)
C35 0.031(3) 0.047(4) 0.042(3) 0.004(3) 0.019(3) -0.004(3)
C34 0.026(3) 0.044(4) 0.044(3) 0.000(3) 0.001(3) -0.010(3)
N2 0.019(2) 0.031(2) 0.0130(19) 0.0041(17) 0.0001(16) -
0.0027(17)
C33 0.028(3) 0.029(3) 0.034(3) 0.008(2) 0.003(2) -0.004(2)
C6 0.024(3) 0.045(3) 0.011(2) 0.002(2) -0.001(2) -0.002(2)
C29 0.034(3) 0.033(3) 0.018(2) -0.003(2) -0.001(2) 0.002(2)
C39 0.022(3) 0.023(3) 0.019(2) 0.0036(19) 0.0026(19) 0.001(2)
C5 0.028(3) 0.042(3) 0.016(2) 0.007(2) -0.002(2) -0.002(2)
```

```
C30 0.029(3) 0.042(3) 0.030(3) -0.004(2) -0.006(2) 0.017(3)
C23 0.037(3) 0.030(3) 0.035(3) 0.002(2) 0.011(3) -0.006(2)
C38 0.027(3) 0.032(3) 0.026(3) 0.000(2) 0.002(2) 0.008(2)
C262 0.035(3) 0.039(3) 0.022(3) -0.003(2) 0.004(2) -0.003(3)
C36 0.016(2) 0.044(3) 0.023(3) 0.005(2) -0.001(2) 0.005(2)
C9 0.033(3) 0.035(3) 0.030(3) -0.012(2) 0.003(2) -0.001(2)
C37 0.028(3) 0.028(3) 0.026(3) 0.005(2) 0.003(2) 0.005(2)
C40 0.020(2) 0.024(3) 0.026(3) -0.004(2) -0.002(2) -0.001(2)
C1 0.017(2) 0.023(2) 0.019(2) 0.0021(19) 0.0045(19) 0.0039(19)
C28 0.041(3) 0.039(3) 0.021(3) 0.008(2) 0.007(2) 0.005(3)
C10 0.035(3) 0.027(3) 0.035(3) -0.007(2) 0.002(2) -0.007(2)
C48 0.024(3) 0.045(3) 0.025(3) -0.008(2) 0.005(2) 0.009(2)
C261 0.027(3) 0.039(3) 0.033(3) 0.002(3) 0.004(2) 0.003(2)
C222 0.044(4) 0.038(3) 0.036(3) 0.011(3) 0.004(3) -0.001(3)
C26 0.022(3) 0.030(3) 0.017(2) 0.003(2) 0.0025(19) -0.004(2)
C260 0.023(3) 0.032(3) 0.025(3) 0.004(2) 0.005(2) 0.000(2)
C27 0.027(3) 0.036(3) 0.023(3) -0.004(2) 0.005(2) 0.006(2)
C41 0.024(3) 0.035(3) 0.028(3) -0.007(2) -0.003(2) 0.005(2)
C25 0.024(3) 0.043(3) 0.026(3) -0.001(2) 0.003(2) -0.002(2)
C42 0.029(3) 0.052(4) 0.049(4) -0.016(3) -0.003(3) 0.015(3)
C47 0.027(3) 0.030(3) 0.023(3) -0.009(2) 0.004(2) 0.000(2)
C8 0.023(3) 0.023(3) 0.021(2) -0.007(2) 0.001(2) -0.003(2)
C21 0.019(2) 0.033(3) 0.019(2) 0.005(2) 0.0060(19) -0.008(2)
C46 0.021(2) 0.024(3) 0.020(2) -0.003(2) 0.001(2) -0.002(2)
C24 0.025(3) 0.040(3) 0.041(3) -0.002(3) 0.009(2) -0.012(2)
C2S 0.082(6) 0.052(5) 0.070(6) 0.004(4) 0.005(5) 0.003(4)
C32 0.035(3) 0.024(3) 0.051(4) 0.003(3) 0.017(3) 0.006(2)
C49 0.018(3) 0.059(4) 0.031(3) -0.001(3) 0.006(2) -0.003(3)
C51 0.027(3) 0.028(3) 0.049(3) 0.000(3) 0.003(3) -0.002(2)
C7 0.021(2) 0.031(3) 0.017(2) -0.006(2) 0.0014(19) -0.004(2)
C1S 0.085(6) 0.056(5) 0.045(4) -0.008(3) -0.005(4) 0.012(4)
C220 0.034(3) 0.029(3) 0.030(3) 0.004(2) 0.007(2) -0.001(2)
C221 0.044(3) 0.031(3) 0.036(3) 0.006(2) 0.010(3) 0.005(3)
C22 0.029(3) 0.029(3) 0.023(3) 0.004(2) 0.006(2) 0.001(2)
C50 0.030(3) 0.050(4) 0.049(4) 0.001(3) 0.005(3) -0.015(3)
C44 0.045(4) 0.051(4) 0.038(3) -0.025(3) -0.009(3) 0.011(3)
C45 0.030(3) 0.038(3) 0.033(3) -0.011(2) -0.007(2) 0.009(2)
C43 0.051(4) 0.048(4) 0.048(4) -0.025(3) 0.001(3) 0.019(3)
C3S 0.099(7) 0.040(4) 0.044(4) -0.006(3) -0.015(4) 0.020(4)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
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involving l.s. planes.
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_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   ?
_diffrn_measurement_method        ?
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             39388
_diffrn_reflns_av_R_equivalents   0.0391
_diffrn_reflns_av_sigmaI/netI     0.0452
_diffrn_reflns_limit_h_min        -14
_diffrn_reflns_limit_h_max        14
_diffrn_reflns_limit_k_min        -16
_diffrn_reflns_limit_k_max        16
_diffrn_reflns_limit_l_min        -27
_diffrn_reflns_limit_l_max        27
_diffrn_reflns_theta_min          1.74
_diffrn_reflns_theta_max          30.52
_reflns_number_total              13332
_reflns_number_gt                 12491
_reflns_threshold_expression      >2\s(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
_computing_data_reduction         ?
_computing_structure_solution     ?
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_computing_structure_refinement   'SHELXL-97 (Sheldrick,
2008)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0526P)^2^+7.4676P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          13332
_refine_ls_number_parameters      405
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0619
_refine_ls_R_factor_gt            0.0573
_refine_ls_wR_factor_ref          0.1648
_refine_ls_wR_factor_gt           0.1622
_refine_ls_goodness_of_fit_ref    1.574
_refine_ls_restrained_S_all       1.574
_refine_ls_shift/su_max           0.001
_refine_ls_shift/su_mean          0.000

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 _atom_site_refinement_flags
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C1 C 0.4466(6) 0.0914(5) 0.2516(3) 0.0219(12) Uani 1 1 d . . .
C5 C 0.5736(6) -0.0409(6) 0.3200(4) 0.0298(14) Uani 1 1 d . .
.
H5A H 0.5590 -0.1223 0.3382 0.036 Uiso 1 1 calc R . .
H5B H 0.6220 -0.0154 0.3497 0.036 Uiso 1 1 calc R . .
C6 C 0.6426(7) -0.0106(7) 0.2424(4) 0.0372(17) Uani 1 1 d . .
.
H6A H 0.7294 0.0178 0.2371 0.045 Uiso 1 1 calc R . .
H6B H 0.6488 -0.0761 0.2226 0.045 Uiso 1 1 calc R . .
C7 C 0.5976(7) 0.1348(6) 0.1322(4) 0.0291(14) Uani 1 1 d . . .
H7A H 0.5444 0.1056 0.1063 0.035 Uiso 1 1 calc R . .
H7B H 0.6875 0.1157 0.1151 0.035 Uiso 1 1 calc R . .
C8 C 0.5836(7) 0.2628(6) 0.1152(4) 0.0289(14) Uani 1 1 d . . .
C9 C 0.6214(8) 0.3107(8) 0.0345(4) 0.0420(19) Uani 1 1 d . . .
H9A H 0.5733 0.2724 0.0114 0.063 Uiso 1 1 calc R . .
H9B H 0.7130 0.2991 0.0189 0.063 Uiso 1 1 calc R . .
H9C H 0.6019 0.3907 0.0225 0.063 Uiso 1 1 calc R . .
C10 C 0.6656(8) 0.3151(8) 0.1541(4) 0.0411(18) Uani 1 1 d . .
.
H10A H 0.6544 0.3964 0.1421 0.062 Uiso 1 1 calc R . .
H10B H 0.7557 0.2967 0.1398 0.062 Uiso 1 1 calc R . .
H10C H 0.6382 0.2851 0.2047 0.062 Uiso 1 1 calc R . .
C21 C 0.3599(6) 0.0288(5) 0.3811(3) 0.0223(12) Uani 1 1 d . .
.
C22 C 0.3769(6) 0.1144(5) 0.4136(3) 0.0249(12) Uani 1 1 d . .
.
C23 C 0.2887(7) 0.1189(6) 0.4765(4) 0.0310(14) Uani 1 1 d . .
.
H23 H 0.2964 0.1761 0.4987 0.037 Uiso 1 1 calc R . .
C24 C 0.1903(7) 0.0398(7) 0.5061(4) 0.0332(15) Uani 1 1 d . .
.
H24 H 0.1321 0.0446 0.5476 0.040 Uiso 1 1 calc R . .
C25 C 0.1777(7) -0.0464(6) 0.4744(4) 0.0309(14) Uani 1 1 d . .
.
H25 H 0.1119 -0.0998 0.4954 0.037 Uiso 1 1 calc R . .
C26 C 0.2627(6) -0.0544(5) 0.4113(3) 0.0243(12) Uani 1 1 d . .
.
C27 C 0.2524(11) -0.0370(9) 0.0271(5) 0.054(2) Uani 1 1 d . .
.
H27A H 0.2107 0.0081 -0.0098 0.080 Uiso 1 1 calc R . .
H27B H 0.2298 -0.1156 0.0363 0.080 Uiso 1 1 calc R . .
H27C H 0.3451 -0.0287 0.0120 0.080 Uiso 1 1 calc R . .
C28 C 0.0245(9) -0.0332(9) 0.1485(5) 0.050(2) Uani 1 1 d . . .
H28A H -0.0034 -0.0165 0.1941 0.075 Uiso 1 1 calc R . .
H28B H 0.0182 -0.1137 0.1542 0.075 Uiso 1 1 calc R . .
H28C H -0.0300 0.0069 0.1166 0.075 Uiso 1 1 calc R . .
```

```
C29 C 0.2961(9) -0.0743(8) 0.1750(5) 0.0448(19) Uani 1 1 d . .
.
H29A H 0.3870 -0.0629 0.1542 0.067 Uiso 1 1 calc R . .
H29B H 0.2757 -0.1535 0.1848 0.067 Uiso 1 1 calc R . .
H29C H 0.2765 -0.0507 0.2187 0.067 Uiso 1 1 calc R . .
C30 C 0.0147(11) 0.2336(11) 0.0134(7) 0.069(3) Uani 1 1 d . .
.
H30A H 0.0061 0.1556 0.0129 0.103 Uiso 1 1 calc R . .
H30B H 0.0031 0.2827 -0.0316 0.103 Uiso 1 1 calc R . .
H30C H -0.0501 0.2510 0.0512 0.103 Uiso 1 1 calc R . .
C31 C 0.1842(17) 0.3988(9) 0.0444(7) 0.086(5) Uani 1 1 d . . .
H31A H 0.1312 0.3984 0.0903 0.129 Uiso 1 1 calc R . .
H31B H 0.1511 0.4545 0.0080 0.129 Uiso 1 1 calc R . .
H31C H 0.2721 0.4173 0.0435 0.129 Uiso 1 1 calc R . .
C32 C 0.3025(15) 0.2626(16) -0.0580(6) 0.104(6) Uani 1 1 d . .
.
H32A H 0.3890 0.2553 -0.0485 0.156 Uiso 1 1 calc R . .
H32B H 0.2939 0.3343 -0.0915 0.156 Uiso 1 1 calc R . .
H32C H 0.2865 0.2016 -0.0776 0.156 Uiso 1 1 calc R . .
C33 C 0.1912(9) 0.5640(7) 0.2954(5) 0.0429(19) Uani 1 1 d . .
.
H33A H 0.1016 0.5624 0.3194 0.064 Uiso 1 1 calc R . .
H33B H 0.2224 0.6409 0.2814 0.064 Uiso 1 1 calc R . .
H33C H 0.2421 0.5171 0.3271 0.064 Uiso 1 1 calc R . .
C34 C 0.3799(8) 0.5330(7) 0.1646(5) 0.0420(19) Uani 1 1 d . .
.
H34A H 0.4369 0.4909 0.1944 0.063 Uiso 1 1 calc R . .
H34B H 0.3991 0.6128 0.1529 0.063 Uiso 1 1 calc R . .
H34C H 0.3923 0.5080 0.1216 0.063 Uiso 1 1 calc R . .
C35 C 0.1036(10) 0.6077(8) 0.1570(5) 0.051(2) Uani 1 1 d . . .
H35A H 0.1072 0.5847 0.1138 0.076 Uiso 1 1 calc R . .
H35B H 0.1360 0.6839 0.1454 0.076 Uiso 1 1 calc R . .
H35C H 0.0151 0.6052 0.1828 0.076 Uiso 1 1 calc R . .
C36 C 0.0258(10) 0.3137(8) 0.3896(4) 0.047(2) Uani 1 1 d . . .
H36A H 0.1016 0.2713 0.4016 0.071 Uiso 1 1 calc R . .
H36B H -0.0508 0.2766 0.4207 0.071 Uiso 1 1 calc R . .
H36C H 0.0301 0.3894 0.3950 0.071 Uiso 1 1 calc R . .
C37 C -0.1307(8) 0.4026(8) 0.2733(6) 0.050(2) Uani 1 1 d . . .
H37A H -0.1285 0.4771 0.2811 0.075 Uiso 1 1 calc R . .
H37B H -0.2065 0.3629 0.3035 0.075 Uiso 1 1 calc R . .
H37C H -0.1338 0.4098 0.2242 0.075 Uiso 1 1 calc R . .
C38 C 0.0019(6) 0.1680(6) 0.2914(4) 0.0270(13) Uani 1 1 d . .
.
C39 C -0.1087(7) 0.1100(7) 0.3094(5) 0.0379(17) Uani 1 1 d . .
.
H39A H -0.1076 0.0341 0.3080 0.046 Uiso 1 1 calc R . .
H39B H -0.1872 0.1453 0.3234 0.046 Uiso 1 1 calc R . .
C220 C 0.4850(7) 0.2022(6) 0.3825(4) 0.0287(13) Uani 1 1 d . .
.
H220 H 0.5452 0.1775 0.3442 0.034 Uiso 1 1 calc R . .
C221 C 0.4305(9) 0.3182(7) 0.3500(5) 0.046(2) Uani 1 1 d . . .
H22A H 0.3866 0.3122 0.3132 0.069 Uiso 1 1 calc R . .
H22B H 0.5004 0.3718 0.3298 0.069 Uiso 1 1 calc R . .
```

```
H22C H 0.3701 0.3439 0.3864 0.069 Uiso 1 1 calc R . .
C222 C 0.5610(9) 0.2091(9) 0.4382(5) 0.047(2) Uani 1 1 d . . .
H22D H 0.5045 0.2346 0.4760 0.070 Uiso 1 1 calc R . .
H22E H 0.6313 0.2619 0.4167 0.070 Uiso 1 1 calc R . .
H22F H 0.5955 0.1352 0.4573 0.070 Uiso 1 1 calc R . .
C260 C 0.2503(7) -0.1525(6) 0.3791(4) 0.0272(13) Uani 1 1 d .
. .
H260 H 0.3099 -0.1380 0.3325 0.033 Uiso 1 1 calc R . .
C261 C 0.1127(8) -0.1602(7) 0.3668(5) 0.0398(18) Uani 1 1 d .
. .
H26A H 0.0533 -0.1815 0.4120 0.060 Uiso 1 1 calc R . .
H26B H 0.1110 -0.2165 0.3409 0.060 Uiso 1 1 calc R . .
H26C H 0.0874 -0.0876 0.3398 0.060 Uiso 1 1 calc R . .
C262 C 0.2906(8) -0.2653(7) 0.4252(4) 0.0382(17) Uani 1 1 d .
. .
H26D H 0.3801 -0.2615 0.4284 0.057 Uiso 1 1 calc R . .
H26E H 0.2802 -0.3259 0.4040 0.057 Uiso 1 1 calc R . .
H26F H 0.2368 -0.2795 0.4722 0.057 Uiso 1 1 calc R . .
N1 N 0.5603(5) 0.0778(5) 0.2082(3) 0.0256(11) Uani 1 1 d . . .
N2 N 0.4497(5) 0.0226(5) 0.3161(3) 0.0227(10) Uani 1 1 d . . .
N3 N 0.2170(6) 0.1559(5) 0.1006(3) 0.0278(12) Uani 1 1 d . . .
N4 N 0.1616(5) 0.3668(5) 0.2343(3) 0.0238(10) Uani 1 1 d . . .
O1 O 0.4496(4) 0.2883(4) 0.1377(2) 0.0266(9) Uani 1 1 d . . .
O2 O 0.1187(4) 0.1177(4) 0.2707(3) 0.0293(10) Uani 1 1 d . . .
Si1 Si 0.1806(2) 0.2559(2) 0.02792(11) 0.0396(5) Uani 1 1 d .
. .
Si2 Si 0.1966(2) 0.01250(18) 0.11089(11) 0.0299(4) Uani 1 1 d
. . .
Si3 Si 0.2062(2) 0.50834(16) 0.21371(11) 0.0303(4) Uani 1 1 d
. . .
Si4 Si 0.01911(18) 0.32082(16) 0.29463(10) 0.0268(4) Uani 1 1
d . . .
U1 U 0.26863(2) 0.218577(19) 0.191674(11) 0.01972(8) Uani 1 1
d . . .

loop_
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 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
C1 0.020(3) 0.027(3) 0.019(3) -0.007(2) -0.002(2) -0.004(2)
C5 0.023(3) 0.035(4) 0.028(3) -0.005(3) -0.003(2) 0.010(3)
C6 0.030(4) 0.046(4) 0.033(4) -0.012(3) -0.002(3) 0.015(3)
C7 0.026(3) 0.038(4) 0.023(3) -0.011(3) 0.001(2) 0.001(3)
C8 0.024(3) 0.036(4) 0.024(3) -0.007(3) 0.002(2) -0.009(3)
C9 0.036(4) 0.050(5) 0.030(4) -0.003(3) 0.006(3) -0.009(3)
C10 0.031(4) 0.055(5) 0.039(4) -0.016(4) -0.003(3) -0.016(3)
C21 0.020(3) 0.026(3) 0.017(3) -0.003(2) -0.001(2) 0.005(2)
C22 0.028(3) 0.021(3) 0.024(3) -0.002(2) -0.006(2) 0.001(2)
C23 0.039(4) 0.029(3) 0.026(3) -0.009(3) -0.007(3) 0.006(3)
```

```
C24 0.034(4) 0.038(4) 0.021(3) -0.004(3) 0.004(3) 0.007(3)
C25 0.031(3) 0.031(3) 0.025(3) -0.001(3) -0.001(3) 0.002(3)
C26 0.024(3) 0.022(3) 0.025(3) -0.002(2) -0.007(2) 0.004(2)
C27 0.071(6) 0.059(6) 0.037(4) -0.028(4) -0.005(4) -0.004(5)
C28 0.042(5) 0.051(5) 0.057(6) -0.017(4) -0.004(4) -0.015(4)
C29 0.054(5) 0.038(4) 0.045(5) -0.012(4) -0.013(4) -0.004(4)
C30 0.063(7) 0.075(8) 0.073(7) -0.007(6) -0.042(6) 0.012(6)
C31 0.168(15) 0.036(5) 0.065(7) 0.007(5) -0.069(9) -0.011(7)
C32 0.108(11) 0.165(16) 0.024(5) 0.005(7) -0.002(6) -0.053(11)
C33 0.059(5) 0.028(4) 0.042(4) -0.014(3) -0.005(4) -0.002(3)
C34 0.047(5) 0.029(4) 0.044(4) -0.008(3) 0.005(4) -0.008(3)
C35 0.064(6) 0.034(4) 0.048(5) 0.004(4) -0.017(4) 0.010(4)
C36 0.062(6) 0.049(5) 0.029(4) -0.015(4) 0.006(4) -0.013(4)
C37 0.029(4) 0.042(5) 0.077(7) -0.019(5) -0.006(4) 0.012(3)
C38 0.023(3) 0.030(3) 0.025(3) -0.005(3) -0.002(2) 0.004(2)
C39 0.025(3) 0.036(4) 0.051(5) -0.012(3) -0.002(3) -0.001(3)
C220 0.029(3) 0.032(4) 0.026(3) -0.008(3) -0.007(3) -0.002(3)
C221 0.052(5) 0.034(4) 0.051(5) 0.000(4) -0.019(4) -0.008(4)
C222 0.039(4) 0.060(6) 0.044(5) -0.010(4) -0.019(4) -0.004(4)
C260 0.027(3) 0.025(3) 0.029(3) -0.007(3) -0.003(3) 0.000(2)
C261 0.034(4) 0.031(4) 0.059(5) -0.015(4) -0.012(4) -0.001(3)
C262 0.046(4) 0.032(4) 0.037(4) -0.010(3) -0.011(3) 0.009(3)
N1 0.019(2) 0.034(3) 0.022(3) -0.008(2) -0.001(2) 0.002(2)
N2 0.020(2) 0.026(3) 0.022(2) -0.005(2) -0.0044(19) 0.0050(19)
N3 0.028(3) 0.036(3) 0.021(3) -0.009(2) -0.005(2) -0.004(2)
N4 0.024(3) 0.022(3) 0.023(2) -0.003(2) 0.000(2) 0.001(2)
O1 0.024(2) 0.029(2) 0.024(2) -0.0034(19) -0.0009(17) -
0.0026(18)
O2 0.022(2) 0.028(2) 0.035(3) -0.008(2) 0.0006(19) -0.0011(18)
Si1 0.0512(13) 0.0431(12) 0.0258(10) -0.0019(9) -0.0167(9) -
0.0094(10)
Si2 0.0318(10) 0.0337(10) 0.0274(9) -0.0133(8) -0.0049(7) -
0.0039(8)
Si3 0.0379(10) 0.0195(8) 0.0290(9) -0.0014(7) -0.0033(8)
0.0004(7)
Si4 0.0252(8) 0.0253(9) 0.0271(9) -0.0064(7) 0.0000(7)
0.0022(7)
U1 0.01825(11) 0.02315(12) 0.01705(11) -0.00457(8) -0.00264(7)
-0.00049(7)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
```

```
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
;

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C1 N2 1.338(8) . ?
C1 N1 1.346(8) . ?
C1 U1 2.630(6) . ?
C5 N2 1.478(8) . ?
C5 C6 1.513(10) . ?
C6 N1 1.454(9) . ?
C7 N1 1.462(9) . ?
C7 C8 1.508(10) . ?
C8 O1 1.426(8) . ?
C8 C10 1.531(10) . ?
C8 C9 1.524(10) . ?
C21 C22 1.397(9) . ?
C21 C26 1.406(9) . ?
C21 N2 1.444(8) . ?
C22 C23 1.399(9) . ?
C22 C220 1.523(9) . ?
C23 C24 1.382(11) . ?
C24 C25 1.380(11) . ?
C25 C26 1.397(9) . ?
C26 C260 1.516(9) . ?
C27 Si2 1.878(8) . ?
C28 Si2 1.863(9) . ?
C29 Si2 1.882(9) . ?
C30 Si1 1.872(11) . ?
C31 Si1 1.855(11) . ?
C32 Si1 1.888(13) . ?
C33 Si3 1.886(8) . ?
C34 Si3 1.879(8) . ?
C35 Si3 1.877(9) . ?
C36 Si4 1.875(8) . ?
C37 Si4 1.875(8) . ?
C38 C39 1.330(10) . ?
C38 O2 1.370(8) . ?
C38 Si4 1.897(7) . ?
C38 U1 3.062(6) . ?
C220 C222 1.513(10) . ?
C220 C221 1.521(11) . ?
C260 C262 1.526(10) . ?
C260 C261 1.528(10) . ?
N3 Si1 1.719(6) . ?
N3 Si2 1.723(6) . ?
N3 U1 2.305(6) . ?
N4 Si4 1.727(6) . ?
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```
N4 Si3 1.731(6) . ?
N4 U1 2.319(5) . ?
O1 U1 2.084(5) . ?
O2 U1 2.151(5) . ?
Si1 U1 3.467(2) . ?
Si4 U1 3.3559(18) . ?

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N2 C1 N1 107.2(5) . . ?
N2 C1 U1 135.5(4) . . ?
N1 C1 U1 116.8(4) . . ?
N2 C5 C6 101.4(5) . . ?
N1 C6 C5 103.6(5) . . ?
N1 C7 C8 114.1(5) . . ?
O1 C8 C7 107.5(5) . . ?
O1 C8 C10 109.3(6) . . ?
C7 C8 C10 111.7(7) . . ?
O1 C8 C9 108.4(6) . . ?
C7 C8 C9 108.7(6) . . ?
C10 C8 C9 111.2(6) . . ?
C22 C21 C26 122.2(6) . . ?
C22 C21 N2 118.6(6) . . ?
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```
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0247P)^2^+1.6070P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     riding
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          9326
_refine_ls_number_parameters      370
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0314
_refine_ls_R_factor_gt            0.0295
_refine_ls_wR_factor_ref          0.0666
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_refine_ls_goodness_of_fit_ref    1.204
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_refine_ls_shift/su_max           0.002
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C1 C 0.5180(4) -0.0099(4) 0.7829(3) 0.0425(10) Uani 1 1 d . .
.
H1A H 0.6120 0.0029 0.7954 0.064 Uiso 1 1 calc R . .
H1B H 0.4744 -0.0721 0.7404 0.064 Uiso 1 1 calc R . .
```

```
H1C H 0.4646 -0.0426 0.8257 0.064 Uiso 1 1 calc R . .
C1S C 0.4562(5) 0.3812(4) 0.5306(3) 0.0479(11) Uani 1 1 d . .
.
H1S H 0.4261 0.2996 0.5517 0.058 Uiso 1 1 calc R . .
C2 C 0.6265(4) 0.2081(4) 0.6761(2) 0.0339(8) Uani 1 1 d . . .
H2A H 0.6330 0.2919 0.6639 0.051 Uiso 1 1 calc R . .
H2B H 0.5808 0.1470 0.6333 0.051 Uiso 1 1 calc R . .
H2C H 0.7192 0.2173 0.6882 0.051 Uiso 1 1 calc R . .
C2S C 0.3803(5) 0.4472(5) 0.5344(3) 0.0496(11) Uani 1 1 d . .
.
H2S H 0.2975 0.4107 0.5581 0.060 Uiso 1 1 calc R . .
C3 C 0.3445(4) 0.1124(4) 0.7246(2) 0.0371(9) Uani 1 1 d . . .
H3A H 0.2832 0.0710 0.7634 0.056 Uiso 1 1 calc R . .
H3B H 0.3130 0.0549 0.6798 0.056 Uiso 1 1 calc R . .
H3C H 0.3430 0.1932 0.7128 0.056 Uiso 1 1 calc R . .
C3S C 0.4239(5) 0.5648(5) 0.5041(3) 0.0467(11) Uani 1 1 d . .
.
H3S H 0.3712 0.6096 0.5070 0.056 Uiso 1 1 calc R . .
C4 C 0.6400(4) 0.1859(4) 0.9823(2) 0.0393(9) Uani 1 1 d . . .
H4A H 0.6230 0.1014 0.9625 0.059 Uiso 1 1 calc R . .
H4B H 0.6052 0.1771 1.0312 0.059 Uiso 1 1 calc R . .
H4C H 0.7392 0.2445 0.9869 0.059 Uiso 1 1 calc R . .
C4S C 0.5372(6) 0.0975(4) 0.4513(3) 0.0536(12) Uani 1 1 d . .
.
H4S H 0.5630 0.1650 0.4176 0.064 Uiso 1 1 calc R . .
C5 C 0.3600(4) 0.1473(4) 0.9193(3) 0.0439(10) Uani 1 1 d . . .
H5A H 0.3098 0.1812 0.8867 0.066 Uiso 1 1 calc R . .
H5B H 0.3351 0.1463 0.9702 0.066 Uiso 1 1 calc R . .
H5C H 0.3357 0.0595 0.9018 0.066 Uiso 1 1 calc R . .
C5S C 0.5926(6) -0.0414(5) 0.5260(3) 0.0540(12) Uani 1 1 d . .
.
H5S H 0.6571 -0.0699 0.5440 0.065 Uiso 1 1 calc R . .
C6 C 0.5879(4) 0.4157(4) 0.9545(2) 0.0354(9) Uani 1 1 d . . .
H6A H 0.6854 0.4755 0.9513 0.053 Uiso 1 1 calc R . .
H6B H 0.5674 0.4112 1.0065 0.053 Uiso 1 1 calc R . .
H6C H 0.5308 0.4461 0.9249 0.053 Uiso 1 1 calc R . .
C6S C 0.6299(5) 0.0565(5) 0.4772(3) 0.0532(12) Uani 1 1 d . .
.
H6S H 0.7202 0.0955 0.4616 0.064 Uiso 1 1 calc R . .
C7 C 0.9265(5) 0.7804(4) 0.9509(2) 0.0419(10) Uani 1 1 d . . .
H7A H 0.8429 0.7874 0.9582 0.063 Uiso 1 1 calc R . .
H7B H 1.0072 0.8566 0.9740 0.063 Uiso 1 1 calc R . .
H7C H 0.9214 0.7030 0.9738 0.063 Uiso 1 1 calc R . .
C7S C 0.9144(5) 0.8788(4) 0.5216(3) 0.0470(11) Uani 1 1 d . .
.
H7S H 0.8549 0.7952 0.5368 0.056 Uiso 1 1 calc R . .
C8 C 1.1012(4) 0.7558(4) 0.8363(2) 0.0369(9) Uani 1 1 d . . .
H8A H 1.0876 0.6701 0.8497 0.055 Uiso 1 1 calc R . .
H8B H 1.1790 0.8215 0.8681 0.055 Uiso 1 1 calc R . .
H8C H 1.1204 0.7684 0.7841 0.055 Uiso 1 1 calc R . .
C8S C 0.8984(5) 0.9115(5) 0.4504(2) 0.0458(11) Uani 1 1 d . .
.
H8S H 0.8284 0.8502 0.4158 0.055 Uiso 1 1 calc R . .
```

```
C9 C 0.9686(4) 0.9263(4) 0.8105(3) 0.0405(10) Uani 1 1 d . . .
H9A H 0.9826 0.9255 0.7577 0.061 Uiso 1 1 calc R . .
H9B H 1.0499 0.9971 0.8374 0.061 Uiso 1 1 calc R . .
H9C H 0.8874 0.9384 0.8161 0.061 Uiso 1 1 calc R . .
C9S C 1.0170(5) 0.9673(5) 0.5715(2) 0.0507(12) Uani 1 1 d . .
.
H9S H 1.0291 0.9444 0.6209 0.061 Uiso 1 1 calc R . .
C10 C 0.6748(4) 0.7480(4) 0.6866(2) 0.0403(10) Uani 1 1 d . .
.
H10A H 0.7430 0.8376 0.6994 0.060 Uiso 1 1 calc R . .
H10B H 0.5864 0.7443 0.6688 0.060 Uiso 1 1 calc R . .
H10C H 0.7063 0.7128 0.6475 0.060 Uiso 1 1 calc R . .
C11 C 0.5878(4) 0.7164(4) 0.8434(2) 0.0364(9) Uani 1 1 d . . .
H11A H 0.5703 0.6631 0.8867 0.055 Uiso 1 1 calc R . .
H11B H 0.5020 0.7158 0.8231 0.055 Uiso 1 1 calc R . .
H11C H 0.6568 0.8049 0.8583 0.055 Uiso 1 1 calc R . .
C12 C 0.5159(4) 0.4838(4) 0.7400(2) 0.0357(9) Uani 1 1 d . . .
H12A H 0.5482 0.4492 0.7010 0.054 Uiso 1 1 calc R . .
H12B H 0.4318 0.4870 0.7204 0.054 Uiso 1 1 calc R . .
H12C H 0.4963 0.4282 0.7824 0.054 Uiso 1 1 calc R . .
C13 C 0.8987(5) 0.5844(4) 0.6351(2) 0.0380(9) Uani 1 1 d . . .
H13A H 0.7996 0.5270 0.6350 0.057 Uiso 1 1 calc R . .
H13B H 0.9185 0.6201 0.5861 0.057 Uiso 1 1 calc R . .
H13C H 0.9270 0.6547 0.6728 0.057 Uiso 1 1 calc R . .
C14 C 1.1837(4) 0.6055(4) 0.6556(3) 0.0434(10) Uani 1 1 d . .
.
H14A H 1.2116 0.6752 0.6936 0.065 Uiso 1 1 calc R . .
H14B H 1.2001 0.6417 0.6065 0.065 Uiso 1 1 calc R . .
H14C H 1.2375 0.5592 0.6658 0.065 Uiso 1 1 calc R . .
C15 C 0.9455(5) 0.3680(4) 0.5788(2) 0.0391(9) Uani 1 1 d . . .
H15A H 0.9992 0.3210 0.5860 0.059 Uiso 1 1 calc R . .
H15B H 0.9639 0.4111 0.5316 0.059 Uiso 1 1 calc R . .
H15C H 0.8471 0.3076 0.5778 0.059 Uiso 1 1 calc R . .
C16 C 1.0932(5) 0.2613(4) 0.7210(2) 0.0404(10) Uani 1 1 d . .
.
H16A H 1.0120 0.1984 0.6898 0.061 Uiso 1 1 calc R . .
H16B H 1.1374 0.2166 0.7487 0.061 Uiso 1 1 calc R . .
H16C H 1.1584 0.3235 0.6894 0.061 Uiso 1 1 calc R . .
C17 C 1.1951(4) 0.4609(4) 0.8480(2) 0.0394(9) Uani 1 1 d . . .
H17A H 1.2549 0.5318 0.8186 0.059 Uiso 1 1 calc R . .
H17B H 1.2451 0.4152 0.8678 0.059 Uiso 1 1 calc R . .
H17C H 1.1674 0.4953 0.8892 0.059 Uiso 1 1 calc R . .
C18 C 0.9196(4) 0.2211(4) 0.8462(2) 0.0346(9) Uani 1 1 d . . .
H18A H 0.8861 0.2607 0.8818 0.052 Uiso 1 1 calc R . .
H18B H 0.9685 0.1800 0.8732 0.052 Uiso 1 1 calc R . .
H18C H 0.8413 0.1563 0.8142 0.052 Uiso 1 1 calc R . .
C19 C 0.9671(3) 0.4914(3) 0.97109(18) 0.0222(6) Uani 1 1 d . .
.
N1 N 0.6028(3) 0.2653(3) 0.82863(15) 0.0219(6) Uani 1 1 d . .
.
N2 N 0.7989(3) 0.6391(3) 0.80411(15) 0.0224(6) Uani 1 1 d . .
.
```

```
N3 N 0.9551(3) 0.4258(3) 0.74280(15) 0.0223(6) Uani 1 1 d . .
.
O1 O 0.8971(2) 0.4742(2) 0.90650(13) 0.0258(5) Uani 1 1 d . .
.
Si1 Si 0.52372(10) 0.14662(9) 0.75818(6) 0.02438(19) Uani 1 1
d . . .
Si2 Si 0.54960(10) 0.25207(9) 0.91764(5) 0.0254(2) Uani 1 1 d
. . .
Si3 Si 0.94167(10) 0.76972(9) 0.84959(6) 0.0263(2) Uani 1 1 d
. . .
Si4 Si 0.65305(10) 0.65084(9) 0.77099(6) 0.0259(2) Uani 1 1 d
. . .
Si5 Si 0.99614(11) 0.49153(10) 0.65748(5) 0.0278(2) Uani 1 1 d
. . .
Si6 Si 1.03931(10) 0.34755(10) 0.78774(5) 0.0261(2) Uani 1 1 d
. . .
U1 U 0.789845(12) 0.443676(11) 0.800485(6) 0.01936(4) Uani 1 1
d . . .

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C1 0.042(2) 0.026(2) 0.058(3) -0.0018(19) -0.001(2) 0.0160(18)
C1S 0.056(3) 0.038(2) 0.040(2) -0.0059(19) -0.007(2) 0.016(2)
C2 0.0295(19) 0.034(2) 0.030(2) -0.0097(16) 0.0007(15)
0.0089(16)
C2S 0.039(2) 0.051(3) 0.047(3) -0.005(2) 0.005(2) 0.011(2)
C3 0.0258(18) 0.040(2) 0.041(2) -0.0095(18) -0.0047(16)
0.0121(17)
C3S 0.042(2) 0.050(3) 0.047(3) -0.013(2) -0.007(2) 0.022(2)
C4 0.044(2) 0.041(2) 0.031(2) 0.0126(18) 0.0047(18) 0.0181(19)
C4S 0.078(4) 0.034(2) 0.042(3) -0.005(2) 0.003(2) 0.021(2)
C5 0.031(2) 0.046(2) 0.044(2) 0.000(2) 0.0099(18) 0.0071(19)
C5S 0.063(3) 0.053(3) 0.054(3) -0.018(2) -0.012(2) 0.037(3)
C6 0.041(2) 0.036(2) 0.029(2) -0.0027(16) 0.0104(17)
0.0170(18)
C6S 0.042(2) 0.046(3) 0.055(3) -0.019(2) 0.009(2) 0.006(2)
C7 0.055(3) 0.036(2) 0.033(2) -0.0053(17) -0.0012(19) 0.021(2)
C7S 0.046(2) 0.042(2) 0.045(3) 0.010(2) 0.006(2) 0.014(2)
C8 0.0264(19) 0.032(2) 0.048(2) -0.0013(18) -0.0011(17)
0.0105(16)
C8S 0.044(2) 0.050(3) 0.033(2) -0.0103(19) -0.0033(19)
0.014(2)
C9 0.039(2) 0.026(2) 0.052(3) 0.0045(18) 0.0007(19) 0.0119(17)
C9S 0.054(3) 0.064(3) 0.026(2) 0.010(2) -0.0013(19) 0.021(2)
C10 0.045(2) 0.044(2) 0.039(2) 0.0124(19) 0.0008(18) 0.027(2)
C11 0.041(2) 0.033(2) 0.044(2) 0.0045(17) 0.0104(18)
0.0236(18)
```

```
C12 0.033(2) 0.034(2) 0.040(2) 0.0012(17) -0.0060(17)
0.0172(17)
C13 0.052(2) 0.045(2) 0.0246(19) 0.0067(17) 0.0062(17)
0.029(2)
C14 0.037(2) 0.043(2) 0.045(2) 0.005(2) 0.0179(19) 0.0125(19)
C15 0.052(2) 0.045(2) 0.0227(19) 0.0043(17) 0.0086(17)
0.023(2)
C16 0.048(2) 0.047(2) 0.039(2) 0.0020(19) 0.0125(19) 0.033(2)
C17 0.0282(19) 0.053(3) 0.038(2) -0.0053(19) -0.0037(17)
0.0207(19)
C18 0.040(2) 0.033(2) 0.037(2) 0.0090(17) 0.0082(17)
0.0212(18)
C19 0.0247(16) 0.0190(15) 0.0233(16) 0.0031(13) 0.0035(12)
0.0102(13)
N1 0.0212(13) 0.0212(14) 0.0230(14) -0.0006(11) 0.0024(11)
0.0096(11)
N2 0.0235(14) 0.0236(14) 0.0216(14) 0.0025(11) 0.0027(11)
0.0120(12)
N3 0.0239(14) 0.0236(14) 0.0193(14) 0.0008(11) 0.0031(11)
0.0107(12)
O1 0.0297(13) 0.0280(13) 0.0204(12) -0.0005(10) -0.0030(10)
0.0149(11)
Si1 0.0217(4) 0.0213(5) 0.0281(5) -0.0034(4) -0.0001(4)
0.0087(4)
Si2 0.0250(5) 0.0250(5) 0.0240(5) 0.0026(4) 0.0059(4)
0.0091(4)
Si3 0.0285(5) 0.0213(5) 0.0291(5) -0.0006(4) 0.0010(4)
0.0117(4)
Si4 0.0281(5) 0.0257(5) 0.0285(5) 0.0051(4) 0.0022(4)
0.0165(4)
Si5 0.0316(5) 0.0307(5) 0.0225(5) 0.0033(4) 0.0081(4)
0.0148(4)
Si6 0.0255(5) 0.0311(5) 0.0260(5) 0.0008(4) 0.0039(4)
0.0166(4)
U1 0.01981(6) 0.01936(7) 0.01853(7) 0.00021(4) 0.00104(4)
0.00892(5)

_geom_special_details
;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
;
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C1S C3S 1.379(7) 2_666 ?
C1S C2S 1.381(7) . ?
C2 Si1 1.879(4) . ?
C2S C3S 1.368(7) . ?
C3 Si1 1.866(4) . ?
C3S C1S 1.379(7) 2_666 ?
C4 Si2 1.867(4) . ?
C4S C5S 1.367(7) 2_656 ?
C4S C6S 1.367(7) . ?
C5 Si2 1.870(4) . ?
C5S C4S 1.367(7) 2_656 ?
C5S C6S 1.378(7) . ?
C6 Si2 1.871(4) . ?
C7 Si3 1.860(4) . ?
C7S C8S 1.365(6) . ?
C7S C9S 1.379(6) . ?
C8 Si3 1.871(4) . ?
C8S C9S 1.373(6) 2_776 ?
C9 Si3 1.872(4) . ?
C9S C8S 1.373(6) 2_776 ?
C10 Si4 1.871(4) . ?
C11 Si4 1.865(4) . ?
C12 Si4 1.882(4) . ?
C13 Si5 1.875(4) . ?
C14 Si5 1.871(4) . ?
C15 Si5 1.879(4) . ?
C16 Si6 1.870(4) . ?
C17 Si6 1.858(4) . ?
C18 Si6 1.866(4) . ?
C19 C19 1.180(7) 2_767 ?
C19 O1 1.304(4) . ?
N1 Si1 1.730(3) . ?
N1 Si2 1.740(3) . ?
N1 U1 2.251(3) . ?
N2 Si4 1.732(3) . ?
N2 Si3 1.742(3) . ?
N2 U1 2.249(3) . ?
N3 Si5 1.725(3) . ?
N3 Si6 1.741(3) . ?
N3 U1 2.259(3) . ?
O1 U1 2.101(2) . ?
Si1 U1 3.3841(10) . ?
Si2 U1 3.4621(9) . ?
Si3 U1 3.4665(10) . ?
Si4 U1 3.4248(9) . ?
Si5 U1 3.4566(10) . ?
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Si6 U1 3.4396(9) . ?

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C2S C3S C1S 120.5(4) . 2_666 ?
C5S C4S C6S 120.0(5) 2_656 . ?
C4S C5S C6S 119.9(5) 2_656 . ?
C4S C6S C5S 120.1(5) . . ?
C8S C7S C9S 119.9(4) . . ?
C7S C8S C9S 120.2(4) . 2_776 ?
C8S C9S C7S 119.9(4) 2_776 . ?
C19 C19 O1 178.6(5) 2_767 . ?
Si1 N1 Si2 124.35(16) . . ?
Si1 N1 U1 115.83(14) . . ?
Si2 N1 U1 119.80(14) . . ?
Si4 N2 Si3 121.34(16) . . ?
Si4 N2 U1 118.13(15) . . ?
Si3 N2 U1 120.06(14) . . ?
Si5 N3 Si6 122.20(16) . . ?
Si5 N3 U1 119.75(14) . . ?
Si6 N3 U1 118.04(14) . . ?
C19 O1 U1 177.5(2) . . ?
N1 Si1 C1 113.41(17) . . ?
N1 Si1 C3 114.80(16) . . ?
C1 Si1 C3 107.24(19) . . ?
N1 Si1 C2 106.58(16) . . ?
C1 Si1 C2 108.9(2) . . ?
C3 Si1 C2 105.48(18) . . ?
C1 Si1 U1 126.53(14) . . ?
C3 Si1 U1 125.01(14) . . ?
C2 Si1 U1 69.80(12) . . ?
N1 Si2 C4 111.80(17) . . ?
N1 Si2 C5 112.88(17) . . ?
C4 Si2 C5 107.7(2) . . ?
N1 Si2 C6 108.63(16) . . ?
C4 Si2 C6 108.9(2) . . ?
C5 Si2 C6 106.7(2) . . ?

C4 Si2 U1 105.92(13) . . ?
C5 Si2 U1 141.21(15) . . ?
C6 Si2 U1 79.58(12) . . ?
N2 Si3 C7 112.13(18) . . ?
N2 Si3 C8 109.61(16) . . ?
C7 Si3 C8 109.1(2) . . ?
N2 Si3 C9 112.07(17) . . ?
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C7 Si3 C9 107.6(2) . . ?
C8 Si3 C9 106.11(19) . . ?
C7 Si3 U1 105.75(14) . . ?
C8 Si3 U1 81.27(13) . . ?
C9 Si3 U1 140.87(15) . . ?
N2 Si4 C11 112.49(17) . . ?
N2 Si4 C10 114.23(17) . . ?
C11 Si4 C10 108.57(19) . . ?
N2 Si4 C12 107.31(15) . . ?
C11 Si4 C12 108.74(19) . . ?
C10 Si4 C12 105.11(19) . . ?
C11 Si4 U1 125.63(13) . . ?
C10 Si4 U1 124.05(14) . . ?
C12 Si4 U1 71.93(12) . . ?
N3 Si5 C14 113.21(18) . . ?
N3 Si5 C13 108.37(16) . . ?
C14 Si5 C13 107.4(2) . . ?
N3 Si5 C15 113.63(17) . . ?
C14 Si5 C15 107.5(2) . . ?
C13 Si5 C15 106.32(19) . . ?
C14 Si5 U1 128.69(14) . . ?
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 'U'  'U'  -9.6767   9.6646
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 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

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_cell_length_b                    15.6531(3)
_cell_length_c                    22.4759(4)
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_cell_angle_beta                  103.691(2)
_cell_angle_gamma                 90.00
_cell_volume                      10263.2(3)
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CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
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(compiled Jan  5 2010,16:28:46)
Empirical absorption correction using spherical harmonics,
 implemented in SCALE3 ABSPACK scaling algorithm.
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Atom C28 is a discrodered C atom in a silyl methyl group. The
thermal ellipsiod is elongated.'


'Alert C The minimum difference density is > 0.1*ZMAX*0.75.
The relevant atom site is U1'

'Alert C Atom C57 has ADP max/min Ratio .....       3.90 prola
Atom C57 shows a long thermal ellipsoid indicating disorder.
Splitting this atom resulted in the split C57 and C57A
becoming non-positive definite'
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_diffrn_measurement_device_type 'Xcalibur, Eos'
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CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
(compiled Jan  5 2010,16:28:46)
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(compiled Jan  5 2010,16:28:46)
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2008)'
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_computing_publication_material   ?

_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
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are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0905P)^2^+0.0000P] where
P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
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H1B H 0.5138 0.5666 0.2903 0.134 Uiso 1 1 calc R . .
H1C H 0.4756 0.6400 0.2805 0.134 Uiso 1 1 calc R . .
C2 C 0.4567(4) 0.5195(7) 0.1633(7) 0.083(5) Uani 1 1 d . . .
H2A H 0.4294 0.5263 0.1797 0.124 Uiso 1 1 calc R . .
H2B H 0.4724 0.4664 0.1790 0.124 Uiso 1 1 calc R . .
H2C H 0.4475 0.5172 0.1185 0.124 Uiso 1 1 calc R . .
C3 C 0.5523(4) 0.5849(7) 0.1723(6) 0.063(3) Uani 1 1 d . . .
H3A H 0.5497 0.5844 0.1280 0.095 Uiso 1 1 calc R . .
H3B H 0.5620 0.5284 0.1893 0.095 Uiso 1 1 calc R . .
H3C H 0.5751 0.6277 0.1914 0.095 Uiso 1 1 calc R . .
C4 C 0.4526(5) 0.8301(7) 0.2377(5) 0.062(4) Uani 1 1 d . . .
H4A H 0.4193 0.8269 0.2219 0.093 Uiso 1 1 calc R . .
H4B H 0.4611 0.8879 0.2529 0.093 Uiso 1 1 calc R . .
H4C H 0.4622 0.7890 0.2712 0.093 Uiso 1 1 calc R . .
C5 C 0.5440(4) 0.8283(9) 0.2052(7) 0.090(5) Uani 1 1 d . . .
H5A H 0.5526 0.8185 0.2496 0.135 Uiso 1 1 calc R . .
H5B H 0.5500 0.8880 0.1966 0.135 Uiso 1 1 calc R . .
H5C H 0.5621 0.7908 0.1851 0.135 Uiso 1 1 calc R . .
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H6A H 0.4702 0.8722 0.0770 0.078 Uiso 1 1 calc R . .
H6B H 0.4606 0.9397 0.1261 0.078 Uiso 1 1 calc R . .
H6C H 0.4226 0.8700 0.0974 0.078 Uiso 1 1 calc R . .
C7 C 0.5411(4) 0.7591(11) 0.0367(5) 0.086(5) Uani 1 1 d . . .
H7A H 0.5366 0.7970 0.0695 0.128 Uiso 1 1 calc R . .
H7B H 0.5717 0.7688 0.0296 0.128 Uiso 1 1 calc R . .
H7C H 0.5384 0.6995 0.0488 0.128 Uiso 1 1 calc R . .
C8 C 0.5113(5) 0.8920(8) -0.0606(7) 0.082(4) Uani 1 1 d . . .
H8A H 0.4936 0.9017 -0.1027 0.124 Uiso 1 1 calc R . .
H8B H 0.5441 0.8952 -0.0593 0.124 Uiso 1 1 calc R . .
H8C H 0.5034 0.9356 -0.0336 0.124 Uiso 1 1 calc R . .
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C9 C 0.5036(4) 0.7041(7) -0.0913(5) 0.062(3) Uani 1 1 d . . .
H9A H 0.5134 0.6493 -0.0713 0.092 Uiso 1 1 calc R . .
H9B H 0.5267 0.7242 -0.1124 0.092 Uiso 1 1 calc R . .
H9C H 0.4742 0.6967 -0.1210 0.092 Uiso 1 1 calc R . .
C10 C 0.4055(5) 0.9563(8) -0.0508(8) 0.097(5) Uani 1 1 d . . .
H10A H 0.4297 0.9761 -0.0700 0.145 Uiso 1 1 calc R . .
H10B H 0.4140 0.9693 -0.0069 0.145 Uiso 1 1 calc R . .
H10C H 0.3767 0.9853 -0.0697 0.145 Uiso 1 1 calc R . .
C11 C 0.3859(5) 0.8148(11) -0.1457(6) 0.102(6) Uani 1 1 d . .
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H11A H 0.4098 0.8409 -0.1628 0.153 Uiso 1 1 calc R . .
H11B H 0.3560 0.8387 -0.1660 0.153 Uiso 1 1 calc R . .
H11C H 0.3856 0.7529 -0.1523 0.153 Uiso 1 1 calc R . .
C12 C 0.3464(4) 0.8062(7) -0.0347(6) 0.056(3) Uani 1 1 d . . .
H12A H 0.3367 0.7487 -0.0494 0.084 Uiso 1 1 calc R . .
H12B H 0.3215 0.8468 -0.0504 0.084 Uiso 1 1 calc R . .
H12C H 0.3538 0.8068 0.0102 0.084 Uiso 1 1 calc R . .
C13 C 0.3761(5) 0.5656(9) -0.0847(7) 0.105(6) Uani 1 1 d . . .
H13A H 0.3608 0.6180 -0.1027 0.158 Uiso 1 1 calc R . .
H13B H 0.3714 0.5205 -0.1159 0.158 Uiso 1 1 calc R . .
H13C H 0.4090 0.5765 -0.0697 0.158 Uiso 1 1 calc R . .
C14 C 0.2888(4) 0.5126(8) -0.0504(7) 0.088(5) Uani 1 1 d . . .
H14A H 0.2762 0.4853 -0.0188 0.132 Uiso 1 1 calc R . .
H14B H 0.2839 0.4754 -0.0865 0.132 Uiso 1 1 calc R . .
H14C H 0.2734 0.5674 -0.0619 0.132 Uiso 1 1 calc R . .
C15 C 0.3783(5) 0.4261(8) 0.0075(8) 0.108(7) Uani 1 1 d . . .
H15A H 0.4117 0.4323 0.0194 0.162 Uiso 1 1 calc R . .
H15B H 0.3700 0.3837 -0.0253 0.162 Uiso 1 1 calc R . .
H15C H 0.3672 0.4073 0.0430 0.162 Uiso 1 1 calc R . .
C16 C 0.2698(4) 0.6686(8) 0.0466(7) 0.072(4) Uani 1 1 d . . .
H16A H 0.2740 0.7195 0.0231 0.109 Uiso 1 1 calc R . .
H16B H 0.2527 0.6839 0.0771 0.109 Uiso 1 1 calc R . .
H16C H 0.2528 0.6252 0.0188 0.109 Uiso 1 1 calc R . .
C17 C 0.3533(4) 0.7064(7) 0.1432(6) 0.064(3) Uani 1 1 d . . .
H17A H 0.3845 0.6887 0.1631 0.097 Uiso 1 1 calc R . .
H17B H 0.3352 0.7120 0.1740 0.097 Uiso 1 1 calc R . .
H17C H 0.3542 0.7616 0.1228 0.097 Uiso 1 1 calc R . .
C18 C 0.3178(5) 0.5263(9) 0.1286(8) 0.104(6) Uani 1 1 d . . .
H18A H 0.2971 0.4875 0.1010 0.156 Uiso 1 1 calc R . .
H18B H 0.3044 0.5417 0.1629 0.156 Uiso 1 1 calc R . .
H18C H 0.3474 0.4980 0.1443 0.156 Uiso 1 1 calc R . .
C19 C 0.4914(4) 0.5252(7) 0.0097(6) 0.055(3) Uani 1 1 d . . .
C20 C 0.1425(3) 0.2059(6) 0.2251(5) 0.043(3) Uani 1 1 d . . .
H20A H 0.1384 0.2503 0.1934 0.065 Uiso 1 1 calc R . .
H20B H 0.1183 0.2113 0.2475 0.065 Uiso 1 1 calc R . .
H20C H 0.1406 0.1495 0.2058 0.065 Uiso 1 1 calc R . .
C21 C 0.2111(4) 0.1313(7) 0.3358(5) 0.061(3) Uani 1 1 d . . .
H21A H 0.2213 0.0806 0.3172 0.091 Uiso 1 1 calc R . .
H21B H 0.1831 0.1178 0.3490 0.091 Uiso 1 1 calc R . .
H21C H 0.2351 0.1490 0.3713 0.091 Uiso 1 1 calc R . .
C22 C 0.1942(5) 0.3173(7) 0.3246(7) 0.083(5) Uani 1 1 d . . .
H22A H 0.2180 0.3168 0.3629 0.124 Uiso 1 1 calc R . .
H22B H 0.1640 0.3184 0.3339 0.124 Uiso 1 1 calc R . .
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H22C H 0.1979 0.3681 0.3007 0.124 Uiso 1 1 calc R . .
C23 C 0.3255(4) 0.2137(7) 0.3401(6) 0.064(3) Uani 1 1 d . . .
H23A H 0.3085 0.2191 0.3721 0.097 Uiso 1 1 calc R . .
H23B H 0.3561 0.2388 0.3545 0.097 Uiso 1 1 calc R . .
H23C H 0.3284 0.1531 0.3306 0.097 Uiso 1 1 calc R . .
C24 C 0.2930(5) 0.3866(8) 0.2910(6) 0.080(4) Uani 1 1 d . . .
H24A H 0.2821 0.4207 0.2538 0.120 Uiso 1 1 calc R . .
H24B H 0.3240 0.4051 0.3117 0.120 Uiso 1 1 calc R . .
H24C H 0.2724 0.3946 0.3184 0.120 Uiso 1 1 calc R . .
C25 C 0.3287(4) 0.2681(8) 0.2131(6) 0.068(4) Uani 1 1 d . . .
H25A H 0.3366 0.2088 0.2060 0.101 Uiso 1 1 calc R . .
H25B H 0.3569 0.3011 0.2282 0.101 Uiso 1 1 calc R . .
H25C H 0.3112 0.2931 0.1746 0.101 Uiso 1 1 calc R . .
C26 C 0.2951(6) 0.0842(10) -0.0194(6) 0.105(6) Uani 1 1 d . .
.
H26A H 0.3137 0.0329 -0.0071 0.157 Uiso 1 1 calc R . .
H26B H 0.3052 0.1131 -0.0526 0.157 Uiso 1 1 calc R . .
H26C H 0.2628 0.0679 -0.0337 0.157 Uiso 1 1 calc R . .
C27 C 0.2706(4) 0.2605(7) 0.0208(6) 0.066(4) Uani 1 1 d . . .
H27A H 0.2383 0.2478 0.0026 0.100 Uiso 1 1 calc R . .
H27B H 0.2844 0.2873 -0.0099 0.100 Uiso 1 1 calc R . .
H27C H 0.2729 0.2996 0.0555 0.100 Uiso 1 1 calc R . .
C28 C 0.3641(4) 0.1903(8) 0.0734(7) 0.078(5) Uani 1 1 d . . .
H28A H 0.3682 0.2305 0.1077 0.117 Uiso 1 1 calc R . .
H28B H 0.3737 0.2176 0.0392 0.117 Uiso 1 1 calc R . .
H28C H 0.3828 0.1393 0.0863 0.117 Uiso 1 1 calc R . .
C29 C 0.3622(4) 0.0009(8) 0.1477(7) 0.085(5) Uani 1 1 d . . .
H29A H 0.3694 0.0033 0.1074 0.127 Uiso 1 1 calc R . .
H29B H 0.3710 -0.0551 0.1663 0.127 Uiso 1 1 calc R . .
H29C H 0.3792 0.0458 0.1740 0.127 Uiso 1 1 calc R . .
C30 C 0.2693(4) -0.0739(7) 0.0936(6) 0.063(3) Uani 1 1 d . . .
H30A H 0.2361 -0.0652 0.0857 0.095 Uiso 1 1 calc R . .
H30B H 0.2776 -0.1270 0.1167 0.095 Uiso 1 1 calc R . .
H30C H 0.2784 -0.0777 0.0546 0.095 Uiso 1 1 calc R . .
C31 C 0.2890(4) 0.0088(7) 0.2169(5) 0.052(3) Uani 1 1 d . . .
H31A H 0.3081 0.0506 0.2439 0.078 Uiso 1 1 calc R . .
H31B H 0.2970 -0.0489 0.2329 0.078 Uiso 1 1 calc R . .
H31C H 0.2566 0.0201 0.2152 0.078 Uiso 1 1 calc R . .
C32 C 0.1101(4) 0.2466(8) -0.0585(5) 0.063(3) Uani 1 1 d . . .
H32A H 0.0913 0.2947 -0.0511 0.095 Uiso 1 1 calc R . .
H32B H 0.0912 0.2071 -0.0878 0.095 Uiso 1 1 calc R . .
H32C H 0.1353 0.2678 -0.0752 0.095 Uiso 1 1 calc R . .
C33 C 0.1650(4) 0.0977(7) -0.0087(5) 0.051(3) Uani 1 1 d . . .
H33A H 0.1862 0.1186 -0.0325 0.077 Uiso 1 1 calc R . .
H33B H 0.1429 0.0584 -0.0339 0.077 Uiso 1 1 calc R . .
H33C H 0.1823 0.0676 0.0277 0.077 Uiso 1 1 calc R . .
C34 C 0.0844(4) 0.1480(7) 0.0437(5) 0.051(3) Uani 1 1 d . . .
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H34B H 0.0650 0.1122 0.0121 0.077 Uiso 1 1 calc R . .
H34C H 0.0664 0.1960 0.0533 0.077 Uiso 1 1 calc R . .
C35 C 0.1025(4) 0.3847(6) 0.0793(5) 0.051(3) Uani 1 1 d . . .
H35A H 0.0807 0.3538 0.0472 0.076 Uiso 1 1 calc R . .
H35B H 0.0973 0.4463 0.0738 0.076 Uiso 1 1 calc R . .
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H35C H 0.0982 0.3677 0.1196 0.076 Uiso 1 1 calc R . .
C36 C 0.1750(4) 0.4194(7) 0.0090(6) 0.064(4) Uani 1 1 d . . .
H36A H 0.2063 0.4070 0.0058 0.096 Uiso 1 1 calc R . .
H36B H 0.1718 0.4807 0.0157 0.096 Uiso 1 1 calc R . .
H36C H 0.1533 0.4023 -0.0290 0.096 Uiso 1 1 calc R . .
C37 C 0.2037(4) 0.4028(6) 0.1443(5) 0.058(3) Uani 1 1 d . . .
H37A H 0.2006 0.3707 0.1806 0.087 Uiso 1 1 calc R . .
H37B H 0.1967 0.4632 0.1493 0.087 Uiso 1 1 calc R . .
H37C H 0.2351 0.3973 0.1393 0.087 Uiso 1 1 calc R . .
C38 C 0.1611(3) -0.0100(6) 0.1574(5) 0.039(2) Uani 1 1 d . . .
C39 C 0.1613(3) -0.0288(6) 0.2144(5) 0.035(2) Uani 1 1 d D . .
C40 C 0.2529(4) -0.1869(7) 0.3252(6) 0.066(4) Uani 1 1 d . . .
H40A H 0.2344 -0.1349 0.3228 0.099 Uiso 1 1 calc R . .
H40B H 0.2810 -0.1743 0.3118 0.099 Uiso 1 1 calc R . .
H40C H 0.2609 -0.2076 0.3676 0.099 Uiso 1 1 calc R . .
C41 C 0.2548(4) -0.3717(8) 0.2842(8) 0.087(5) Uani 1 1 d . . .
H41A H 0.2547 -0.3983 0.3236 0.130 Uiso 1 1 calc R . .
H41B H 0.2864 -0.3582 0.2827 0.130 Uiso 1 1 calc R . .
H41C H 0.2416 -0.4112 0.2509 0.130 Uiso 1 1 calc R . .
C42 C 0.2141(4) -0.2377(8) 0.1951(5) 0.065(3) Uani 1 1 d . . .
H42A H 0.1929 -0.2764 0.1681 0.097 Uiso 1 1 calc R . .
H42B H 0.2442 -0.2403 0.1853 0.097 Uiso 1 1 calc R . .
H42C H 0.2023 -0.1792 0.1893 0.097 Uiso 1 1 calc R . .
C43 C 0.1937(5) -0.3323(8) 0.4237(6) 0.075(4) Uani 1 1 d . . .
H43A H 0.2261 -0.3386 0.4230 0.112 Uiso 1 1 calc R . .
H43B H 0.1862 -0.3729 0.4531 0.112 Uiso 1 1 calc R . .
H43C H 0.1882 -0.2739 0.4360 0.112 Uiso 1 1 calc R . .
C44 C 0.1644(5) -0.4701(7) 0.3278(7) 0.078(4) Uani 1 1 d . . .
H44A H 0.1503 -0.4804 0.2844 0.117 Uiso 1 1 calc R . .
H44B H 0.1495 -0.5061 0.3531 0.117 Uiso 1 1 calc R . .
H44C H 0.1971 -0.4841 0.3362 0.117 Uiso 1 1 calc R . .
C45 C 0.0959(4) -0.3447(7) 0.3518(5) 0.057(3) Uani 1 1 d . . .
H45A H 0.0909 -0.2884 0.3681 0.085 Uiso 1 1 calc R . .
H45B H 0.0892 -0.3892 0.3791 0.085 Uiso 1 1 calc R . .
H45C H 0.0755 -0.3516 0.3110 0.085 Uiso 1 1 calc R . .
C46 C 0.0777(4) 0.0417(6) 0.3067(5) 0.056(3) Uani 1 1 d . . .
H46A H 0.0952 0.0401 0.2749 0.083 Uiso 1 1 calc R . .
H46B H 0.0905 0.0857 0.3369 0.083 Uiso 1 1 calc R . .
H46C H 0.0456 0.0551 0.2879 0.083 Uiso 1 1 calc R . .
C47 C 0.1429(3) -0.0905(7) 0.3829(5) 0.045(3) Uani 1 1 d . . .
H47A H 0.1442 -0.1401 0.4099 0.068 Uiso 1 1 calc R . .
H47B H 0.1571 -0.0412 0.4069 0.068 Uiso 1 1 calc R . .
H47C H 0.1595 -0.1035 0.3513 0.068 Uiso 1 1 calc R . .
C48 C 0.0501(4) -0.0557(7) 0.4079(5) 0.060(3) Uani 1 1 d . . .
H48A H 0.0178 -0.0421 0.3900 0.090 Uiso 1 1 calc R . .
H48B H 0.0639 -0.0101 0.4361 0.090 Uiso 1 1 calc R . .
H48C H 0.0521 -0.1099 0.4302 0.090 Uiso 1 1 calc R . .
C49 C -0.0142(4) -0.2334(8) 0.3406(6) 0.059(3) Uani 1 1 d . .
.
H49A H 0.0000 -0.2901 0.3458 0.089 Uiso 1 1 calc R . .
H49B H -0.0476 -0.2395 0.3312 0.089 Uiso 1 1 calc R . .
H49C H -0.0040 -0.2006 0.3785 0.089 Uiso 1 1 calc R . .
```

```
C50 C -0.0391(4) -0.0863(8) 0.2513(6) 0.067(4) Uani 1 1 d . .
.
H50A H -0.0344 -0.0423 0.2832 0.101 Uiso 1 1 calc R . .
H50B H -0.0705 -0.1082 0.2441 0.101 Uiso 1 1 calc R . .
H50C H -0.0341 -0.0616 0.2134 0.101 Uiso 1 1 calc R . .
C51 C -0.0054(3) -0.2532(7) 0.2117(5) 0.051(3) Uani 1 1 d . .
.
H51A H 0.0061 -0.2277 0.1784 0.077 Uiso 1 1 calc R . .
H51B H -0.0381 -0.2662 0.1970 0.077 Uiso 1 1 calc R . .
H51C H 0.0115 -0.3060 0.2254 0.077 Uiso 1 1 calc R . .
C52 C 0.0949(4) -0.3902(7) 0.1670(6) 0.067(4) Uani 1 1 d . . .
H52A H 0.1267 -0.3809 0.1899 0.101 Uiso 1 1 calc R . .
H52B H 0.0916 -0.4486 0.1508 0.101 Uiso 1 1 calc R . .
H52C H 0.0742 -0.3820 0.1944 0.101 Uiso 1 1 calc R . .
C53 C 0.0210(4) -0.3390(8) 0.0574(6) 0.072(4) Uani 1 1 d . . .
H53A H -0.0009 -0.3300 0.0829 0.108 Uiso 1 1 calc R . .
H53B H 0.0199 -0.3988 0.0443 0.108 Uiso 1 1 calc R . .
H53C H 0.0131 -0.3019 0.0213 0.108 Uiso 1 1 calc R . .
C54 C 0.1216(4) -0.3337(9) 0.0533(6) 0.074(4) Uani 1 1 d . . .
H54A H 0.1205 -0.2864 0.0244 0.110 Uiso 1 1 calc R . .
H54B H 0.1133 -0.3870 0.0305 0.110 Uiso 1 1 calc R . .
H54C H 0.1527 -0.3387 0.0792 0.110 Uiso 1 1 calc R . .
C55 C 0.0539(4) -0.1261(9) 0.0140(5) 0.075(4) Uani 1 1 d . . .
H55A H 0.0748 -0.1578 -0.0054 0.112 Uiso 1 1 calc R . .
H55B H 0.0488 -0.0689 -0.0041 0.112 Uiso 1 1 calc R . .
H55C H 0.0246 -0.1564 0.0074 0.112 Uiso 1 1 calc R . .
C56 C 0.1363(3) -0.0616(6) 0.1000(4) 0.039(2) Uani 1 1 d . . .
H56A H 0.1579 -0.1060 0.0929 0.046 Uiso 1 1 calc R . .
H56B H 0.1313 -0.0221 0.0646 0.046 Uiso 1 1 calc R . .
N1 N 0.4723(3) 0.7006(5) 0.1476(3) 0.0335(18) Uani 1 1 d . . .
N2 N 0.4432(3) 0.7746(6) -0.0200(3) 0.050(2) Uani 1 1 d . . .
N3 N 0.3623(3) 0.6071(5) 0.0371(4) 0.045(2) Uani 1 1 d . . .
N4 N 0.2408(3) 0.2264(4) 0.2378(4) 0.0325(18) Uani 1 1 d . . .
N5 N 0.2796(3) 0.1172(5) 0.1058(4) 0.0375(19) Uani 1 1 d . . .
N6 N 0.1699(2) 0.2486(5) 0.0706(3) 0.0327(18) Uani 1 1 d . . .
N7 N 0.1669(3) -0.2845(4) 0.2898(4) 0.0358(19) Uani 1 1 d . .
.
N8 N 0.0594(3) -0.1439(4) 0.2938(3) 0.0292(17) Uani 1 1 d . .
.
N9 N 0.0846(3) -0.2140(5) 0.1355(4) 0.042(2) Uani 1 1 d . . .
O1 O 0.4679(3) 0.5879(5) 0.0289(4) 0.067(2) Uani 1 1 d . . .
O2 O 0.1846(2) 0.0629(4) 0.1453(3) 0.0405(16) Uani 1 1 d . . .
O3 O 0.1401(2) -0.0979(4) 0.2300(3) 0.0342(15) Uani 1 1 d . .
.
Si1 Si 0.49608(11) 0.61204(19) 0.18760(13) 0.0453(7) Uani 1 1
d . . .
Si2 Si 0.48133(10) 0.80441(17) 0.17533(13) 0.0397(7) Uani 1 1
d . . .
Si3 Si 0.49729(11) 0.7818(2) -0.03405(14) 0.0544(8) Uani 1 1 d
. . .
Si4 Si 0.39787(11) 0.8373(3) -0.06192(16) 0.0619(10) Uani 1 1
d . . .
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Si5 Si 0.35178(12) 0.5310(2) -0.02006(19) 0.0650(11) Uani 1 1
d . . .
Si6 Si 0.32658(11) 0.6254(2) 0.08577(17) 0.0559(9) Uani 1 1 d
. . .
Si7 Si 0.19953(10) 0.21887(18) 0.27923(13) 0.0425(7) Uani 1 1
d . . .
Si8 Si 0.29415(10) 0.27079(19) 0.26988(14) 0.0464(7) Uani 1 1
d . . .
Si9 Si 0.30186(11) 0.1588(2) 0.04823(16) 0.0564(9) Uani 1 1 d
. . .
Si10 Si 0.29928(10) 0.01750(19) 0.13876(14) 0.0454(7) Uani 1 1
d . . .
Si11 Si 0.13388(10) 0.18962(18) 0.01502(13) 0.0388(7) Uani 1 1
d . . .
Si12 Si 0.16242(10) 0.35875(17) 0.07452(13) 0.0384(7) Uani 1 1
d . . .
Si13 Si 0.21971(10) -0.26984(19) 0.27509(15) 0.0449(7) Uani 1
1 d . . .
Si14 Si 0.15728(11) -0.35414(18) 0.34634(14) 0.0467(8) Uani 1
1 d . . .
Si15 Si 0.08129(10) -0.06532(17) 0.34555(13) 0.0373(6) Uani 1
1 d . . .
Si16 Si 0.00271(9) -0.17660(18) 0.27681(14) 0.0400(7) Uani 1 1
d . . .
Si17 Si 0.08025(11) -0.3127(2) 0.10262(14) 0.0496(8) Uani 1 1
d . . .
Si18 Si 0.07949(10) -0.11673(19) 0.09724(13) 0.0432(7) Uani 1
1 d . . .
U1 U 0.428428(14) 0.68484(3) 0.051062(17) 0.04055(12) Uani 1 1
d . . .
U2 U 0.222360(12) 0.17420(2) 0.141088(16) 0.03292(11) Uani 1 1
d . . .
U3 U 0.105101(12) -0.20813(2) 0.239304(15) 0.03006(10) Uani 1
1 d . . .
C57 C 0.0422(4) -0.0500(10) 0.1277(6) 0.098(6) Uani 1 1 d . .
.
H57A H 0.0128 -0.0791 0.1243 0.148 Uiso 1 1 calc R . .
H57B H 0.0371 0.0037 0.1046 0.148 Uiso 1 1 calc R . .
H57C H 0.0561 -0.0378 0.1708 0.148 Uiso 1 1 calc R . .
H39 H 0.181(4) 0.008(7) 0.245(5) 0.118 Uiso 1 1 d D . .

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C2 0.067(9) 0.052(8) 0.116(12) 0.031(8) -0.004(9) 0.005(6)
C3 0.053(8) 0.053(7) 0.085(9) 0.002(7) 0.021(7) 0.026(6)
C4 0.092(10) 0.057(7) 0.034(6) -0.008(5) 0.006(6) 0.033(7)
```

C5 0.044(8) 0.107(11) 0.107(12) -0.051(10) -0.003(8) -0.009(7)
C6 0.070(8) 0.034(6) 0.058(7) 0.008(5) 0.030(6) 0.016(5)
C7 0.029(7) 0.186(15) 0.044(7) 0.011(9) 0.012(6) 0.010(8)
C8 0.075(10) 0.069(9) 0.122(13) -0.014(9) 0.059(9) -0.010(7)
C9 0.059(8) 0.065(8) 0.056(7) -0.001(6) 0.005(6) 0.021(6)
C10 0.061(9) 0.084(10) 0.143(15) 0.060(10) 0.020(10) 0.003(7)
C11 0.047(8) 0.211(19) 0.040(7) 0.021(9) -0.006(6) 0.006(10)
C12 0.047(7) 0.055(7) 0.072(8) 0.016(6) 0.023(6) 0.005(5)
C13 0.057(9) 0.121(13) 0.142(15) -0.100(12) 0.031(10) -
0.020(8)
C14 0.057(9) 0.060(8) 0.127(13) -0.030(8) -0.019(9) -0.007(6)
C15 0.068(10) 0.050(8) 0.173(17) -0.014(10) -0.037(10) -
0.003(7)
C16 0.042(7) 0.071(9) 0.113(12) -0.010(8) 0.035(8) -0.006(6)
C17 0.049(8) 0.068(8) 0.085(9) -0.010(7) 0.031(7) 0.003(6)
C18 0.076(11) 0.104(12) 0.139(15) 0.057(11) 0.040(11) -
0.015(9)
C19 0.045(7) 0.050(8) 0.062(8) -0.017(6) -0.003(6) 0.013(5)
C20 0.041(6) 0.040(6) 0.052(6) 0.015(5) 0.019(5) 0.018(5)
C21 0.060(8) 0.070(8) 0.046(7) 0.014(6) 0.000(6) -0.009(6)
C22 0.125(13) 0.036(7) 0.112(12) -0.020(7) 0.078(11) -0.011(7)
C23 0.053(8) 0.071(8) 0.060(8) 0.002(7) -0.006(6) 0.001(6)
C24 0.079(10) 0.066(9) 0.084(10) -0.020(8) -0.002(8) -0.019(7)
C25 0.045(7) 0.092(10) 0.068(8) 0.000(7) 0.016(6) -0.021(7)
C26 0.124(14) 0.144(14) 0.063(9) 0.008(9) 0.056(10) 0.071(12)
C27 0.055(8) 0.073(8) 0.083(9) 0.046(7) 0.040(7) 0.028(6)
C28 0.039(7) 0.096(10) 0.117(12) 0.054(9) 0.057(8) 0.017(6)
C29 0.038(7) 0.088(10) 0.134(13) 0.046(9) 0.033(8) 0.037(7)
C30 0.080(9) 0.048(7) 0.066(8) -0.006(6) 0.024(7) 0.010(6)
C31 0.063(8) 0.048(7) 0.044(6) 0.008(5) 0.012(6) 0.015(5)
C32 0.068(9) 0.077(9) 0.039(6) 0.009(6) 0.001(6) 0.029(7)
C33 0.057(7) 0.056(7) 0.045(6) 0.004(5) 0.020(6) 0.014(5)
C34 0.040(6) 0.063(7) 0.054(7) -0.011(6) 0.018(5) 0.005(5)
C35 0.050(7) 0.041(6) 0.065(7) 0.005(5) 0.021(6) 0.016(5)
C36 0.064(8) 0.055(7) 0.084(9) 0.040(7) 0.040(7) 0.024(6)
C37 0.069(8) 0.028(6) 0.068(8) 0.028(5) 0.001(6) 0.005(5)
C38 0.044(6) 0.034(6) 0.047(6) 0.021(5) 0.027(5) 0.022(4)
C39 0.037(6) 0.031(5) 0.039(6) -0.004(4) 0.011(5) 0.005(4)
C40 0.042(7) 0.071(8) 0.075(9) -0.002(7) -0.005(6) -0.013(6)
C41 0.061(9) 0.061(9) 0.145(15) 0.019(9) 0.038(9) 0.021(7)
C42 0.041(7) 0.093(9) 0.062(8) -0.018(7) 0.017(6) -0.009(6)
C43 0.080(10) 0.082(10) 0.050(7) 0.019(7) -0.008(7) 0.002(7)
C44 0.080(10) 0.044(7) 0.114(12) 0.016(7) 0.029(9) 0.023(7)
C45 0.076(9) 0.039(6) 0.061(8) 0.014(6) 0.027(7) 0.000(6)
C46 0.069(8) 0.035(6) 0.065(8) 0.000(5) 0.020(7) 0.012(5)
C47 0.043(6) 0.050(6) 0.041(6) -0.009(5) 0.007(5) -0.005(5)
C48 0.063(8) 0.070(8) 0.053(7) -0.014(6) 0.026(6) 0.004(6)
C49 0.038(7) 0.075(8) 0.072(8) 0.016(7) 0.026(6) -0.005(6)
C50 0.041(7) 0.073(8) 0.091(10) 0.010(7) 0.020(7) 0.022(6)
C51 0.030(6) 0.062(7) 0.064(7) -0.003(6) 0.015(5) -0.016(5)
C52 0.093(10) 0.042(7) 0.068(8) -0.028(6) 0.019(7) -0.027(6)
C53 0.069(9) 0.089(10) 0.058(8) -0.038(7) 0.018(7) -0.037(7)
C54 0.052(8) 0.117(11) 0.056(8) -0.036(8) 0.020(6) -0.027(7)

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C55 0.060(8) 0.122(12) 0.035(6) 0.004(7) -0.004(6) -0.020(8)
C56 0.040(6) 0.042(6) 0.035(5) 0.009(5) 0.010(5) -0.006(4)
N1 0.038(5) 0.036(4) 0.028(4) -0.004(3) 0.010(4) 0.011(3)
N2 0.026(5) 0.103(7) 0.022(4) 0.002(4) 0.008(4) -0.010(5)
N3 0.042(5) 0.026(4) 0.066(6) -0.009(4) 0.007(4) -0.001(4)
N4 0.036(5) 0.018(4) 0.044(5) 0.003(3) 0.010(4) 0.004(3)
N5 0.033(5) 0.046(5) 0.039(5) 0.009(4) 0.019(4) 0.015(4)
N6 0.030(4) 0.036(4) 0.037(4) 0.014(4) 0.018(4) 0.012(3)
N7 0.037(5) 0.026(4) 0.038(4) 0.004(3) -0.003(4) 0.005(3)
N8 0.039(5) 0.018(4) 0.034(4) 0.001(3) 0.015(4) 0.005(3)
N9 0.032(5) 0.054(5) 0.036(5) -0.001(4) 0.001(4) -0.020(4)
O1 0.041(5) 0.088(6) 0.072(6) -0.042(5) 0.012(4) 0.007(4)
O2 0.040(4) 0.047(4) 0.037(4) 0.011(3) 0.014(3) 0.012(3)
O3 0.037(4) 0.039(4) 0.030(3) 0.005(3) 0.014(3) -0.006(3)
Si1 0.0488(19) 0.0472(18) 0.0417(16) 0.0094(14) 0.0143(14)
0.0220(14)
Si2 0.0403(16) 0.0389(16) 0.0357(15) -0.0134(12) 0.0005(13)
0.0037(12)
Si3 0.0390(18) 0.088(2) 0.0379(16) -0.0038(17) 0.0125(14)
0.0002(16)
Si4 0.0339(18) 0.105(3) 0.0456(18) 0.0231(19) 0.0068(15) -
0.0026(17)
Si5 0.046(2) 0.0387(18) 0.099(3) -0.0277(19) -0.0050(19) -
0.0017(14)
Si6 0.0427(19) 0.0499(19) 0.081(2) 0.0070(17) 0.0259(17) -
0.0076(14)
Si7 0.0467(18) 0.0468(17) 0.0368(15) 0.0050(13) 0.0155(14)
0.0075(13)
Si8 0.0391(17) 0.0452(18) 0.0493(18) -0.0025(14) -0.0005(14) -
0.0044(13)
Si9 0.047(2) 0.071(2) 0.062(2) 0.0284(17) 0.0358(17)
0.0322(16)
Si10 0.0380(17) 0.0473(18) 0.0537(18) 0.0084(14) 0.0167(14)
0.0220(13)
Si11 0.0370(16) 0.0463(17) 0.0350(14) 0.0073(12) 0.0122(12)
0.0118(12)
Si12 0.0364(16) 0.0341(15) 0.0469(16) 0.0200(13) 0.0146(13)
0.0090(12)
Si13 0.0283(15) 0.0456(17) 0.0584(19) -0.0046(15) 0.0051(14)
0.0071(12)
Si14 0.054(2) 0.0371(16) 0.0463(17) 0.0085(14) 0.0060(15)
0.0115(14)
Si15 0.0400(16) 0.0330(15) 0.0419(16) -0.0044(12) 0.0153(13)
0.0048(12)
Si16 0.0281(15) 0.0485(17) 0.0467(17) 0.0030(14) 0.0158(13)
0.0013(12)
Si17 0.0432(18) 0.069(2) 0.0383(16) -0.0212(15) 0.0134(14) -
0.0213(15)
Si18 0.0335(16) 0.0576(19) 0.0377(16) 0.0075(14) 0.0065(13) -
0.0016(13)
U1 0.0382(2) 0.0541(3) 0.02894(19) -0.01174(17) 0.00701(16) -
0.01079(18)
```

```
U2 0.0329(2) 0.0370(2) 0.03038(19) 0.00675(15) 0.01052(15)
0.01547(15)
U3 0.02808(19) 0.0342(2) 0.02830(18) 0.00036(15) 0.00747(14)
0.00576(14)
C57 0.035(7) 0.184(16) 0.089(10) 0.099(11) 0.038(7) 0.037(8)

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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
;

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C2 Si1 1.868(12) . ?
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C4 Si2 1.855(11) . ?
C5 Si2 1.880(12) . ?
C6 Si2 1.891(10) . ?
C7 Si3 1.844(11) . ?
C8 Si3 1.904(12) . ?
C9 Si3 1.813(11) . ?
C10 Si4 1.886(14) . ?
C11 Si4 1.865(13) . ?
C12 Si4 1.857(11) . ?
C13 Si5 1.855(17) . ?
C14 Si5 1.874(12) . ?
C15 Si5 1.866(13) . ?
C16 Si6 1.851(12) . ?
C17 Si6 1.851(12) . ?
C18 Si6 1.876(13) . ?
C19 C19 1.09(2) 3_665 ?
C19 O1 1.338(12) . ?
C20 Si7 1.863(10) . ?
C21 Si7 1.846(11) . ?
C22 Si7 1.875(11) . ?
C23 Si8 1.864(11) . ?
C24 Si8 1.877(12) . ?
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C26 Si9 1.890(14) . ?
C27 Si9 1.876(10) . ?
C28 Si9 1.886(12) . ?
C29 Si10 1.871(11) . ?
C30 Si10 1.859(11) . ?
C31 Si10 1.859(11) . ?
C32 Si11 1.864(10) . ?
C33 Si11 1.862(10) . ?
C34 Si11 1.872(11) . ?
C35 Si12 1.872(10) . ?
C36 Si12 1.864(11) . ?
C37 Si12 1.884(11) . ?
C38 C39 1.312(13) . ?
C38 O2 1.402(11) . ?
C38 C56 1.555(13) . ?
C39 O3 1.343(11) . ?
C40 Si13 1.847(11) . ?
C41 Si13 1.896(11) . ?
C42 Si13 1.836(13) . ?
C43 Si14 1.854(12) . ?
C44 Si14 1.886(11) . ?
C45 Si14 1.883(12) . ?
C46 Si15 1.881(10) . ?
C47 Si15 1.884(10) . ?
C48 Si15 1.867(11) . ?
C49 Si16 1.857(11) . ?
C50 Si16 1.887(11) . ?
C51 Si16 1.863(11) . ?
C52 Si17 1.860(13) . ?
C53 Si17 1.874(12) . ?
C54 Si17 1.879(12) . ?
C55 Si18 1.853(11) . ?
C56 Si18 1.899(9) . ?
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N1 Si2 1.739(8) . ?
N1 U1 2.269(7) . ?
N2 Si3 1.731(9) . ?
N2 Si4 1.758(9) . ?
N2 U1 2.249(8) . ?
N3 Si5 1.726(9) . ?
N3 Si6 1.728(9) . ?
N3 U1 2.285(8) . ?
N4 Si7 1.722(8) . ?
N4 Si8 1.737(8) . ?
N4 U2 2.266(8) . ?
N5 Si9 1.719(8) . ?
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N5 U2 2.241(7) . ?
N6 Si11 1.716(8) . ?
N6 Si12 1.743(8) . ?
N6 U2 2.273(7) . ?
N7 Si13 1.710(9) . ?
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N7 Si14 1.749(8) . ?
N7 U3 2.273(7) . ?
N8 Si15 1.714(8) . ?
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Si4 N2 U1 N3 39.5(6) . . . . ?
Si3 N2 U1 Si2 75.2(5) . . . . ?
Si4 N2 U1 Si2 -105.3(5) . . . . ?
Si3 N2 U1 Si4 -179.5(9) . . . . ?
Si3 N2 U1 Si1 31.4(7) . . . . ?
Si4 N2 U1 Si1 -149.1(3) . . . . ?
Si3 N2 U1 Si5 -115.1(5) . . . . ?
Si4 N2 U1 Si5 64.4(5) . . . . ?
Si3 N2 U1 Si6 -171.3(3) . . . . ?
Si4 N2 U1 Si6 8.2(7) . . . . ?
Si1 N1 U1 O1 -36.7(5) . . . . ?
Si2 N1 U1 O1 141.0(5) . . . . ?
Si1 N1 U1 N2 -133.1(5) . . . . ?
Si2 N1 U1 N2 44.6(5) . . . . ?
Si1 N1 U1 N3 62.6(5) . . . . ?
Si2 N1 U1 N3 -119.7(4) . . . . ?
Si1 N1 U1 Si2 -177.7(8) . . . . ?
Si1 N1 U1 Si4 -161.5(3) . . . . ?
Si2 N1 U1 Si4 16.2(6) . . . . ?
Si2 N1 U1 Si1 177.7(8) . . . . ?
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Si1 N1 U1 Si5 35.9(6) . . . . ?
Si2 N1 U1 Si5 -146.4(3) . . . . ?
Si1 N1 U1 Si6 81.1(4) . . . . ?
Si2 N1 U1 Si6 -101.2(4) . . . . ?
Si5 N3 U1 O1 -34.4(5) . . . . ?
Si6 N3 U1 O1 143.6(5) . . . . ?
Si5 N3 U1 N2 64.2(6) . . . . ?
Si6 N3 U1 N2 -117.8(5) . . . . ?
Si5 N3 U1 N1 -132.6(4) . . . . ?
Si6 N3 U1 N1 45.4(5) . . . . ?
Si5 N3 U1 Si2 -162.8(3) . . . . ?
Si6 N3 U1 Si2 15.2(6) . . . . ?
Si5 N3 U1 Si4 81.2(4) . . . . ?
Si6 N3 U1 Si4 -100.8(4) . . . . ?
Si5 N3 U1 Si1 -109.1(4) . . . . ?
Si6 N3 U1 Si1 68.9(4) . . . . ?
Si6 N3 U1 Si5 178.0(9) . . . . ?
Si5 N3 U1 Si6 -178.0(9) . . . . ?
N1 Si2 U1 O1 -43.6(5) . . . . ?
C4 Si2 U1 O1 -132.4(5) . . . . ?
C5 Si2 U1 O1 28.9(7) . . . . ?
C6 Si2 U1 O1 130.5(5) . . . . ?
N1 Si2 U1 N2 -140.7(5) . . . . ?
C4 Si2 U1 N2 130.6(5) . . . . ?
C5 Si2 U1 N2 -68.2(7) . . . . ?
C6 Si2 U1 N2 33.5(4) . . . . ?
C4 Si2 U1 N1 -88.7(6) . . . . ?
C5 Si2 U1 N1 72.5(8) . . . . ?
C6 Si2 U1 N1 174.2(6) . . . . ?
N1 Si2 U1 N3 77.4(5) . . . . ?
C4 Si2 U1 N3 -11.3(5) . . . . ?
C5 Si2 U1 N3 149.9(7) . . . . ?
C6 Si2 U1 N3 -108.4(4) . . . . ?
N1 Si2 U1 Si4 -167.1(5) . . . . ?
C4 Si2 U1 Si4 104.2(4) . . . . ?
C5 Si2 U1 Si4 -94.5(7) . . . . ?
C6 Si2 U1 Si4 7.1(4) . . . . ?
N1 Si2 U1 Si1 -1.2(4) . . . . ?
C4 Si2 U1 Si1 -90.0(4) . . . . ?
C5 Si2 U1 Si1 71.3(7) . . . . ?
C6 Si2 U1 Si1 172.9(4) . . . . ?
N1 Si2 U1 Si5 60.9(5) . . . . ?
C4 Si2 U1 Si5 -27.9(5) . . . . ?
C5 Si2 U1 Si5 133.4(7) . . . . ?
C6 Si2 U1 Si5 -124.9(4) . . . . ?
N1 Si2 U1 Si6 84.2(5) . . . . ?
C4 Si2 U1 Si6 -4.5(4) . . . . ?
C5 Si2 U1 Si6 156.7(7) . . . . ?
C6 Si2 U1 Si6 -101.6(4) . . . . ?
N2 Si4 U1 O1 -45.2(6) . . . . ?
C12 Si4 U1 O1 132.9(5) . . . . ?
C11 Si4 U1 O1 33.9(6) . . . . ?
C10 Si4 U1 O1 -129.0(6) . . . . ?
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C12 Si4 U1 N2 178.2(7) . . . . ?
C11 Si4 U1 N2 79.2(8) . . . . ?
C10 Si4 U1 N2 -83.8(8) . . . . ?
N2 Si4 U1 N1 71.5(6) . . . . ?
C12 Si4 U1 N1 -110.3(5) . . . . ?
C11 Si4 U1 N1 150.7(6) . . . . ?
C10 Si4 U1 N1 -12.2(6) . . . . ?
N2 Si4 U1 N3 -147.1(6) . . . . ?
C12 Si4 U1 N3 31.1(5) . . . . ?
C11 Si4 U1 N3 -67.9(6) . . . . ?
C10 Si4 U1 N3 129.2(6) . . . . ?
N2 Si4 U1 Si2 79.0(5) . . . . ?
C12 Si4 U1 Si2 -102.9(4) . . . . ?
C11 Si4 U1 Si2 158.1(6) . . . . ?
C10 Si4 U1 Si2 -4.8(6) . . . . ?
N2 Si4 U1 Si1 54.5(6) . . . . ?
C12 Si4 U1 Si1 -127.3(4) . . . . ?
C11 Si4 U1 Si1 133.7(6) . . . . ?
C10 Si4 U1 Si1 -29.2(6) . . . . ?
N2 Si4 U1 Si5 -121.0(5) . . . . ?
C12 Si4 U1 Si5 57.1(4) . . . . ?
C11 Si4 U1 Si5 -41.9(6) . . . . ?
C10 Si4 U1 Si5 155.2(6) . . . . ?
N2 Si4 U1 Si6 -173.6(5) . . . . ?
C12 Si4 U1 Si6 4.5(4) . . . . ?
C11 Si4 U1 Si6 -94.5(6) . . . . ?
C10 Si4 U1 Si6 102.6(6) . . . . ?
N1 Si1 U1 O1 141.7(5) . . . . ?
C1 Si1 U1 O1 -171.2(9) . . . . ?
C3 Si1 U1 O1 36.7(5) . . . . ?
C2 Si1 U1 O1 -69.0(5) . . . . ?
N1 Si1 U1 N2 61.3(6) . . . . ?
C1 Si1 U1 N2 108.4(10) . . . . ?
C3 Si1 U1 N2 -43.7(5) . . . . ?
C2 Si1 U1 N2 -149.4(6) . . . . ?
C1 Si1 U1 N1 47.2(10) . . . . ?
C3 Si1 U1 N1 -105.0(6) . . . . ?
C2 Si1 U1 N1 149.4(7) . . . . ?
N1 Si1 U1 N3 -126.2(5) . . . . ?
C1 Si1 U1 N3 -79.0(9) . . . . ?
C3 Si1 U1 N3 128.8(4) . . . . ?
C2 Si1 U1 N3 23.2(5) . . . . ?
N1 Si1 U1 Si2 1.3(5) . . . . ?
C1 Si1 U1 Si2 48.5(9) . . . . ?
C3 Si1 U1 Si2 -103.7(4) . . . . ?
C2 Si1 U1 Si2 150.7(5) . . . . ?
N1 Si1 U1 Si4 31.9(5) . . . . ?
C1 Si1 U1 Si4 79.0(9) . . . . ?
C3 Si1 U1 Si4 -73.1(4) . . . . ?
C2 Si1 U1 Si4 -178.8(5) . . . . ?
N1 Si1 U1 Si5 -152.9(5) . . . . ?
C1 Si1 U1 Si5 -105.7(9) . . . . ?
C3 Si1 U1 Si5 102.2(4) . . . . ?
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C2 Si1 U1 Si5 -3.5(5) . . . . ?
N1 Si1 U1 Si6 -101.9(5) . . . . ?
C1 Si1 U1 Si6 -54.7(9) . . . . ?
C3 Si1 U1 Si6 153.1(4) . . . . ?
C2 Si1 U1 Si6 47.5(5) . . . . ?
N3 Si5 U1 O1 144.4(6) . . . . ?
C13 Si5 U1 O1 -66.3(6) . . . . ?
C15 Si5 U1 O1 39.0(7) . . . . ?
C14 Si5 U1 O1 -172.0(9) . . . . ?
N3 Si5 U1 N2 -126.9(5) . . . . ?
C13 Si5 U1 N2 22.3(6) . . . . ?
C15 Si5 U1 N2 127.7(7) . . . . ?
C14 Si5 U1 N2 -83.4(9) . . . . ?
N3 Si5 U1 N1 63.5(6) . . . . ?
C13 Si5 U1 N1 -147.2(6) . . . . ?
C15 Si5 U1 N1 -41.9(7) . . . . ?
C14 Si5 U1 N1 107.1(9) . . . . ?
C13 Si5 U1 N3 149.3(7) . . . . ?
C15 Si5 U1 N3 -105.4(8) . . . . ?
C14 Si5 U1 N3 43.6(10) . . . . ?
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C15 Si5 U1 Si2 -75.1(7) . . . . ?
C14 Si5 U1 Si2 73.8(9) . . . . ?
N3 Si5 U1 Si4 -102.9(5) . . . . ?
C13 Si5 U1 Si4 46.4(5) . . . . ?
C15 Si5 U1 Si4 151.8(6) . . . . ?
C14 Si5 U1 Si4 -59.3(9) . . . . ?
N3 Si5 U1 Si1 79.4(5) . . . . ?
C13 Si5 U1 Si1 -131.3(5) . . . . ?
C15 Si5 U1 Si1 -26.0(7) . . . . ?
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N3 Si5 U1 Si6 1.1(5) . . . . ?
C13 Si5 U1 Si6 150.4(5) . . . . ?
C15 Si5 U1 Si6 -104.3(7) . . . . ?
C14 Si5 U1 Si6 44.7(9) . . . . ?
N3 Si6 U1 O1 -41.2(5) . . . . ?
C16 Si6 U1 O1 -124.7(6) . . . . ?
C17 Si6 U1 O1 136.7(5) . . . . ?
C18 Si6 U1 O1 36.9(8) . . . . ?
N3 Si6 U1 N2 81.5(6) . . . . ?
C16 Si6 U1 N2 -2.0(6) . . . . ?
C17 Si6 U1 N2 -100.5(5) . . . . ?
C18 Si6 U1 N2 159.6(8) . . . . ?
N3 Si6 U1 N1 -140.7(5) . . . . ?
C16 Si6 U1 N1 135.8(6) . . . . ?
C17 Si6 U1 N1 37.3(5) . . . . ?
C18 Si6 U1 N1 -62.6(7) . . . . ?
C16 Si6 U1 N3 -83.5(7) . . . . ?
C17 Si6 U1 N3 177.9(7) . . . . ?
C18 Si6 U1 N3 78.1(9) . . . . ?
N3 Si6 U1 Si2 -167.9(5) . . . . ?
C16 Si6 U1 Si2 108.7(5) . . . . ?
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C17 Si6 U1 Si2 10.1(4) . . . . ?
C18 Si6 U1 Si2 -89.7(7) . . . . ?
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C17 Si6 U1 Si4 -96.7(4) . . . . ?
C18 Si6 U1 Si4 163.4(7) . . . . ?
N3 Si6 U1 Si1 -115.3(5) . . . . ?
C16 Si6 U1 Si1 161.3(5) . . . . ?
C17 Si6 U1 Si1 62.7(4) . . . . ?
C18 Si6 U1 Si1 -37.1(7) . . . . ?
N3 Si6 U1 Si5 -1.1(5) . . . . ?
C16 Si6 U1 Si5 -84.6(5) . . . . ?
C17 Si6 U1 Si5 176.8(4) . . . . ?
C18 Si6 U1 Si5 77.0(7) . . . . ?
Si9 N5 U2 O2 135.4(5) . . . . ?
Si10 N5 U2 O2 -40.4(5) . . . . ?
Si9 N5 U2 N4 -112.1(5) . . . . ?
Si10 N5 U2 N4 72.1(5) . . . . ?
Si9 N5 U2 N6 30.6(6) . . . . ?
Si10 N5 U2 N6 -145.3(4) . . . . ?
Si9 N5 U2 Si10 175.8(9) . . . . ?
Si9 N5 U2 Si11 56.8(5) . . . . ?
Si10 N5 U2 Si11 -119.0(4) . . . . ?
Si9 N5 U2 Si7 -133.3(4) . . . . ?
Si10 N5 U2 Si7 50.9(6) . . . . ?
Si7 N4 U2 O2 -38.9(4) . . . . ?
Si8 N4 U2 O2 140.3(4) . . . . ?
Si7 N4 U2 N5 -147.5(4) . . . . ?
Si8 N4 U2 N5 31.7(5) . . . . ?
Si7 N4 U2 N6 70.8(4) . . . . ?
Si8 N4 U2 N6 -110.1(4) . . . . ?
Si7 N4 U2 Si10 -119.4(3) . . . . ?
Si8 N4 U2 Si10 59.8(4) . . . . ?
Si7 N4 U2 Si11 48.6(5) . . . . ?
Si8 N4 U2 Si11 -132.3(3) . . . . ?
Si8 N4 U2 Si7 179.1(7) . . . . ?
Si11 N6 U2 O2 -32.6(4) . . . . ?
Si12 N6 U2 O2 142.2(4) . . . . ?
Si11 N6 U2 N5 71.8(5) . . . . ?
Si12 N6 U2 N5 -113.4(5) . . . . ?
Si11 N6 U2 N4 -145.7(4) . . . . ?
Si12 N6 U2 N4 29.1(5) . . . . ?
Si11 N6 U2 Si10 48.5(5) . . . . ?
Si12 N6 U2 Si10 -136.6(3) . . . . ?
Si12 N6 U2 Si11 174.8(8) . . . . ?
Si11 N6 U2 Si7 -119.4(4) . . . . ?
Si12 N6 U2 Si7 55.4(4) . . . . ?
N5 Si10 U2 O2 138.9(5) . . . . ?
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C29 Si10 U2 O2 -166.6(8) . . . . ?
C31 Si10 U2 N5 153.9(6) . . . . ?
C30 Si10 U2 N5 -102.3(6) . . . . ?
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C29 Si10 U2 N4 -63.7(8) . . . . ?
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C31 Si10 U2 N6 -157.5(5) . . . . ?
C30 Si10 U2 N6 -53.7(5) . . . . ?
C29 Si10 U2 N6 103.1(8) . . . . ?
N5 Si10 U2 Si11 70.8(5) . . . . ?
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C30 Si10 U2 Si11 -31.6(4) . . . . ?
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C32 Si11 U2 O2 -168.3(7) . . . . ?
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C32 Si11 U2 N6 44.8(8) . . . . ?
C34 Si11 U2 N6 -107.9(5) . . . . ?
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C34 Si11 U2 Si10 107.2(4) . . . . ?
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C33 Si11 U2 Si7 -144.9(4) . . . . ?
C32 Si11 U2 Si7 115.2(7) . . . . ?
C34 Si11 U2 Si7 -37.5(4) . . . . ?
N4 Si7 U2 O2 142.6(4) . . . . ?
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C20 Si7 U2 O2 -57.8(3) . . . . ?
C22 Si7 U2 O2 -153.8(8) . . . . ?
N4 Si7 U2 N5 45.7(5) . . . . ?
C21 Si7 U2 N5 -48.1(5) . . . . ?
C20 Si7 U2 N5 -154.8(4) . . . . ?
C22 Si7 U2 N5 109.3(8) . . . . ?
C21 Si7 U2 N4 -93.8(6) . . . . ?
C20 Si7 U2 N4 159.6(5) . . . . ?
C22 Si7 U2 N4 63.6(8) . . . . ?
N4 Si7 U2 N6 -119.1(4) . . . . ?
C21 Si7 U2 N6 147.1(5) . . . . ?
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C20 Si7 U2 N6 40.5(4) . . . . ?
C22 Si7 U2 N6 -55.5(8) . . . . ?
N4 Si7 U2 Si10 70.2(4) . . . . ?
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C20 Si7 U2 Si10 -130.2(3) . . . . ?
C22 Si7 U2 Si10 133.8(8) . . . . ?
N4 Si7 U2 Si11 -145.4(4) . . . . ?
C21 Si7 U2 Si11 120.9(4) . . . . ?
C20 Si7 U2 Si11 14.2(3) . . . . ?
C22 Si7 U2 Si11 -81.7(8) . . . . ?
Si17 N9 U3 O3 144.9(5) . . . . ?
Si18 N9 U3 O3 -29.8(4) . . . . ?
Si17 N9 U3 N7 48.9(5) . . . . ?
Si18 N9 U3 N7 -125.8(4) . . . . ?
Si17 N9 U3 N8 -121.9(4) . . . . ?
Si18 N9 U3 N8 63.3(5) . . . . ?
Si18 N9 U3 Si17 -174.7(8) . . . . ?
Si17 N9 U3 Si16 -100.5(4) . . . . ?
Si18 N9 U3 Si16 84.8(4) . . . . ?
Si17 N9 U3 Si18 174.7(8) . . . . ?
Si17 N9 U3 Si14 18.9(6) . . . . ?
Si18 N9 U3 Si14 -155.9(3) . . . . ?
Si17 N9 U3 Si15 -150.3(3) . . . . ?
Si18 N9 U3 Si15 34.9(6) . . . . ?
Si13 N7 U3 O3 -33.2(5) . . . . ?
Si14 N7 U3 O3 143.9(4) . . . . ?
Si13 N7 U3 N9 57.2(5) . . . . ?
Si14 N7 U3 N9 -125.7(4) . . . . ?
Si13 N7 U3 N8 -131.7(4) . . . . ?
Si14 N7 U3 N8 45.4(5) . . . . ?
Si13 N7 U3 Si17 77.2(4) . . . . ?
Si14 N7 U3 Si17 -105.7(4) . . . . ?
Si13 N7 U3 Si16 -162.5(3) . . . . ?
Si14 N7 U3 Si16 14.6(5) . . . . ?
Si13 N7 U3 Si18 27.6(6) . . . . ?
Si14 N7 U3 Si18 -155.3(3) . . . . ?
Si13 N7 U3 Si14 -177.1(8) . . . . ?
Si13 N7 U3 Si15 -108.3(4) . . . . ?
Si14 N7 U3 Si15 68.8(4) . . . . ?
Si15 N8 U3 O3 -36.8(4) . . . . ?
Si16 N8 U3 O3 140.6(4) . . . . ?
Si15 N8 U3 N9 -126.0(4) . . . . ?
Si16 N8 U3 N9 51.4(5) . . . . ?
Si15 N8 U3 N7 63.2(5) . . . . ?
Si16 N8 U3 N7 -119.4(4) . . . . ?
Si15 N8 U3 Si17 -156.4(3) . . . . ?
Si16 N8 U3 Si17 21.0(5) . . . . ?
Si15 N8 U3 Si16 -177.4(7) . . . . ?
Si15 N8 U3 Si18 -100.8(4) . . . . ?
Si16 N8 U3 Si18 76.6(4) . . . . ?
Si15 N8 U3 Si14 82.6(4) . . . . ?
Si16 N8 U3 Si14 -100.0(4) . . . . ?
Si16 N8 U3 Si15 177.4(7) . . . . ?
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N9 Si17 U3 O3 -37.3(5) . . . . ?
C52 Si17 U3 O3 142.6(5) . . . . ?
C53 Si17 U3 O3 -120.0(6) . . . . ?
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C52 Si17 U3 N9 179.9(7) . . . . ?
C53 Si17 U3 N9 -82.7(7) . . . . ?
C54 Si17 U3 N9 84.4(7) . . . . ?
N9 Si17 U3 N7 -137.9(5) . . . . ?
C52 Si17 U3 N7 42.0(5) . . . . ?
C53 Si17 U3 N7 139.4(6) . . . . ?
C54 Si17 U3 N7 -53.5(6) . . . . ?
N9 Si17 U3 N8 76.5(5) . . . . ?
C52 Si17 U3 N8 -103.6(5) . . . . ?
C53 Si17 U3 N8 -6.2(6) . . . . ?
C54 Si17 U3 N8 160.9(6) . . . . ?
N9 Si17 U3 Si16 86.3(5) . . . . ?
C52 Si17 U3 Si16 -93.8(4) . . . . ?
C53 Si17 U3 Si16 3.6(6) . . . . ?
C54 Si17 U3 Si16 170.7(6) . . . . ?
N9 Si17 U3 Si18 -3.0(5) . . . . ?
C52 Si17 U3 Si18 176.9(5) . . . . ?
C53 Si17 U3 Si18 -85.7(5) . . . . ?
C54 Si17 U3 Si18 81.4(6) . . . . ?
N9 Si17 U3 Si14 -165.4(5) . . . . ?
C52 Si17 U3 Si14 14.5(4) . . . . ?
C53 Si17 U3 Si14 111.9(5) . . . . ?
C54 Si17 U3 Si14 -81.1(6) . . . . ?
N9 Si17 U3 Si15 53.9(5) . . . . ?
C52 Si17 U3 Si15 -126.2(5) . . . . ?
C53 Si17 U3 Si15 -28.7(6) . . . . ?
C54 Si17 U3 Si15 138.3(6) . . . . ?
N8 Si16 U3 O3 -44.1(4) . . . . ?
C49 Si16 U3 O3 -130.3(5) . . . . ?
C51 Si16 U3 O3 131.8(4) . . . . ?
C50 Si16 U3 O3 34.9(6) . . . . ?
N8 Si16 U3 N9 -136.8(4) . . . . ?
C49 Si16 U3 N9 137.0(5) . . . . ?
C51 Si16 U3 N9 39.1(4) . . . . ?
C50 Si16 U3 N9 -57.7(6) . . . . ?
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are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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P=(Fo^2^+2Fc^2^)/3'
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H27A H 0.1105 -0.0331 0.0586 0.042 Uiso 1 1 calc R . .
H27B H 0.1762 0.0827 0.0429 0.042 Uiso 1 1 calc R . .
C12 C 0.22956(11) -0.1116(2) 0.07761(11) 0.0270(4) Uani 1 1 d
. . .
C13 C 0.28361(14) -0.1026(2) 0.02933(13) 0.0368(5) Uani 1 1 d
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H25 H 0.2747 -0.0284 -0.0104 0.044 Uiso 1 1 calc R . .
C14 C 0.34686(15) -0.1956(3) 0.03810(15) 0.0452(6) Uani 1 1 d
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H24 H 0.3818 -0.1865 0.0046 0.054 Uiso 1 1 calc R . .
C15 C 0.36185(14) -0.3058(3) 0.09605(16) 0.0485(6) Uani 1 1 d
. . .
H23 H 0.4073 -0.3703 0.1022 0.058 Uiso 1 1 calc R . .
C16 C 0.31109(15) -0.3215(2) 0.14442(14) 0.0412(5) Uani 1 1 d
. . .
H22 H 0.3211 -0.3976 0.1831 0.049 Uiso 1 1 calc R . .
C17 C 0.24586(12) -0.2270(2) 0.13662(12) 0.0288(4) Uani 1 1 d
. . .
C18 C 0.2268(2) -0.3305(3) 0.26389(16) 0.0562(7) Uani 1 1 d .
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H19A H 0.2325 -0.4279 0.2467 0.084 Uiso 1 1 calc R . .
H19B H 0.1875 -0.3287 0.2953 0.084 Uiso 1 1 calc R . .
H19C H 0.2830 -0.2952 0.2994 0.084 Uiso 1 1 calc R . .
C19 C 0.10704(17) -0.2868(3) 0.13699(19) 0.0576(7) Uani 1 1 d
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H20A H 0.0860 -0.2298 0.0858 0.086 Uiso 1 1 calc R . .
H20B H 0.0682 -0.2764 0.1686 0.086 Uiso 1 1 calc R . .
H20C H 0.1096 -0.3866 0.1222 0.086 Uiso 1 1 calc R . .
C21 C 0.18091(12) 0.2736(2) 0.22880(15) 0.0356(4) Uani 1 1 d .
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H18A H 0.2036 0.3318 0.2801 0.043 Uiso 1 1 calc R . .
H18B H 0.1776 0.3277 0.1780 0.043 Uiso 1 1 calc R . .
C22 C 0.10674(11) 0.1949(2) 0.22204(12) 0.0274(4) Uani 1 1 d .
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C23 C 0.03483(13) 0.1986(3) 0.14659(14) 0.0400(5) Uani 1 1 d .
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H16 H 0.0346 0.2638 0.1041 0.048 Uiso 1 1 calc R . .
C24 C -0.03263(13) 0.1128(3) 0.13376(17) 0.0540(8) Uani 1 1 d
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H15 H -0.0801 0.1184 0.0830 0.065 Uiso 1 1 calc R . .
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C25 C -0.03308(16) 0.0148(3) 0.1953(2) 0.0605(9) Uani 1 1 d .
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H14 H -0.0812 -0.0453 0.1857 0.073 Uiso 1 1 calc R . .
C26 C 0.03516(16) 0.0042(3) 0.26942(19) 0.0458(6) Uani 1 1 d .
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H13 H 0.0340 -0.0627 0.3106 0.055 Uiso 1 1 calc R . .
C27 C 0.10494(11) 0.0911(2) 0.28331(12) 0.0278(4) Uani 1 1 d .
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C28 C 0.19199(16) 0.1952(3) 0.41873(15) 0.0539(7) Uani 1 1 d .
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H10A H 0.1832 0.2857 0.3888 0.081 Uiso 1 1 calc R . .
H10B H 0.2502 0.1917 0.4598 0.081 Uiso 1 1 calc R . .
H10C H 0.1505 0.1862 0.4475 0.081 Uiso 1 1 calc R . .
C29 C 0.1872(2) -0.0570(3) 0.40487(19) 0.0654(9) Uani 1 1 d .
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H11A H 0.1426 -0.0605 0.4301 0.098 Uiso 1 1 calc R . .
H11B H 0.2436 -0.0620 0.4490 0.098 Uiso 1 1 calc R . .
H11C H 0.1802 -0.1373 0.3666 0.098 Uiso 1 1 calc R . .
C31 C 0.39517(12) -0.0592(2) 0.34563(13) 0.0313(4) Uani 1 1 d
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H9A H 0.3909 -0.1179 0.3921 0.038 Uiso 1 1 calc R . .
H9B H 0.4344 -0.1016 0.3199 0.038 Uiso 1 1 calc R . .
C32 C 0.40896(10) 0.0897(2) 0.36465(11) 0.0253(4) Uani 1 1 d .
. .
C33 C 0.42289(12) 0.1440(3) 0.44825(12) 0.0352(5) Uani 1 1 d .
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H7 H 0.4288 0.0786 0.4923 0.042 Uiso 1 1 calc R . .
C34 C 0.42782(13) 0.2862(3) 0.46578(13) 0.0415(5) Uani 1 1 d .
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H6 H 0.4381 0.3175 0.5214 0.050 Uiso 1 1 calc R . .
C35 C 0.41768(13) 0.3851(3) 0.40188(14) 0.0377(5) Uani 1 1 d .
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H5 H 0.4207 0.4835 0.4141 0.045 Uiso 1 1 calc R . .
C36 C 0.40297(11) 0.3385(2) 0.31924(12) 0.0286(4) Uani 1 1 d .
. .
H4 H 0.3961 0.4062 0.2762 0.034 Uiso 1 1 calc R . .
C37 C 0.39835(10) 0.1950(2) 0.30010(10) 0.0213(3) Uani 1 1 d .
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C38 C 0.45443(12) 0.0764(2) 0.20205(12) 0.0298(4) Uani 1 1 d .
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H1A H 0.4356 0.0205 0.1504 0.045 Uiso 1 1 calc R . .
H1B H 0.4826 0.0142 0.2497 0.045 Uiso 1 1 calc R . .
H1C H 0.4948 0.1493 0.1984 0.045 Uiso 1 1 calc R . .
C39 C 0.34717(12) 0.2495(2) 0.14566(11) 0.0304(4) Uani 1 1 d .
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H2A H 0.3927 0.3163 0.1475 0.046 Uiso 1 1 calc R . .
H2B H 0.2993 0.3009 0.1533 0.046 Uiso 1 1 calc R . .
H2C H 0.3273 0.2012 0.0914 0.046 Uiso 1 1 calc R . .
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N2 N 0.17983(11) 0.0768(2) 0.35798(11) 0.0358(4) Uani 1 1 d .
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0.0052(11)
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0.0174(11)
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0.0090(10)
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0.0002(7)
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0.0176(13)
C29 0.094(2) 0.0632(19) 0.0503(16) 0.0245(14) 0.0387(16)
0.0357(17)
C31 0.0271(9) 0.0288(10) 0.0332(10) 0.0098(8) 0.0043(7)
0.0021(8)
C32 0.0170(7) 0.0343(10) 0.0217(8) 0.0026(7) 0.0030(6) -
0.0009(7)
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C33 0.0267(9) 0.0572(14) 0.0208(8) 0.0010(8) 0.0072(7) -
0.0083(9)
C34 0.0329(10) 0.0663(16) 0.0290(10) -0.0208(10) 0.0155(8) -
0.0162(10)
C35 0.0318(10) 0.0390(12) 0.0465(12) -0.0204(10) 0.0190(9) -
0.0114(9)
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C37 0.0167(7) 0.0263(9) 0.0204(7) -0.0022(6) 0.0059(6) -
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0.0010(6)
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0.00034(3)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
(compiled Jan  5 2010,16:28:46)
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 implemented in SCALE3 ABSPACK scaling algorithm.
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 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
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factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
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factors based
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on F, and R-
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P=(Fo^2^+2Fc^2^)/3'
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d . . .
H13 H 0.3780 -0.2181 1.1177 0.043 Uiso 1 1 calc R . .
C14 C 0.40446(12) -0.34539(16) 1.03115(13) 0.0433(5) Uani 1 1
d . . .
H14 H 0.4602 -0.3678 1.0677 0.052 Uiso 1 1 calc R . .
C15 C 0.37330(12) -0.40197(15) 0.94938(13) 0.0416(4) Uani 1 1
d . . .
H15 H 0.4055 -0.4654 0.9311 0.050 Uiso 1 1 calc R . .
C16 C 0.29471(11) -0.36595(13) 0.89377(12) 0.0340(4) Uani 1 1
d . . .
H16 H 0.2740 -0.4035 0.8360 0.041 Uiso 1 1 calc R . .
C17 C 0.24597(10) -0.27500(12) 0.92200(10) 0.0243(3) Uani 1 1
d . . .
C18 C 0.16668(14) -0.26087(13) 0.75848(11) 0.0389(4) Uani 1 1
d . . .
H18A H 0.2273 -0.2422 0.7334 0.058 Uiso 1 1 calc R . .
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H18B H 0.1159 -0.2228 0.7206 0.058 Uiso 1 1 calc R . .
H18C H 0.1565 -0.3393 0.7531 0.058 Uiso 1 1 calc R . .
C19 C 0.07551(11) -0.26119(14) 0.89798(12) 0.0376(4) Uani 1 1
d . . .
H19A H 0.0663 -0.3392 0.8876 0.056 Uiso 1 1 calc R . .
H19B H 0.0243 -0.2213 0.8626 0.056 Uiso 1 1 calc R . .
H19C H 0.0756 -0.2450 0.9675 0.056 Uiso 1 1 calc R . .
C21 C 0.07640(10) 0.05116(13) 0.88271(10) 0.0269(3) Uani 1 1 d
. . .
H21A H 0.0443 0.0390 0.9430 0.032 Uiso 1 1 calc R . .
H21B H 0.0870 0.1298 0.8746 0.032 Uiso 1 1 calc R . .
C22 C 0.02158(10) 0.00521(12) 0.79749(10) 0.0241(3) Uani 1 1 d
. . .
C23 C -0.07020(11) -0.03626(13) 0.80088(12) 0.0331(4) Uani 1 1
d . . .
H23 H -0.1003 -0.0310 0.8599 0.040 Uiso 1 1 calc R . .
C24 C -0.11815(12) -0.08425(14) 0.72161(14) 0.0431(5) Uani 1 1
d . . .
H24 H -0.1801 -0.1113 0.7267 0.052 Uiso 1 1 calc R . .
C25 C -0.07593(13) -0.09298(14) 0.63487(14) 0.0441(5) Uani 1 1
d . . .
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C26 C 0.01539(12) -0.05445(13) 0.62875(11) 0.0336(4) Uani 1 1
d . . .
H26 H 0.0448 -0.0607 0.5694 0.040 Uiso 1 1 calc R . .
C27 C 0.06360(10) -0.00718(11) 0.70843(10) 0.0230(3) Uani 1 1
d . . .
C28 C 0.16626(11) 0.14773(12) 0.69776(11) 0.0286(3) Uani 1 1 d
. . .
H28A H 0.1390 0.1691 0.6333 0.043 Uiso 1 1 calc R . .
H28B H 0.2322 0.1711 0.7055 0.043 Uiso 1 1 calc R . .
H28C H 0.1308 0.1820 0.7478 0.043 Uiso 1 1 calc R . .
C29 C 0.21281(12) -0.01862(14) 0.62851(10) 0.0340(4) Uani 1 1
d . . .
H29A H 0.2066 -0.0977 0.6289 0.051 Uiso 1 1 calc R . .
H29B H 0.2796 0.0011 0.6379 0.051 Uiso 1 1 calc R . .
H29C H 0.1864 0.0099 0.5661 0.051 Uiso 1 1 calc R . .
N3 N 0.31168(8) 0.10010(10) 0.95827(8) 0.0248(3) Uani 1 1 d .
. .
N1 N 0.16708(9) -0.22800(10) 0.86198(8) 0.0256(3) Uani 1 1 d .
. .
N2 N 0.16138(8) 0.02794(9) 0.70779(8) 0.0230(3) Uani 1 1 d . .
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Sc1 Sc 0.215943(18) -0.04397(2) 0.884846(18) 0.01913(8) Uani 1
1 d . . .

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0.0011(6)
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0.0005(7)
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0.0108(8)
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0.0044(7)
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0.0031(6)
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0.0068(8)
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0.0048(7)
C12 0.0289(8) 0.0277(8) 0.0237(8) 0.0098(6) 0.0017(6) -
0.0066(7)
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0.0106(8)
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0.0014(8)
C15 0.0338(9) 0.0373(10) 0.0553(11) 0.0149(9) 0.0139(8)
0.0092(8)
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0.0004(7)
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0.0031(6)
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N2 0.0246(6) 0.0226(7) 0.0223(6) 0.0001(5) 0.0045(5) 0.0027(5)
Sc1 0.01886(13) 0.01927(13) 0.01944(14) -0.00096(11)
0.00254(9) -0.00017(12)

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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C27 N2 1.4579(18) . ?
C28 N2 1.4862(18) . ?
C29 N2 1.4762(18) . ?
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N1 Sc1 2.3883(12) . ?
N2 Sc1 2.6616(12) . ?

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C17 N1 Sc1 N2 144.02(8) . . . . ?
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C29 N2 Sc1 N3 102.73(10) . . . . ?
C28 N2 Sc1 N3 -20.98(10) . . . . ?
C27 N2 Sc1 C12 79.24(11) . . . . ?
C29 N2 Sc1 C12 -41.52(14) . . . . ?
C28 N2 Sc1 C12 -165.24(9) . . . . ?
C17 C12 Sc1 C11 140.90(14) . . . . ?
C13 C12 Sc1 C11 -101.8(2) . . . . ?
C17 C12 Sc1 C31 -81.08(9) . . . . ?
C13 C12 Sc1 C31 36.18(17) . . . . ?
C11 C12 Sc1 C31 138.02(11) . . . . ?
C17 C12 Sc1 C21 102.68(9) . . . . ?
C13 C12 Sc1 C21 -140.06(16) . . . . ?
C11 C12 Sc1 C21 -38.22(12) . . . . ?
C17 C12 Sc1 N1 22.23(8) . . . . ?
C13 C12 Sc1 N1 139.49(18) . . . . ?
C11 C12 Sc1 N1 -118.67(11) . . . . ?
C17 C12 Sc1 N3 -152.64(8) . . . . ?
C13 C12 Sc1 N3 -35.38(17) . . . . ?
C11 C12 Sc1 N3 66.46(10) . . . . ?
C17 C12 Sc1 N2 -7.67(13) . . . . ?
C13 C12 Sc1 N2 109.59(17) . . . . ?
C11 C12 Sc1 N2 -148.57(10) . . . . ?

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 'Sc'  'Sc'   0.3119   1.5331
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loop_
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 'x, y, z'
 '-x, -y, -z'

_cell_length_a                    9.5340(3)
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_cell_length_c                    18.2650(5)
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_cell_angle_beta                  94.203(2)
_cell_angle_gamma                 114.173(3)
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_cell_formula_units_Z             2
_cell_measurement_temperature     100(2)
_cell_measurement_reflns_used     9061
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_exptl_crystal_F_000              664
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_exptl_absorpt_correction_T_max   0.9207
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CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.64 (release 22-03-2010 CrysAlis171 .NET)
(compiled Mar 22 2010,13:57:49)
Empirical absorption correction using spherical harmonics,
 implemented in SCALE3 ABSPACK scaling algorithm.
;

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Alert level B and C
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min)..4.47
Ratio
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for
C260

The thermal ellipsoid of C262 is noted as elongated in the
direction
of normal thermal motion for this group. C262 is directly
bound to
C260.
;

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_diffrn_measurement_device_type   'SuperNova, Dual, Cu at
zero, Atlas'
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_diffrn_reflns_limit_k_max         13
_diffrn_reflns_limit_l_min         -22
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_diffrn_reflns_theta_min           2.55
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CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.64 (release 22-03-2010 CrysAlis171 .NET)
(compiled Mar 22 2010,13:57:49)
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Version 1.171.33.64 (release 22-03-2010 CrysAlis171 .NET)
(compiled Mar 22 2010,13:57:49)
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Version 1.171.33.64 (release 22-03-2010 CrysAlis171 .NET)
(compiled Mar 22 2010,13:57:49)
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_computing_structure_refinement    'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics      'ORTEP (Farrugia, 1997)'
_computing_publication_material    ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
```

```
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0527P)^2^+0.0000P] where
P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     riding
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          6660
_refine_ls_number_parameters      398
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_refine_ls_wR_factor_ref          0.0969
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_refine_ls_goodness_of_fit_ref    0.952
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 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
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C1 C 0.1310(2) -0.0077(2) 0.79081(12) 0.0194(4) Uani 1 1 d . .
.
C5 C -0.1376(2) -0.1515(3) 0.78132(13) 0.0365(6) Uani 1 1 d .
. .
H5A H -0.1795 -0.2519 0.7683 0.044 Uiso 1 1 calc R . .
H5B H -0.2239 -0.1286 0.7679 0.044 Uiso 1 1 calc R . .
C6 C -0.0601(2) -0.0816(2) 0.86547(13) 0.0274(5) Uani 1 1 d .
. .
H6A H -0.1078 -0.0238 0.8917 0.033 Uiso 1 1 calc R . .
H6B H -0.0673 -0.1490 0.8926 0.033 Uiso 1 1 calc R . .
C7 C 0.2217(2) 0.0861(2) 0.93238(12) 0.0225(4) Uani 1 1 d . .
.
```

```
H7A H 0.3078 0.0585 0.9316 0.027 Uiso 1 1 calc R . .
H7B H 0.1743 0.0684 0.9773 0.027 Uiso 1 1 calc R . .
C8 C 0.2909(2) 0.2396(2) 0.94320(12) 0.0227(4) Uani 1 1 d . .
.
C9 C 0.1637(3) 0.2882(2) 0.94504(14) 0.0323(5) Uani 1 1 d . .
.
H9A H 0.2112 0.3866 0.9523 0.048 Uiso 1 1 calc R . .
H9B H 0.1110 0.2698 0.9878 0.048 Uiso 1 1 calc R . .
H9C H 0.0871 0.2395 0.8962 0.048 Uiso 1 1 calc R . .
C10 C 0.4121(3) 0.3126(2) 1.01955(13) 0.0303(5) Uani 1 1 d . .
.
H10A H 0.4938 0.2810 1.0168 0.045 Uiso 1 1 calc R . .
H10B H 0.3599 0.2918 1.0621 0.045 Uiso 1 1 calc R . .
H10C H 0.4597 0.4115 1.0284 0.045 Uiso 1 1 calc R . .
C21 C -0.0249(2) -0.16428(19) 0.66092(12) 0.0192(4) Uani 1 1 d
. . .
C22 C -0.1183(2) -0.1476(2) 0.60468(12) 0.0218(4) Uani 1 1 d .
. .
C23 C -0.1440(2) -0.2240(2) 0.52774(12) 0.0268(5) Uani 1 1 d .
. .
H23 H -0.2082 -0.2151 0.4892 0.032 Uiso 1 1 calc R . .
C24 C -0.0779(3) -0.3118(2) 0.50692(13) 0.0306(5) Uani 1 1 d .
. .
H24 H -0.0958 -0.3624 0.4542 0.037 Uiso 1 1 calc R . .
C25 C 0.0149(2) -0.3269(2) 0.56255(13) 0.0291(5) Uani 1 1 d .
. .
H25 H 0.0616 -0.3868 0.5472 0.035 Uiso 1 1 calc R . .
C26 C 0.0410(2) -0.2565(2) 0.63998(12) 0.0232(4) Uani 1 1 d .
. .
C27 C 0.5058(2) 0.0239(2) 0.82343(13) 0.0236(4) Uani 1 1 d . .
.
H27A H 0.4276 -0.0536 0.8368 0.028 Uiso 1 1 calc R . .
H27B H 0.5529 -0.0115 0.7819 0.028 Uiso 1 1 calc R . .
C28 C 0.6267(2) 0.1234(2) 0.89154(12) 0.0220(4) Uani 1 1 d . .
.
C29 C 0.6535(2) 0.0940(2) 0.95986(13) 0.0263(5) Uani 1 1 d . .
.
H29 H 0.6034 0.0020 0.9600 0.032 Uiso 1 1 calc R . .
C30 C 0.7506(2) 0.1946(2) 1.02750(13) 0.0295(5) Uani 1 1 d . .
.
H30 H 0.7633 0.1708 1.0730 0.035 Uiso 1 1 calc R . .
C31 C 0.8283(2) 0.3283(2) 1.02862(13) 0.0279(5) Uani 1 1 d . .
.
H31 H 0.8943 0.3973 1.0747 0.033 Uiso 1 1 calc R . .
C32 C 0.8087(2) 0.3614(2) 0.96107(12) 0.0233(4) Uani 1 1 d . .
.
H32 H 0.8635 0.4531 0.9609 0.028 Uiso 1 1 calc R . .
C33 C 0.7107(2) 0.2621(2) 0.89495(12) 0.0208(4) Uani 1 1 d . .
.
C34 C 0.7703(2) 0.2570(2) 0.76792(13) 0.0265(5) Uani 1 1 d . .
.
H34A H 0.8822 0.3171 0.7886 0.040 Uiso 1 1 calc R . .
H34B H 0.7394 0.2685 0.7188 0.040 Uiso 1 1 calc R . .
```

```
H34C H 0.7506 0.1618 0.7596 0.040 Uiso 1 1 calc R . .
C35 C 0.7138(2) 0.4374(2) 0.83697(13) 0.0248(4) Uani 1 1 d . .
.
H35A H 0.6557 0.4637 0.8748 0.037 Uiso 1 1 calc R . .
H35B H 0.6831 0.4505 0.7883 0.037 Uiso 1 1 calc R . .
H35C H 0.8266 0.4944 0.8567 0.037 Uiso 1 1 calc R . .
C36 C 0.3826(2) 0.0968(2) 0.65505(12) 0.0231(4) Uani 1 1 d . .
.
H36A H 0.4423 0.0434 0.6402 0.028 Uiso 1 1 calc R . .
H36B H 0.2722 0.0404 0.6273 0.028 Uiso 1 1 calc R . .
C37 C 0.4511(2) 0.2251(2) 0.63458(12) 0.0217(4) Uani 1 1 d . .
.
C38 C 0.5544(2) 0.2469(2) 0.58308(12) 0.0268(5) Uani 1 1 d . .
.
H38 H 0.5769 0.1743 0.5574 0.032 Uiso 1 1 calc R . .
C39 C 0.6250(3) 0.3712(2) 0.56843(14) 0.0335(5) Uani 1 1 d . .
.
H39 H 0.6965 0.3829 0.5342 0.040 Uiso 1 1 calc R . .
C40 C 0.5919(3) 0.4774(2) 0.60315(14) 0.0333(5) Uani 1 1 d . .
.
H40 H 0.6370 0.5611 0.5916 0.040 Uiso 1 1 calc R . .
C41 C 0.4918(2) 0.4606(2) 0.65521(13) 0.0284(5) Uani 1 1 d . .
.
H41 H 0.4689 0.5336 0.6797 0.034 Uiso 1 1 calc R . .
C42 C 0.4246(2) 0.3374(2) 0.67188(12) 0.0213(4) Uani 1 1 d . .
.
C43 C 0.3566(3) 0.4492(2) 0.78831(13) 0.0282(5) Uani 1 1 d . .
.
H43A H 0.4693 0.5088 0.8064 0.042 Uiso 1 1 calc R . .
H43B H 0.3087 0.4301 0.8323 0.042 Uiso 1 1 calc R . .
H43C H 0.3079 0.4946 0.7637 0.042 Uiso 1 1 calc R . .
C44 C 0.1624(2) 0.2419(2) 0.69865(14) 0.0296(5) Uani 1 1 d . .
.
H44A H 0.1278 0.2958 0.6741 0.044 Uiso 1 1 calc R . .
H44B H 0.1044 0.2223 0.7397 0.044 Uiso 1 1 calc R . .
H44C H 0.1425 0.1558 0.6601 0.044 Uiso 1 1 calc R . .
C220 C -0.1958(2) -0.0535(2) 0.62527(13) 0.0253(4) Uani 1 1 d
. . .
H220 H -0.1435 0.0105 0.6786 0.030 Uiso 1 1 calc R . .
C221 C -0.1816(3) 0.0317(2) 0.57006(14) 0.0332(5) Uani 1 1 d .
. .
H22A H -0.0725 0.0738 0.5638 0.050 Uiso 1 1 calc R . .
H22B H -0.2138 0.1033 0.5914 0.050 Uiso 1 1 calc R . .
H22C H -0.2495 -0.0276 0.5197 0.050 Uiso 1 1 calc R . .
C222 C -0.3701(2) -0.1369(2) 0.62473(14) 0.0315(5) Uani 1 1 d
. . .
H22D H -0.4228 -0.2020 0.5731 0.047 Uiso 1 1 calc R . .
H22E H -0.4190 -0.0752 0.6383 0.047 Uiso 1 1 calc R . .
H22F H -0.3797 -0.1868 0.6624 0.047 Uiso 1 1 calc R . .
C260 C 0.1313(3) -0.2853(2) 0.70010(14) 0.0323(5) Uani 1 1 d .
. .
H260 H 0.1669 -0.2076 0.7490 0.039 Uiso 1 1 calc R . .
```

```
C261 C 0.2743(3) -0.2970(3) 0.67644(17) 0.0402(6) Uani 1 1 d .
. .
H26A H 0.3365 -0.3015 0.7199 0.060 Uiso 1 1 calc R . .
H26B H 0.3378 -0.2170 0.6613 0.060 Uiso 1 1 calc R . .
H26C H 0.2417 -0.3800 0.6327 0.060 Uiso 1 1 calc R . .
C262 C 0.0250(3) -0.4151(4) 0.7167(2) 0.0857(14) Uani 1 1 d .
. .
H26D H -0.0050 -0.4939 0.6706 0.129 Uiso 1 1 calc R . .
H26E H -0.0694 -0.4083 0.7306 0.129 Uiso 1 1 calc R . .
H26F H 0.0809 -0.4265 0.7596 0.129 Uiso 1 1 calc R . .
N1 N 0.10330(18) 0.00167(17) 0.86208(10) 0.0223(4) Uani 1 1 d
. . .
N2 N -0.00745(18) -0.09537(17) 0.74099(10) 0.0199(4) Uani 1 1
d . . .
N3 N 0.67767(18) 0.29255(17) 0.82356(10) 0.0209(4) Uani 1 1 d
. . .
N4 N 0.33254(19) 0.32007(17) 0.73210(10) 0.0222(4) Uani 1 1 d
. . .
O1 O 0.36611(15) 0.26400(14) 0.88147(8) 0.0219(3) Uani 1 1 d .
. .
Sc1 Sc 0.39483(4) 0.15419(4) 0.78773(2) 0.01748(10) Uani 1 1 d
. . .

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0.0137(9)
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0.0032(10)
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0.0086(9)
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0.0108(9)
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0.0126(9)
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0.0218(11)
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0.0112(10)
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0.0041(8)
C22 0.0207(9) 0.0212(10) 0.0205(11) 0.0083(9) 0.0027(8)
0.0055(8)
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0.0084(9)
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0.0120(10)
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0.0134(10)
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0.0077(9)
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0.0129(9)
C28 0.0205(9) 0.0281(11) 0.0215(11) 0.0092(9) 0.0025(8)
0.0138(9)
C29 0.0262(10) 0.0275(11) 0.0275(12) 0.0129(10) 0.0020(9)
0.0122(9)
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0.0167(10)
C31 0.0225(10) 0.0337(12) 0.0225(12) 0.0062(10) -0.0024(9)
0.0104(9)
C32 0.0203(9) 0.0283(11) 0.0219(12) 0.0087(9) 0.0026(8)
0.0111(9)
C33 0.0186(9) 0.0256(10) 0.0211(11) 0.0087(9) 0.0029(8)
0.0117(8)
C34 0.0230(10) 0.0355(12) 0.0240(12) 0.0112(10) 0.0068(9)
0.0145(10)
C35 0.0236(10) 0.0225(10) 0.0268(12) 0.0095(9) 0.0006(9)
0.0083(9)
C36 0.0304(10) 0.0249(10) 0.0160(11) 0.0069(9) 0.0028(9)
0.0140(9)
C37 0.0225(9) 0.0280(11) 0.0130(10) 0.0074(9) -0.0015(8)
0.0098(9)
C38 0.0265(10) 0.0333(12) 0.0177(11) 0.0060(9) -0.0003(9)
0.0124(10)
C39 0.0275(11) 0.0408(13) 0.0247(13) 0.0122(11) 0.0073(10)
0.0065(10)
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0.0042(10)
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0.0090(9)
C42 0.0205(9) 0.0252(10) 0.0161(11) 0.0079(9) -0.0016(8)
0.0081(9)
C43 0.0368(12) 0.0314(12) 0.0228(12) 0.0089(10) 0.0040(10)
0.0211(10)
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0.0142(10)
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 All s.u.'s (except the s.u. in the dihedral angle between two
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 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;
```

```
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_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0281P)^2^+0.0000P] where
P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     riding
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          8681
_refine_ls_number_parameters      385
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_refine_ls_shift/su_mean          0.000

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Y1 Y 0.481708(16) 0.984611(15) 0.115326(10) 0.01933(5) Uani 1
1 d . . .
Si1 Si 0.70868(5) 0.71739(5) 0.17680(3) 0.03298(13) Uani 1 1 d
. . .
Si2 Si 0.45633(6) 1.24924(5) 0.21380(3) 0.03481(14) Uani 1 1 d
. . .
O1 O 0.39625(10) 0.93222(9) 0.01295(7) 0.0206(3) Uani 1 1 d .
. .
N1 N 0.28508(13) 0.74139(12) 0.18380(8) 0.0214(3) Uani 1 1 d .
. .
N2 N 0.28248(13) 0.78997(12) 0.29962(8) 0.0217(3) Uani 1 1 d .
. .
C8 C 0.28402(16) 0.86256(15) 0.02359(10) 0.0238(4) Uani 1 1 d
. . .
```

```
C21 C 0.26239(17) 0.86546(15) 0.35359(10) 0.0248(4) Uani 1 1 d
. . .
C26 C 0.34934(18) 0.85413(17) 0.41612(11) 0.0310(5) Uani 1 1 d
. . .
C22 C 0.15207(17) 0.94079(17) 0.34632(11) 0.0302(4) Uani 1 1 d
. . .
C1 C 0.31755(15) 0.82627(14) 0.21323(10) 0.0204(4) Uani 1 1 d
. . .
C7 C 0.30032(18) 0.74232(15) 0.09378(10) 0.0261(4) Uani 1 1 d
. . .
H7A H 0.2378 0.6895 0.0877 0.031 Uiso 1 1 calc R . .
H7B H 0.3860 0.7095 0.0826 0.031 Uiso 1 1 calc R . .
C10 C 0.27446(19) 0.83470(18) -0.06022(11) 0.0381(5) Uani 1 1
d . . .
H10A H 0.3513 0.7911 -0.0725 0.057 Uiso 1 1 calc R . .
H10B H 0.2662 0.9075 -0.1074 0.057 Uiso 1 1 calc R . .
H10C H 0.1999 0.7880 -0.0534 0.057 Uiso 1 1 calc R . .
C220 C 0.05143(18) 0.94798(18) 0.28363(12) 0.0358(5) Uani 1 1
d . . .
H220 H 0.0843 0.8987 0.2477 0.043 Uiso 1 1 calc R . .
C31 C 0.39687(18) 1.13390(16) 0.17760(12) 0.0335(5) Uani 1 1 d
. . .
H31A H 0.3358 1.1782 0.1370 0.040 Uiso 1 1 calc R . .
H31B H 0.3434 1.0884 0.2287 0.040 Uiso 1 1 calc R . .
C24 C 0.2175(2) 1.0013(2) 0.46182(14) 0.0492(6) Uani 1 1 d . .
.
H24 H 0.2030 1.0482 0.4977 0.059 Uiso 1 1 calc R . .
C6 C 0.22990(17) 0.63676(15) 0.25121(10) 0.0256(4) Uani 1 1 d
. . .
H6A H 0.2865 0.5670 0.2571 0.031 Uiso 1 1 calc R . .
H6B H 0.1451 0.6209 0.2387 0.031 Uiso 1 1 calc R . .
C5 C 0.2205(2) 0.67370(16) 0.33196(11) 0.0367(5) Uani 1 1 d .
. .
H5A H 0.1309 0.6812 0.3543 0.044 Uiso 1 1 calc R . .
H5B H 0.2669 0.6174 0.3772 0.044 Uiso 1 1 calc R . .
C23 C 0.13186(19) 1.00879(19) 0.40137(13) 0.0424(5) Uani 1 1 d
. . .
H23 H 0.0595 1.0602 0.3975 0.051 Uiso 1 1 calc R . .
C260 C 0.46351(18) 0.76601(17) 0.42906(12) 0.0357(5) Uani 1 1
d . . .
H260 H 0.4765 0.7373 0.3790 0.043 Uiso 1 1 calc R . .
C9 C 0.16350(17) 0.93242(17) 0.04268(12) 0.0355(5) Uani 1 1 d
. . .
H9A H 0.1521 1.0021 -0.0066 0.053 Uiso 1 1 calc R . .
H9B H 0.1728 0.9554 0.0927 0.053 Uiso 1 1 calc R . .
H9C H 0.0892 0.8840 0.0540 0.053 Uiso 1 1 calc R . .
C27 C 0.64623(18) 0.85583(16) 0.19318(12) 0.0326(5) Uani 1 1 d
. . .
H27A H 0.7210 0.9043 0.1846 0.039 Uiso 1 1 calc R . .
H27B H 0.6151 0.8355 0.2543 0.039 Uiso 1 1 calc R . .
C261 C 0.58936(19) 0.8235(2) 0.43445(13) 0.0490(6) Uani 1 1 d
. . .
H26A H 0.5804 0.8482 0.4851 0.073 Uiso 1 1 calc R . .
```

```
H26B H 0.6054 0.8912 0.3834 0.073 Uiso 1 1 calc R . .
H26C H 0.6607 0.7669 0.4382 0.073 Uiso 1 1 calc R . .
C222 C -0.0765(2) 0.8973(2) 0.33294(14) 0.0615(7) Uani 1 1 d .
. .
H22A H -0.1189 0.9515 0.3604 0.092 Uiso 1 1 calc R . .
H22B H -0.0597 0.8225 0.3764 0.092 Uiso 1 1 calc R . .
H22C H -0.1313 0.8858 0.2930 0.092 Uiso 1 1 calc R . .
C262 C 0.4368(2) 0.6592(2) 0.51116(13) 0.0574(7) Uani 1 1 d .
. .
H26D H 0.3662 0.6163 0.5041 0.086 Uiso 1 1 calc R . .
H26E H 0.4144 0.6863 0.5603 0.086 Uiso 1 1 calc R . .
H26F H 0.5130 0.6080 0.5206 0.086 Uiso 1 1 calc R . .
C30 C 0.88357(19) 0.6821(2) 0.19838(15) 0.0522(6) Uani 1 1 d .
. .
H30A H 0.8924 0.6714 0.2583 0.078 Uiso 1 1 calc R . .
H30B H 0.9358 0.7463 0.1619 0.078 Uiso 1 1 calc R . .
H30C H 0.9117 0.6106 0.1859 0.078 Uiso 1 1 calc R . .
C25 C 0.3236(2) 0.9251(2) 0.46926(13) 0.0436(6) Uani 1 1 d . .
.
H25 H 0.3799 0.9206 0.5107 0.052 Uiso 1 1 calc R . .
C221 C 0.0275(2) 1.0729(2) 0.22276(16) 0.0624(7) Uani 1 1 d .
. .
H22D H 0.1077 1.1033 0.1903 0.094 Uiso 1 1 calc R . .
H22E H -0.0064 1.1231 0.2561 0.094 Uiso 1 1 calc R . .
H22F H -0.0338 1.0714 0.1834 0.094 Uiso 1 1 calc R . .
C32 C 0.6077(2) 1.1980(2) 0.26990(14) 0.0589(7) Uani 1 1 d . .
.
H32A H 0.6745 1.1792 0.2304 0.088 Uiso 1 1 calc R . .
H32B H 0.5904 1.1286 0.3195 0.088 Uiso 1 1 calc R . .
H32C H 0.6357 1.2598 0.2886 0.088 Uiso 1 1 calc R . .
C34 C 0.3411(2) 1.29434(19) 0.29542(14) 0.0558(6) Uani 1 1 d .
. .
H34A H 0.3308 1.2287 0.3484 0.084 Uiso 1 1 calc R . .
H34B H 0.2585 1.3175 0.2727 0.084 Uiso 1 1 calc R . .
H34C H 0.3752 1.3599 0.3069 0.084 Uiso 1 1 calc R . .
C28 C 0.6131(2) 0.58937(19) 0.24974(15) 0.0542(6) Uani 1 1 d .
. .
H28A H 0.5239 0.6019 0.2377 0.081 Uiso 1 1 calc R . .
H28B H 0.6194 0.5827 0.3093 0.081 Uiso 1 1 calc R . .
H28C H 0.6471 0.5176 0.2397 0.081 Uiso 1 1 calc R . .
C33 C 0.4883(2) 1.38912(17) 0.11959(14) 0.0532(6) Uani 1 1 d .
. .
H33A H 0.4073 1.4267 0.1004 0.080 Uiso 1 1 calc R . .
H33B H 0.5387 1.3699 0.0727 0.080 Uiso 1 1 calc R . .
H33C H 0.5352 1.4421 0.1376 0.080 Uiso 1 1 calc R . .
C29 C 0.7012(2) 0.7241(2) 0.06069(14) 0.0587(7) Uani 1 1 d . .
.
H29A H 0.7400 0.7955 0.0222 0.088 Uiso 1 1 calc R . .
H29B H 0.6124 0.7238 0.0497 0.088 Uiso 1 1 calc R . .
H29C H 0.7476 0.6565 0.0510 0.088 Uiso 1 1 calc R . .
C1S C 0.1092(3) 0.4670(3) 0.54099(18) 0.0776(9) Uani 1 1 d U .
.
H1S H 0.1843 0.4438 0.5692 0.093 Uiso 1 1 calc R . .
```

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C2S C 0.0810(3) 0.4108(3) 0.48404(19) 0.0811(9) Uani 1 1 d U .
.
H2S H 0.1369 0.3513 0.4741 0.097 Uiso 1 1 calc R . .
C3S C 0.0296(3) 0.5570(3) 0.55778(18) 0.0786(9) Uani 1 1 d U .
.
C31S C 0.0600(6) 0.6213(5) 0.6139(4) 0.0935(19) Uani 0.50 1 d
PU . .
H31C H 0.1475 0.6473 0.5984 0.140 Uiso 0.50 1 calc PR . .
H31D H 0.0512 0.5702 0.6733 0.140 Uiso 0.50 1 calc PR . .
H31E H 0.0015 0.6889 0.6073 0.140 Uiso 0.50 1 calc PR . .
C1T C 0.8776(4) 0.4582(4) 0.0308(4) 0.093(3) Uani 0.50 1 d
PGDU A -1
H1T H 0.7924 0.4521 0.0205 0.111 Uiso 0.50 1 calc PR A -1
C2T C 0.9188(6) 0.4000(4) 0.1126(4) 0.101(2) Uani 0.50 1 d
PGDU A -1
H2T H 0.8612 0.3550 0.1570 0.122 Uiso 0.50 1 calc PR A -1
C3T C 1.0461(7) 0.4092(6) 0.1279(4) 0.146(4) Uani 0.50 1 d
PGDU A -1
H3T H 1.0736 0.3702 0.1826 0.176 Uiso 0.50 1 calc PR A -1
C4T C 1.1321(5) 0.4765(6) 0.0614(5) 0.141(4) Uani 0.50 1 d
PGDU A -1
H4T H 1.2172 0.4826 0.0716 0.169 Uiso 0.50 1 calc PR A -1
C5T C 1.0909(5) 0.5347(5) -0.0204(4) 0.105(3) Uani 0.50 1 d
PGDU A -1
H5T H 1.1485 0.5797 -0.0649 0.126 Uiso 0.50 1 calc PR A -1
C6T C 0.9636(6) 0.5255(5) -0.0357(3) 0.090(2) Uani 0.50 1 d
PGDU A -1
C61T C 0.9310(11) 0.5928(10) -0.1183(6) 0.177(6) Uani 0.50 1 d
PDU A -1
H61A H 0.8414 0.5828 -0.1226 0.266 Uiso 0.50 1 calc PR A -1
H61B H 0.9842 0.5671 -0.1612 0.266 Uiso 0.50 1 calc PR A -1
H61C H 0.9450 0.6750 -0.1279 0.266 Uiso 0.50 1 calc PR A -1

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 _atom_site_aniso_U_33
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0.00567(7)
Si1 0.0280(3) 0.0362(3) 0.0341(3) -0.0100(3) -0.0065(2)
0.0019(3)
Si2 0.0570(4) 0.0244(3) 0.0248(3) -0.0100(2) -0.0042(3) -
0.0029(3)
O1 0.0192(6) 0.0256(6) 0.0184(6) -0.0081(5) -0.0006(5) -
0.0078(5)
N1 0.0265(8) 0.0209(8) 0.0170(7) -0.0058(6) 0.0009(6) -
0.0083(7)
N2 0.0251(8) 0.0226(8) 0.0166(7) -0.0043(6) 0.0021(6) -
0.0109(7)
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C8 0.0230(9) 0.0297(10) 0.0195(9) -0.0070(8) -0.0021(8) -
0.0124(8)
C21 0.0297(10) 0.0299(10) 0.0154(9) -0.0085(8) 0.0069(8) -
0.0138(9)
C26 0.0337(11) 0.0403(11) 0.0190(10) -0.0091(9) 0.0048(8) -
0.0157(10)
C22 0.0285(10) 0.0359(11) 0.0276(10) -0.0143(9) 0.0099(8) -
0.0108(9)
C1 0.0184(9) 0.0226(9) 0.0204(9) -0.0074(7) -0.0021(7) -
0.0009(8)
C7 0.0316(10) 0.0284(10) 0.0228(10) -0.0135(8) 0.0007(8) -
0.0100(9)
C10 0.0450(12) 0.0473(13) 0.0248(11) -0.0113(9) -0.0024(9) -
0.0238(11)
C220 0.0276(11) 0.0475(13) 0.0341(11) -0.0184(10) 0.0045(9)
0.0000(10)
C31 0.0436(12) 0.0295(11) 0.0266(10) -0.0105(9) 0.0065(9) -
0.0044(10)
C24 0.0508(14) 0.0658(16) 0.0447(14) -0.0396(13) 0.0145(12) -
0.0174(13)
C6 0.0280(10) 0.0216(9) 0.0257(10) -0.0046(8) -0.0024(8) -
0.0070(8)
C5 0.0502(13) 0.0323(11) 0.0253(10) -0.0049(9) 0.0033(9) -
0.0203(10)
C23 0.0339(12) 0.0525(14) 0.0480(13) -0.0290(11) 0.0094(10) -
0.0079(11)
C260 0.0382(12) 0.0454(12) 0.0254(11) -0.0109(9) -0.0068(9) -
0.0106(10)
C9 0.0242(10) 0.0402(12) 0.0348(11) -0.0012(9) -0.0035(9) -
0.0045(9)
C27 0.0342(11) 0.0358(11) 0.0270(10) -0.0071(9) -0.0069(9) -
0.0047(9)
C261 0.0405(13) 0.0684(16) 0.0425(13) -0.0203(12) -0.0096(11)
-0.0111(12)
C222 0.0424(14) 0.100(2) 0.0517(15) -0.0358(15) 0.0054(12) -
0.0296(14)
C262 0.0678(17) 0.0578(15) 0.0408(13) -0.0015(12) -0.0171(12)
-0.0146(13)
C30 0.0329(12) 0.0606(15) 0.0621(16) -0.0187(13) -0.0065(11)
0.0034(12)
C25 0.0440(13) 0.0640(15) 0.0324(12) -0.0269(11) 0.0020(10) -
0.0199(12)
C221 0.0433(14) 0.0590(16) 0.0764(18) -0.0077(14) -0.0179(13)
0.0045(13)
C32 0.0789(18) 0.0668(17) 0.0429(14) -0.0303(13) -0.0206(13)
0.0047(14)
C34 0.0873(18) 0.0399(13) 0.0441(13) -0.0217(11) -0.0013(13)
0.0033(13)
C28 0.0480(14) 0.0407(13) 0.0718(16) -0.0117(12) -0.0129(12) -
0.0068(12)
C33 0.0765(17) 0.0313(12) 0.0492(14) -0.0075(10) -0.0064(13) -
0.0112(12)

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C29 0.0681(16) 0.0647(16) 0.0514(15) -0.0304(13) -0.0142(13)
0.0162(14)
C1S 0.0661(19) 0.083(2) 0.0551(18) 0.0204(16) -0.0025(15) -
0.0279(18)
C2S 0.079(2) 0.073(2) 0.0633(19) 0.0159(16) 0.0066(17) -
0.0222(18)
C3S 0.088(2) 0.076(2) 0.0524(18) 0.0059(16) 0.0084(18) -
0.0342(19)
C31S 0.101(5) 0.089(5) 0.076(4) -0.010(3) 0.012(4) -0.021(4)
C1T 0.059(4) 0.048(5) 0.185(7) -0.057(5) -0.018(5) 0.001(4)
C2T 0.104(5) 0.048(4) 0.175(7) -0.062(4) -0.041(5) 0.013(4)
C3T 0.186(8) 0.079(7) 0.223(10) -0.100(7) -0.096(7) 0.045(6)
C4T 0.089(5) 0.104(7) 0.290(11) -0.133(7) -0.078(6) 0.034(5)
C5T 0.060(4) 0.056(6) 0.204(9) -0.066(6) 0.049(5) -0.016(4)
C6T 0.119(5) 0.031(4) 0.128(6) -0.041(3) -0.009(4) 0.018(4)
C61T 0.329(17) 0.082(9) 0.099(7) -0.023(6) 0.008(9) 0.060(10)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
;

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Y1 O1 2.2537(10) . ?
Y1 O1 2.2796(10) 2_675 ?
Y1 C27 2.3965(18) . ?
Y1 C31 2.3997(17) . ?
Y1 C1 2.6234(16) . ?
Y1 Y1 3.6453(3) 2_675 ?
Si1 C27 1.8235(19) . ?
Si1 C28 1.867(2) . ?
Si1 C30 1.881(2) . ?
Si1 C29 1.884(2) . ?
Si2 C31 1.8334(17) . ?
Si2 C32 1.873(2) . ?
Si2 C34 1.877(2) . ?
Si2 C33 1.882(2) . ?
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O1 C8 1.4395(18) . ?
O1 Y1 2.2796(10) 2_675 ?
N1 C1 1.3325(19) . ?
N1 C7 1.459(2) . ?
N1 C6 1.4682(19) . ?
N2 C1 1.349(2) . ?
N2 C21 1.445(2) . ?
N2 C5 1.478(2) . ?
C8 C9 1.515(2) . ?
C8 C10 1.527(2) . ?
C8 C7 1.528(2) . ?
C21 C22 1.397(3) . ?
C21 C26 1.407(2) . ?
C26 C25 1.394(3) . ?
C26 C260 1.514(3) . ?
C22 C23 1.388(2) . ?
C22 C220 1.523(2) . ?
C220 C221 1.519(3) . ?
C220 C222 1.526(3) . ?
C24 C25 1.369(3) . ?
C24 C23 1.380(3) . ?
C6 C5 1.515(2) . ?
C260 C262 1.532(3) . ?
C260 C261 1.541(2) . ?
C1S C2S 1.379(4) . ?
C1S C3S 1.389(4) . ?
C2S C3S 1.371(4) 2_566 ?
C3S C2S 1.371(4) 2_566 ?
C3S C31S 1.446(6) . ?
C1T C2T 1.3900 . ?
C1T C6T 1.3900 . ?
C2T C3T 1.3900 . ?
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C5T C6T 1.3900 . ?
C6T C61T 1.391(8) . ?

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O1 Y1 C27 117.95(5) . . ?
O1 Y1 C27 98.41(5) 2_675 . ?
O1 Y1 C31 126.70(6) . . ?
O1 Y1 C31 110.63(5) 2_675 . ?
C27 Y1 C31 114.03(6) . . ?
O1 Y1 C1 79.53(4) . . ?
O1 Y1 C1 150.80(4) 2_675 . ?
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C27 Y1 C1 85.83(6) . . ?
C31 Y1 C1 93.48(6) . . ?
O1 Y1 Y1 36.72(3) . 2_675 ?
O1 Y1 Y1 36.23(2) 2_675 2_675 ?
C27 Y1 Y1 112.41(5) . 2_675 ?
C31 Y1 Y1 126.14(5) . 2_675 ?
C1 Y1 Y1 115.69(3) . 2_675 ?
C27 Si1 C28 110.85(10) . . ?
C27 Si1 C30 113.50(9) . . ?
C28 Si1 C30 107.15(10) . . ?
C27 Si1 C29 110.88(9) . . ?
C28 Si1 C29 108.60(10) . . ?
C30 Si1 C29 105.59(10) . . ?
C31 Si2 C32 111.50(10) . . ?
C31 Si2 C34 114.41(9) . . ?
C32 Si2 C34 104.29(10) . . ?
C31 Si2 C33 111.02(9) . . ?
C32 Si2 C33 109.43(11) . . ?
C34 Si2 C33 105.80(10) . . ?
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Y1 O1 Y1 107.05(4) . 2_675 ?
C1 N1 C7 126.91(13) . . ?
C1 N1 C6 114.68(13) . . ?
C7 N1 C6 118.40(12) . . ?
C1 N2 C21 125.73(14) . . ?
C1 N2 C5 113.46(13) . . ?
C21 N2 C5 117.67(13) . . ?
O1 C8 C9 109.27(14) . . ?
O1 C8 C10 109.10(13) . . ?
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C26 C21 N2 118.81(16) . . ?
C25 C26 C21 117.05(19) . . ?
C25 C26 C260 120.32(17) . . ?
C21 C26 C260 122.59(16) . . ?
C23 C22 C21 117.85(17) . . ?
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C21 C22 C220 123.16(16) . . ?
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N1 C1 Y1 118.73(11) . . ?
N2 C1 Y1 131.79(11) . . ?
N1 C7 C8 116.77(14) . . ?
C221 C220 C22 113.27(16) . . ?
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Si2 C31 Y1 139.04(10) . . ?
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N1 C6 C5 102.26(12) . . ?
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Si1 C27 Y1 125.34(9) . . ?
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C2S C1S C3S 122.5(3) . . ?
C3S C2S C1S 119.7(3) 2_566 . ?
C2S C3S C1S 117.8(3) 2_566 . ?
C2S C3S C31S 118.6(4) 2_566 . ?
C1S C3S C31S 123.6(4) . . ?
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C5T C4T C3T 120.0 . . ?
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C5 N2 C21 C22 -86.11(19) . . . . ?
C1 N2 C21 C26 -112.22(19) . . . . ?
C5 N2 C21 C26 89.18(19) . . . . ?
C22 C21 C26 C25 -2.3(2) . . . . ?
N2 C21 C26 C25 -177.46(15) . . . . ?
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C7 N1 C1 N2 177.97(16) . . . . ?
C6 N1 C1 N2 -2.8(2) . . . . ?
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O1 Y1 C1 N2 165.23(12) 2_675 . . . ?
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C31 Y1 C1 N2 -48.44(16) . . . . ?
Y1 Y1 C1 N2 178.33(14) 2_675 . . . ?
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Y1 Y1 C31 Si2 -95.40(15) 2_675 . . . ?
C1 N1 C6 C5 5.0(2) . . . . ?
C7 N1 C6 C5 -175.75(15) . . . . ?
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C21 N2 C5 C6 164.83(15) . . . . ?
N1 C6 C5 N2 -4.71(18) . . . . ?
C25 C24 C23 C22 -0.8(3) . . . . ?
C21 C22 C23 C24 -0.6(3) . . . . ?
C220 C22 C23 C24 177.16(17) . . . . ?
C25 C26 C260 C262 73.2(2) . . . . ?
C21 C26 C260 C262 -104.3(2) . . . . ?
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C21 C26 C260 C261 133.13(17) . . . . ?
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C29 Si1 C27 Y1 30.29(14) . . . . ?
O1 Y1 C27 Si1 -0.17(13) . . . . ?
O1 Y1 C27 Si1 -75.27(11) 2_675 . . . ?
C31 Y1 C27 Si1 167.60(10) . . . . ?
C1 Y1 C27 Si1 75.65(11) . . . . ?
Y1 Y1 C27 Si1 -40.46(12) 2_675 . . . ?
C23 C24 C25 C26 0.6(3) . . . . ?
C21 C26 C25 C24 0.9(3) . . . . ?
C260 C26 C25 C24 -176.75(18) . . . . ?
C3S C1S C2S C3S -0.5(4) . . . 2_566 ?
C2S C1S C3S C2S 0.5(4) . . . 2_566 ?
C2S C1S C3S C31S -176.9(3) . . . . ?
C6T C1T C2T C3T 0.0 . . . . ?
C1T C2T C3T C4T 0.0 . . . . ?
C2T C3T C4T C5T 0.0 . . . . ?
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C4T C5T C6T C1T 0.0 . . . . ?
C4T C5T C6T C61T 176.4(8) . . . . ?
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data_po0011

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 'x, y, z'
 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

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CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
(compiled Jan  5 2010,16:28:46)
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Empirical absorption correction using spherical harmonics,
 implemented in SCALE3 ABSPACK scaling algorithm.
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# SQUEEZE RESULTS (APPEND TO CIF)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
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   1 -0.002  0.000  0.500       318        77 ' '
   2 -0.046  0.500  0.000       318        77 ' '

Alert level A
PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS
of .     325.00 A**3
Squeeze procedure used to removed solvent molecules for which
the disorder could
not be reconciled. See SQUEEZE RESULTS above.

;

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Source'
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zero, Atlas'
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Version 1.171.33.64 (release 22-03-2010 CrysAlis171 .NET)
(compiled Mar 22 2010,13:57:49)
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1997)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   ?

_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-
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 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
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P=(Fo^2^+2Fc^2^)/3'
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C5 C 0.4592(2) 0.23841(9) 0.18965(10) 0.0300(4) Uani 1 1 d . .
.
H5A H 0.5213 0.2797 0.1894 0.036 Uiso 1 1 calc R . .
H5B H 0.4139 0.2387 0.2320 0.036 Uiso 1 1 calc R . .
C6 C 0.34866(19) 0.23641(9) 0.12605(9) 0.0275(3) Uani 1 1 d .
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H6A H 0.2512 0.2348 0.1383 0.033 Uiso 1 1 calc R . .
H6B H 0.3576 0.2771 0.0961 0.033 Uiso 1 1 calc R . .
C7 C 0.29673(19) 0.14809(9) 0.03096(9) 0.0273(3) Uani 1 1 d .
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H7A H 0.3443 0.1610 -0.0089 0.033 Uiso 1 1 calc R . .
H7B H 0.2055 0.1736 0.0268 0.033 Uiso 1 1 calc R . .
C8 C 0.26494(18) 0.06963(9) 0.02726(9) 0.0236(3) Uani 1 1 d .
. .
C9 C 0.21960(19) 0.04145(10) 0.09367(9) 0.0287(3) Uani 1 1 d .
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H9A H 0.1918 -0.0074 0.0873 0.043 Uiso 1 1 calc R . .
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H9B H 0.1390 0.0685 0.1053 0.043 Uiso 1 1 calc R . .
H9C H 0.2990 0.0452 0.1308 0.043 Uiso 1 1 calc R . .
C10 C 0.14265(18) 0.06047(9) -0.03140(9) 0.0288(4) Uani 1 1 d
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H10A H 0.1704 0.0796 -0.0737 0.043 Uiso 1 1 calc R . .
H10B H 0.0586 0.0851 -0.0202 0.043 Uiso 1 1 calc R . .
H10C H 0.1208 0.0109 -0.0377 0.043 Uiso 1 1 calc R . .
C21 C 0.62672(19) 0.14800(8) 0.24425(8) 0.0235(3) Uani 1 1 d .
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C22 C 0.5602(2) 0.11168(9) 0.29330(9) 0.0286(4) Uani 1 1 d . .
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C23 C 0.6449(2) 0.08990(10) 0.35288(9) 0.0336(4) Uani 1 1 d .
. .
H23 H 0.6027 0.0650 0.3865 0.040 Uiso 1 1 calc R . .
C24 C 0.7887(2) 0.10364(10) 0.36419(9) 0.0345(4) Uani 1 1 d .
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H24 H 0.8447 0.0877 0.4049 0.041 Uiso 1 1 calc R . .
C25 C 0.8512(2) 0.14087(10) 0.31587(10) 0.0312(4) Uani 1 1 d .
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H25 H 0.9499 0.1508 0.3243 0.037 Uiso 1 1 calc R . .
C26 C 0.77185(19) 0.16393(9) 0.25527(9) 0.0250(3) Uani 1 1 d .
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C27 C 0.75009(18) 0.11875(8) 0.03405(8) 0.0234(3) Uani 1 1 d .
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H27A H 0.8060 0.1323 0.0782 0.028 Uiso 1 1 calc R . .
H27B H 0.8149 0.0897 0.0107 0.028 Uiso 1 1 calc R . .
C28 C 0.6640(3) 0.18291(14) -0.10726(11) 0.0511(6) Uani 1 1 d
. . .
H28A H 0.7288 0.1523 -0.1279 0.077 Uiso 1 1 calc R . .
H28B H 0.6534 0.2269 -0.1326 0.077 Uiso 1 1 calc R . .
H28C H 0.5711 0.1604 -0.1091 0.077 Uiso 1 1 calc R . .
C29 C 0.9159(2) 0.24280(11) -0.01693(13) 0.0429(5) Uani 1 1 d
. . .
H29A H 0.9600 0.2516 0.0302 0.064 Uiso 1 1 calc R . .
H29B H 0.9035 0.2869 -0.0419 0.064 Uiso 1 1 calc R . .
H29C H 0.9768 0.2119 -0.0397 0.064 Uiso 1 1 calc R . .
C30 C 0.6233(3) 0.26898(12) 0.01690(13) 0.0504(6) Uani 1 1 d .
. .
H30A H 0.5248 0.2527 0.0121 0.076 Uiso 1 1 calc R . .
H30B H 0.6283 0.3118 -0.0096 0.076 Uiso 1 1 calc R . .
H30C H 0.6570 0.2782 0.0653 0.076 Uiso 1 1 calc R . .
C31 C 0.6365(2) -0.02172(9) 0.16153(8) 0.0261(3) Uani 1 1 d .
. .
H31A H 0.6205 0.0135 0.1963 0.031 Uiso 1 1 calc R . .
H31B H 0.5508 -0.0515 0.1574 0.031 Uiso 1 1 calc R . .
C32 C 0.9507(2) -0.03950(11) 0.22162(13) 0.0454(5) Uani 1 1 d
. . .
H32A H 0.9782 -0.0314 0.1761 0.068 Uiso 1 1 calc R . .
H32B H 1.0183 -0.0716 0.2473 0.068 Uiso 1 1 calc R . .
H32C H 0.9509 0.0047 0.2463 0.068 Uiso 1 1 calc R . .
C33 C 0.7250(3) -0.09321(11) 0.30172(11) 0.0482(6) Uani 1 1 d
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H33A H 0.7326 -0.0491 0.3269 0.072 Uiso 1 1 calc R . .
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H33B H 0.7923 -0.1268 0.3253 0.072 Uiso 1 1 calc R . .
H33C H 0.6283 -0.1114 0.2996 0.072 Uiso 1 1 calc R . .
C34 C 0.7707(2) -0.16918(10) 0.17495(12) 0.0390(4) Uani 1 1 d
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H34A H 0.6739 -0.1835 0.1570 0.059 Uiso 1 1 calc R . .
H34B H 0.8106 -0.2017 0.2108 0.059 Uiso 1 1 calc R . .
H34C H 0.8295 -0.1693 0.1378 0.059 Uiso 1 1 calc R . .
C220 C 0.4021(2) 0.09710(11) 0.28459(10) 0.0362(4) Uani 1 1 d
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H220 H 0.3589 0.1164 0.2394 0.043 Uiso 1 1 calc R . .
C221 C 0.3697(3) 0.01901(12) 0.28526(12) 0.0452(5) Uani 1 1 d
. . .
H22A H 0.4103 -0.0008 0.3294 0.068 Uiso 1 1 calc R . .
H22B H 0.4113 -0.0040 0.2483 0.068 Uiso 1 1 calc R . .
H22C H 0.2667 0.0119 0.2784 0.068 Uiso 1 1 calc R . .
C222 C 0.3330(3) 0.13362(13) 0.34128(12) 0.0438(5) Uani 1 1 d
. . .
H22D H 0.3708 0.1139 0.3859 0.066 Uiso 1 1 calc R . .
H22E H 0.2300 0.1267 0.3330 0.066 Uiso 1 1 calc R . .
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C260 C 0.84026(19) 0.20719(9) 0.20498(9) 0.0280(4) Uani 1 1 d
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H260 H 0.7766 0.2063 0.1602 0.034 Uiso 1 1 calc R . .
C261 C 0.9858(2) 0.17825(12) 0.19299(11) 0.0383(4) Uani 1 1 d
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H26A H 1.0538 0.1843 0.2346 0.057 Uiso 1 1 calc R . .
H26B H 1.0193 0.2033 0.1550 0.057 Uiso 1 1 calc R . .
H26C H 0.9767 0.1287 0.1817 0.057 Uiso 1 1 calc R . .
C262 C 0.8556(2) 0.28334(11) 0.22882(12) 0.0414(5) Uani 1 1 d
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N2 N 0.53984(15) 0.17333(7) 0.18374(7) 0.0222(3) Uani 1 1 d .
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O1 O 0.38816(12) 0.03333(6) 0.01285(6) 0.0208(2) Uani 1 1 d .
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Sc1 Sc 0.59305(3) 0.041012(15) 0.065299(14) 0.01881(8) Uani 1
1 d . . .
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0.0059(6)
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0.0013(8)
C26 0.0279(8) 0.0216(7) 0.0255(8) -0.0057(6) 0.0040(7) -
0.0014(7)
C27 0.0220(8) 0.0223(7) 0.0260(8) -0.0024(6) 0.0038(6)
0.0002(6)
C28 0.0563(14) 0.0614(14) 0.0330(10) 0.0117(10) -0.0035(10) -
0.0122(12)
C29 0.0320(10) 0.0345(10) 0.0607(13) 0.0178(9) 0.0008(9) -
0.0025(8)
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0.00111(10) 0.00237(11)
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 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C27 Sc1 2.2579(17) . ?
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O1 C8 C7 109.14(14) . . ?
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_diffrn_measurement_device_type   'Bruker SMART APEX CCD area
detector'
_diffrn_measurement_method        'omega scans'
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             98382
_diffrn_reflns_av_R_equivalents   0.0637
_diffrn_reflns_av_sigmaI/netI     0.0386
_diffrn_reflns_limit_h_min        -13
_diffrn_reflns_limit_h_max        13
_diffrn_reflns_limit_k_min        -28
_diffrn_reflns_limit_k_max        30
_diffrn_reflns_limit_l_min        -51
_diffrn_reflns_limit_l_max        51
_diffrn_reflns_theta_min          1.07
_diffrn_reflns_theta_max          28.94
_reflns_number_total              10956
_reflns_number_gt                 9564
_reflns_threshold_expression      >2\s(I)

_computing_data_collection        'SMART (Siemens, 1993)'
_computing_cell_refinement        'SAINT (Siemens, 1995)'
```

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_computing_data_reduction          'SAINT (Siemens, 1995)'
_computing_structure_solution      'SIR-92 (Giacovazzo, 1994)'
_computing_structure_refinement    'SHELXL-97 (Sheldrick,
2008)'
_computing_molecular_graphics      'ORTEP (Farrugia, 1997)'
_computing_publication_material    'enCIFer (Allen et al.,
2004)'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0375P)^2^+12.1028P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     riding
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          10956
_refine_ls_number_parameters      412
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0932
_refine_ls_R_factor_gt            0.0790
_refine_ls_wR_factor_ref          0.1607
_refine_ls_wR_factor_gt           0.1543
_refine_ls_goodness_of_fit_ref    1.281
_refine_ls_restrained_S_all       1.281
_refine_ls_shift/su_max           0.000
_refine_ls_shift/su_mean          0.000

loop_
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 _atom_site_fract_x
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 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
C1 C 0.4750(2) 0.57338(11) 0.11415(6) 0.0199(5) Uani 1 1 d . .
.
C5 C 0.3445(3) 0.65820(13) 0.10004(7) 0.0279(6) Uani 1 1 d . .
.
H5A H 0.3800 0.6994 0.1018 0.034 Uiso 1 1 calc R . .
H5B H 0.2471 0.6595 0.1018 0.034 Uiso 1 1 calc R . .
C6 C 0.3888(3) 0.62782(12) 0.06635(7) 0.0245(6) Uani 1 1 d . .
.
H6A H 0.3126 0.6119 0.0531 0.029 Uiso 1 1 calc R . .
H6B H 0.4387 0.6558 0.0512 0.029 Uiso 1 1 calc R . .
C7 C 0.5313(3) 0.53918(12) 0.05311(6) 0.0238(5) Uani 1 1 d . .
.
H7A H 0.5693 0.5642 0.0342 0.029 Uiso 1 1 calc R . .
H7B H 0.4590 0.5154 0.0426 0.029 Uiso 1 1 calc R . .
C8 C 0.6382(3) 0.49566(12) 0.06561(7) 0.0229(5) Uani 1 1 d . .
.
C9 C 0.7577(3) 0.52812(13) 0.08055(8) 0.0294(6) Uani 1 1 d . .
.
H9A H 0.7314 0.5506 0.1014 0.044 Uiso 1 1 calc R . .
H9B H 0.7929 0.5558 0.0630 0.044 Uiso 1 1 calc R . .
H9C H 0.8256 0.4988 0.0868 0.044 Uiso 1 1 calc R . .
C10 C 0.6801(3) 0.45943(14) 0.03331(7) 0.0319(6) Uani 1 1 d .
. .
H10A H 0.7474 0.4301 0.0400 0.048 Uiso 1 1 calc R . .
H10B H 0.7163 0.4865 0.0156 0.048 Uiso 1 1 calc R . .
H10C H 0.6033 0.4385 0.0237 0.048 Uiso 1 1 calc R . .
C21 C 0.3881(3) 0.63169(11) 0.16343(7) 0.0215(5) Uani 1 1 d .
. .
C22 C 0.2797(3) 0.60864(13) 0.18172(7) 0.0278(6) Uani 1 1 d .
. .
C23 C 0.2699(4) 0.62232(14) 0.21729(8) 0.0394(8) Uani 1 1 d .
. .
H23 H 0.1972 0.6075 0.2304 0.047 Uiso 1 1 calc R . .
C24 C 0.3634(4) 0.65670(16) 0.23372(8) 0.0472(9) Uani 1 1 d .
. .
H24 H 0.3563 0.6644 0.2581 0.057 Uiso 1 1 calc R . .
C25 C 0.4677(4) 0.68026(15) 0.21499(8) 0.0383(7) Uani 1 1 d .
. .
H25 H 0.5311 0.7045 0.2266 0.046 Uiso 1 1 calc R . .
C26 C 0.4810(3) 0.66888(13) 0.17949(7) 0.0268(6) Uani 1 1 d .
. .
C27 C 0.3253(3) 0.37205(14) 0.05804(8) 0.0331(7) Uani 1 1 d .
. .
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```
H27A H 0.3614 0.3860 0.0354 0.040 Uiso 1 1 calc R . .
H27B H 0.3095 0.3286 0.0554 0.040 Uiso 1 1 calc R . .
C28 C 0.0603(4) 0.37152(18) 0.09716(10) 0.0512(9) Uani 1 1 d .
. .
H28A H 0.0537 0.3283 0.0931 0.077 Uiso 1 1 calc R . .
H28B H -0.0282 0.3891 0.0972 0.077 Uiso 1 1 calc R . .
H28C H 0.1026 0.3788 0.1198 0.077 Uiso 1 1 calc R . .
C29 C 0.0617(3) 0.40136(19) 0.02053(9) 0.0506(9) Uani 1 1 d .
. .
H29A H 0.1160 0.4139 0.0006 0.076 Uiso 1 1 calc R . .
H29B H -0.0155 0.4275 0.0224 0.076 Uiso 1 1 calc R . .
H29C H 0.0327 0.3599 0.0170 0.076 Uiso 1 1 calc R . .
C30 C 0.1744(3) 0.48808(15) 0.07189(10) 0.0425(8) Uani 1 1 d .
. .
H30A H 0.2305 0.4936 0.0925 0.064 Uiso 1 1 calc R . .
H30B H 0.0864 0.5043 0.0766 0.064 Uiso 1 1 calc R . .
H30C H 0.2133 0.5091 0.0519 0.064 Uiso 1 1 calc R . .
C31 C 0.6365(3) 0.30538(13) 0.09315(7) 0.0280(6) Uani 1 1 d .
. .
H31A H 0.7249 0.3241 0.0931 0.034 Uiso 1 1 calc R . .
H31B H 0.6293 0.2830 0.1154 0.034 Uiso 1 1 calc R . .
C32 C 0.6258(4) 0.28503(15) 0.01394(8) 0.0411(8) Uani 1 1 d .
. .
H32A H 0.5412 0.3060 0.0120 0.062 Uiso 1 1 calc R . .
H32B H 0.6317 0.2542 -0.0043 0.062 Uiso 1 1 calc R . .
H32C H 0.6981 0.3138 0.0110 0.062 Uiso 1 1 calc R . .
C33 C 0.4956(4) 0.19655(15) 0.06375(9) 0.0424(8) Uani 1 1 d .
. .
H33A H 0.5036 0.1758 0.0862 0.064 Uiso 1 1 calc R . .
H33B H 0.4955 0.1672 0.0447 0.064 Uiso 1 1 calc R . .
H33C H 0.4130 0.2193 0.0633 0.064 Uiso 1 1 calc R . .
C34 C 0.7928(4) 0.20274(15) 0.05679(9) 0.0429(8) Uani 1 1 d .
. .
H34A H 0.8692 0.2291 0.0538 0.064 Uiso 1 1 calc R . .
H34B H 0.7882 0.1746 0.0372 0.064 Uiso 1 1 calc R . .
H34C H 0.8016 0.1804 0.0787 0.064 Uiso 1 1 calc R . .
C35 C 0.4155(3) 0.39905(12) 0.15102(7) 0.0282(6) Uani 1 1 d .
. .
H35A H 0.4841 0.4216 0.1639 0.034 Uiso 1 1 calc R . .
H35B H 0.3372 0.4253 0.1491 0.034 Uiso 1 1 calc R . .
C36 C 0.3186(4) 0.27029(14) 0.14779(9) 0.0416(8) Uani 1 1 d .
. .
H36A H 0.2454 0.2835 0.1329 0.062 Uiso 1 1 calc R . .
H36B H 0.2903 0.2361 0.1620 0.062 Uiso 1 1 calc R . .
H36C H 0.3932 0.2584 0.1330 0.062 Uiso 1 1 calc R . .
C37 C 0.2276(4) 0.34626(16) 0.20757(9) 0.0486(9) Uani 1 1 d .
. .
H37A H 0.2503 0.3782 0.2241 0.073 Uiso 1 1 calc R . .
H37B H 0.2083 0.3094 0.2205 0.073 Uiso 1 1 calc R . .
H37C H 0.1499 0.3581 0.1940 0.073 Uiso 1 1 calc R . .
C38 C 0.5131(4) 0.3070(2) 0.20395(11) 0.0637(12) Uani 1 1 d .
. .
H38A H 0.5904 0.3020 0.1888 0.096 Uiso 1 1 calc R . .
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```
H38B H 0.4915 0.2686 0.2150 0.096 Uiso 1 1 calc R . .
H38C H 0.5325 0.3367 0.2221 0.096 Uiso 1 1 calc R . .
C39 C 0.7882(3) 0.44056(17) 0.16696(9) 0.0430(8) Uani 1 1 d .
. .
H39A H 0.8617 0.4549 0.1521 0.052 Uiso 1 1 calc R . .
H39B H 0.7500 0.4043 0.1561 0.052 Uiso 1 1 calc R . .
C40 C 0.8363(4) 0.42689(16) 0.20325(9) 0.0424(8) Uani 1 1 d .
. .
H40A H 0.9323 0.4187 0.2033 0.051 Uiso 1 1 calc R . .
H40B H 0.7893 0.3920 0.2133 0.051 Uiso 1 1 calc R . .
C41 C 0.8049(4) 0.48331(17) 0.22317(9) 0.0474(9) Uani 1 1 d .
. .
H41A H 0.7938 0.4751 0.2485 0.057 Uiso 1 1 calc R . .
H41B H 0.8746 0.5139 0.2200 0.057 Uiso 1 1 calc R . .
C42 C 0.6780(4) 0.50265(17) 0.20684(8) 0.0436(8) Uani 1 1 d .
. .
H42A H 0.6024 0.4819 0.2179 0.052 Uiso 1 1 calc R . .
H42B H 0.6657 0.5464 0.2094 0.052 Uiso 1 1 calc R . .
C220 C 0.1746(3) 0.57130(14) 0.16409(8) 0.0340(7) Uani 1 1 d .
. .
H220 H 0.2034 0.5638 0.1395 0.041 Uiso 1 1 calc R . .
C221 C 0.1571(3) 0.51066(14) 0.18198(10) 0.0442(8) Uani 1 1 d
. . .
H22A H 0.2431 0.4911 0.1844 0.066 Uiso 1 1 calc R . .
H22B H 0.0986 0.4854 0.1678 0.066 Uiso 1 1 calc R . .
H22C H 0.1182 0.5165 0.2052 0.066 Uiso 1 1 calc R . .
C222 C 0.0429(4) 0.60415(17) 0.16281(11) 0.0501(9) Uani 1 1 d
. . .
H22D H 0.0120 0.6117 0.1867 0.075 Uiso 1 1 calc R . .
H22E H -0.0219 0.5795 0.1504 0.075 Uiso 1 1 calc R . .
H22F H 0.0541 0.6423 0.1505 0.075 Uiso 1 1 calc R . .
C260 C 0.5924(3) 0.69760(13) 0.15899(7) 0.0290(6) Uani 1 1 d .
. .
H260 H 0.5690 0.6949 0.1336 0.035 Uiso 1 1 calc R . .
C261 C 0.7217(3) 0.66423(17) 0.16406(10) 0.0455(8) Uani 1 1 d
. . .
H26A H 0.7485 0.6668 0.1887 0.068 Uiso 1 1 calc R . .
H26B H 0.7899 0.6823 0.1493 0.068 Uiso 1 1 calc R . .
H26C H 0.7099 0.6221 0.1575 0.068 Uiso 1 1 calc R . .
C262 C 0.6083(4) 0.76371(15) 0.16788(12) 0.0545(10) Uani 1 1 d
. . .
H26D H 0.5226 0.7838 0.1661 0.082 Uiso 1 1 calc R . .
H26E H 0.6705 0.7822 0.1515 0.082 Uiso 1 1 calc R . .
H26F H 0.6419 0.7677 0.1918 0.082 Uiso 1 1 calc R . .
N1 N 0.4738(2) 0.57911(10) 0.07928(5) 0.0212(4) Uani 1 1 d . .
.
N2 N 0.4022(2) 0.61852(10) 0.12690(5) 0.0221(4) Uani 1 1 d . .
.
O1 O 0.58505(18) 0.45599(8) 0.09070(5) 0.0225(4) Uani 1 1 d .
. .
O2 O 0.6889(2) 0.48646(9) 0.17051(5) 0.0323(5) Uani 1 1 d . .
.
```

```
Si1 Si 0.16088(8) 0.40640(4) 0.06169(2) 0.02817(18) Uani 1 1 d
. . .
Si2 Si 0.63817(8) 0.24897(3) 0.05810(2) 0.02599(17) Uani 1 1 d
. . .
Si3 Si 0.36999(8) 0.33292(4) 0.17714(2) 0.02675(17) Uani 1 1 d
. . .
Sc1 Sc 0.49107(5) 0.38035(2) 0.096481(13) 0.02053(12) Uani 1 1
d . . .
Li1 Li 0.5568(5) 0.4938(2) 0.13473(12) 0.0269(10) Uani 1 1 d .
. .

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 _atom_site_aniso_U_33
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 _atom_site_aniso_U_13
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C1 0.0187(12) 0.0207(12) 0.0205(12) 0.0009(9) 0.0000(9) -
0.0004(10)
C5 0.0315(15) 0.0278(14) 0.0245(13) 0.0022(11) -0.0034(11)
0.0103(12)
C6 0.0272(14) 0.0230(13) 0.0234(12) 0.0034(10) -0.0060(10)
0.0033(11)
C7 0.0280(14) 0.0264(13) 0.0171(11) 0.0000(10) 0.0024(10)
0.0021(11)
C8 0.0234(13) 0.0241(13) 0.0212(12) 0.0023(10) 0.0061(10)
0.0013(10)
C9 0.0207(13) 0.0326(15) 0.0347(15) 0.0011(12) 0.0040(11) -
0.0030(11)
C10 0.0343(16) 0.0347(16) 0.0267(14) -0.0029(12) 0.0105(12)
0.0042(13)
C21 0.0244(13) 0.0197(12) 0.0204(12) 0.0009(9) 0.0005(10)
0.0062(10)
C22 0.0300(15) 0.0261(14) 0.0274(13) 0.0031(11) 0.0058(11)
0.0032(12)
C23 0.052(2) 0.0367(17) 0.0298(15) 0.0008(13) 0.0151(14) -
0.0040(15)
C24 0.072(3) 0.047(2) 0.0226(15) -0.0042(14) 0.0098(16) -
0.0084(19)
C25 0.049(2) 0.0400(17) 0.0261(14) -0.0049(13) -0.0042(13) -
0.0107(15)
C26 0.0266(14) 0.0285(14) 0.0252(13) 0.0010(11) -0.0004(11)
0.0038(11)
C27 0.0265(15) 0.0370(16) 0.0358(16) -0.0081(13) -0.0044(12)
0.0055(12)
C28 0.0343(19) 0.057(2) 0.062(2) 0.0087(19) 0.0041(17) -
0.0081(17)
C29 0.0324(18) 0.072(3) 0.047(2) -0.0132(19) -0.0133(15)
0.0068(18)
C30 0.0330(17) 0.0367(18) 0.058(2) -0.0095(16) -0.0020(15)
0.0015(14)
```

```
C31 0.0269(14) 0.0270(14) 0.0303(14) -0.0004(11) -0.0021(11)
0.0024(11)
C32 0.057(2) 0.0395(18) 0.0267(15) 0.0043(13) 0.0056(15)
0.0123(16)
C33 0.053(2) 0.0350(17) 0.0389(17) -0.0108(14) 0.0133(16) -
0.0102(16)
C34 0.048(2) 0.0388(18) 0.0418(18) -0.0013(14) 0.0035(15)
0.0186(16)
C35 0.0311(15) 0.0237(13) 0.0300(14) -0.0004(11) 0.0063(12) -
0.0046(11)
C36 0.051(2) 0.0262(15) 0.0474(19) -0.0090(14) 0.0066(16) -
0.0084(15)
C37 0.057(2) 0.044(2) 0.0446(19) -0.0109(16) 0.0244(17) -
0.0172(17)
C38 0.059(3) 0.077(3) 0.054(2) 0.026(2) -0.021(2) -0.004(2)
C39 0.0384(18) 0.051(2) 0.0391(17) -0.0086(15) -0.0056(14)
0.0148(16)
C40 0.0407(19) 0.0421(19) 0.0445(19) 0.0089(15) -0.0055(15)
0.0026(15)
C41 0.052(2) 0.058(2) 0.0314(17) 0.0008(15) -0.0065(15) -
0.0054(18)
C42 0.048(2) 0.049(2) 0.0346(17) -0.0116(15) -0.0035(15)
0.0054(17)
C220 0.0306(16) 0.0346(16) 0.0367(16) 0.0004(13) 0.0049(13) -
0.0053(13)
C221 0.0355(18) 0.0283(16) 0.069(2) -0.0001(16) 0.0027(17) -
0.0001(14)
C222 0.0367(19) 0.043(2) 0.070(3) 0.0149(18) -0.0052(18)
0.0011(16)
C260 0.0242(14) 0.0353(15) 0.0275(14) -0.0007(12) -0.0012(11)
-0.0015(12)
C261 0.0345(18) 0.050(2) 0.052(2) 0.0007(17) 0.0010(15)
0.0058(16)
C262 0.048(2) 0.0347(19) 0.081(3) 0.0026(18) 0.024(2) -
0.0049(16)
N1 0.0231(11) 0.0218(11) 0.0188(10) 0.0011(8) -0.0001(8)
0.0030(9)
N2 0.0243(11) 0.0221(11) 0.0198(10) 0.0010(8) -0.0013(8)
0.0054(9)
O1 0.0255(9) 0.0198(9) 0.0222(9) 0.0012(7) 0.0048(7) 0.0008(7)
O2 0.0351(12) 0.0351(11) 0.0267(10) -0.0049(8) -0.0066(9)
0.0066(9)
Si1 0.0212(4) 0.0330(4) 0.0303(4) -0.0062(3) -0.0023(3) -
0.0005(3)
Si2 0.0299(4) 0.0228(4) 0.0253(4) 0.0010(3) 0.0046(3)
0.0057(3)
Si3 0.0311(4) 0.0255(4) 0.0237(4) 0.0008(3) 0.0017(3) -
0.0067(3)
Sc1 0.0201(2) 0.0184(2) 0.0230(2) -0.00191(19) 0.00000(19)
0.00074(19)
Li1 0.033(3) 0.025(2) 0.023(2) -0.0019(18) -0.0030(19)
0.004(2)
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;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
;

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C1 N2 1.341(3) . ?
C1 Li1 2.114(5) . ?
C5 N2 1.477(3) . ?
C5 C6 1.523(4) . ?
C6 N1 1.474(3) . ?
C7 N1 1.461(3) . ?
C7 C8 1.533(4) . ?
C8 O1 1.412(3) . ?
C8 C9 1.523(4) . ?
C8 C10 1.536(4) . ?
C21 C26 1.398(4) . ?
C21 C22 1.401(4) . ?
C21 N2 1.434(3) . ?
C22 C23 1.397(4) . ?
C22 C220 1.512(4) . ?
C23 C24 1.372(5) . ?
C24 C25 1.382(5) . ?
C25 C26 1.387(4) . ?
C26 C260 1.517(4) . ?
C27 Si1 1.840(3) . ?
C27 Sc1 2.240(3) . ?
C28 Si1 1.867(4) . ?
C29 Si1 1.870(3) . ?
C30 Si1 1.871(3) . ?
C31 Si2 1.839(3) . ?
C31 Sc1 2.235(3) . ?
C32 Si2 1.874(3) . ?
C33 Si2 1.873(3) . ?
C34 Si2 1.878(3) . ?
C35 Si3 1.841(3) . ?
```

```
C35 Sc1 2.260(3) . ?
C36 Si3 1.867(3) . ?
C37 Si3 1.877(3) . ?
C38 Si3 1.869(4) . ?
C39 O2 1.443(4) . ?
C39 C40 1.502(4) . ?
C40 C41 1.506(5) . ?
C41 C42 1.494(5) . ?
C42 O2 1.439(4) . ?
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Si1 C27 Sc1 126.55(15) . . ?
Si2 C31 Sc1 124.13(14) . . ?
Si3 C35 Sc1 115.88(14) . . ?
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C39 C40 C41 103.2(3) . . ?
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C261 C260 C262 110.8(3) . . ?
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C1 N1 C6 114.2(2) . . ?
C7 N1 C6 117.0(2) . . ?
C1 N2 C21 124.3(2) . . ?
C1 N2 C5 114.6(2) . . ?
C21 N2 C5 120.9(2) . . ?
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Li1 C1 N2 C5 -167.3(3) . . . . ?
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C22 C21 N2 C1 -94.9(3) . . . . ?
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C9 C8 O1 Sc1 -149.4(2) . . . . ?
C7 C8 O1 Sc1 86.4(3) . . . . ?
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Si2 C31 Sc1 O1 -114.61(17) . . . . ?
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 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
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 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
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P=(Fo^2^+2Fc^2^)/3'
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H1B H 0.2957 0.8727 0.4802 0.057 Uiso 1 1 calc R . .
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C2 C 0.3097(3) 0.9837(3) 0.42791(13) 0.0659(11) Uani 1 1 d . .
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H2B H 0.3693 0.9388 0.4177 0.079 Uiso 1 1 calc R . .
C3 C 0.3558(3) 1.0760(3) 0.45885(14) 0.0737(11) Uani 1 1 d . .
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H3A H 0.4286 1.0560 0.4764 0.088 Uiso 1 1 calc R . .
H3B H 0.3648 1.1420 0.4398 0.088 Uiso 1 1 calc R . .
C4 C 0.2741(3) 1.0960(3) 0.49188(13) 0.0611(10) Uani 1 1 d . .
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H4A H 0.3115 1.0997 0.5248 0.073 Uiso 1 1 calc R . .
H4B H 0.2342 1.1654 0.4841 0.073 Uiso 1 1 calc R . .
C5 C 0.3374(2) 0.8225(3) 0.17644(11) 0.0536(9) Uani 1 1 d . .
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H5A H 0.3006 0.8869 0.1603 0.064 Uiso 1 1 calc R . .
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C6 C 0.3517(3) 0.7351(3) 0.14182(12) 0.0574(9) Uani 1 1 d . .
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H6A H 0.3626 0.7662 0.1110 0.069 Uiso 1 1 calc R . .
H6B H 0.2874 0.6852 0.1374 0.069 Uiso 1 1 calc R . .
C7 C 0.4536(3) 0.6776(3) 0.16467(13) 0.0675(10) Uani 1 1 d . .
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H7A H 0.4358 0.6249 0.1887 0.081 Uiso 1 1 calc R . .
H7B H 0.4904 0.6384 0.1410 0.081 Uiso 1 1 calc R . .
C8 C 0.5238(3) 0.7672(2) 0.18666(12) 0.0523(9) Uani 1 1 d . .
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H8A H 0.5717 0.7409 0.2152 0.063 Uiso 1 1 calc R . .
H8B H 0.5711 0.7966 0.1643 0.063 Uiso 1 1 calc R . .
C9 C 0.7016(3) 1.1482(3) 0.33286(11) 0.0515(8) Uani 1 1 d . .
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H9A H 0.7018 1.1973 0.3055 0.062 Uiso 1 1 calc R . .
H9B H 0.7678 1.1009 0.3355 0.062 Uiso 1 1 calc R . .
C10 C 0.6993(3) 1.2127(3) 0.37722(11) 0.0599(9) Uani 1 1 d . .
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H10A H 0.7748 1.2325 0.3920 0.072 Uiso 1 1 calc R . .
H10B H 0.6548 1.2799 0.3711 0.072 Uiso 1 1 calc R . .
C11 C 0.6463(3) 1.1344(3) 0.40750(11) 0.0591(9) Uani 1 1 d . .
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H11A H 0.7019 1.0845 0.4244 0.071 Uiso 1 1 calc R . .
H11B H 0.6091 1.1743 0.4309 0.071 Uiso 1 1 calc R . .
C12 C 0.5640(3) 1.0723(3) 0.37392(10) 0.0627(10) Uani 1 1 d .
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H12A H 0.5621 0.9947 0.3833 0.075 Uiso 1 1 calc R . .
H12B H 0.4892 1.1037 0.3732 0.075 Uiso 1 1 calc R . .
C13 C 0.5572(3) 1.2934(2) 0.22010(11) 0.0486(8) Uani 1 1 d . .
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H13A H 0.5415 1.2694 0.1869 0.058 Uiso 1 1 calc R . .
H13B H 0.6379 1.2905 0.2302 0.058 Uiso 1 1 calc R . .
C14 C 0.5150(3) 1.4061(2) 0.22532(11) 0.0538(8) Uani 1 1 d . .
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H14A H 0.4496 1.4211 0.2017 0.065 Uiso 1 1 calc R . .
H14B H 0.5727 1.4612 0.2220 0.065 Uiso 1 1 calc R . .
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O1 O 0.19829(16) 1.00412(15) 0.48571(8) 0.0450(6) Uani 1 1 d .
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O2 O 0.44815(14) 0.85060(14) 0.19894(6) 0.0383(5) Uani 1 1 d .
. .
O3 O 0.60105(15) 1.08266(15) 0.32797(6) 0.0417(5) Uani 1 1 d .
. .
O4 O 0.5000 1.22356(19) 0.2500 0.0352(6) Uani 1 2 d S . .
Ce1 Ce 0.0000 1.0000 0.5000 0.03060(10) Uani 1 2 d S . .
Ce2 Ce 0.5000 1.015957(17) 0.2500 0.02626(9) Uani 1 2 d S . .
B1 B -0.0241 1.203870(17) 0.4648 0.0584(11) Uani 1 1 d RD . .
H11 H -0.0373 1.2873 0.4487 0.070 Uiso 0.52(2) 1 d PRD A 1
H12 H 0.0538 1.2037 0.4908 0.070 Uiso 0.52(2) 1 d PRD A 1
H13 H -0.0167 1.1423 0.4364 0.070 Uiso 0.52(2) 1 d PRD A 1
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B2 B -0.0739 0.910648(17) 0.4073 0.0498(10) Uani 1 1 d RD . .
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H31 H 0.2277 1.0087 0.2996 0.047 Uiso 1 1 d RD . .
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H12' H -0.018(4) 1.2909(15) 0.4517(18) 0.047 Uiso 0.48(2) 1 d
PD A 2
H13' H -0.030(4) 1.195(4) 0.5038(7) 0.047 Uiso 0.48(2) 1 d PD
A 2
H14' H -0.098(2) 1.149(3) 0.4530(18) 0.047 Uiso 0.48(2) 1 d PD
A 2
H32' H 0.3710(18) 0.960(4) 0.3062(15) 0.047 Uiso 0.40(3) 1 d
PD B 2
H33' H 0.2950(18) 0.983(5) 0.2473(8) 0.047 Uiso 0.40(3) 1 d PD
B 2
H34' H 0.337(3) 1.0988(11) 0.284(2) 0.047 Uiso 0.40(3) 1 d PD
B 2

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0.0108(16)
C2 0.093(3) 0.057(2) 0.053(2) 0.0160(19) 0.027(2) 0.028(2)
C3 0.060(2) 0.079(3) 0.086(3) 0.017(2) 0.022(2) -0.013(2)
C4 0.050(2) 0.057(2) 0.077(3) -0.0205(19) 0.0142(19) -
0.0170(18)
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C6 0.065(2) 0.050(2) 0.053(2) -0.0149(17) -0.0057(17) -
0.0049(18)
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C8 0.050(2) 0.0443(19) 0.063(2) -0.0134(17) 0.0088(17)
0.0104(16)
C9 0.049(2) 0.058(2) 0.043(2) -0.0057(16) -0.0048(15) -
0.0209(17)
C10 0.066(2) 0.060(2) 0.049(2) -0.0138(18) -0.0104(17) -
0.0133(19)
C11 0.061(2) 0.075(2) 0.039(2) -0.0166(18) -0.0032(17)
0.0038(19)
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0.021(2)
C13 0.050(2) 0.0399(18) 0.060(2) 0.0123(16) 0.0230(16)
0.0005(15)
C14 0.060(2) 0.0387(18) 0.063(2) 0.0063(16) 0.0085(17)
0.0006(16)
O1 0.0343(12) 0.0462(13) 0.0573(14) -0.0201(10) 0.0163(10) -
0.0023(9)
O2 0.0322(11) 0.0373(11) 0.0445(12) -0.0113(9) 0.0021(9)
0.0031(9)
O3 0.0501(13) 0.0467(12) 0.0264(11) -0.0009(9) -0.0015(9) -
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O4 0.0375(16) 0.0300(15) 0.0407(16) 0.000 0.0152(13) 0.000
Ce1 0.03001(16) 0.03207(15) 0.02927(16) -0.00624(9)
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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C5 C6 1.488(4) . ?
C6 C7 1.499(4) . ?
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C8 O2 1.455(3) . ?
C9 O3 1.459(3) . ?
C9 C10 1.502(4) . ?
C10 C11 1.501(5) . ?
C11 C12 1.499(4) . ?
C12 O3 1.459(3) . ?
C13 O4 1.458(3) . ?
C13 C14 1.490(4) . ?
C14 C14 1.512(6) 2_655 ?
O1 Ce1 2.5178(19) . ?
O2 Ce2 2.5279(17) . ?
O3 Ce2 2.5337(17) . ?
O4 C13 1.458(3) 2_655 ?
O4 Ce2 2.543(2) . ?
Ce1 O1 2.5178(19) 5_576 ?
Ce1 B1 2.6944 5_576 ?
Ce1 B1 2.6944 . ?
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Ce1 B2 2.9000 . ?
Ce2 O2 2.5279(17) 2_655 ?
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O2 C5 C6 106.0(2) . . ?
C5 C6 C7 102.4(3) . . ?
C8 C7 C6 103.6(3) . . ?
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O3 C9 C10 104.7(2) . . ?
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O4 C13 C14 106.5(2) . . ?
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C1 O1 C4 107.9(2) . . ?
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C4 O1 Ce1 127.51(16) . . ?
C8 O2 C5 108.1(2) . . ?
C8 O2 Ce2 125.93(16) . . ?
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 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
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 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
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H25 H 0.0787 0.6118 0.2628 0.037 Uiso 1 1 calc R . .
N2 N -0.2898(7) 0.3708(5) 0.3097(4) 0.0298(15) Uani 1 1 d . .
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O1 O -0.2410(8) 0.1304(5) 0.4656(3) 0.0443(18) Uani 1 1 d . .
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C45 C -0.0523(9) -0.1770(7) 0.5769(4) 0.0296(16) Uani 1 1 d .
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H45 H -0.0195 -0.2399 0.5518 0.036 Uiso 1 1 calc R . .
O2 O -0.0535(8) 0.3769(5) 0.4771(3) 0.0440(17) Uani 1 1 d . .
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C011 C -0.3640(9) 0.3337(8) 0.5676(4) 0.0334(18) Uani 1 1 d .
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C16 C 0.2324(12) 0.2567(7) 0.6458(5) 0.045(2) Uani 1 1 d . . .
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H16B H 0.3412 0.2545 0.6445 0.054 Uiso 1 1 calc R . .
C6 C -0.4564(10) 0.2312(7) 0.2694(5) 0.0364(19) Uani 1 1 d . .
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H6A H -0.5521 0.2330 0.2934 0.044 Uiso 1 1 calc R . .
H6B H -0.4647 0.1840 0.2266 0.044 Uiso 1 1 calc R . .
C260 C 0.0021(11) 0.4018(9) 0.2394(5) 0.046(2) Uani 1 1 d . .
.
H260 H -0.0374 0.3279 0.2527 0.055 Uiso 1 1 calc R . .
C41 C -0.0231(8) 0.0147(6) 0.6108(4) 0.0203(13) Uani 1 1 d . .
.
C220 C -0.4388(10) 0.5529(9) 0.3841(5) 0.042(2) Uani 1 1 d . .
.
H220 H -0.4724 0.4761 0.3736 0.050 Uiso 1 1 calc R . .
N1 N -0.3345(8) 0.1935(6) 0.3187(4) 0.0327(15) Uani 1 1 d . .
.
C42 C -0.1611(8) 0.0088(8) 0.6487(4) 0.0318(19) Uani 1 1 d . .
.
```

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C422 C -0.2244(10) 0.1008(8) 0.7669(4) 0.0363(18) Uani 1 1 d .
. .
H42A H -0.2869 0.1576 0.7876 0.055 Uiso 1 1 calc R . .
H42B H -0.1243 0.1073 0.7867 0.055 Uiso 1 1 calc R . .
H42C H -0.2639 0.0279 0.7780 0.055 Uiso 1 1 calc R . .
C24 C -0.0854(9) 0.6914(7) 0.3183(5) 0.0329(17) Uani 1 1 d . .
.
H24 H -0.0413 0.7623 0.3196 0.039 Uiso 1 1 calc R . .
C17 C 0.1886(10) 0.3747(6) 0.5321(6) 0.039(2) Uani 1 1 d . . .
H17A H 0.2325 0.3559 0.4859 0.047 Uiso 1 1 calc R . .
H17B H 0.2599 0.4215 0.5587 0.047 Uiso 1 1 calc R . .
C7 C -0.3349(12) 0.0832(7) 0.3504(6) 0.047(2) Uani 1 1 d . . .
H7A H -0.2391 0.0480 0.3409 0.056 Uiso 1 1 calc R . .
H7B H -0.4119 0.0391 0.3256 0.056 Uiso 1 1 calc R . .
C420 C -0.2216(12) 0.1158(9) 0.6861(4) 0.048(2) Uani 1 1 d . .
.
H420 H -0.1453 0.1735 0.6780 0.057 Uiso 1 1 calc R . .
C18 C 0.0465(12) 0.4412(8) 0.5180(5) 0.044(2) Uani 1 1 d . . .
C44 C -0.1816(9) -0.1824(6) 0.6124(4) 0.0291(16) Uani 1 1 d .
. .
H44 H -0.2367 -0.2488 0.6118 0.035 Uiso 1 1 calc R . .
C262 C -0.0130(12) 0.4185(10) 0.1593(5) 0.052(3) Uani 1 1 d .
. .
H26A H -0.1175 0.4202 0.1454 0.077 Uiso 1 1 calc R . .
H26B H 0.0355 0.3578 0.1348 0.077 Uiso 1 1 calc R . .
H26C H 0.0333 0.4882 0.1462 0.077 Uiso 1 1 calc R . .
C11 C 0.0661(9) 0.1935(7) 0.5536(5) 0.0307(17) Uani 1 1 d . .
.
C23 C -0.2221(8) 0.6726(5) 0.3501(4) 0.0227(14) Uani 1 1 d . .
.
H23 H -0.2703 0.7319 0.3728 0.027 Uiso 1 1 calc R . .
C10 C -0.3545(12) -0.0474(7) 0.4531(6) 0.053(3) Uani 1 1 d . .
.
H10A H -0.2657 -0.0823 0.4350 0.079 Uiso 1 1 calc R . .
H10B H -0.4416 -0.0863 0.4347 0.079 Uiso 1 1 calc R . .
H10C H -0.3526 -0.0505 0.5052 0.079 Uiso 1 1 calc R . .
C5 C -0.4032(9) 0.3472(7) 0.2510(5) 0.036(2) Uani 1 1 d . . .
H5A H -0.3579 0.3489 0.2036 0.043 Uiso 1 1 calc R . .
H5B H -0.4851 0.4009 0.2518 0.043 Uiso 1 1 calc R . .
C8 C -0.3604(12) 0.0763(8) 0.4283(6) 0.054(3) Uani 1 1 d . . .
C1 C -0.2420(9) 0.2789(6) 0.3410(4) 0.0272(15) Uani 1 1 d . .
.
C9 C -0.5152(12) 0.1331(9) 0.4455(7) 0.057(3) Uani 1 1 d . . .
H9A H -0.5416 0.1163 0.4945 0.086 Uiso 1 1 calc R . .
H9B H -0.5915 0.1047 0.4128 0.086 Uiso 1 1 calc R . .
H9C H -0.5069 0.2130 0.4396 0.086 Uiso 1 1 calc R . .
C20 C 0.0869(12) 0.5482(7) 0.4774(5) 0.042(2) Uani 1 1 d . . .
H20A H 0.1471 0.5295 0.4366 0.063 Uiso 1 1 calc R . .
H20B H 0.1424 0.5974 0.5093 0.063 Uiso 1 1 calc R . .
H20C H -0.0034 0.5850 0.4608 0.063 Uiso 1 1 calc R . .
C222 C -0.5570(10) 0.6316(9) 0.3516(7) 0.049(3) Uani 1 1 d . .
.
H22A H -0.5423 0.7058 0.3709 0.074 Uiso 1 1 calc R . .
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H22B H -0.6552 0.6053 0.3637 0.074 Uiso 1 1 calc R . .
H22C H -0.5481 0.6335 0.2998 0.074 Uiso 1 1 calc R . .
C462 C 0.2962(10) -0.1527(9) 0.5785(6) 0.048(2) Uani 1 1 d . .
.
H46A H 0.3097 -0.1255 0.6272 0.072 Uiso 1 1 calc R . .
H46B H 0.3909 -0.1518 0.5545 0.072 Uiso 1 1 calc R . .
H46C H 0.2581 -0.2280 0.5795 0.072 Uiso 1 1 calc R . .
C221 C -0.4185(13) 0.5623(17) 0.4689(6) 0.090(6) Uani 1 1 d .
. .
H22D H -0.3512 0.5047 0.4860 0.135 Uiso 1 1 calc R . .
H22E H -0.5142 0.5533 0.4912 0.135 Uiso 1 1 calc R . .
H22F H -0.3777 0.6346 0.4812 0.135 Uiso 1 1 calc R . .
C461 C 0.1680(13) -0.1174(11) 0.4598(6) 0.056(3) Uani 1 1 d .
. .
H46D H 0.1251 -0.1914 0.4593 0.085 Uiso 1 1 calc R . .
H46E H 0.2650 -0.1195 0.4382 0.085 Uiso 1 1 calc R . .
H46F H 0.1037 -0.0671 0.4329 0.085 Uiso 1 1 calc R . .
C19 C -0.0226(13) 0.4754(9) 0.5930(6) 0.052(3) Uani 1 1 d . .
.
H19A H -0.0859 0.5400 0.5864 0.078 Uiso 1 1 calc R . .
H19B H 0.0569 0.4928 0.6271 0.078 Uiso 1 1 calc R . .
H19C H -0.0809 0.4141 0.6112 0.078 Uiso 1 1 calc R . .
C421 C -0.3604(14) 0.1592(12) 0.6497(7) 0.067(3) Uani 1 1 d .
. .
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H42E H -0.3545 0.1476 0.5983 0.100 Uiso 1 1 calc R . .
H42F H -0.3703 0.2380 0.6595 0.100 Uiso 1 1 calc R . .
C261 C 0.1746(11) 0.4060(10) 0.2551(6) 0.050(2) Uani 1 1 d . .
.
H26D H 0.2108 0.4807 0.2468 0.074 Uiso 1 1 calc R . .
H26E H 0.2243 0.3546 0.2235 0.074 Uiso 1 1 calc R . .
H26F H 0.1949 0.3852 0.3046 0.074 Uiso 1 1 calc R . .
C43 C -0.2339(8) -0.0915(8) 0.6496(4) 0.0327(19) Uani 1 1 d .
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0.0267(12)
C25 0.023(4) 0.043(4) 0.027(4) 0.005(3) 0.004(3) -0.001(3)
N2 0.029(3) 0.022(3) 0.038(4) -0.003(3) -0.021(3) 0.010(2)
O1 0.063(4) 0.034(3) 0.035(3) 0.022(3) -0.032(3) -0.034(3)
C45 0.038(4) 0.030(4) 0.021(3) 0.008(3) 0.005(3) 0.006(3)
O2 0.072(4) 0.030(3) 0.029(3) 0.011(2) -0.027(3) -0.026(3)
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C26 0.029(4) 0.026(3) 0.016(3) 0.001(3) -0.003(3) 0.010(3)
C011 0.026(4) 0.051(5) 0.023(4) 0.013(3) 0.009(3) 0.020(3)
N3 0.033(4) 0.030(4) 0.027(3) 0.000(3) -0.012(3) -0.006(3)
C460 0.036(4) 0.036(4) 0.027(4) 0.013(3) 0.016(3) 0.007(3)
C15 0.039(4) 0.031(4) 0.031(4) -0.009(3) -0.024(3) 0.013(3)
N4 0.029(3) 0.019(3) 0.030(3) 0.007(2) -0.021(3) 0.000(2)
C22 0.029(4) 0.016(3) 0.024(3) 0.015(3) 0.004(3) 0.006(3)
C46 0.013(3) 0.024(3) 0.027(3) 0.002(3) -0.003(2) 0.003(3)
C16 0.058(6) 0.028(4) 0.047(5) 0.007(4) -0.041(5) 0.000(4)
C6 0.029(4) 0.035(4) 0.045(5) 0.000(4) -0.020(4) -0.003(3)
C260 0.039(5) 0.060(6) 0.037(5) -0.010(4) -0.004(4) 0.025(4)
C41 0.023(3) 0.021(3) 0.017(3) 0.004(2) -0.012(2) 0.005(3)
C220 0.025(4) 0.065(6) 0.036(5) 0.005(4) 0.008(3) -0.001(4)
N1 0.038(4) 0.028(3) 0.031(4) -0.007(3) -0.012(3) -0.006(3)
C42 0.022(4) 0.058(5) 0.015(3) -0.004(3) -0.005(3) 0.025(4)
C422 0.038(4) 0.046(5) 0.026(4) -0.005(3) 0.008(3) -0.007(4)
C24 0.035(4) 0.026(4) 0.037(4) 0.008(3) -0.002(3) -0.008(3)
C17 0.036(4) 0.018(4) 0.063(6) 0.006(4) -0.020(4) -0.012(3)
C7 0.058(6) 0.019(4) 0.062(6) -0.008(4) -0.030(5) 0.000(4)
C420 0.063(6) 0.061(6) 0.020(4) -0.010(4) -0.002(4) 0.035(5)
C18 0.068(6) 0.034(4) 0.030(4) 0.011(3) -0.022(4) -0.035(4)
C44 0.030(4) 0.022(4) 0.035(4) 0.009(3) -0.002(3) -0.008(3)
C262 0.060(6) 0.062(6) 0.033(5) -0.020(4) 0.011(4) 0.019(5)
C11 0.025(4) 0.029(4) 0.038(4) 0.007(3) -0.014(3) -0.006(3)
C23 0.034(4) 0.007(3) 0.028(3) 0.001(2) 0.004(3) 0.007(3)
C10 0.066(6) 0.021(4) 0.068(7) 0.017(4) -0.039(5) -0.029(4)
C5 0.027(4) 0.036(4) 0.044(5) 0.016(4) -0.022(3) -0.012(3)
C8 0.067(7) 0.033(5) 0.061(6) 0.017(4) -0.034(5) -0.041(5)
C1 0.032(4) 0.026(4) 0.023(4) -0.005(3) 0.001(3) -0.001(3)
C9 0.043(5) 0.052(6) 0.076(8) 0.007(5) -0.012(5) -0.015(5)
C20 0.058(6) 0.021(4) 0.046(5) 0.004(4) 0.000(4) -0.010(4)
C222 0.019(4) 0.056(6) 0.074(7) 0.004(5) 0.010(4) 0.005(4)
C462 0.031(5) 0.065(6) 0.048(5) -0.004(5) 0.012(4) 0.019(4)
C221 0.040(6) 0.200(18) 0.030(5) 0.012(7) 0.013(4) -0.024(8)
C461 0.056(6) 0.075(7) 0.039(5) 0.019(5) 0.024(5) 0.014(6)
C19 0.064(7) 0.046(6) 0.045(6) -0.025(5) -0.014(5) 0.003(5)
C421 0.063(7) 0.082(8) 0.056(7) -0.014(6) 0.007(6) 0.041(6)
C261 0.039(5) 0.067(7) 0.042(5) -0.004(5) -0.002(4) 0.016(5)
C43 0.012(3) 0.065(6) 0.021(3) 0.011(4) 0.009(3) 0.005(3)

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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
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 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C21 C26 C260 C261 -139.0(8) . . . . ?
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expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
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P=(Fo^2^+2Fc^2^)/3'
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C9 C 0.19242(17) 1.12051(18) 0.65606(13) 0.0734(8) Uani 1 1 d
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C220 C 0.62779(16) 1.27617(11) 0.61762(11) 0.0420(5) Uani 1 1
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C221 C 0.6089(2) 1.31576(15) 0.68934(13) 0.0766(8) Uani 1 1 d
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C222 C 0.6374(2) 1.33486(15) 0.55647(14) 0.0788(8) Uani 1 1 d
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C260 C 0.79436(16) 1.01194(11) 0.60685(12) 0.0456(5) Uani 1 1
d . . .
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H26B H 0.7868 0.9131 0.6675 0.151 Uiso 1 1 calc R . .
H26C H 0.7333 0.9841 0.7040 0.151 Uiso 1 1 calc R . .
C262 C 0.88022(19) 0.98246(14) 0.56329(15) 0.0692(7) Uani 1 1
d . . .
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H26E H 0.8695 0.9279 0.5535 0.104 Uiso 1 1 calc R . .
H26F H 0.9492 0.9905 0.5926 0.104 Uiso 1 1 calc R . .
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N2 N 0.61386(11) 1.11462(8) 0.58226(7) 0.0286(3) Uani 1 1 d .
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0.0330(15)
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0.0009(10)
C26 0.0262(10) 0.0449(11) 0.0309(10) 0.0039(8) 0.0045(8)
0.0010(8)
C220 0.0427(12) 0.0374(11) 0.0477(12) -0.0053(9) 0.0134(10) -
0.0004(9)
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0.0270(15)
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0.0008(6)
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distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
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C5 C 0.4513(4) 0.2770(5) 0.2038(3) 0.061(2) Uani 1 1 d . . .
H5A H 0.4222 0.3265 0.1876 0.073 Uiso 1 1 calc R . .
H5B H 0.4426 0.2652 0.2362 0.073 Uiso 1 1 calc R . .
C6 C 0.4321(4) 0.2006(5) 0.1678(3) 0.060(2) Uani 1 1 d . . .
H6A H 0.4175 0.1522 0.1844 0.072 Uiso 1 1 calc R . .
H6B H 0.3919 0.2136 0.1358 0.072 Uiso 1 1 calc R . .
C7 C 0.5085(3) 0.1149(4) 0.1243(3) 0.0428(16) Uani 1 1 d . . .
H7A H 0.5185 0.1391 0.0947 0.051 Uiso 1 1 calc R . .
H7B H 0.4601 0.0866 0.1115 0.051 Uiso 1 1 calc R . .
C8 C 0.5676(3) 0.0492(4) 0.1487(3) 0.0397(15) Uani 1 1 d . . .
C9 C 0.5515(4) -0.0230(5) 0.1091(3) 0.059(2) Uani 1 1 d . . .
H9A H 0.5470 -0.0003 0.0756 0.088 Uiso 1 1 calc R . .
H9B H 0.5054 -0.0506 0.1075 0.088 Uiso 1 1 calc R . .
H9C H 0.5919 -0.0633 0.1194 0.088 Uiso 1 1 calc R . .
C10 C 0.5661(4) 0.0189(5) 0.1999(3) 0.0535(19) Uani 1 1 d . .
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H10A H 0.6001 -0.0281 0.2114 0.080 Uiso 1 1 calc R . .
H10B H 0.5161 0.0010 0.1966 0.080 Uiso 1 1 calc R . .
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C11 C 0.8759(3) -0.0042(4) 0.1819(3) 0.0391(15) Uani 1 1 d . .
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C15 C 1.0028(4) -0.0401(7) 0.2087(5) 0.096(4) Uani 1 1 d . . .
H15A H 1.0377 -0.0272 0.2430 0.115 Uiso 1 1 calc R . .
H15B H 1.0218 -0.0880 0.1945 0.115 Uiso 1 1 calc R . .
C16 C 0.9910(4) 0.0347(5) 0.1741(3) 0.059(2) Uani 1 1 d . . .
H16A H 1.0203 0.0830 0.1920 0.071 Uiso 1 1 calc R . .
H16B H 1.0040 0.0221 0.1434 0.071 Uiso 1 1 calc R . .
C17 C 0.8769(3) 0.1256(4) 0.1315(3) 0.0430(16) Uani 1 1 d . .
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H17A H 0.8384 0.1074 0.0997 0.052 Uiso 1 1 calc R . .
H17B H 0.9149 0.1560 0.1217 0.052 Uiso 1 1 calc R . .
C18 C 0.8415(3) 0.1871(4) 0.1603(3) 0.0427(16) Uani 1 1 d . .
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C19 C 0.8936(3) 0.2037(5) 0.2140(3) 0.056(2) Uani 1 1 d . . .
H19A H 0.8741 0.2491 0.2292 0.084 Uiso 1 1 calc R . .
H19B H 0.9422 0.2194 0.2127 0.084 Uiso 1 1 calc R . .
H19C H 0.8983 0.1532 0.2346 0.084 Uiso 1 1 calc R . .
C21 C 0.5728(3) 0.3566(4) 0.2447(2) 0.0386(15) Uani 1 1 d . .
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C22 C 0.6054(3) 0.3403(4) 0.2987(3) 0.0425(15) Uani 1 1 d . .
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C23 C 0.6459(4) 0.4054(5) 0.3294(3) 0.0513(18) Uani 1 1 d . .
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H23 H 0.6685 0.3965 0.3648 0.062 Uiso 1 1 calc R . .
C24 C 0.6537(4) 0.4833(5) 0.3087(3) 0.0550(19) Uani 1 1 d . .
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H24 H 0.6822 0.5259 0.3300 0.066 Uiso 1 1 calc R . .
C25 C 0.6186(4) 0.4980(4) 0.2559(3) 0.0467(17) Uani 1 1 d . .
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H25 H 0.6234 0.5508 0.2420 0.056 Uiso 1 1 calc R . .
C26 C 0.5768(3) 0.4353(4) 0.2239(3) 0.0425(16) Uani 1 1 d . .
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C27 C 0.7422(3) 0.2982(5) 0.2331(3) 0.0507(19) Uani 1 1 d . .
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C28 C 0.7669(4) 0.2529(6) 0.2772(3) 0.062(2) Uani 1 1 d . . .
C29 C 0.8181(4) 0.2856(7) 0.3248(4) 0.076(3) Uani 1 1 d . . .
C30 C 0.8364(4) 0.3672(8) 0.3255(4) 0.074(3) Uani 1 1 d . . .
C31 C 0.8122(4) 0.4159(6) 0.2840(4) 0.070(3) Uani 1 1 d . . .
C32 C 0.7664(4) 0.3788(6) 0.2375(3) 0.059(2) Uani 1 1 d . . .
C33 C 0.6281(4) 0.2849(5) 0.0909(3) 0.059(2) Uani 1 1 d . . .
H33A H 0.6124 0.3369 0.1035 0.071 Uiso 1 1 calc R . .
H33B H 0.6741 0.3001 0.0847 0.071 Uiso 1 1 calc R . .
C34 C 0.4616(7) 0.3138(12) 0.0370(7) 0.187(8) Uani 1 1 d . . .
H34A H 0.4553 0.2806 0.0648 0.280 Uiso 1 1 calc R . .
H34B H 0.4208 0.3025 0.0056 0.280 Uiso 1 1 calc R . .
H34C H 0.4621 0.3731 0.0454 0.280 Uiso 1 1 calc R . .
C35 C 0.5627(7) 0.3694(7) -0.0157(4) 0.113(4) Uani 1 1 d . . .
H35A H 0.5518 0.4209 -0.0007 0.170 Uiso 1 1 calc R . .
H35B H 0.5248 0.3600 -0.0488 0.170 Uiso 1 1 calc R . .
H35C H 0.6110 0.3743 -0.0200 0.170 Uiso 1 1 calc R . .
C36 C 0.5342(8) 0.1820(8) -0.0050(4) 0.129(5) Uani 1 1 d . . .
H36A H 0.5736 0.1408 0.0078 0.193 Uiso 1 1 calc R . .
H36B H 0.5228 0.1889 -0.0417 0.193 Uiso 1 1 calc R . .
H36C H 0.4901 0.1627 0.0018 0.193 Uiso 1 1 calc R . .
C41 C 0.9169(4) -0.1244(5) 0.2435(3) 0.056(2) Uani 1 1 d . . .
C42 C 0.9355(4) -0.1087(5) 0.2968(4) 0.062(2) Uani 1 1 d . . .
C43 C 0.9286(5) -0.1757(8) 0.3290(4) 0.088(3) Uani 1 1 d . . .
H43 H 0.9396 -0.1665 0.3643 0.105 Uiso 1 1 calc R . .
C44 C 0.9054(5) -0.2556(8) 0.3082(5) 0.085(3) Uani 1 1 d . . .
H44 H 0.9007 -0.2995 0.3297 0.102 Uiso 1 1 calc R . .
C45 C 0.8897(4) -0.2696(5) 0.2575(5) 0.079(3) Uani 1 1 d . . .
H45 H 0.8741 -0.3236 0.2444 0.095 Uiso 1 1 calc R . .
C46 C 0.8961(4) -0.2047(6) 0.2227(4) 0.066(2) Uani 1 1 d . . .
C47 C 0.7211(4) -0.0983(5) 0.1952(4) 0.064(2) Uani 1 1 d . . .
C48 C 0.7412(5) -0.0860(7) 0.2473(5) 0.078(3) Uani 1 1 d . . .
C49 C 0.7369(6) -0.1423(9) 0.2827(5) 0.090(3) Uani 1 1 d . . .
C50 C 0.7129(7) -0.2181(12) 0.2677(7) 0.118(6) Uani 1 1 d . .
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C51 C 0.6879(6) -0.2407(7) 0.2140(8) 0.120(5) Uani 1 1 d . . .
C52 C 0.6931(5) -0.1794(6) 0.1792(5) 0.082(3) Uani 1 1 d . . .
C53 C 0.7161(4) -0.0105(6) 0.0704(3) 0.067(2) Uani 1 1 d . . .
H53A H 0.6815 -0.0575 0.0671 0.081 Uiso 1 1 calc R . .
H53B H 0.6842 0.0368 0.0537 0.081 Uiso 1 1 calc R . .
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H54B H 0.6548 -0.1248 -0.0325 0.900 Uiso 1 1 calc R . .
H54C H 0.7168 -0.1838 0.0044 0.900 Uiso 1 1 calc R . .
C55 C 0.7444(16) 0.062(3) -0.0225(12) 0.55(4) Uani 1 1 d . . .
H55A H 0.6926 0.0791 -0.0352 0.831 Uiso 1 1 calc R . .
H55B H 0.7609 0.0490 -0.0512 0.831 Uiso 1 1 calc R . .
H55C H 0.7743 0.1078 -0.0026 0.831 Uiso 1 1 calc R . .
C56 C 0.8552(5) -0.0675(9) 0.0459(4) 0.115(4) Uani 1 1 d . . .
H56A H 0.8623 -0.1141 0.0698 0.172 Uiso 1 1 calc R . .
H56B H 0.8845 -0.0197 0.0634 0.172 Uiso 1 1 calc R . .
H56C H 0.8710 -0.0841 0.0174 0.172 Uiso 1 1 calc R . .
C110 C 0.8268(4) 0.2684(5) 0.1283(4) 0.070(2) Uani 1 1 d . . .
H11A H 0.7925 0.2568 0.0941 0.104 Uiso 1 1 calc R . .
H11B H 0.8733 0.2894 0.1259 0.104 Uiso 1 1 calc R . .
H11C H 0.8053 0.3104 0.1447 0.104 Uiso 1 1 calc R . .
C220 C 0.5921(4) 0.2592(5) 0.3237(3) 0.0528(18) Uani 1 1 d . .
.
H220 H 0.5732 0.2171 0.2959 0.063 Uiso 1 1 calc R . .
C221 C 0.6599(5) 0.2213(6) 0.3632(4) 0.080(3) Uani 1 1 d . . .
H22A H 0.6971 0.2089 0.3473 0.119 Uiso 1 1 calc R . .
H22B H 0.6460 0.1698 0.3765 0.119 Uiso 1 1 calc R . .
H22C H 0.6802 0.2609 0.3911 0.119 Uiso 1 1 calc R . .
C222 C 0.5296(5) 0.2728(6) 0.3477(4) 0.081(3) Uani 1 1 d . . .
H22D H 0.5475 0.3102 0.3770 0.121 Uiso 1 1 calc R . .
H22E H 0.5161 0.2191 0.3588 0.121 Uiso 1 1 calc R . .
H22F H 0.4863 0.2975 0.3223 0.121 Uiso 1 1 calc R . .
C260 C 0.5325(4) 0.4563(5) 0.1664(3) 0.0537(18) Uani 1 1 d . .
.
H260 H 0.5153 0.4025 0.1482 0.064 Uiso 1 1 calc R . .
C261 C 0.5765(5) 0.5025(6) 0.1383(4) 0.083(3) Uani 1 1 d . . .
H26A H 0.5473 0.5063 0.1021 0.124 Uiso 1 1 calc R . .
H26B H 0.6223 0.4723 0.1424 0.124 Uiso 1 1 calc R . .
H26C H 0.5882 0.5587 0.1524 0.124 Uiso 1 1 calc R . .
C262 C 0.4619(5) 0.5087(7) 0.1645(4) 0.095(3) Uani 1 1 d . . .
H26D H 0.4758 0.5670 0.1727 0.143 Uiso 1 1 calc R . .
H26E H 0.4408 0.4862 0.1893 0.143 Uiso 1 1 calc R . .
H26F H 0.4253 0.5053 0.1303 0.143 Uiso 1 1 calc R . .
C420 C 0.9643(6) -0.0259(7) 0.3230(4) 0.092(3) Uani 1 1 d . .
.
H420 H 0.9596 0.0156 0.2953 0.110 Uiso 1 1 calc R . .
C421 C 0.9225(7) 0.0111(9) 0.3572(5) 0.121(4) Uani 1 1 d . . .
H42A H 0.8698 -0.0012 0.3422 0.182 Uiso 1 1 calc R . .
H42B H 0.9297 0.0716 0.3599 0.182 Uiso 1 1 calc R . .
H42C H 0.9416 -0.0138 0.3912 0.182 Uiso 1 1 calc R . .
C422 C 1.0486(6) -0.0320(8) 0.3548(6) 0.135(5) Uani 1 1 d . .
.
H42D H 1.0571 -0.0796 0.3781 0.202 Uiso 1 1 calc R . .
H42E H 1.0645 0.0193 0.3744 0.202 Uiso 1 1 calc R . .
H42F H 1.0769 -0.0396 0.3317 0.202 Uiso 1 1 calc R . .
C460 C 0.8858(5) -0.2244(7) 0.1645(5) 0.101(4) Uani 1 1 d . .
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H460 H 0.8666 -0.1728 0.1443 0.121 Uiso 1 1 calc R . .
C461 C 0.8284(7) -0.2961(9) 0.1426(7) 0.161(7) Uani 1 1 d . .
.
H46A H 0.8182 -0.3010 0.1059 0.242 Uiso 1 1 calc R . .
H46B H 0.7826 -0.2832 0.1491 0.242 Uiso 1 1 calc R . .
H46C H 0.8485 -0.3489 0.1592 0.242 Uiso 1 1 calc R . .
C462 C 0.9595(7) -0.2482(12) 0.1567(5) 0.156(7) Uani 1 1 d . .
.
H46D H 0.9946 -0.2022 0.1680 0.233 Uiso 1 1 calc R . .
H46E H 0.9505 -0.2592 0.1205 0.233 Uiso 1 1 calc R . .
H46F H 0.9798 -0.2983 0.1765 0.233 Uiso 1 1 calc R . .
N1 N 0.5031(3) 0.1842(3) 0.1585(2) 0.0411(13) Uani 1 1 d . . .
N2 N 0.5328(3) 0.2894(3) 0.2123(2) 0.0401(12) Uani 1 1 d . . .
N3 N 0.9113(3) 0.0506(4) 0.1609(2) 0.0406(13) Uani 1 1 d . . .
N4 N 0.9257(3) -0.0581(4) 0.2106(3) 0.0557(16) Uani 1 1 d . .
.
O1 O 0.64194(19) 0.0844(3) 0.15506(15) 0.0340(9) Uani 1 1 d .
. .
O2 O 0.77226(19) 0.1508(3) 0.16136(15) 0.0342(9) Uani 1 1 d .
. .
F1 F 0.7505(3) 0.1703(4) 0.2766(2) 0.0886(16) Uani 1 1 d . . .
F2 F 0.8436(3) 0.2358(5) 0.3668(2) 0.112(2) Uani 1 1 d . . .
F3 F 0.8839(3) 0.4008(5) 0.3712(2) 0.125(3) Uani 1 1 d . . .
F4 F 0.8316(3) 0.5002(4) 0.2844(3) 0.108(2) Uani 1 1 d . . .
F5 F 0.7462(3) 0.4307(3) 0.1951(2) 0.0834(15) Uani 1 1 d . . .
F6 F 0.7662(3) -0.0049(4) 0.2647(2) 0.1052(19) Uani 1 1 d . .
.
F7 F 0.7572(5) -0.1255(7) 0.3327(4) 0.169(4) Uani 1 1 d . . .
F8 F 0.7102(4) -0.2861(5) 0.2989(4) 0.177(4) Uani 1 1 d . . .
F9 F 0.6644(4) -0.3185(4) 0.1964(5) 0.206(5) Uani 1 1 d . . .
F10 F 0.6698(4) -0.1990(4) 0.1286(3) 0.127(3) Uani 1 1 d . . .
Si1 Si 0.5639(3) 0.2811(2) 0.02682(11) 0.1413(19) Uani 1 1 d .
. .
Si2 Si 0.75554(14) -0.0381(3) 0.02157(10) 0.1085(13) Uani 1 1
d . . .
Sc1 Sc 0.67301(6) 0.21226(7) 0.16355(4) 0.0336(3) Uani 1 1 d .
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Sc2 Sc 0.74032(6) 0.02285(8) 0.15202(5) 0.0360(3) Uani 1 1 d .
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C1 0.032(3) 0.030(4) 0.043(3) -0.002(3) 0.011(3) 0.003(3)
C5 0.042(4) 0.069(6) 0.078(5) -0.025(4) 0.029(4) -0.007(4)
C6 0.039(4) 0.061(5) 0.091(6) -0.023(4) 0.035(4) -0.010(3)
C7 0.029(3) 0.045(4) 0.054(4) -0.014(3) 0.014(3) -0.008(3)
C8 0.034(3) 0.035(4) 0.055(4) -0.010(3) 0.022(3) -0.010(3)
```

C9 0.045(4) 0.047(5) 0.086(5) -0.022(4) 0.024(4) -0.016(3)
C10 0.043(4) 0.045(4) 0.081(5) 0.005(4) 0.031(3) -0.006(3)
C11 0.035(3) 0.032(4) 0.054(4) -0.004(3) 0.020(3) -0.003(3)
C15 0.045(5) 0.096(8) 0.161(10) 0.054(7) 0.054(5) 0.008(5)
C16 0.037(4) 0.073(6) 0.072(5) 0.008(4) 0.025(3) 0.006(3)
C17 0.042(3) 0.042(4) 0.051(4) 0.004(3) 0.022(3) -0.002(3)
C18 0.032(3) 0.031(4) 0.070(5) 0.001(3) 0.024(3) -0.004(3)
C19 0.031(3) 0.061(5) 0.080(5) -0.024(4) 0.023(3) -0.015(3)
C21 0.039(3) 0.032(4) 0.051(4) -0.009(3) 0.023(3) -0.001(3)
C22 0.049(4) 0.034(4) 0.049(4) -0.005(3) 0.022(3) 0.004(3)
C23 0.057(4) 0.049(5) 0.047(4) -0.007(4) 0.016(3) 0.002(3)
C24 0.053(4) 0.047(5) 0.064(5) -0.019(4) 0.020(4) -0.004(3)
C25 0.058(4) 0.027(4) 0.060(5) -0.002(3) 0.026(3) 0.003(3)
C26 0.043(3) 0.036(4) 0.055(4) -0.001(3) 0.023(3) 0.010(3)
C27 0.031(3) 0.053(5) 0.069(5) -0.021(4) 0.019(3) 0.004(3)
C28 0.055(4) 0.071(6) 0.061(5) -0.019(5) 0.023(4) -0.007(4)
C29 0.050(5) 0.102(8) 0.077(6) -0.023(6) 0.023(4) -0.013(5)
C30 0.053(5) 0.098(8) 0.065(6) -0.041(6) 0.013(4) -0.014(5)
C31 0.036(4) 0.071(6) 0.105(7) -0.037(6) 0.027(4) -0.013(4)
C32 0.036(4) 0.059(5) 0.081(6) -0.019(5) 0.018(4) 0.002(4)
C33 0.067(5) 0.053(5) 0.059(5) 0.007(4) 0.022(4) 0.004(4)
C34 0.081(9) 0.24(2) 0.231(19) 0.062(17) 0.045(10) 0.026(10)
C35 0.151(10) 0.077(8) 0.089(8) 0.027(6) 0.011(7) 0.009(7)
C36 0.190(13) 0.119(11) 0.058(6) -0.013(7) 0.016(7) -0.033(9)
C41 0.038(4) 0.044(5) 0.088(6) 0.017(4) 0.023(4) 0.008(3)
C42 0.054(4) 0.053(5) 0.089(6) 0.022(5) 0.038(4) 0.016(4)
C43 0.073(6) 0.103(9) 0.101(7) 0.039(7) 0.047(5) 0.042(6)
C44 0.075(6) 0.086(8) 0.113(9) 0.041(7) 0.057(6) 0.032(6)
C45 0.044(4) 0.042(5) 0.147(10) 0.014(6) 0.027(5) 0.013(4)
C46 0.042(4) 0.061(6) 0.096(7) 0.024(5) 0.025(4) 0.015(4)
C47 0.042(4) 0.046(5) 0.110(7) 0.011(5) 0.033(4) 0.004(3)
C48 0.059(5) 0.068(7) 0.113(8) 0.024(6) 0.038(5) 0.018(5)
C49 0.074(6) 0.107(10) 0.104(9) 0.052(8) 0.051(6) 0.031(6)
C50 0.073(7) 0.134(14) 0.173(14) 0.097(12) 0.076(9) 0.029(8)
C51 0.059(6) 0.049(7) 0.262(18) 0.040(10) 0.067(9) 0.003(5)
C52 0.059(5) 0.042(5) 0.148(10) 0.016(6) 0.039(6) 0.004(4)
C53 0.059(5) 0.085(7) 0.060(5) -0.023(5) 0.023(4) -0.015(4)
C54 0.173(19) 0.91(8) 0.79(7) -0.76(7) 0.25(3) -0.31(4)
C55 0.34(3) 1.06(10) 0.37(4) 0.58(6) 0.27(3) 0.45(5)
C56 0.094(7) 0.171(13) 0.087(7) -0.059(8) 0.042(6) 0.008(7)
C110 0.056(5) 0.047(5) 0.116(7) 0.020(5) 0.042(5) -0.001(4)
C220 0.073(5) 0.045(5) 0.051(4) 0.006(3) 0.035(4) 0.007(4)
C221 0.083(6) 0.077(7) 0.082(6) 0.028(5) 0.033(5) 0.020(5)
C222 0.089(6) 0.079(7) 0.095(7) 0.020(5) 0.058(5) 0.021(5)
C260 0.066(4) 0.041(4) 0.053(4) 0.003(3) 0.019(3) 0.007(3)
C261 0.093(7) 0.080(7) 0.078(6) 0.023(5) 0.031(5) 0.012(5)
C262 0.083(6) 0.127(9) 0.067(6) 0.017(6) 0.013(5) 0.052(6)
C420 0.099(7) 0.078(8) 0.100(8) 0.018(6) 0.035(6) 0.025(6)
C421 0.134(10) 0.134(11) 0.099(8) -0.014(8) 0.045(7) 0.030(8)
C422 0.085(8) 0.093(9) 0.187(13) 0.000(9) -0.008(8) 0.002(6)
C460 0.078(7) 0.070(7) 0.119(9) -0.005(6) -0.013(6) 0.023(5)
C461 0.093(8) 0.115(11) 0.241(18) -0.096(12) 0.010(9) -
0.010(7)

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C462 0.092(8) 0.29(2) 0.087(8) -0.040(11) 0.037(6) -0.027(10)
N1 0.030(3) 0.040(3) 0.057(3) -0.013(3) 0.019(2) -0.004(2)
N2 0.035(3) 0.040(3) 0.049(3) -0.005(3) 0.020(2) 0.001(2)
N3 0.033(3) 0.046(3) 0.048(3) -0.002(3) 0.019(2) -0.001(2)
N4 0.029(3) 0.049(4) 0.091(5) 0.015(3) 0.023(3) 0.003(3)
O1 0.0252(19) 0.031(2) 0.049(2) -0.0056(19) 0.0163(16) -
0.0054(17)
O2 0.0238(19) 0.033(2) 0.049(2) -0.0017(19) 0.0166(16) -
0.0037(16)
F1 0.104(4) 0.084(4) 0.090(4) -0.015(3) 0.048(3) -0.029(3)
F2 0.095(4) 0.159(6) 0.070(4) 0.005(4) 0.010(3) 0.011(4)
F3 0.085(4) 0.184(7) 0.099(4) -0.077(5) 0.020(3) -0.045(4)
F4 0.078(3) 0.078(4) 0.176(6) -0.069(4) 0.054(4) -0.033(3)
F5 0.076(3) 0.062(3) 0.108(4) -0.005(3) 0.025(3) 0.001(3)
F6 0.115(5) 0.098(5) 0.092(4) -0.011(4) 0.021(3) 0.015(4)
F7 0.165(7) 0.239(11) 0.136(7) 0.088(7) 0.093(5) 0.107(7)
F8 0.101(5) 0.162(7) 0.300(11) 0.156(8) 0.112(6) 0.033(4)
F9 0.119(5) 0.053(4) 0.415(16) 0.059(7) 0.048(7) -0.026(4)
F10 0.118(5) 0.073(4) 0.153(6) -0.034(4) -0.001(4) 0.015(3)
Si1 0.238(5) 0.077(2) 0.0534(16) 0.0181(16) -0.025(2) -
0.043(3)
Si2 0.0613(15) 0.205(4) 0.0542(14) -0.044(2) 0.0131(11)
0.0128(19)
Sc1 0.0303(6) 0.0304(7) 0.0418(7) -0.0037(5) 0.0142(5) -
0.0010(5)
Sc2 0.0313(6) 0.0308(7) 0.0487(7) -0.0034(6) 0.0171(5) -
0.0016(5)

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 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C7 C8 1.503(9) . ?
C8 O1 1.463(7) . ?
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C8 C9 1.526(9) . ?
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C11 Sc2 2.449(6) . ?
C15 C16 1.479(11) . ?
C15 N4 1.501(9) . ?
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C18 C110 1.522(10) . ?
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C45 C46 1.427(12) . ?
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C56 Si2 1.832(10) . ?
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C420 C421 1.528(14) . ?
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C460 C461 1.541(15) . ?
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O2 Sc1 2.126(4) . ?
Sc1 Sc2 3.2946(17) . ?

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N1 C6 C5 102.6(5) . . ?
N1 C7 C8 115.5(5) . . ?
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O1 C8 C7 109.5(5) . . ?
C10 C8 C7 113.0(5) . . ?
O1 C8 C9 108.8(5) . . ?
C10 C8 C9 111.5(6) . . ?
C7 C8 C9 104.8(5) . . ?
N4 C11 N3 108.3(5) . . ?
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N3 C11 Sc2 111.3(4) . . ?
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O2 C18 C110 110.7(5) . . ?
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O2 C18 C17 108.4(5) . . ?
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C26 C21 N2 120.2(6) . . ?
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F5 C32 C31 115.6(8) . . ?
Si1 C33 Sc1 143.9(5) . . ?
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loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x, y, -z+1/2'
 'x+1/2, y+1/2, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y, z-1/2'
 '-x+1/2, -y+1/2, -z'
 'x+1/2, -y+1/2, z-1/2'

_cell_length_a                    38.7236(16)
```

```
_cell_length_b                    23.2484(10)
_cell_length_c                    20.6479(8)
_cell_angle_alpha                 90.00
_cell_angle_beta                  110.141(5)
_cell_angle_gamma                 90.00
_cell_volume                      17451.8(12)
_cell_formula_units_Z             16
_cell_measurement_temperature     100(2)
_cell_measurement_reflns_used     17263
_cell_measurement_theta_min     2.2539
_cell_measurement_theta_max     63.9887

_exptl_crystal_description        block
_exptl_crystal_colour             colourless
_exptl_crystal_size_max           0.1721
_exptl_crystal_size_mid           0.1682
_exptl_crystal_size_min           0.0708
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.241
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              6912
_exptl_absorpt_coefficient_mu     1.951
_exptl_absorpt_correction_type    'multi-scan'
_exptl_absorpt_correction_T_min   0.57150
_exptl_absorpt_correction_T_max   1.00000
_exptl_absorpt_process_details
;
CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
(compiled Jan  5 2010,16:28:46)
Empirical absorption correction using spherical harmonics,
 implemented in SCALE3 ABSPACK scaling algorithm.
;
_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       100(2)
_diffrn_radiation_wavelength      1.54180
_diffrn_radiation_type            CuK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type
'SuperNova, Dual, Cu at zero, Atlas'
_diffrn_measurement_method        'omega scans'
_diffrn_detector_area_resol_mean 10.3147
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             62621
_diffrn_reflns_av_R_equivalents   0.0589
```

```
_diffrn_reflns_av_sigmaI/netI     0.0558
_diffrn_reflns_limit_h_min        -44
_diffrn_reflns_limit_h_max        44
_diffrn_reflns_limit_k_min        -26
_diffrn_reflns_limit_k_max        22
_diffrn_reflns_limit_l_min        -23
_diffrn_reflns_limit_l_max        23
_diffrn_reflns_theta_min          2.26
_diffrn_reflns_theta_max          64.08
_reflns_number_total              13666
_reflns_number_gt                 9691
_reflns_threshold_expression      >2\s(I)

_computing_data_collection
;
CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
(compiled Jan  5 2010,16:28:46)
;
_computing_cell_refinement
;
CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
(compiled Jan  5 2010,16:28:46)
;
_computing_data_reduction
;
CrysAlisPro, Oxford Diffraction Ltd.,
Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET)
(compiled Jan  5 2010,16:28:46)
;
_computing_structure_solution     'SIR-92 (Giacovazzo, 1994)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     'ORTEP (Farrugia, 1997)'
_computing_publication_material   'enCIFer (Allen et al.,
2004)'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-
factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R
are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt)
etc. and is
 not relevant to the choice of reflections for refinement.  R-
factors based
 on F^2^ are statistically about twice as large as those based
on F, and R-
 factors based on ALL data will be even larger.
```

```
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.2000P)^2^+0.0000P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     riding
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          13666
_refine_ls_number_parameters      1033
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.1448
_refine_ls_R_factor_gt            0.1030
_refine_ls_wR_factor_ref          0.3881
_refine_ls_wR_factor_gt           0.3423
_refine_ls_goodness_of_fit_ref    1.591
_refine_ls_restrained_S_all       1.591
_refine_ls_shift/su_max           0.000
_refine_ls_shift/su_mean          0.000

loop_
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
C00A C 0.33388(16) 0.2160(3) -0.0681(3) 0.0367(15) Uani 1 1 d
. . .
H00A H 0.3520 0.1937 -0.0318 0.055 Uiso 1 1 calc R . .
H00B H 0.3253 0.1933 -0.1107 0.055 Uiso 1 1 calc R . .
H00C H 0.3130 0.2254 -0.0537 0.055 Uiso 1 1 calc R . .
C1 C 0.63235(14) 0.1141(3) 1.1213(3) 0.0255(13) Uani 1 1 d . .
.
C1A C 0.38079(14) 0.3612(3) 0.1335(3) 0.0249(13) Uani 1 1 d .
. .
C5 C 0.64124(16) 0.0858(3) 1.2354(3) 0.0387(17) Uani 1 1 d . .
.
H5A H 0.6584 0.0540 1.2567 0.046 Uiso 1 1 calc R . .
H5B H 0.6232 0.0898 1.2594 0.046 Uiso 1 1 calc R . .
```

```
C5A C 0.38700(15) 0.3290(3) 0.2453(3) 0.0357(16) Uani 1 1 d .
. .
H5A1 H 0.4047 0.2979 0.2666 0.043 Uiso 1 1 calc R . .
H5A2 H 0.3680 0.3303 0.2673 0.043 Uiso 1 1 calc R . .
C6 C 0.66189(16) 0.1422(3) 1.2369(3) 0.0371(16) Uani 1 1 d . .
.
H6A H 0.6512 0.1740 1.2557 0.044 Uiso 1 1 calc R . .
H6B H 0.6883 0.1383 1.2647 0.044 Uiso 1 1 calc R . .
C6A C 0.40632(16) 0.3869(3) 0.2504(3) 0.0389(17) Uani 1 1 d .
. .
H6A1 H 0.3937 0.4172 0.2675 0.047 Uiso 1 1 calc R . .
H6A2 H 0.4323 0.3846 0.2812 0.047 Uiso 1 1 calc R . .
C7 C 0.67154(16) 0.2026(3) 1.1431(3) 0.0377(17) Uani 1 1 d . .
.
H7A H 0.6911 0.2182 1.1841 0.045 Uiso 1 1 calc R . .
H7B H 0.6519 0.2320 1.1273 0.045 Uiso 1 1 calc R . .
C7A C 0.41862(16) 0.4509(3) 0.1618(3) 0.0359(16) Uani 1 1 d .
. .
H7A1 H 0.4368 0.4666 0.2046 0.043 Uiso 1 1 calc R . .
H7A2 H 0.3985 0.4794 0.1446 0.043 Uiso 1 1 calc R . .
C8 C 0.68773(15) 0.1927(3) 1.0857(3) 0.0379(17) Uani 1 1 d . .
.
C8A C 0.43742(15) 0.4439(3) 0.1075(3) 0.0388(17) Uani 1 1 d .
. .
C9 C 0.71898(16) 0.1504(3) 1.1090(3) 0.0387(16) Uani 1 1 d . .
.
H9A H 0.7098 0.1132 1.1186 0.058 Uiso 1 1 calc R . .
H9B H 0.7379 0.1647 1.1510 0.058 Uiso 1 1 calc R . .
H9C H 0.7297 0.1456 1.0727 0.058 Uiso 1 1 calc R . .
C9A C 0.46975(16) 0.4020(3) 0.1335(3) 0.0379(16) Uani 1 1 d .
. .
H9A1 H 0.4607 0.3642 0.1413 0.057 Uiso 1 1 calc R . .
H9A2 H 0.4874 0.4164 0.1769 0.057 Uiso 1 1 calc R . .
H9A3 H 0.4818 0.3986 0.0991 0.057 Uiso 1 1 calc R . .
C10 C 0.70098(17) 0.2507(3) 1.0688(3) 0.0437(18) Uani 1 1 d .
. .
H10A H 0.7137 0.2452 1.0356 0.066 Uiso 1 1 calc R . .
H10B H 0.7179 0.2679 1.1111 0.066 Uiso 1 1 calc R . .
H10C H 0.6798 0.2762 1.0489 0.066 Uiso 1 1 calc R . .
C10A C 0.44947(19) 0.5031(3) 0.0932(3) 0.0481(19) Uani 1 1 d .
. .
H10D H 0.4616 0.5002 0.0588 0.072 Uiso 1 1 calc R . .
H10E H 0.4667 0.5193 0.1360 0.072 Uiso 1 1 calc R . .
H10F H 0.4279 0.5282 0.0757 0.072 Uiso 1 1 calc R . .
C11 C 0.59777(15) 0.1501(3) 0.8762(3) 0.0311(15) Uani 1 1 d .
. .
C11A C 0.35215(14) 0.4009(3) -0.1108(3) 0.0299(15) Uani 1 1 d
. . .
C15 C 0.5896(2) 0.1790(4) 0.7623(3) 0.051(2) Uani 1 1 d . . .
H15A H 0.6089 0.1776 0.7409 0.061 Uiso 1 1 calc R . .
H15B H 0.5712 0.2084 0.7385 0.061 Uiso 1 1 calc R . .
C15A C 0.34269(19) 0.4340(4) -0.2235(3) 0.0467(19) Uani 1 1 d
. . .
```

```
H15C H 0.3632 0.4287 -0.2412 0.056 Uiso 1 1 calc R . .
H15D H 0.3265 0.4652 -0.2496 0.056 Uiso 1 1 calc R . .
C16 C 0.5720(2) 0.1206(4) 0.7606(3) 0.063(3) Uani 1 1 d . . .
H16A H 0.5453 0.1218 0.7335 0.076 Uiso 1 1 calc R . .
H16B H 0.5838 0.0910 0.7408 0.076 Uiso 1 1 calc R . .
C16A C 0.3215(2) 0.3786(4) -0.2275(3) 0.053(2) Uani 1 1 d . .
.
H16C H 0.2946 0.3856 -0.2448 0.064 Uiso 1 1 calc R . .
H16D H 0.3275 0.3500 -0.2574 0.064 Uiso 1 1 calc R . .
C17 C 0.56585(16) 0.0558(3) 0.8550(3) 0.0350(16) Uani 1 1 d .
. .
H17A H 0.5546 0.0315 0.8137 0.042 Uiso 1 1 calc R . .
H17B H 0.5465 0.0649 0.8747 0.042 Uiso 1 1 calc R . .
C17A C 0.32122(15) 0.3056(3) -0.1364(3) 0.0325(15) Uani 1 1 d
. . .
H17C H 0.3111 0.2818 -0.1784 0.039 Uiso 1 1 calc R . .
H17D H 0.3009 0.3140 -0.1190 0.039 Uiso 1 1 calc R . .
C18 C 0.59677(15) 0.0210(3) 0.9089(3) 0.0353(16) Uani 1 1 d .
. .
C18A C 0.35123(15) 0.2703(3) -0.0807(3) 0.0329(15) Uani 1 1 d
. . .
C19 C 0.62830(17) 0.0084(4) 0.8818(3) 0.0458(19) Uani 1 1 d .
. .
H19A H 0.6390 0.0448 0.8736 0.069 Uiso 1 1 calc R . .
H19B H 0.6188 -0.0132 0.8386 0.069 Uiso 1 1 calc R . .
H19C H 0.6473 -0.0143 0.9160 0.069 Uiso 1 1 calc R . .
C19A C 0.38369(15) 0.2573(3) -0.1048(3) 0.0379(17) Uani 1 1 d
. . .
H19D H 0.3947 0.2935 -0.1124 0.057 Uiso 1 1 calc R . .
H19E H 0.3750 0.2354 -0.1479 0.057 Uiso 1 1 calc R . .
H19F H 0.4021 0.2347 -0.0694 0.057 Uiso 1 1 calc R . .
C21 C 0.60512(16) 0.0219(3) 1.1371(3) 0.0331(16) Uani 1 1 d .
. .
C21A C 0.35338(14) 0.2674(3) 0.1427(3) 0.0285(14) Uani 1 1 d .
. .
C22 C 0.56737(16) 0.0163(3) 1.1238(3) 0.0349(16) Uani 1 1 d .
. .
C22A C 0.31506(14) 0.2609(3) 0.1259(3) 0.0304(15) Uani 1 1 d .
. .
C23 C 0.55158(18) -0.0380(3) 1.1035(3) 0.0408(18) Uani 1 1 d .
. .
H23 H 0.5260 -0.0429 1.0942 0.049 Uiso 1 1 calc R . .
C23A C 0.29946(16) 0.2079(3) 0.1017(3) 0.0328(15) Uani 1 1 d .
. .
H23A H 0.2737 0.2028 0.0902 0.039 Uiso 1 1 calc R . .
C24 C 0.5721(2) -0.0843(4) 1.0965(3) 0.047(2) Uani 1 1 d . . .
H24 H 0.5607 -0.1205 1.0821 0.057 Uiso 1 1 calc R . .
C24A C 0.32065(17) 0.1623(3) 0.0939(3) 0.0326(15) Uani 1 1 d .
. .
H24A H 0.3093 0.1266 0.0762 0.039 Uiso 1 1 calc R . .
C25 C 0.60959(19) -0.0777(4) 1.1108(3) 0.0459(19) Uani 1 1 d .
. .
H25 H 0.6238 -0.1098 1.1064 0.055 Uiso 1 1 calc R . .
```

```
C25A C 0.35849(17) 0.1687(3) 0.1121(3) 0.0363(16) Uani 1 1 d .
. .
H25A H 0.3730 0.1370 0.1074 0.044 Uiso 1 1 calc R . .
C26 C 0.62671(18) -0.0250(3) 1.1314(3) 0.0406(18) Uani 1 1 d .
. .
C26A C 0.37536(15) 0.2207(3) 0.1368(3) 0.0305(15) Uani 1 1 d .
. .
C41 C 0.62831(16) 0.2416(3) 0.8619(3) 0.0359(16) Uani 1 1 d .
. .
C41A C 0.38039(16) 0.4944(3) -0.1222(3) 0.0305(15) Uani 1 1 d
. . .
C42 C 0.61317(17) 0.2910(4) 0.8775(3) 0.0409(18) Uani 1 1 d .
. .
C42A C 0.36527(16) 0.5461(3) -0.1117(3) 0.0326(15) Uani 1 1 d
. . .
C43 C 0.63550(19) 0.3397(4) 0.8974(3) 0.0444(18) Uani 1 1 d .
. .
H43 H 0.6255 0.3744 0.9077 0.053 Uiso 1 1 calc R . .
C43A C 0.38864(17) 0.5938(3) -0.0891(3) 0.0364(16) Uani 1 1 d
. . .
H43A H 0.3788 0.6296 -0.0816 0.044 Uiso 1 1 calc R . .
C44 C 0.67212(19) 0.3381(4) 0.9023(3) 0.0453(18) Uani 1 1 d .
. .
H44 H 0.6872 0.3713 0.9161 0.054 Uiso 1 1 calc R . .
C44A C 0.42609(16) 0.5890(3) -0.0778(3) 0.0358(16) Uani 1 1 d
. . .
H44A H 0.4418 0.6213 -0.0625 0.043 Uiso 1 1 calc R . .
C45 C 0.68650(18) 0.2869(3) 0.8865(3) 0.0426(18) Uani 1 1 d .
. .
H45 H 0.7117 0.2856 0.8905 0.051 Uiso 1 1 calc R . .
C45A C 0.44038(16) 0.5363(3) -0.0890(3) 0.0331(15) Uani 1 1 d
. . .
H45A H 0.4660 0.5331 -0.0809 0.040 Uiso 1 1 calc R . .
C46 C 0.66526(17) 0.2387(3) 0.8656(3) 0.0397(17) Uani 1 1 d .
. .
C46A C 0.41816(16) 0.4889(3) -0.1116(3) 0.0382(17) Uani 1 1 d
. . .
C47 C 0.56047(15) 0.1845(3) 1.0042(3) 0.0335(15) Uani 1 1 d .
. .
C47A C 0.31069(15) 0.4328(3) 0.0076(3) 0.0321(14) Uani 1 1 d .
. .
C48 C 0.55938(15) 0.2172(3) 1.0606(3) 0.0351(16) Uani 1 1 d .
. .
C48A C 0.27979(15) 0.4387(3) -0.0509(3) 0.0329(15) Uani 1 1 d
. . .
C49 C 0.53004(16) 0.2483(3) 1.0634(3) 0.0338(15) Uani 1 1 d .
. .
C49A C 0.24911(16) 0.4714(3) -0.0564(3) 0.0342(15) Uani 1 1 d
. . .
C50 C 0.49851(15) 0.2512(3) 1.0059(3) 0.0359(16) Uani 1 1 d .
. .
C50A C 0.24796(16) 0.5013(3) 0.0002(3) 0.0370(16) Uani 1 1 d .
. .
```

```
C51 C 0.49749(15) 0.2207(3) 0.9483(3) 0.0317(14) Uani 1 1 d .
. .
C51A C 0.27745(16) 0.4974(3) 0.0606(3) 0.0365(16) Uani 1 1 d .
. .
C52 C 0.52775(15) 0.1892(3) 0.9491(3) 0.0334(15) Uani 1 1 d .
. .
C52A C 0.30723(16) 0.4653(3) 0.0626(3) 0.0373(16) Uani 1 1 d .
. .
C110 C 0.58055(18) -0.0348(3) 0.9240(3) 0.0434(17) Uani 1 1 d
. . .
H11A H 0.5999 -0.0573 0.9578 0.065 Uiso 1 1 calc R . .
H11B H 0.5702 -0.0570 0.8813 0.065 Uiso 1 1 calc R . .
H11C H 0.5611 -0.0261 0.9428 0.065 Uiso 1 1 calc R . .
C220 C 0.54366(16) 0.0662(3) 1.1306(3) 0.0381(17) Uani 1 1 d .
. .
H220 H 0.5597 0.1010 1.1442 0.046 Uiso 1 1 calc R . .
C221 C 0.51302(18) 0.0791(4) 1.0618(3) 0.051(2) Uani 1 1 d . .
.
H22A H 0.5240 0.0891 1.0270 0.077 Uiso 1 1 calc R . .
H22B H 0.4982 0.1114 1.0678 0.077 Uiso 1 1 calc R . .
H22C H 0.4974 0.0451 1.0466 0.077 Uiso 1 1 calc R . .
C222 C 0.52727(18) 0.0545(4) 1.1875(3) 0.0438(18) Uani 1 1 d .
. .
H22D H 0.5110 0.0210 1.1748 0.066 Uiso 1 1 calc R . .
H22E H 0.5132 0.0881 1.1927 0.066 Uiso 1 1 calc R . .
H22F H 0.5472 0.0469 1.2312 0.066 Uiso 1 1 calc R . .
C260 C 0.66812(18) -0.0196(3) 1.1478(3) 0.0420(17) Uani 1 1 d
. . .
H260 H 0.6753 0.0213 1.1608 0.050 Uiso 1 1 calc R . .
C261 C 0.6786(2) -0.0347(4) 1.0851(4) 0.0487(19) Uani 1 1 d .
. .
H26A H 0.6742 -0.0757 1.0747 0.073 Uiso 1 1 calc R . .
H26B H 0.7047 -0.0261 1.0950 0.073 Uiso 1 1 calc R . .
H26C H 0.6637 -0.0120 1.0454 0.073 Uiso 1 1 calc R . .
C262 C 0.6889(2) -0.0580(4) 1.2092(4) 0.064(2) Uani 1 1 d . .
.
H26D H 0.6802 -0.0502 1.2477 0.096 Uiso 1 1 calc R . .
H26E H 0.7153 -0.0500 1.2235 0.096 Uiso 1 1 calc R . .
H26F H 0.6844 -0.0985 1.1957 0.096 Uiso 1 1 calc R . .
C420 C 0.57291(18) 0.2939(4) 0.8723(3) 0.053(2) Uani 1 1 d . .
.
H420 H 0.5627 0.2540 0.8680 0.064 Uiso 1 1 calc R . .
C421 C 0.5687(2) 0.3229(4) 0.9362(4) 0.0502(19) Uani 1 1 d . .
.
H42A H 0.5827 0.3012 0.9777 0.075 Uiso 1 1 calc R . .
H42B H 0.5427 0.3236 0.9316 0.075 Uiso 1 1 calc R . .
H42C H 0.5781 0.3624 0.9401 0.075 Uiso 1 1 calc R . .
C422 C 0.5510(3) 0.3285(6) 0.8080(4) 0.095(4) Uani 1 1 d . . .
H42D H 0.5602 0.3682 0.8127 0.142 Uiso 1 1 calc R . .
H42E H 0.5249 0.3287 0.8030 0.142 Uiso 1 1 calc R . .
H42F H 0.5540 0.3109 0.7671 0.142 Uiso 1 1 calc R . .
C460 C 0.68237(17) 0.1832(3) 0.8492(3) 0.0392(16) Uani 1 1 d .
. .
```

```
H460 H 0.6622 0.1547 0.8292 0.047 Uiso 1 1 calc R . .
C461 C 0.71007(19) 0.1572(4) 0.9146(3) 0.050(2) Uani 1 1 d . .
.
H46A H 0.7196 0.1210 0.9031 0.075 Uiso 1 1 calc R . .
H46B H 0.6979 0.1496 0.9482 0.075 Uiso 1 1 calc R . .
H46C H 0.7304 0.1841 0.9344 0.075 Uiso 1 1 calc R . .
C462 C 0.70074(19) 0.1950(4) 0.7957(3) 0.0464(18) Uani 1 1 d .
. .
H46D H 0.7191 0.2255 0.8126 0.070 Uiso 1 1 calc R . .
H46E H 0.6821 0.2071 0.7523 0.070 Uiso 1 1 calc R . .
H46F H 0.7128 0.1599 0.7880 0.070 Uiso 1 1 calc R . .
C620 C 0.29098(15) 0.3101(3) 0.1324(3) 0.0334(15) Uani 1 1 d .
. .
H620 H 0.3071 0.3444 0.1494 0.040 Uiso 1 1 calc R . .
C621 C 0.26223(16) 0.3257(4) 0.0626(3) 0.0440(19) Uani 1 1 d .
. .
H62A H 0.2747 0.3385 0.0311 0.066 Uiso 1 1 calc R . .
H62B H 0.2465 0.3566 0.0689 0.066 Uiso 1 1 calc R . .
H62C H 0.2471 0.2918 0.0432 0.066 Uiso 1 1 calc R . .
C622 C 0.27198(17) 0.2966(3) 0.1850(3) 0.0405(17) Uani 1 1 d .
. .
H62D H 0.2549 0.2644 0.1682 0.061 Uiso 1 1 calc R . .
H62E H 0.2583 0.3306 0.1909 0.061 Uiso 1 1 calc R . .
H62F H 0.2906 0.2864 0.2294 0.061 Uiso 1 1 calc R . .
C660 C 0.41711(15) 0.2267(3) 0.1584(3) 0.0356(16) Uani 1 1 d .
. .
H660 H 0.4239 0.2672 0.1737 0.043 Uiso 1 1 calc R . .
C661 C 0.43017(17) 0.2140(3) 0.0975(3) 0.0403(17) Uani 1 1 d .
. .
H66A H 0.4264 0.1732 0.0854 0.060 Uiso 1 1 calc R . .
H66B H 0.4564 0.2234 0.1105 0.060 Uiso 1 1 calc R . .
H66C H 0.4160 0.2374 0.0577 0.060 Uiso 1 1 calc R . .
C662 C 0.43619(17) 0.1864(4) 0.2191(3) 0.0473(19) Uani 1 1 d .
. .
H66D H 0.4261 0.1929 0.2560 0.071 Uiso 1 1 calc R . .
H66E H 0.4627 0.1943 0.2364 0.071 Uiso 1 1 calc R . .
H66F H 0.4319 0.1464 0.2036 0.071 Uiso 1 1 calc R . .
C820 C 0.32436(17) 0.5533(4) -0.1248(3) 0.0445(18) Uani 1 1 d
. . .
H820 H 0.3123 0.5148 -0.1355 0.053 Uiso 1 1 calc R . .
C821 C 0.31733(19) 0.5781(4) -0.0613(4) 0.052(2) Uani 1 1 d .
. .
H82A H 0.3273 0.5518 -0.0222 0.078 Uiso 1 1 calc R . .
H82B H 0.2908 0.5826 -0.0717 0.078 Uiso 1 1 calc R . .
H82C H 0.3294 0.6156 -0.0495 0.078 Uiso 1 1 calc R . .
C822 C 0.30702(19) 0.5932(5) -0.1877(4) 0.071(3) Uani 1 1 d .
. .
H82D H 0.3191 0.6309 -0.1786 0.106 Uiso 1 1 calc R . .
H82E H 0.2807 0.5978 -0.1957 0.106 Uiso 1 1 calc R . .
H82F H 0.3103 0.5761 -0.2286 0.106 Uiso 1 1 calc R . .
C860 C 0.43488(17) 0.4331(3) -0.1253(3) 0.0371(16) Uani 1 1 d
. . .
H860 H 0.4149 0.4035 -0.1394 0.045 Uiso 1 1 calc R . .
```

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C861 C 0.46545(18) 0.4106(4) -0.0613(3) 0.0461(19) Uani 1 1 d
. . .
H86A H 0.4853 0.4390 -0.0462 0.069 Uiso 1 1 calc R . .
H86B H 0.4751 0.3744 -0.0726 0.069 Uiso 1 1 calc R . .
H86C H 0.4555 0.4039 -0.0243 0.069 Uiso 1 1 calc R . .
C862 C 0.4493(2) 0.4406(4) -0.1852(3) 0.051(2) Uani 1 1 d . .
.
H86D H 0.4289 0.4507 -0.2272 0.076 Uiso 1 1 calc R . .
H86E H 0.4606 0.4046 -0.1926 0.076 Uiso 1 1 calc R . .
H86F H 0.4678 0.4714 -0.1741 0.076 Uiso 1 1 calc R . .
F1 F 0.58932(9) 0.21796(18) 1.11980(16) 0.0402(10) Uani 1 1 d
. . .
F1A F 0.27786(9) 0.40996(18) -0.11001(16) 0.0415(10) Uani 1 1
d . . .
F2 F 0.53136(9) 0.27816(19) 1.12076(17) 0.0437(10) Uani 1 1 d
. . .
F2A F 0.22032(9) 0.47449(19) -0.11655(17) 0.0450(10) Uani 1 1
d . . .
F3 F 0.46969(9) 0.28300(18) 1.00671(18) 0.0434(10) Uani 1 1 d
. . .
F3A F 0.21871(9) 0.53447(19) -0.00394(19) 0.0480(11) Uani 1 1
d . . .
F4 F 0.46700(9) 0.2233(2) 0.89091(17) 0.0457(11) Uani 1 1 d .
. .
F4A F 0.27668(10) 0.5271(2) 0.11696(18) 0.0487(11) Uani 1 1 d
. . .
F5 F 0.52362(9) 0.15962(19) 0.88927(17) 0.0451(10) Uani 1 1 d
. . .
F5A F 0.33492(9) 0.46372(18) 0.12487(17) 0.0439(10) Uani 1 1 d
. . .
N1 N 0.65645(12) 0.1517(2) 1.1632(2) 0.0309(12) Uani 1 1 d . .
.
N1A N 0.40349(12) 0.3977(2) 0.1784(2) 0.0301(12) Uani 1 1 d .
. .
N2 N 0.62278(12) 0.0766(3) 1.1607(2) 0.0340(13) Uani 1 1 d . .
.
N2A N 0.37033(12) 0.3213(2) 0.1697(2) 0.0292(12) Uani 1 1 d .
. .
N3 N 0.57836(13) 0.1089(3) 0.8338(2) 0.0366(14) Uani 1 1 d . .
.
N3A N 0.33445(12) 0.3598(3) -0.1550(2) 0.0326(13) Uani 1 1 d .
. .
N4 N 0.60572(13) 0.1906(3) 0.8376(2) 0.0387(14) Uani 1 1 d . .
.
N4A N 0.35652(13) 0.4460(3) -0.1482(2) 0.0355(13) Uani 1 1 d .
. .
O1 O 0.65995(10) 0.1728(2) 1.02658(19) 0.0319(10) Uani 1 1 d .
. .
O1A O 0.41164(10) 0.42240(19) 0.04599(17) 0.0295(10) Uani 1 1
d . . .
O2 O 0.60986(11) 0.0544(2) 0.96910(19) 0.0339(10) Uani 1 1 d .
. .
```

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O2A O 0.36327(10) 0.3036(2) -0.01999(18) 0.0334(10) Uani 1 1 d
. . .
Sc1 Sc 0.61372(3) 0.13308(5) 0.99914(5) 0.0267(4) Uani 1 1 d .
. .
Sc1A Sc 0.36585(3) 0.38199(5) 0.01146(5) 0.0265(4) Uani 1 1 d
. . .

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 _atom_site_aniso_U_12
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C1 0.025(3) 0.024(4) 0.026(3) -0.001(2) 0.007(2) 0.001(2)
C1A 0.022(3) 0.027(4) 0.024(3) 0.001(2) 0.006(2) 0.003(2)
C5 0.035(3) 0.060(5) 0.018(3) -0.001(3) 0.005(2) -0.003(3)
C5A 0.029(3) 0.058(5) 0.017(3) -0.001(3) 0.004(2) -0.005(3)
C6 0.034(3) 0.057(5) 0.017(3) -0.002(3) 0.006(2) -0.006(3)
C6A 0.035(3) 0.062(5) 0.018(3) -0.001(3) 0.007(2) -0.009(3)
C7 0.031(3) 0.053(5) 0.027(3) -0.007(3) 0.007(2) -0.011(3)
C7A 0.031(3) 0.048(5) 0.026(3) -0.007(3) 0.006(2) -0.010(3)
C8 0.023(3) 0.066(6) 0.022(3) -0.001(3) 0.004(2) -0.008(3)
C8A 0.029(3) 0.064(6) 0.022(3) -0.003(3) 0.006(2) -0.011(3)
C9 0.031(3) 0.047(5) 0.038(3) 0.000(3) 0.011(3) -0.002(3)
C9A 0.032(3) 0.048(5) 0.032(3) -0.002(3) 0.008(2) -0.003(3)
C10 0.035(3) 0.061(6) 0.033(3) 0.000(3) 0.009(3) -0.013(3)
C10A 0.044(4) 0.061(6) 0.037(3) -0.001(3) 0.012(3) -0.022(4)
C11 0.028(3) 0.043(5) 0.021(3) -0.007(3) 0.006(2) -0.003(3)
C11A 0.021(3) 0.044(5) 0.022(3) -0.002(3) 0.003(2) 0.002(3)
C15 0.058(4) 0.070(6) 0.018(3) 0.002(3) 0.006(3) -0.020(4)
C15A 0.051(4) 0.062(6) 0.017(3) 0.003(3) -0.003(3) -0.011(4)
C16 0.070(5) 0.097(8) 0.014(3) -0.002(3) 0.004(3) -0.038(5)
C16A 0.059(4) 0.068(6) 0.019(3) 0.001(3) -0.004(3) -0.026(4)
C17 0.035(3) 0.044(5) 0.025(3) -0.008(3) 0.009(2) -0.010(3)
C17A 0.025(3) 0.041(5) 0.029(3) -0.003(3) 0.006(2) -0.002(3)
C18 0.031(3) 0.048(5) 0.028(3) -0.009(3) 0.013(2) -0.005(3)
C18A 0.026(3) 0.049(5) 0.025(3) -0.004(3) 0.009(2) -0.002(3)
C19 0.036(3) 0.066(6) 0.039(3) -0.017(3) 0.018(3) -0.003(3)
C19A 0.026(3) 0.059(5) 0.028(3) -0.006(3) 0.009(2) 0.002(3)
C21 0.034(3) 0.045(5) 0.021(3) -0.001(3) 0.009(2) -0.007(3)
C21A 0.023(3) 0.042(5) 0.017(2) 0.004(2) 0.003(2) -0.005(3)
C22 0.038(3) 0.047(5) 0.018(3) 0.001(3) 0.008(2) -0.010(3)
C22A 0.024(3) 0.046(5) 0.018(2) 0.004(3) 0.001(2) -0.002(3)
C23 0.043(3) 0.057(6) 0.024(3) -0.001(3) 0.013(3) -0.016(3)
C23A 0.028(3) 0.045(5) 0.022(3) 0.003(3) 0.004(2) -0.007(3)
C24 0.065(4) 0.052(6) 0.031(3) -0.007(3) 0.024(3) -0.020(4)
C24A 0.044(3) 0.028(4) 0.024(3) -0.004(3) 0.010(2) -0.014(3)
C25 0.055(4) 0.053(6) 0.036(3) 0.001(3) 0.024(3) -0.008(4)
C25A 0.037(3) 0.047(5) 0.026(3) 0.006(3) 0.012(2) 0.001(3)
C26 0.042(3) 0.054(6) 0.028(3) 0.006(3) 0.015(3) -0.002(3)
```

C26A 0.029(3) 0.039(5) 0.023(3) 0.008(3) 0.009(2) -0.002(3)
C41 0.033(3) 0.051(5) 0.020(3) 0.012(3) 0.005(2) -0.006(3)
C41A 0.034(3) 0.035(5) 0.019(2) 0.010(3) 0.005(2) -0.001(3)
C42 0.034(3) 0.062(6) 0.023(3) 0.004(3) 0.006(2) -0.001(3)
C42A 0.031(3) 0.039(5) 0.023(3) 0.008(3) 0.003(2) -0.007(3)
C43 0.050(4) 0.048(5) 0.035(3) 0.003(3) 0.015(3) 0.002(4)
C43A 0.043(3) 0.038(5) 0.029(3) 0.004(3) 0.012(3) 0.006(3)
C44 0.051(4) 0.046(6) 0.042(3) 0.001(3) 0.019(3) -0.014(4)
C44A 0.037(3) 0.039(5) 0.027(3) 0.002(3) 0.005(2) -0.014(3)
C45 0.042(3) 0.051(6) 0.037(3) 0.002(3) 0.016(3) -0.008(3)
C45A 0.033(3) 0.034(5) 0.029(3) 0.007(3) 0.006(2) -0.002(3)
C46 0.037(3) 0.053(5) 0.028(3) 0.007(3) 0.009(3) -0.008(3)
C46A 0.034(3) 0.059(5) 0.019(3) 0.006(3) 0.006(2) -0.001(3)
C47 0.027(3) 0.045(5) 0.027(3) 0.004(3) 0.008(2) -0.002(3)
C47A 0.029(3) 0.034(4) 0.033(3) 0.002(3) 0.011(2) -0.004(3)
C48 0.024(3) 0.049(5) 0.026(3) 0.002(3) 0.001(2) 0.000(3)
C48A 0.029(3) 0.039(5) 0.031(3) -0.002(3) 0.012(2) -0.002(3)
C49 0.035(3) 0.039(5) 0.029(3) -0.004(3) 0.013(2) -0.004(3)
C49A 0.029(3) 0.033(5) 0.037(3) 0.009(3) 0.007(2) 0.000(3)
C50 0.025(3) 0.050(5) 0.033(3) 0.007(3) 0.011(2) 0.004(3)
C50A 0.028(3) 0.046(5) 0.040(3) 0.007(3) 0.015(3) 0.006(3)
C51 0.025(3) 0.032(4) 0.033(3) 0.007(3) 0.002(2) -0.003(3)
C51A 0.036(3) 0.038(5) 0.038(3) -0.003(3) 0.015(3) -0.004(3)
C52 0.031(3) 0.042(5) 0.026(3) -0.005(3) 0.008(2) -0.005(3)
C52A 0.027(3) 0.049(5) 0.032(3) 0.007(3) 0.006(2) 0.000(3)
C110 0.042(4) 0.047(5) 0.042(3) -0.003(3) 0.016(3) -0.007(3)
C220 0.031(3) 0.056(5) 0.026(3) 0.002(3) 0.009(2) -0.008(3)
C221 0.035(3) 0.081(7) 0.034(3) 0.011(4) 0.008(3) -0.007(4)
C222 0.042(3) 0.060(6) 0.031(3) -0.002(3) 0.016(3) -0.006(3)
C260 0.041(3) 0.038(5) 0.046(4) 0.005(3) 0.014(3) 0.003(3)
C261 0.050(4) 0.043(5) 0.060(4) 0.011(4) 0.028(3) 0.006(3)
C262 0.058(5) 0.081(8) 0.049(4) 0.013(4) 0.011(4) 0.019(4)
C420 0.034(3) 0.079(7) 0.042(4) 0.000(4) 0.008(3) 0.009(4)
C421 0.053(4) 0.046(6) 0.058(4) -0.006(4) 0.027(3) -0.008(4)
C422 0.066(6) 0.149(12) 0.055(5) 0.011(6) 0.003(4) 0.039(6)
C460 0.038(3) 0.045(5) 0.035(3) 0.000(3) 0.013(3) -0.007(3)
C461 0.051(4) 0.061(6) 0.044(4) 0.012(4) 0.024(3) 0.006(4)
C462 0.050(4) 0.056(6) 0.034(3) 0.003(3) 0.016(3) -0.002(4)
C620 0.024(3) 0.045(5) 0.028(3) 0.004(3) 0.005(2) -0.004(3)
C621 0.026(3) 0.071(6) 0.031(3) 0.008(3) 0.004(2) 0.000(3)
C622 0.034(3) 0.057(6) 0.030(3) 0.002(3) 0.010(3) 0.001(3)
C660 0.025(3) 0.048(5) 0.033(3) 0.006(3) 0.008(2) 0.004(3)
C661 0.036(3) 0.045(5) 0.044(3) 0.010(3) 0.019(3) 0.005(3)
C662 0.032(3) 0.070(6) 0.037(3) 0.010(3) 0.009(3) 0.002(3)
C820 0.032(3) 0.055(6) 0.045(4) 0.010(3) 0.010(3) 0.001(3)
C821 0.048(4) 0.049(6) 0.068(5) -0.002(4) 0.031(4) -0.005(4)
C822 0.033(4) 0.107(9) 0.060(5) 0.028(5) 0.002(3) 0.004(4)
C860 0.038(3) 0.042(5) 0.030(3) 0.006(3) 0.011(3) -0.001(3)
C861 0.040(3) 0.063(6) 0.035(3) 0.010(3) 0.013(3) 0.007(3)
C862 0.058(4) 0.062(6) 0.034(3) 0.008(3) 0.018(3) 0.017(4)
F1 0.0319(17) 0.054(3) 0.0281(16) -0.0071(16) 0.0023(14)
0.0075(17)

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F1A 0.0323(18) 0.054(3) 0.0335(17) -0.0063(17) 0.0051(14)
0.0047(17)
F2 0.0382(19) 0.061(3) 0.0328(18) -0.0098(17) 0.0131(15)
0.0039(18)
F2A 0.0281(17) 0.065(3) 0.0361(18) 0.0051(18) 0.0043(14)
0.0058(17)
F3 0.0274(17) 0.058(3) 0.046(2) 0.0068(18) 0.0138(15)
0.0093(17)
F3A 0.0329(18) 0.063(3) 0.051(2) 0.011(2) 0.0173(16)
0.0155(18)
F4 0.0273(17) 0.068(3) 0.0333(18) 0.0009(18) -0.0003(14)
0.0004(17)
F4A 0.040(2) 0.068(3) 0.040(2) -0.0101(19) 0.0160(16)
0.0062(19)
F5 0.0342(18) 0.064(3) 0.0313(17) -0.0106(18) 0.0042(14)
0.0030(18)
F5A 0.0363(18) 0.057(3) 0.0329(18) -0.0083(17) 0.0047(15)
0.0093(18)
N1 0.029(2) 0.044(4) 0.018(2) -0.002(2) 0.0054(18) -0.004(2)
N1A 0.026(2) 0.044(4) 0.018(2) -0.007(2) 0.0049(18) -0.004(2)
N2 0.030(2) 0.053(4) 0.016(2) -0.003(2) 0.0050(18) -0.005(2)
N2A 0.023(2) 0.045(4) 0.017(2) 0.000(2) 0.0025(17) -0.003(2)
N3 0.037(3) 0.055(4) 0.018(2) -0.001(2) 0.008(2) -0.008(3)
N3A 0.029(2) 0.048(4) 0.017(2) 0.001(2) 0.0028(18) -0.006(2)
N4 0.035(3) 0.060(5) 0.017(2) 0.004(2) 0.004(2) -0.007(3)
N4A 0.034(3) 0.049(4) 0.017(2) 0.004(2) 0.0000(19) -0.008(2)
O1 0.030(2) 0.039(3) 0.0257(19) -0.0021(18) 0.0075(16) -
0.0082(18)
O1A 0.029(2) 0.032(3) 0.0237(18) 0.0001(17) 0.0047(15) -
0.0064(18)
O2 0.035(2) 0.040(3) 0.0261(19) -0.0042(18) 0.0102(16) -
0.0032(19)
O2A 0.031(2) 0.043(3) 0.0252(19) -0.0038(18) 0.0080(16) -
0.0038(19)
Sc1 0.0242(6) 0.0355(9) 0.0185(5) -0.0020(4) 0.0049(4) -
0.0018(5)
Sc1A 0.0222(5) 0.0360(9) 0.0188(5) -0.0006(4) 0.0038(4) -
0.0018(5)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
s.u.'s are taken
 into account individually in the estimation of s.u.'s in
distances, angles
 and torsion angles; correlations between s.u.'s in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s
involving l.s. planes.
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C1 N2 1.330(8) . ?
C1 N1 1.351(8) . ?
C1 Sc1 2.413(5) . ?
C1A N2A 1.339(8) . ?
C1A N1A 1.339(7) . ?
C1A Sc1A 2.431(5) . ?
C5 N2 1.475(7) . ?
C5 C6 1.530(10) . ?
C5A N2A 1.480(6) . ?
C5A C6A 1.526(10) . ?
C6 N1 1.480(7) . ?
C6A N1A 1.475(7) . ?
C7 N1 1.443(9) . ?
C7 C8 1.537(8) . ?
C7A N1A 1.459(8) . ?
C7A C8A 1.542(8) . ?
C8 O1 1.399(7) . ?
C8 C9 1.505(9) . ?
C8 C10 1.524(10) . ?
C8A O1A 1.409(6) . ?
C8A C10A 1.515(10) . ?
C8A C9A 1.529(9) . ?
C11 N3 1.339(8) . ?
C11 N4 1.337(8) . ?
C11 Sc1 2.429(5) . ?
C11A N3A 1.336(8) . ?
C11A N4A 1.347(8) . ?
C11A Sc1A 2.434(5) . ?
C15 N4 1.487(7) . ?
C15 C16 1.517(11) . ?
C15A N4A 1.487(7) . ?
C15A C16A 1.514(10) . ?
C16 N3 1.470(7) . ?
C16A N3A 1.471(7) . ?
C17 N3 1.448(9) . ?
C17 C18 1.552(9) . ?
C17A N3A 1.461(8) . ?
C17A C18A 1.557(8) . ?
C18 O2 1.403(7) . ?
C18 C110 1.520(10) . ?
C18 C19 1.536(8) . ?
C18A O2A 1.408(7) . ?
C18A C19A 1.533(7) . ?
C21 C22 1.398(8) . ?
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C21 C26 1.402(10) . ?
C21 N2 1.447(9) . ?
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C43 C42 C420 C422 73.4(9) . . . . ?
C41 C42 C420 C421 134.3(7) . . . . ?
C43 C42 C420 C421 -46.8(9) . . . . ?
C45 C46 C460 C462 -54.6(7) . . . . ?
C41 C46 C460 C462 127.5(6) . . . . ?
C45 C46 C460 C461 68.4(7) . . . . ?
C41 C46 C460 C461 -109.5(6) . . . . ?
C23A C22A C620 C621 -60.4(7) . . . . ?
C21A C22A C620 C621 118.3(6) . . . . ?
C23A C22A C620 C622 63.1(7) . . . . ?
C21A C22A C620 C622 -118.1(6) . . . . ?
C25A C26A C660 C662 -62.7(7) . . . . ?
C21A C26A C660 C662 116.3(7) . . . . ?
C25A C26A C660 C661 60.0(8) . . . . ?
C21A C26A C660 C661 -121.0(6) . . . . ?
C41A C42A C820 C821 126.5(7) . . . . ?
C43A C42A C820 C821 -54.4(8) . . . . ?
C41A C42A C820 C822 -111.5(8) . . . . ?
C43A C42A C820 C822 67.6(8) . . . . ?
C45A C46A C860 C861 59.1(7) . . . . ?
C41A C46A C860 C861 -121.9(6) . . . . ?
C45A C46A C860 C862 -64.7(7) . . . . ?
C41A C46A C860 C862 114.3(6) . . . . ?
N2 C1 N1 C7 -173.9(6) . . . . ?
Sc1 C1 N1 C7 1.8(8) . . . . ?
N2 C1 N1 C6 -4.6(7) . . . . ?
Sc1 C1 N1 C6 171.0(4) . . . . ?
C8 C7 N1 C1 -50.3(8) . . . . ?
C8 C7 N1 C6 141.1(5) . . . . ?
C5 C6 N1 C1 8.3(7) . . . . ?
C5 C6 N1 C7 178.5(5) . . . . ?
N2A C1A N1A C7A -173.5(5) . . . . ?
Sc1A C1A N1A C7A 3.8(7) . . . . ?
N2A C1A N1A C6A -6.4(7) . . . . ?
Sc1A C1A N1A C6A 170.9(4) . . . . ?
C8A C7A N1A C1A -51.8(8) . . . . ?
C8A C7A N1A C6A 141.8(5) . . . . ?
C5A C6A N1A C1A 10.7(7) . . . . ?
C5A C6A N1A C7A 178.9(5) . . . . ?
N1 C1 N2 C21 -163.6(5) . . . . ?
Sc1 C1 N2 C21 22.0(9) . . . . ?
N1 C1 N2 C5 -1.4(7) . . . . ?
Sc1 C1 N2 C5 -175.8(4) . . . . ?
C22 C21 N2 C1 -102.5(6) . . . . ?
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C26 C21 N2 C1 80.6(7) . . . . ?
C22 C21 N2 C5 96.1(6) . . . . ?
C26 C21 N2 C5 -80.8(7) . . . . ?
C6 C5 N2 C1 6.3(7) . . . . ?
C6 C5 N2 C21 169.6(5) . . . . ?
N1A C1A N2A C21A -164.4(5) . . . . ?
Sc1A C1A N2A C21A 18.9(9) . . . . ?
N1A C1A N2A C5A -1.1(7) . . . . ?
Sc1A C1A N2A C5A -177.8(4) . . . . ?
C22A C21A N2A C1A -102.2(6) . . . . ?
C26A C21A N2A C1A 81.3(7) . . . . ?
C22A C21A N2A C5A 95.4(6) . . . . ?
C26A C21A N2A C5A -81.1(6) . . . . ?
C6A C5A N2A C1A 7.5(7) . . . . ?
C6A C5A N2A C21A 171.8(5) . . . . ?
N4 C11 N3 C17 176.7(5) . . . . ?
Sc1 C11 N3 C17 0.7(8) . . . . ?
N4 C11 N3 C16 -0.1(8) . . . . ?
Sc1 C11 N3 C16 -176.1(5) . . . . ?
C18 C17 N3 C11 -52.4(8) . . . . ?
C18 C17 N3 C16 124.2(7) . . . . ?
C15 C16 N3 C11 -2.3(9) . . . . ?
C15 C16 N3 C17 -179.2(6) . . . . ?
N4A C11A N3A C17A -174.2(5) . . . . ?
Sc1A C11A N3A C17A 2.9(7) . . . . ?
N4A C11A N3A C16A -7.4(7) . . . . ?
Sc1A C11A N3A C16A 169.6(5) . . . . ?
C18A C17A N3A C11A -53.6(8) . . . . ?
C18A C17A N3A C16A 140.4(6) . . . . ?
C15A C16A N3A C11A 14.4(8) . . . . ?
C15A C16A N3A C17A -178.0(6) . . . . ?
N3 C11 N4 C41 -175.9(6) . . . . ?
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Sc1 C11 N4 C15 177.5(5) . . . . ?
C42 C41 N4 C11 -85.0(8) . . . . ?
C46 C41 N4 C11 97.8(7) . . . . ?
C42 C41 N4 C15 96.7(7) . . . . ?
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C16 C15 N4 C11 -3.8(8) . . . . ?
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N3A C11A N4A C41A -166.5(6) . . . . ?
Sc1A C11A N4A C41A 17.2(9) . . . . ?
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Sc1A C11A N4A C15A -179.7(5) . . . . ?
C42A C41A N4A C11A -102.9(7) . . . . ?
C46A C41A N4A C11A 80.6(7) . . . . ?
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C16A C15A N4A C11A 11.9(8) . . . . ?
C16A C15A N4A C41A 176.3(6) . . . . ?
C9 C8 O1 Sc1 96.9(7) . . . . ?
C10 C8 O1 Sc1 -141.5(5) . . . . ?
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C7 C8 O1 Sc1 -24.8(10) . . . . ?
C10A C8A O1A Sc1A -137.6(6) . . . . ?
C9A C8A O1A Sc1A 99.7(6) . . . . ?
C7A C8A O1A Sc1A -20.9(10) . . . . ?
C110 C18 O2 Sc1 -143.3(5) . . . . ?
C19 C18 O2 Sc1 95.2(7) . . . . ?
C17 C18 O2 Sc1 -25.2(7) . . . . ?
C00A C18A O2A Sc1A -140.1(5) . . . . ?
C19A C18A O2A Sc1A 97.6(6) . . . . ?
C17A C18A O2A Sc1A -22.9(7) . . . . ?
C8 O1 Sc1 O2 -106.0(7) . . . . ?
C8 O1 Sc1 C1 -12.1(7) . . . . ?
C8 O1 Sc1 C47 73.5(7) . . . . ?
C8 O1 Sc1 C11 170.2(7) . . . . ?
C18 O2 Sc1 O1 -105.4(5) . . . . ?
C18 O2 Sc1 C1 169.2(5) . . . . ?
C18 O2 Sc1 C47 75.1(6) . . . . ?
C18 O2 Sc1 C11 -13.3(5) . . . . ?
N2 C1 Sc1 O1 -161.6(6) . . . . ?
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N2 C1 Sc1 O2 -41.1(6) . . . . ?
N1 C1 Sc1 O2 144.7(4) . . . . ?
N2 C1 Sc1 C47 79.9(6) . . . . ?
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C52 C47 Sc1 C1 -152.0(6) . . . . ?
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C52 C47 Sc1 C11 28.2(6) . . . . ?
C48 C47 Sc1 C11 -146.2(6) . . . . ?
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N3 C11 Sc1 O2 26.7(4) . . . . ?
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N3 C11 Sc1 C1 92(4) . . . . ?
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N3 C11 Sc1 C47 -94.0(5) . . . . ?
N4 C11 Sc1 C47 91.3(6) . . . . ?
C8A O1A Sc1A O2A -108.3(7) . . . . ?
C8A O1A Sc1A C47A 72.2(7) . . . . ?
C8A O1A Sc1A C1A -14.9(7) . . . . ?
C8A O1A Sc1A C11A 166.6(7) . . . . ?
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C48A C47A Sc1A O2A -54.0(6) . . . . ?
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C48A C47A Sc1A C1A -153.3(6) . . . . ?
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N2A C1A Sc1A C47A 82.3(6) . . . . ?
N1A C1A Sc1A C47A -94.1(4) . . . . ?
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N1A C1A Sc1A C11A 99(8) . . . . ?
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N4A C11A Sc1A O1A -37.7(6) . . . . ?
N3A C11A Sc1A O2A 25.4(4) . . . . ?
N4A C11A Sc1A O2A -158.7(6) . . . . ?
N3A C11A Sc1A C47A -95.6(4) . . . . ?
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N3A C11A Sc1A C1A 71(8) . . . . ?
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_refine_diff_density_rms    0.177
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