

# An unsupported transition metal–lanthanide bond; synthesis and crystal structure of an Nd–Fe amido N-heterocyclic carbene complex†

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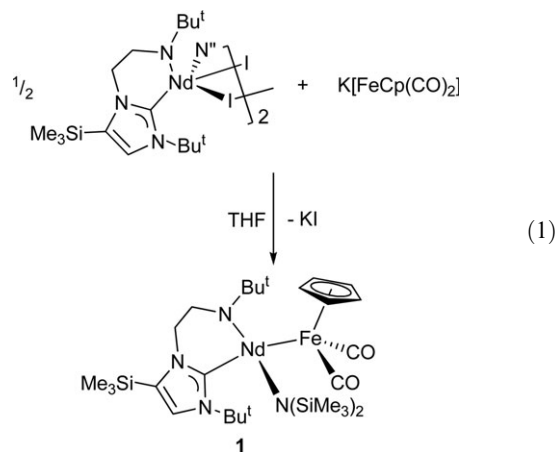
**A salt-elimination reaction between the neodymium monoiodide [Nd(L')(N'')(I)]<sub>2</sub> [L' = Bu<sup>t</sup>NCH<sub>2</sub>CH<sub>2</sub>{C(NCSiMe<sub>3</sub>CHNBu<sup>t</sup>)}; N'' = N(SiMe<sub>3</sub>)<sub>2</sub>] and K[FeCp(CO)<sub>2</sub>] affords the first complex with an unsupported 4f–3d metal–metal bond that is sufficiently stable to be isolated; the bond is identified as principally ionic in nature by DFT calculations.**

Although metal–metal bonds are found in a wide variety of structurally and synthetically important complexes of the d- and p-block metals, complexes of the f-elements with unsupported bonds to a transition metal are very rare. In the 1980's, Marks reported the metallocene complexes [Cp\*<sub>2</sub>(I)Th–RuCp(CO)<sub>2</sub>] (Cp\* = C<sub>5</sub>Me<sub>5</sub>),<sup>1</sup> [Cp<sub>3</sub>Th–RuCp(CO)<sub>2</sub>],<sup>2</sup> and [Cp<sub>3</sub>U–Fe(CO)<sub>2</sub>Cp].<sup>3a</sup> Comparisons of these with the Group 14 complexes Cp<sub>3</sub>U–MPh<sub>3</sub> (M = Sn, Ge, Si) suggested weak heterobimetallic bonding.<sup>3b</sup> Beletskaya showed that crystalline [Cp<sub>2</sub>(thf)Lu–RuCp(CO)<sub>2</sub>] was stable and possesses a polarised covalent Lu–Ru bond of 2.995(2) Å.<sup>4</sup> But despite the stability of the actinide heterobimetallics, the Lu–Ru complex was unstable towards disproportionation, and they were unable to stabilise the Lu–Fe analogue sufficiently to isolate it. We have shown that the salt-elimination reaction between a neodymium monoiodide and [K(NMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>){Ga(NArCH)<sub>2</sub>}] (Ar = 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>) affords [Nd(L')(N'')(thf){Ga(NArCH)<sub>2</sub>}] **A** [L' = Bu<sup>t</sup>NCH<sub>2</sub>CH<sub>2</sub>{C(NCSiMe<sub>3</sub>CHNBu<sup>t</sup>)}; N'' = N(SiMe<sub>3</sub>)<sub>2</sub>]. X-Ray crystallography and DFT calculations reveal a Nd–Ga bond in this compound, which exhibits a parent ion mass peak in the EI mass spectrum, and which is thermally stable up to 100 °C in toluene.<sup>5</sup>

Neutral adducts are also formed between Eu<sup>II</sup>, Yb<sup>II</sup>, and either Al<sup>I</sup> or Ga<sup>I</sup>: in the complexes [(Cp\*)<sub>2</sub>Ln–Al(Cp\*)] (Ln = Eu, Yb), the dative Ln–Al bonds are essentially ionic;<sup>6</sup> in [(Cp\*)<sub>2</sub>Ln–{Ga(Cp\*)<sub>n</sub>(thf)<sub>m</sub>}] (Ln = Eu, n = 2, m = 0, Yb, n = 1, m = 1), the metal–metal bond is significantly more stable in solution than in the Al analogues.<sup>7</sup> Arnold *et al.* has more recently demonstrated that [(CpSiMe<sub>3</sub>)<sub>3</sub>U–Al(Cp\*)] (CpSiMe<sub>3</sub> = C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>) is stable in solution, and the U–Al bond exhibits some covalent character, according to

DFT calculations, owing to charge transfer from the Cp\*Al ligand onto uranium.<sup>8</sup> Kempe *et al.* also recently showed that protonolysis routes can afford the first unsupported Y–Re and Yb–Re bonds in [(Cp)<sub>2</sub>Ln–ReCp<sub>2</sub>] (Ln = Y, Yb), which were demonstrated by DFT calculations to be very polar.<sup>9</sup>

We have been studying the chemistry of NHC ligands with an incorporated anionic functional group to permit the isolation of discrete carbene complexes of Lewis acidic transition metal cations and lanthanides.<sup>10</sup> N-heterocyclic carbenes (NHCs) are widely used as σ-bases in homogeneous late metal catalyst systems, and as rate-accelerating additives in organic reactions catalysed by Lewis acidic metal cations.<sup>11</sup> During the course of our studies, we have found routes to mono halide-substituted lanthanide complexes,<sup>12</sup> and have taken the opportunity to explore their salt metathesis chemistry (see also **A** above).<sup>13</sup> Herein, we show how this salt-elimination strategy can be used to isolate the first thermally stable complex containing an unsupported bond between a 3d and a 4f metal.



Treatment of the neodymium iodide complex [Nd(L')(N'')(μ-I)]<sub>2</sub> with an equivalent of the potassium salt of the CpFe(CO)<sub>2</sub> anion fragment, K[CpFe(CO)<sub>2</sub>] (KFp), affords a brown solution, and a precipitate of KI. After work-up to remove the KI by filtration, and evaporation to dryness, an orange powder is afforded. The product may be recrystallised from diethyl ether to afford analytically pure [Nd(L')(N'')(FeCp(CO)<sub>2</sub>)] **1**, in excellent yield,‡ and single crystals suitable for X-ray structural analysis, Fig. 1.§

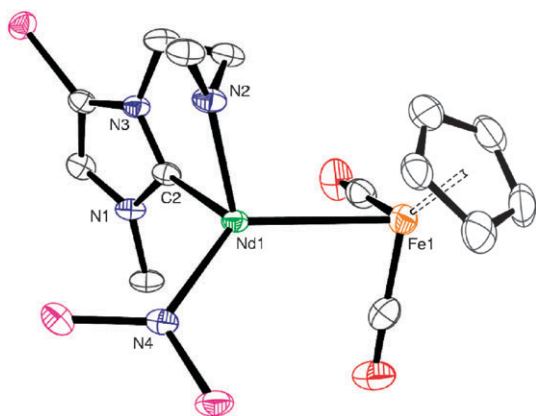
The <sup>1</sup>H NMR spectrum of **1** contains paramagnetically shifted resonances, which fall within the range 70 to –6 ppm, and a solution magnetic moment was calculated by the NMR spectroscopic method as 3.41 B.M. The mass spectrum (EI) contains fragments in which silylmethyl and carbonyl

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† Electronic supplementary information (ESI) available: Full synthetic, crystallographic and computational details for compound **1**. CCDC 689392. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b819072k



**Fig. 1** Displacement ellipsoid drawing of **1**, methyl groups and hydrogens omitted for clarity. Selected distances (Å) and angles (°): Nd1–Fe1 2.9942(7), Nd1–C2 2.606(4), Nd1–N2 2.204(3), Nd1–N4 2.342(3), N1–C2 1.363(5), N3–C2 1.354(5), N2–Nd1–Fe1 104.73(9), C2–Nd1–Fe1 107.37(9), N4–Nd1–Fe1 127.51(8), N2–Nd1–C2 83.34(12), N3–C2–N1 104.0(3).

groups have been lost from the molecular ion of **1**, but retaining the Nd and Fe core. This suggests a good stability of the metal–metal bond in the gas phase.

The coordination sphere about the Nd cation is approximately *pseudo*-tetrahedral. The N2–Nd1–C2 angle is small, 83.34(12)°, presumably because of the ligand bite angle imposed by the bidentate NHC–amide ligand. The Nd–Fe distance is 2.9942(7) Å which is much less than the sum of the covalent radii for Nd and Fe (3.15 Å).

Shorter bond distances to metals of comparable radius to Nd (six-coordinate covalent radius of Nd is 1.123 Å) may be found in [PbMe<sub>2</sub>Fp<sub>2</sub>],<sup>14</sup> Pb–Fe = 2.735, 2.737 Å (four-coordinate lead radius 1.12 Å) and [Bi(S<sub>2</sub>NEt<sub>2</sub>)<sub>2</sub>Fp],<sup>15</sup> Bi–Fe = 2.641 Å (five-coordinate bismuth radius 1.10 Å).<sup>16</sup>

The Fp fragment has been shown to bind to a variety of main group metal fragments, predominantly based on the metals tin and gallium, but also antimony, mercury, indium, and bismuth. However, a few examples of binding to more electropositive metals exist, for example, [(N{CMe<sub>2</sub>CH<sub>2</sub>}<sub>2</sub>–CH<sub>2</sub>)<sub>2</sub>AlFp], [Cp<sub>2</sub>(H)NbFp], [(NMe<sub>2</sub>)<sub>3</sub>TiFp], [HC{SiMe<sub>2</sub>N(*p*-tol)}<sub>3</sub>TiFp], and [{N(SiMe<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(SiMe<sub>3</sub>)ZrFp]<sub>2</sub>.<sup>17</sup>

The Nd–C<sub>carbene</sub> distance of 2.606(4) Å is not significantly different from that in the parent, unsilylated four-coordinate NHC complex [Nd(L)(N'')<sub>2</sub>] (L = Bu<sup>1</sup>NCH<sub>2</sub>CH<sub>2</sub>–{C(NCHCHNBu<sup>1</sup>)}) in which it is 2.609(3) Å.<sup>18</sup> It is shorter than in the five-coordinate starting material, [Nd(L')(N'')(μ-I)]<sub>2</sub> [Nd–C(NHC) = 2.656(5) Å] and in the five-coordinate Nd–Ga complex **A** [Nd–C(NHC) = 2.669(2) Å].<sup>5</sup> The other distances and angles fall within the expected ranges for these interactions.

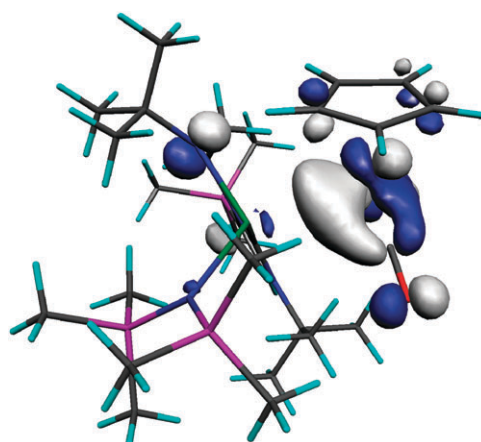
The FTIR spectrum of **1** reveals an asymmetric  $\nu(\text{CO})_{\text{as}}$  stretch at 1845 cm<sup>−1</sup> which is 75 cm<sup>−1</sup> greater than the  $\nu(\text{CO})_{\text{as}}$  stretch in K[Fp] ( $\nu(\text{CO})_{\text{as}}$  = 1770 cm<sup>−1</sup>). ( $\delta\nu_{\text{as}}$  = 75 cm<sup>−1</sup>). The magnitude of the shift ( $\delta\nu_{\text{as}}$ ) between that in K[Fp] and a complex containing a metal bound Fp anion is a useful reporter of the electron density presence between the two metals. This magnitude of this shift is less than in [Me(CH<sub>2</sub>SiMe<sub>3</sub>N)<sub>3</sub>Ti–Fp] ( $\nu_{\text{as}}$  = 1916 cm<sup>−1</sup>,  $\delta\nu_{\text{as}}$  = 146 cm<sup>−1</sup>)

in which a significant Ti–Fe  $\pi$ -bonding component was ascribed,<sup>19</sup> and in [(Me<sub>2</sub>N)<sub>3</sub>Ti–Fp], ( $\nu_{\text{as}}$  = 1898 cm<sup>−1</sup>,  $\delta\nu_{\text{as}}$  = 128 cm<sup>−1</sup>).<sup>17a</sup>

DFT calculations were carried out on the model geometry **1** in order to probe the nature of the Nd–Fe interaction in **1**. The DFT geometry optimisation of **1** reproduces successfully the principal features of the structure of **1** as determined by X-ray crystallography; the Nd(1)–Fe(1) and Nd(1)–C(2) distances are 3.02 and 2.64 Å, respectively, *ca.* 0.03 to 0.04 Å longer than in the X-ray crystal structure of **1**. In addition, frequency calculations on **1** and a geometry optimised [Fp]<sup>−</sup> fragment yield calculated  $\nu(\text{CO})_{\text{as}}$  of 1834 and 1794 cm<sup>−1</sup>, respectively, reproducing qualitatively the experimental trend observed for **1** and K[FeCp(CO)<sub>2</sub>]. The data suggest that these calculations should provide a reasonable, qualitative description of the electronic structure of **1**.

The calculated interaction energy between the {Fp}<sup>−</sup> and {Nd}<sup>+</sup> fragments, corrected for thermal and zero point energies, the preparation energies for the fragments and for basis set superposition errors, is 384 kJ mol<sup>−1</sup>. This is similar to the Nd–Ga bond energy calculated for **A** (386 kJ mol<sup>−1</sup>),<sup>5</sup> and is of a similar order of magnitude to the experimentally determined bond disruption energy for the Sm–C bond in Cp'<sub>2</sub>Sm–CCPh [D(Sm–C) = 390 kJ mol<sup>−1</sup>] in toluene.<sup>20</sup> However, the calculated interaction energy between the [Fp]<sup>−</sup> and {Nd}<sup>+</sup> fragments in **1** is *ca.* 255 kJ mol<sup>−1</sup> greater than the experimentally determined U–Fe disruption energy in [Cp<sub>3</sub>U–Fp] [D(U–Fe) = 129 kJ mol<sup>−1</sup>] in toluene<sup>3a</sup> and it has also been argued that actinide compounds are reasonable thermochemical models of 4f centres.<sup>3a</sup> We suggest that this discrepancy in calculated and experimental energies may reflect the gas-phase nature of the theoretical study *versus* the solution phase of the experimental determinations.

A natural bond orbital (NBO) analysis of **1** reveals natural charges for Nd(1) and Fe(1) of +2.51 and −0.42, respectively, consistent with some charge transfer involving a formally anionic Fe(0) centre to a Nd(III) centre in **1**. The Wiberg bond order (0.13) for the Nd–Fe interaction is substantially less than that for the Nd–Ga bond in **A**<sup>5</sup> (0.83) and, in contrast to **A**, an NBO analysis for **1** does not identify a formal covalent Nd–Fe bond in **1**.



**Fig. 2** The Kohn–Sham representation of the HOMO of **1** at the 0.05 e<sup>−3</sup> isosurface.

This suggests that the Nd–Fe interaction is principally ionic in character and this is supported by the nature of the HOMO in **1** (Fig. 2). This orbital is 84.6% localised on the [Fp]<sup>−</sup> fragment, principally within the Fe 3d (33.9%) and 4p (12.2%) orbitals. The remaining 15.4% is localised on the amide N(2) atom (10.4%) with essentially no delocalisation (0.4%) onto the Nd centre. The HOMO orbital is  $\pi$ -bonding with respect to the Fe–C(O) bonds and  $\pi$ -antibonding with respect to the C–O bonds. Polarisation of the electron density within this orbital towards the {Nd}<sup>+</sup> fragment could provide the mechanism for the observed and calculated increase in  $\nu(\text{CO})_{\text{as}}$  on the coordination of the {Fp}<sup>−</sup> unit to the {Nd}<sup>+</sup> fragment.

To conclude, this work demonstrates that complexes containing bound d- and an f-block metal fragments are accessible if appropriately designed salt-elimination strategies can be designed. These strategies provide a driving force for the formation of the product by ensuring a strong electrostatic contribution to the interaction between the d- and f-block fragments in addition to favourable salt-elimination.

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## Notes and references

† To cold (−78 °C) [Nd(L')(N'')(μ-D)]<sub>2</sub> (1.35 g, 1.86 mmol) and K[FeCp(CO)<sub>2</sub>] (0.33 g, 1.86 mmol) was added 30 ml thf; the orange-brown turbid mixture was allowed to warm to 298 K. Yield of **1**, orange solid, 96% (1.32 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K);  $\delta$  70.15 (s, 2H, CH<sub>2</sub>), 20.12 (br s, 2H, CH<sub>2</sub>), 4.74 (s, 9H, Bu<sup>1</sup>), 1.12 (s, 5H, Cp), −1.91 (s, 9H, SiMe<sub>3</sub>), −4.26 (br s, 27H, N{SiMe<sub>3</sub>}<sub>2</sub> and Bu<sup>1</sup>), −5.75 (s, 1H, CH). MS (ES): *m/z* 627 ([M − 2(SiMe<sub>3</sub>)<sub>2</sub> − 2H], 8 %).  $\mu_{\text{eff}}$  298 K: 3.41 B.M. FTIR ( $\nu$ , cm): 1916 (s), 1845 (s). Anal. calc. (found) for C<sub>29</sub>H<sub>55</sub>N<sub>4</sub>O<sub>2</sub>Si<sub>3</sub>FeNd: C 44.88 (44.87); H 7.14 (7.10); N 7.22 (7.32). § CCDC 689392. Crystal data C<sub>29</sub>H<sub>55</sub>FeN<sub>4</sub>NdO<sub>2</sub>Si<sub>3</sub>, *M*<sub>r</sub> 776.13, triclinic, *P*1̄, 150 (2) K, *a*, *b*, *c* (Å) 11.1340 (9), 11.7943 (9), 15.6599 (12),  $\alpha$ ,  $\beta$ ,  $\gamma$  (°) 94.396 (2), 107.987 (2), 100.847 (2), *V* 1900.9 (3) Å<sup>3</sup>, *Z* 2, *D*<sub>x</sub> 1.356 mg m<sup>−3</sup>,  $\mu$  1.86 mm<sup>−1</sup>, yellow block, 0.36 × 0.23 × 0.14(mm), *T*<sub>min</sub> *T*<sub>max</sub> 0.555, 0.781, no. of measured, independent and observed reflections *I* > 2 $\sigma$ (*I*) 13589, 6642, 6078, *R*<sub>int</sub> 0.024,  $\theta_{\text{max}}$  25.0°, *R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)], *wR*(*F*<sup>2</sup>), *S* 0.038, 0.085, 1, 10, 6642 reflections, 376 parameters, ( $\Delta/\sigma$ )<sub>max</sub> 0.002,  $\Delta\rho_{\text{max}}$ ,  $\Delta\rho_{\text{min}}$  (e Å<sup>−3</sup>) 1.41, −1.02.

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