APPLICATIONS OF TRANSITION METAL COMPLEXES IN ORGANIC SYNTHESIS

by

ROBERT C. DAVIS

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The following is a statement of postgraduate courses attended during the last three years.

"Recent developments in the Theory of Concerted Processes"
Dr. A. J. Bellamy

"Organometallic Reagents in Organic Syntheses"
Professor P. L. Pauson

"Industrial Research and Development"
Dr. B. Gravenor

"Carbonium Ions"
Dr. B. Capon

"Molecular Rearrangements"
Dr. G. Tennant

"Lab 10, intra-departmental seminars"
(2 years)

"Annual Conference of the Chemical Society"
April 7-11, 1975

To my parents, Robert and Jean, my brother, Ronald

and my wife, Patricia

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This investigation has been concerned with reactions of cyclopalladated complexes of nitrogen and sulphur donor ligands involving replacement of palladium by non-metallic atoms or groups, with a view to obtaining organic products which could be used as precursors for the syntheses of novel heterocyclic systems.

The cyclopalladation reactions of the nitrogen donor ligands, azobenzene, 2-phenylpyridine, 2-styrylpyridine and benzylideneaniline were investigated together with those of the sulphur donor ligand, quinolizine-4-thione. Four basic types of cyclopalladated complexes were synthesised: 1) chloride-bridged dimeric complexes; 2) acetate-bridged dimeric complexes; 3) monomeric triethylphosphine complexes; 4) monomeric dithiocarbamato and dithiophosphato complexes.

All the ligands except 2-styrylpyridine gave chloride-bridged complexes and all but quinolizine-4-thione gave acetate-bridged complexes. Monomeric triethylphosphine complexes were obtained from the [2-(2-pyridyl)phenyl]- and (4-thionoquinolizin-6-yl)-palladium chloride dimers. The O, O-diethyl dithiophosphato-derivative of 2-phenylazophenyl-palladium was prepared and dithiocarbamato-derivatives were obtained from the palladium complexes of all the ligands except quinolizine-4-thione.

Four main types of approach to the replacement of palladium were investigated: 1) attempts to effect replacement of palladium by sulphur using nucleophilic sulphur reagents; 2) attempted reductive elimination reactions of dithiocarbamato and phosphine complexes; 3) reactions with substances, other than thiocyanogen, containing disulphide bonds; 4) reactions of the complexes with electrophiles.

Very little success was achieved in the first three types of approach but successful metal replacement was observed in the reactions of dithiocarbamato-complexes with the electrophilic reagents, bromine and thiocyanogen. Quinolizine-4-thione could not be substituted in this way since the required dithiocarbamato-complex was not obtained.

2-(2-Thiocyanatophenyl)pyridine, the product obtained from the reaction of the dithiocarbamato[2-(2-pyridyl)phenyl]palladium complex with thiocyanogen, was converted into a benzisothiazolo-pyridinium salt, thus demonstrating the synthetic potential of the products obtained by this new route.

INTRODUCTION

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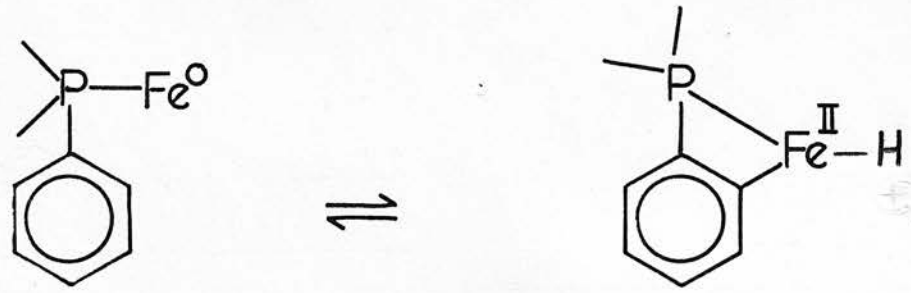

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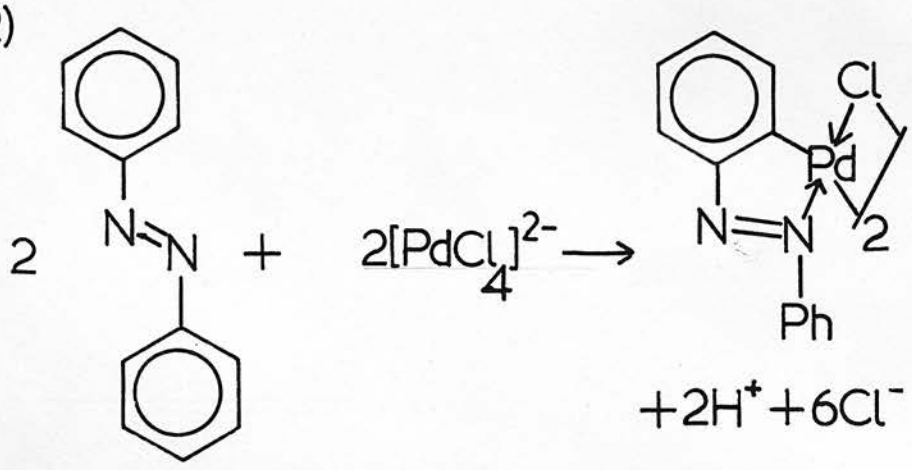

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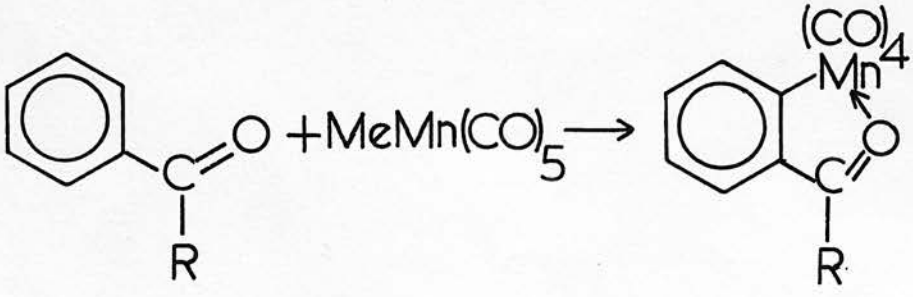

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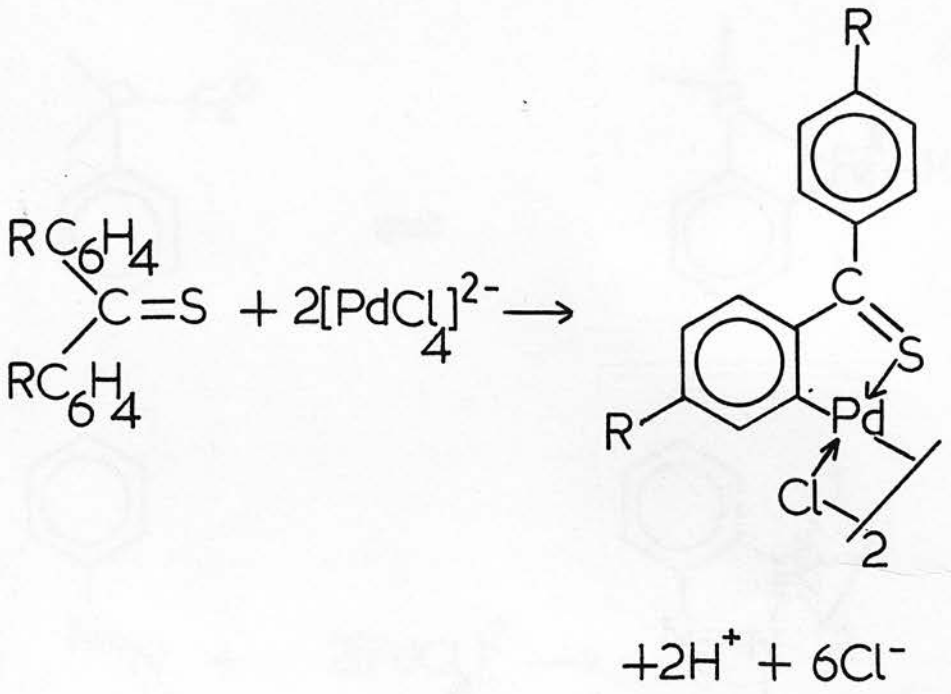
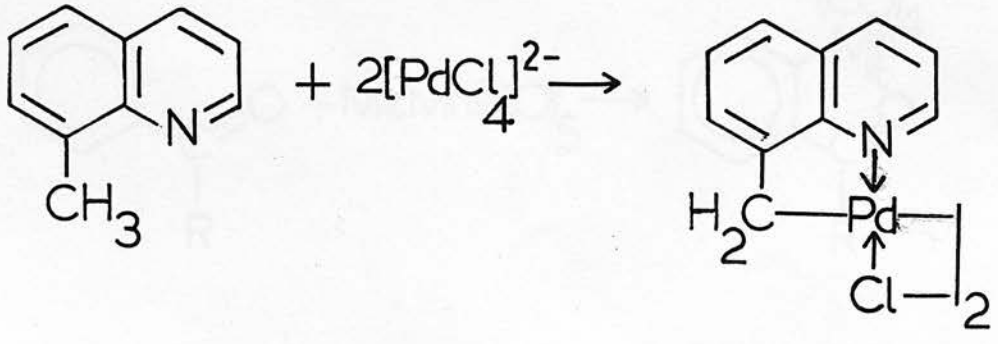


$+2H^{+} + 6Cl^{-}$

(5)



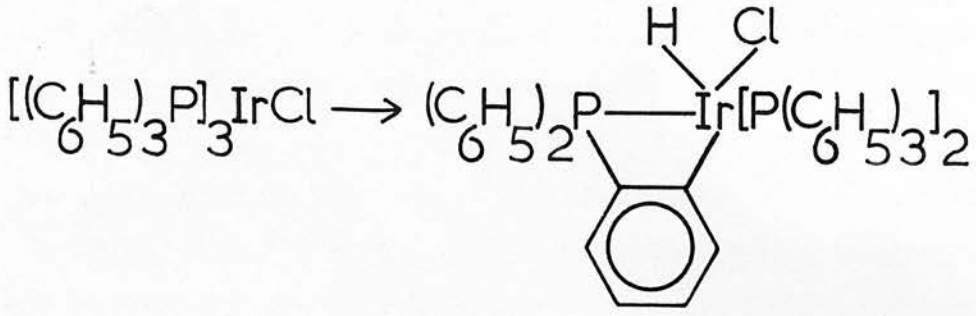
$+2H^{+} + 6Cl^{-}$

Although a few compounds with transition metal-carbon bonds have been known for a long time, it is only comparatively recently that it has become clearly recognised that the formation of bonds to carbon is a general and characteristic property of all the d-group transition metals. The metals can form a variety of compounds in which there is a normal σ-bond to carbon, although the binary alkyls and aryls are usually less stable thermally and chemically than those in which other ligands, notably π-bonding ligands, are, in addition, bound to the metal atom. The unique characteristics of d-orbitals also allow certain types of unsaturated hydrocarbons and some of their derivatives to be bound to metals in a non-classical manner to give molecules or ions with structures which have no counterpart elsewhere in chemistry.

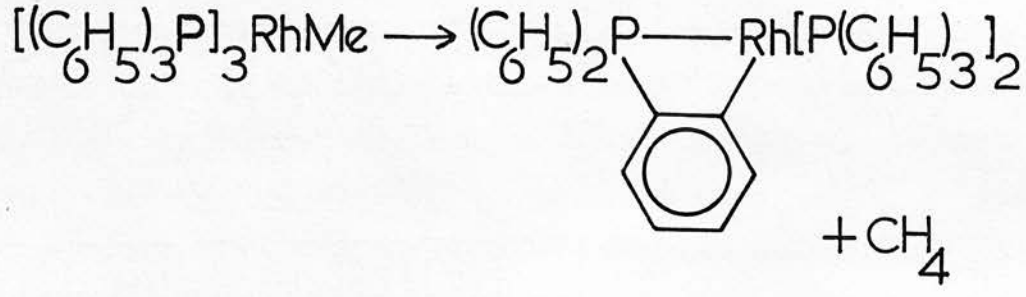
More recently, certain types of aromatic systems have been shown[1] to form carbon-metal σ-bonds when complexed with transition metals. These compounds arise from an intramolecular aromatic substitution reaction in transition metal complexes. In this reaction an aryl carbon-hydrogen bond in a donor ligand of a transition metal complex reacts with the central metal atom to form a metal-carbon σ-bond. The hydrogen originally attached to carbon adds to the metal to form a metal-hydrogen bond (1),[1] is eliminated as H^+ (2) and (4),[2,3] or is eliminated in the form of an alkane (3).[4] The reactions shown illustrate this substitution reaction leading to the cyclometallated complexes and also show examples of the four types of donor ligands known to undergo cyclometallation reactions. These reactions have been commonly referred to as ortho-metallation reactions but in some cases, such as (5),[5] this terminology is misleading and inappropriate. Thus, the term cyclometallation will be used where applicable, and ortho-metallation when it accurately represents the situation involved.

Most of the work carried out in connection with these compounds to date has been concerned with nitrogen and phosphorus donor ligands. Our research has been concerned with nitrogen

(6)


[(C6H5)3P]3IrCl
H
Cl
(C6H5)2P
Ir[P(C6H5)3]2

(7)


[(C6H5)3P]3RhMe
(C6H5)2P
Rh[P(C6H5)3]2
+CH4

and to a lesser extent sulphur donor ligands and in this review it is proposed to deal principally with work related to transition metal complexes with nitrogen donor ligands. A great deal of work has been carried out on phosphorus donor ligand transition metal complexes and, whilst not attempting to review this in anything but the most basic terms, it is perhaps worthwhile to mention a few examples of this type since they differ in several aspects from the nitrogen donor ligand complexes.

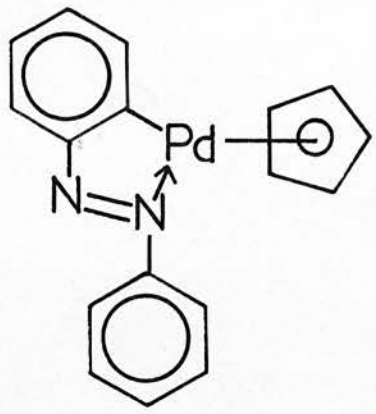
Phosphorus Donor Ligands

Triarylphosphine and triaryl phosphite complexes of many group VIII metals undergo intramolecular aromatic substitution.[1] As with nitrogen donor ligands of certain types, ortho-substitution occurs, but the role of the metal atom is more complex. For example, the substitution may involve a formal oxidation of the metal, as shown in the example (6). More commonly, the initial and final oxidation states of the metal are the same since, as in (7), substitution is accompanied by elimination.

The oxidative substitutions such as those of (6) are typical examples of the oxidative addition reactions now recognised in transition metal chemistry, since the metal undergoes an increase in both formal oxidation state and coordination number. The acceleration of this reaction by electron-donating substituents on the aromatic ring can be attributed either to: (1), an enhancement of the electron density in the ring which could promote electrophilic substitution as has been shown[1] for nitrogen donor complexes; or (2), enhanced electron density on the metal atom which could promote oxidative addition to the metal.

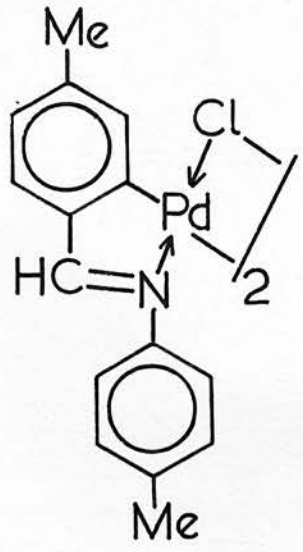
The more common type of ortho-substitution, exemplified by reaction (7), may also involve oxidative addition. In the thermolysis of the rhodium complex, which occurs even at $0^{\circ}C$, the first step may be addition of an ortho carbon-hydrogen bond to the metal atom to give a six-coordinate rhodium (III) species, very

(8)



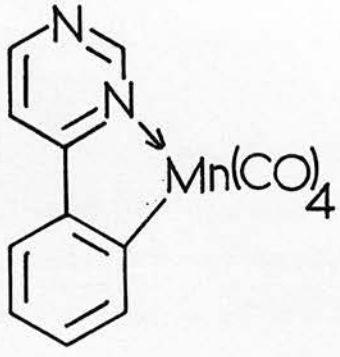
Azobenzene

(9)



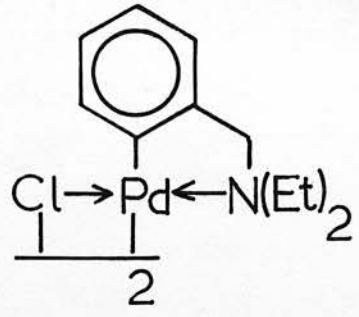
Benzylideneaniline

(10)



4-Phenylpyrimidine

(11)



N, N-Diethylbenzylamine

similar to the metallated iridium product in (6). This intermediate may then undergo reductive elimination of methane to give the observed ortho-metallated product. Consistent with this postulated reaction sequence, pyrolysis of $[(C_6D_5)_3P]_3RhCH_3$ produces CH_3D.

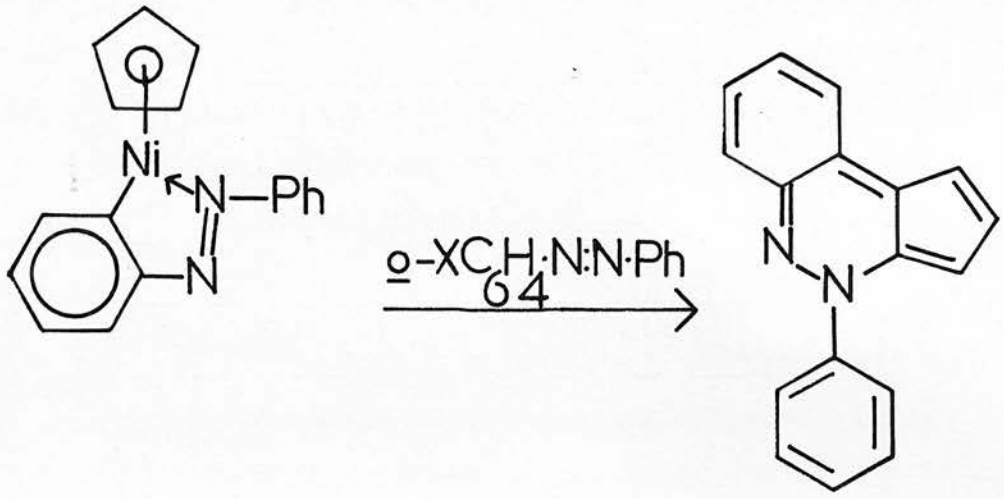
These examples illustrate the type of intramolecular aromatic substitution reactions undergone by phosphorus donor ligand transition metal complexes forming carbon-metal σ-bonds.

Nitrogen Donor Ligands

A great number of nitrogen donor ligands have now been metallated by a variety of transition metals and it is necessary, in some way, to classify their complexes. They can be classified according to either the metal atom or the ligand. For our purposes we shall classify the complexes according to the type of ligand, since our work was more concerned with the organic implications and potential of these compounds than with the inorganic aspects. The nitrogen donor ligands which have been most frequently studied are of four main types which are exemplified in the cyclometallated complexes (8), (9), (10), and (11). Ligands of the first type are azobenzene and its derivatives, the second type are the isostructurally related Schiff's bases, the third type are phenyl-substituted nitrogen heterocycles and the fourth, N, N-dialkylbenzylamines. There are others outwith this classification, which will be referred to later.

(a) Azobenzene and its Derivatives

The earliest example of cyclometallation involving nitrogen donor ligands was reported by Kleiman and Dubeck[6] in 1963. Azobenzene was metallated by nickel in the reaction of azobenzene and nickelocene to give the ortho-metallated complex (12). The complex was represented as shown, with a metal-carbon σ-bond and a π-coordination of the azo group double bond to the metal. This was later shown to be incorrect and in fact the nickel coordinates to only one of



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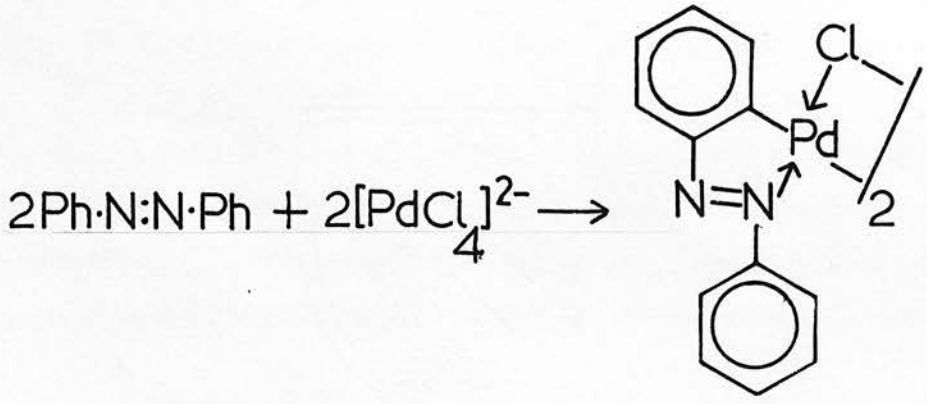
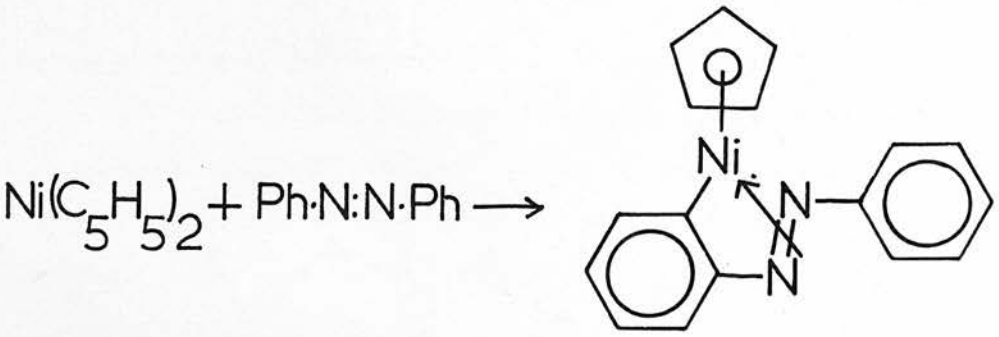


(14)

$+2H^{+} +6Cl^{-}$



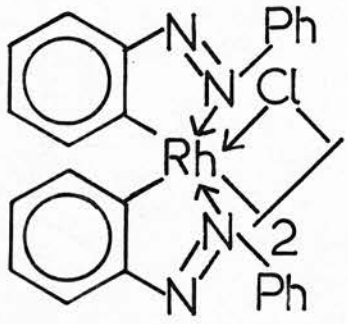
(12)

the azo-nitrogens, that farthest away from it, by means of a co-ordinate bond using a nitrogen lone pair of electrons. Since its discovery, this compound has been studied in greater detail by Ustynyuk and his coworkers.[7,8]

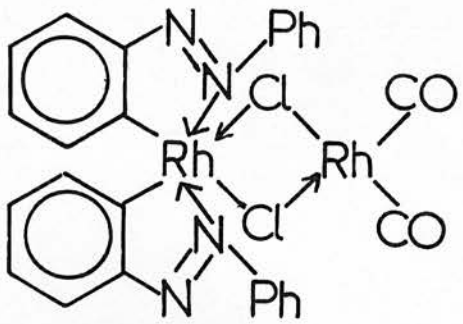
Ustynyuk[7] investigated initially, the reactions of the (h^5-cyclopentadienyl)[2-(phenylazo)phenyl]nickel complex with mercuric acetate and with mercuric chloride. In both cases good yields of the ortho-mercurated azobenzenes were obtained. These compounds, in turn, were halogenated yielding 2-halogenoazobenzenes in almost quantitative amounts. With perbenzoic acid, the complex reacted to give both 2-hydroxyazobenzene and a new pseudo-azulene, 4-phenyl-4H-cyclopenta[c]cinnoline (13). Nickelocene was also found[8] to interact with ortho-halogenoazobenzenes in two steps. Cyclopentadienyl [2-(phenylazo)phenyl]nickel, formed initially by halogen abstraction, reacted with more of the ortho-halogenoazobenzene to give 4-phenyl-4H-cyclopenta[c]cinnoline. The formation of this new heterocyclic system involves ligand coupling and loss of two hydrogen atoms which, it is presumed, are transferred to the halogenoazobenzene.

Cope, in 1965, reported[2] the synthesis of another ortho-metallated complex, that of di-μ-chlorobis[2-(phenylazo)phenyl] dipalladium (II) (14). The platinum analogue was also prepared by the same method.

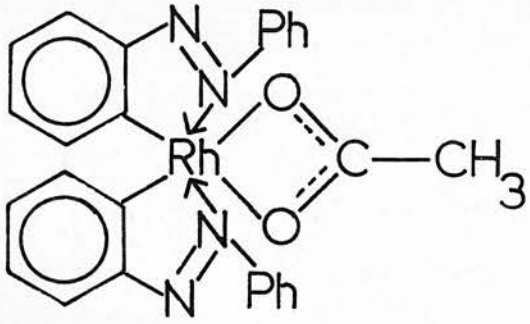
Direct cyclometallation reactions of azobenzene and its derivatives are not confined solely to the metals of the nickel sub-



(15)



(16)



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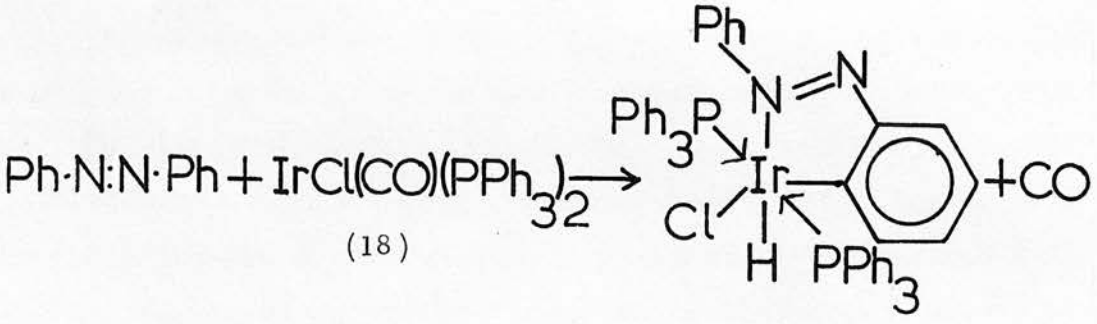

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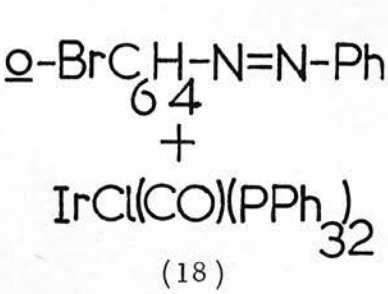
(19)



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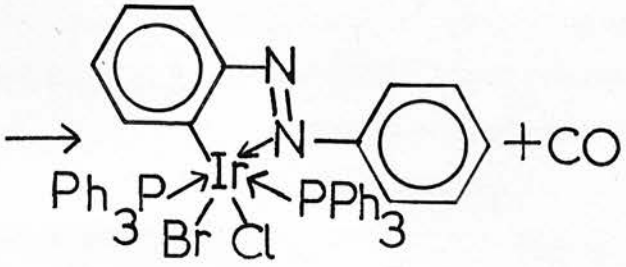


(20)

group, but are also observed with metals of other sub-groups of group VIII, with metals of group VII, with the group VI metal, molybdenum, and with the main group metal, mercury.

Two metals of the cobalt sub-group, rhodium[9] and iridium,[10] have both been reported to metallate azobenzene directly, affording ortho-metallated complexes containing azobenzene as a chelating nitrogen donor ligand.

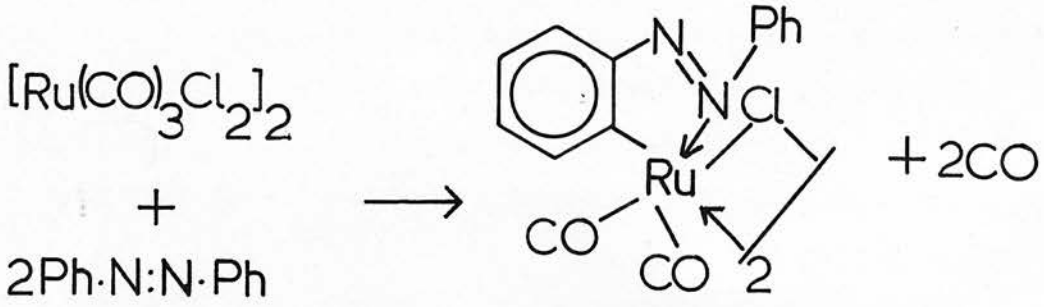
The rhodium complexes (15) and (16) have been obtained from the respective reactions of azobenzene with rhodium trichloride and with dimeric dicarbonylrhodium dichloride.[9] The product (16) of the second reaction is unusual among rhodium complexes in containing rhodium atoms in both of the common oxidation states, Rh (I) and Rh (III).

The dimeric complex (15) was converted to the monomeric rhodium complex (17), the structure of which was established[11, 12] by X-ray crystallography. The use of ligand exchange reactions to obtain complexes more suitable for crystallographic study is well established and will be dealt with in greater detail later.

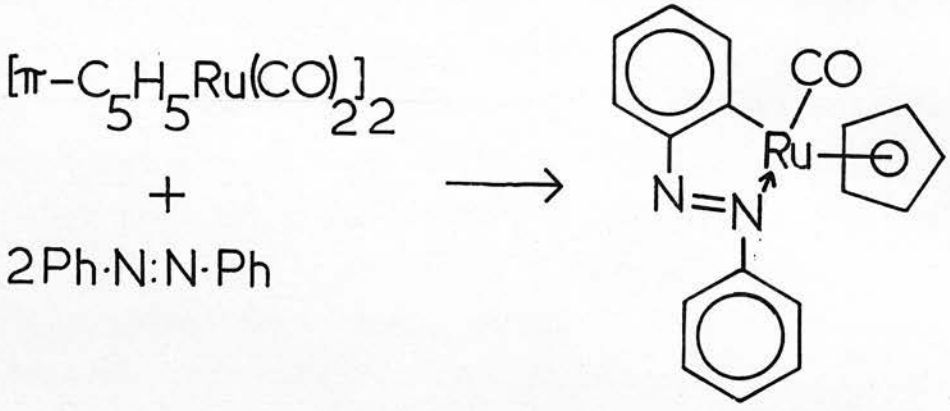
Cyclometallated iridium (III) complexes of azobenzene have been reported[10] only relatively recently. They have been obtained by the reaction of azobenzene or 2-bromoazobenzene with Vaska's complex (18). The cyclometallated products (19) and (20) were formed, it was thought, by direct oxidative additions of aryl carbon-hydrogen bonds to the iridium (I) centre, a mode of formation related to the cyclometallation reactions of tertiary phosphines and phosphites.

Although no direct cyclometallations of azobenzene by cobalt are known, cyclometallated cobalt complexes of azobenzene have been obtained indirectly, by metal-exchange reactions of palladium complexes.[13] These cobalt derivatives have been suggested as intermediates in the octacarbonyldicobalt-catalysed carbonylation of azobenzene. Both the cobalt complexes, and the carbonylation reaction will be referred to later in more detail.

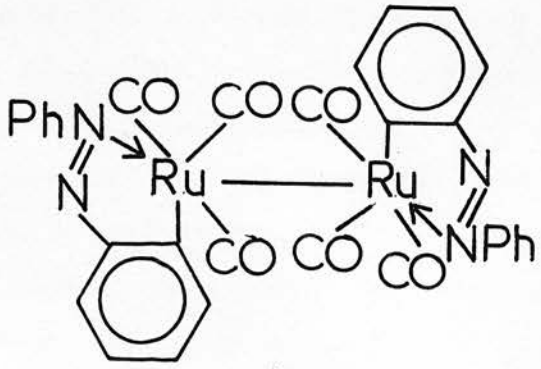
Of the iron sub-group metals, both ruthenium[14] and iron[15]


[Ru(CO)3Cl2]2
+
2Ph·N:N·Ph
Ph
N
N
Cl
Ru
CO
CO
2
+2CO

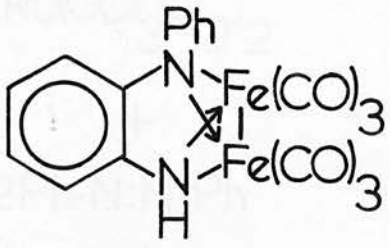
(21)


[π-C5H5Ru(CO)2]2
+
2Ph·N:N·Ph
CO
Ru
N=N

(22)


PhN
N
CO
CO
CO
Ru
Ru
N
CO
CO
CO
NPh

(23)



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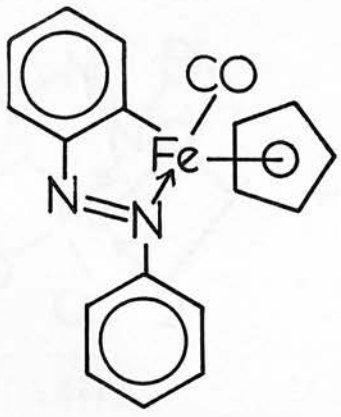

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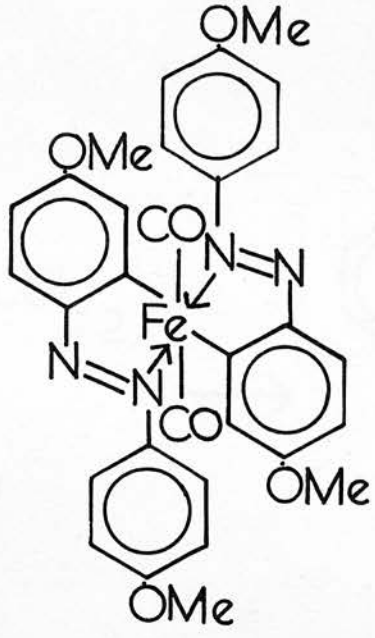


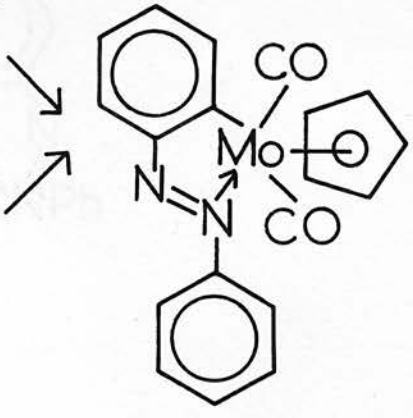
(25)

$$(CO)_3MeMo(\pi\text{-}C_5H_5) + Ph{\cdot}N{:}N{\cdot}Ph$$

(30)

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Ph{\cdot}N{:}N{\cdot}Ph$$

(31)



(29)

metallate azobenzene directly to afford ortho-metallated complexes. The ruthenium complexes are formed more easily and have been more extensively studied.[14, 16, 17]

The reaction of dimeric tricarbonylruthenium dichloride with azobenzene gave the dimeric complex (21) and various reactions of this complex have been reported.[16]

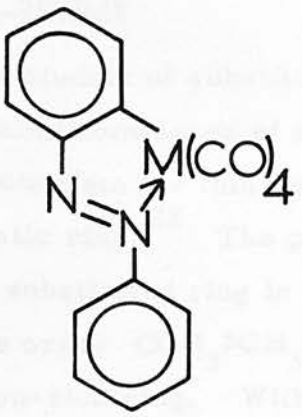
π-Cyclopentadienyldicarbonylruthenium, also a dimeric complex, reacted[17] with azobenzene to form the ortho-metallated monomeric complex, carbonyl-π-cyclopentadienyl(phenylazophenyl-C^3, N') ruthenium (22).

Another method of preparing cyclometallated complexes of ruthenium was reported,[14] involving the reaction of dodecacarbonyltriruthenium and azobenzene. This reaction produced three major products, two of which were complexes of the rearranged ligand o-semidine. The third product was a binuclear complex (23) containing ortho-metallated azobenzene ligands.

The formation of the rearranged ortho-semidine ligand had previously been observed by Pauson[15, 18] in the reactions of azobenzene with iron carbonyls. Pauson[18] showed that the major products obtained from the reactions of azobenzenes and iron carbonyls, were ortho-semidine complexes such as (24). Small amounts of the cyclometallated complex (25), were however obtained with 4, 4'-dimethoxyazobenzene.

Bruce[17] and his co-workers later described better routes to cyclometallated iron derivatives of azobenzene by reaction with the dimeric π-cyclopentadienyl dicarbonyliron and with the monomeric dicarbonyl-π-cyclopentadienyl methyliron complexes. Both these reactions gave the complex (26), the yield being greater in the reaction with the dimeric iron compound.

The same workers also reported[17] the formation of complexes (27) and (28) containing the group VII metals, manganese and rhenium. Decacarbonyldimanganese and decacarbonyldirhenium reacted with azobenzene giving low yields of (27) and (28). However, the thermal

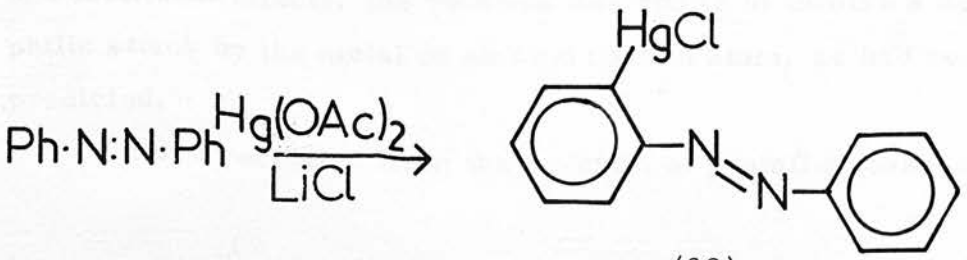


(27), M = Mn
(28), M = Re

reaction of methylpentacarbonylmanganese and -rhenium with azobenzene, produced nearly quantitative yields of the same complexes.

A direct metallation reaction has also been reported[17] for the group VI metal, molybdenum. A cyclometallated azobenzene complex (29) was obtained in very low yield from the reactions of azobenzene with both π-cyclopentadienyl tricarbonyl methylmolybdenum and the dimeric π-cyclopentadienyl tricarbonyl molybdenum (30) and (31). It was found that these reactions were complex, the initially formed ortho-metallated product reacting with an excess of reactants to form products containing rearranged ortho-semidine ligands.

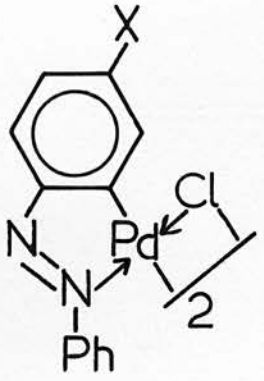
The only other metal known to metallate azobenzene directly is mercury, a main group metal. ortho-Mercurated azobenzene was obtained by Rausch and his co-workers.[19] Azobenzene and mercuric acetate were refluxed in methanol and subsequently treated with excess lithium chloride to yield 2-chloromercuriazobenzene (32). Sokalov[20] has recently extended this work to substituted azobenzenes. Cross[21] had earlier reported the preparation of the same complexes in better yields by reaction of the corresponding azobenzene-2-sulphinic acids with mercuric chloride.



(32)

Mechanistic Studies

Early studies of substituent effects on the formation of ortho-palladated complexes of azobenzene, suggested that the probable mechanism for this reaction involved electrophilic attack on the aromatic ring.[22] The preference for attachment of the metal to the substituted ring in the complex (33), was found to decrease in the order $OCH_3 > CH_3 > H > Cl$, indicating metallation of the more electron-rich ring. With 4-methoxyazobenzene, only the substituted ring was attacked to give the ortho-metallated product (33; $X=OCH_3$) but with 4-chloroazobenzene, metallation of the unsubstituted ring predominated.



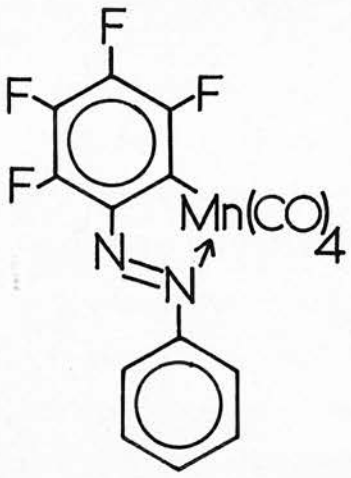
$X = OCH_3,\ CH_3,\ H,\ Cl$

(33)

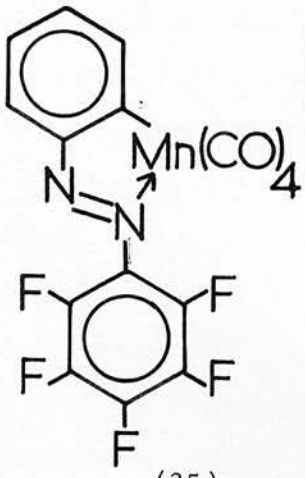
A little later, another study of the mechanistic aspects of the cyclopalladation reaction reported[23] results consistent with an electrophilic substitution mechanism, but showed that ortho-substitution, generally, depended upon the nature of the metal and associated ligands.

Metallation of azobenzene by methylpentacarbonylmanganese gave the complex (27), previously described. Methylpentacarbonylmanganese, being a low-valent electron-rich complex, was thought unlikely to react via an electrophilic mechanism and, from a study of substituent effects, the reaction was shown to involve a nucleophilic attack by the metal on an aryl carbon atom, as had been predicted.

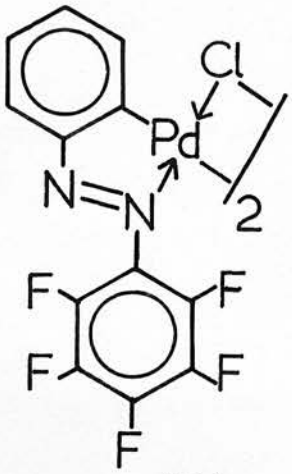
More recently, from the reaction of pentafluoroazobenzene



(34)

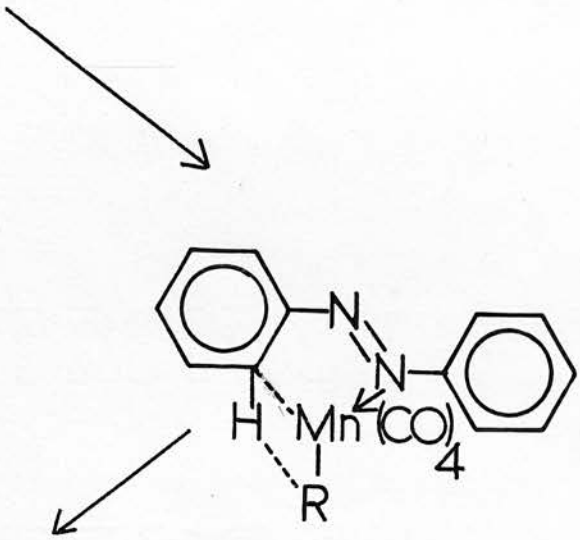


(35)

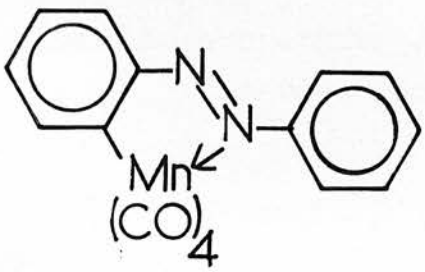


(36)

$$RMn(CO)_5 + Ph{\cdot}N{:}N{\cdot}Ph$$



(37)



with decacarbonyldimanganese, two products were obtained[27] in low yields. The complexes were identified as compounds in which the pentafluorophenyl and the unsubstituted phenyl rings, respectively, had been metallated (34) and (35). The reaction of pentafluoroazobenzene and palladium chloride, however, produced only the phenyl substituted complex (36) as was expected for an electrophilic palladation reaction. These results confirmed the earlier observations.

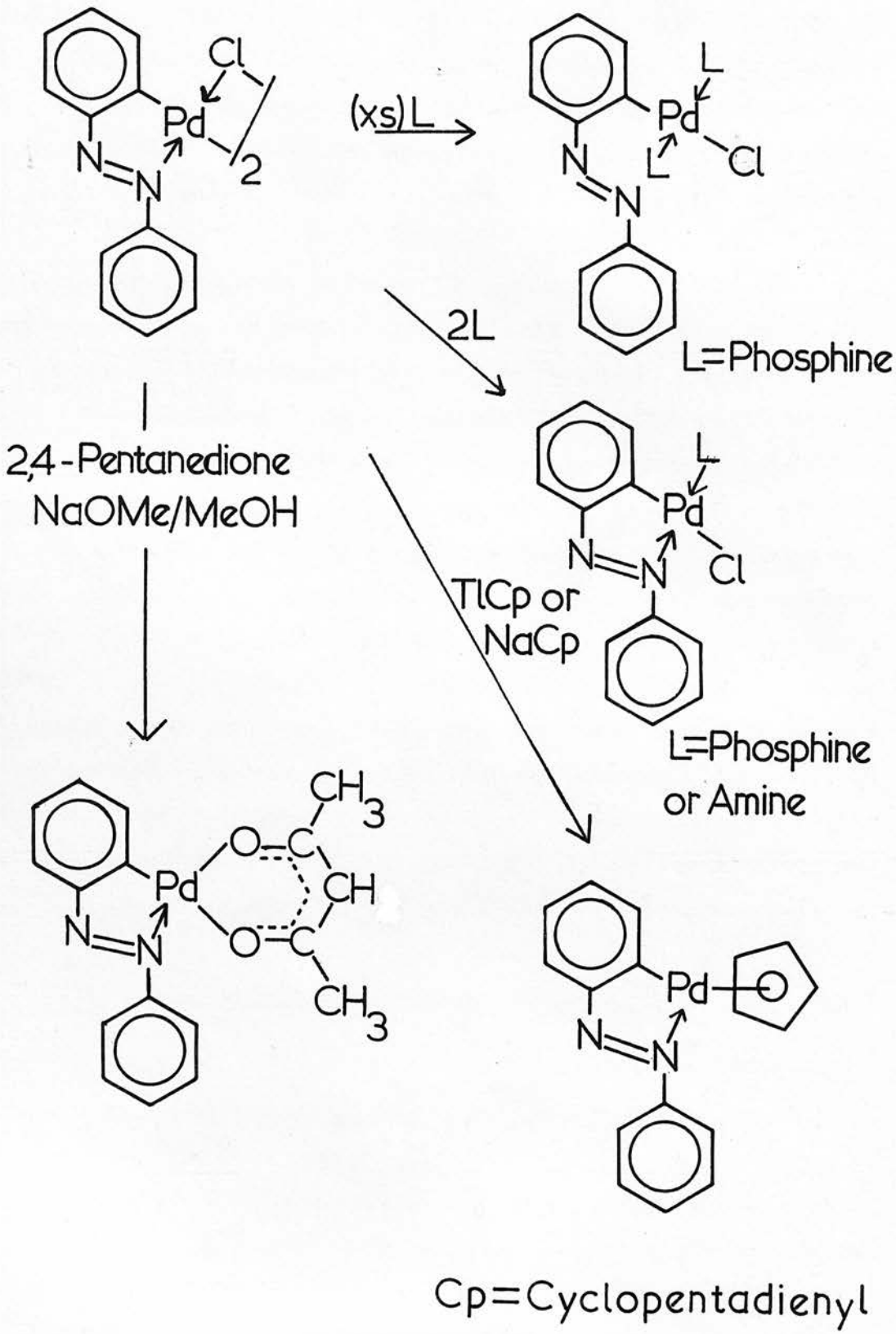
The effects of different R groups in alkylpentacarbonylmanganese complexes, $RMn(CO)_5$, on internal metallation reactions with azobenzene, were studied.[25] It was found that, by replacing methyl with benzyl, a more efficient metallation reaction was achieved. This was thought to be due to the greater thermodynamic stability of the resulting hydrocarbon, toluene, as against methane. The results were consistent with a mechanism involving an initial coordination of one of the azobenzene nitrogens to manganese, which resulted in a build-up of electron density on the metal atom. A partial transfer of electron density onto the leaving group, R, might also occur to a greater or lesser extent, depending on the nature of R. The final step envisaged is a concerted reaction involving cleavage of both the manganese-carbon bond and the ortho-aryl carbon-hydrogen bond, to give the hydrocarbon, RH, and the metallated complex. A four-centre transition state as shown in (37) was proposed.

Reactions of Cyclometallated Complexes of Azobenzenes

(1) Ligand Exchange

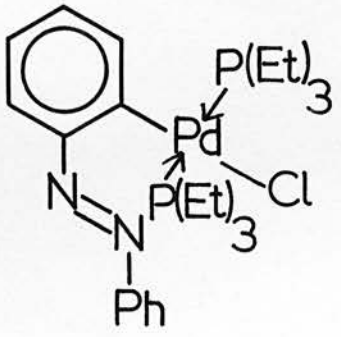
Ligand exchange reactions of cyclometallated complexes have been limited mainly to the cleavage of cyclometallated halogen-bridged dimers with phosphines[26] and amines.[2] The monomeric derivatives obtained in this way, have been found more amenable to characterisation and crystallographic study[27] than the corresponding dimers, owing to the increased solubility in organic solvents of the monomeric complexes relative to the dimeric ones. Substitution

Fig (i)

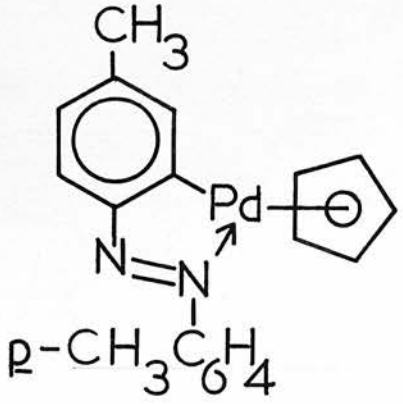

Cl
Pd
N=N
2
(xs) L
L
Pd
L
Cl
N=N
2L
L=Phosphine
2,4-Pentanedione
NaOMe/MeOH
L
Pd
N=N
Cl
TlCp or
NaCp
L=Phosphine
or Amine
CH3
O=C
Pd
CH
O=C
CH3
Pd
O
N=N
Cp=Cyclopentadienyl

reactions[13] with both the conjugate base of acetylacetone and with sodium or thallium (I) cyclopentadienide have also afforded more tractable derivatives of the halogen-bridged dimers. Both types of reactions are summarised briefly in Fig. (i), the di-μ-chlorobis-[2-(phenylazo)phenyl-2C, N']dipalladium (II) complex being used to exemplify them. Phosphines were found to cleave not only the halogen bridges, but also, in some cases, the nitrogen-palladium coordinate bond.

Both the phosphine complex[27] (38) and the π-cyclopentadienyl complex[28] (39) have been the subject of X-ray crystallographic studies. In both cases the results confirmed the presence of an ortho-carbon-palladium bond and, in the case of (39), a nitrogen-palladium co-ordinate bond, involving the nitrogen furthest away from the metallated ortho-carbon atom of the aromatic ring.



(38)

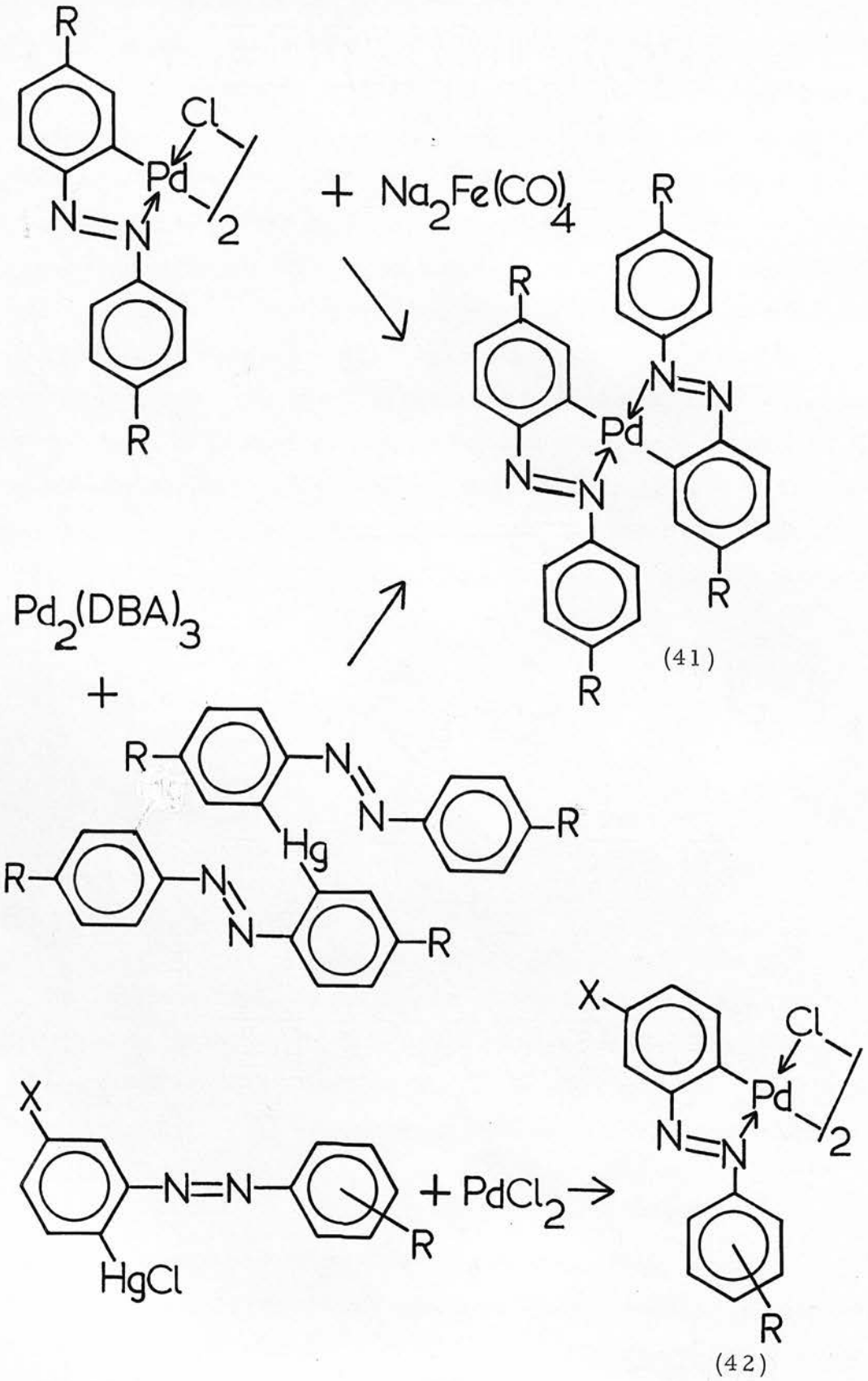


(39)

Ligand exchange reactions are not confined solely to palladium complexes and from other metal complexes, notably ruthenium and rhodium complexes, ligand exchange products have been obtained by Bruce[16, 29] and his co-workers.

(2) Metal-Exchange Reactions

The first examples of cyclometallated complexes of azobenzene undergoing metal exchange reactions were reported in 1968 by Heck,[13] who showed that palladated azobenzenes react by metal-exchange with anions of cobalt, manganese, and rhenium. The manganese and rhenium complexes (27) and (28), obtained by this method, have since

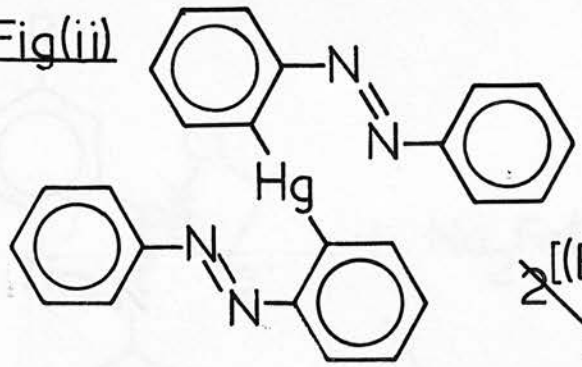


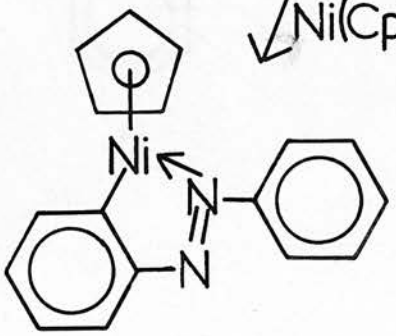
(41)

(42)

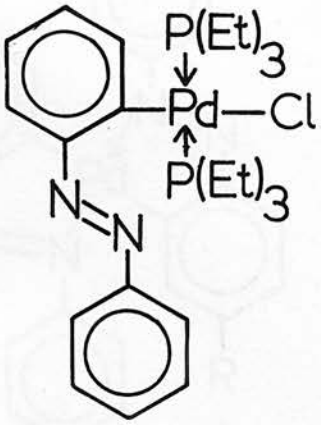
X = H; R = H and X = Cl; R = 2-Me, 3-Me, 4-Me or 3, 5-Br_2

Fig(ii)

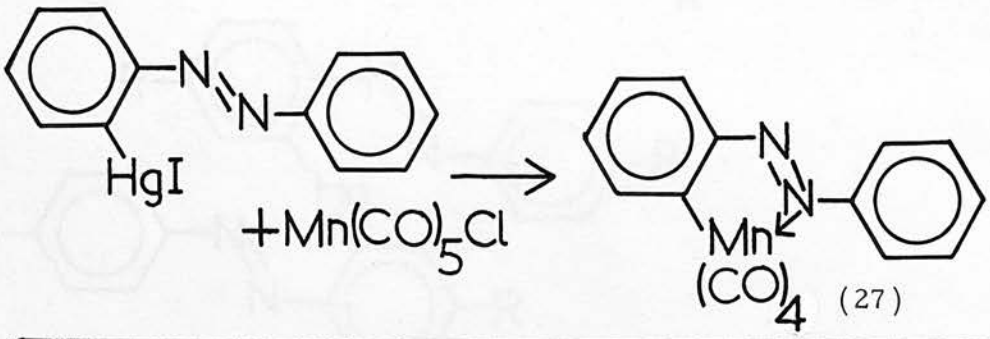




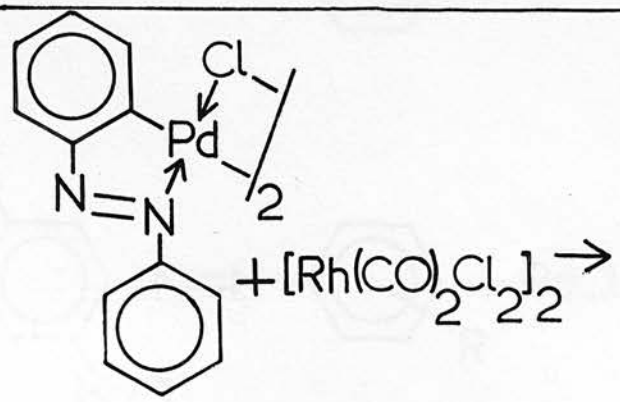
(12)



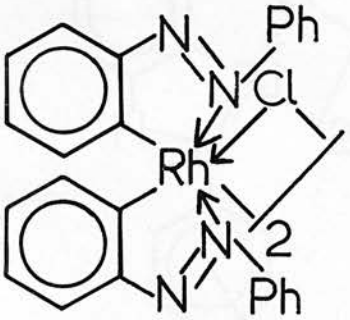
(38)



(27)

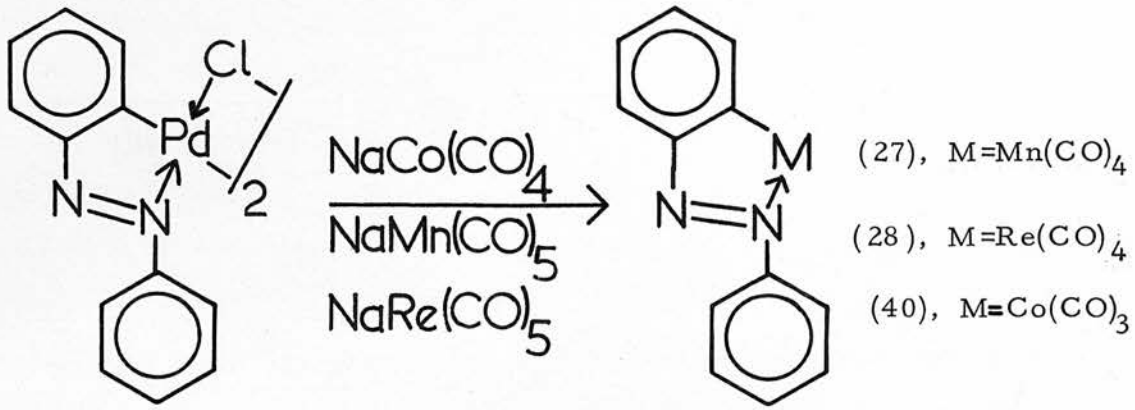


(14)



(15)

been prepared directly, as previously described.[17] Formation of the cobalt complex (40), however, has not been reported by any route other than Heck's.

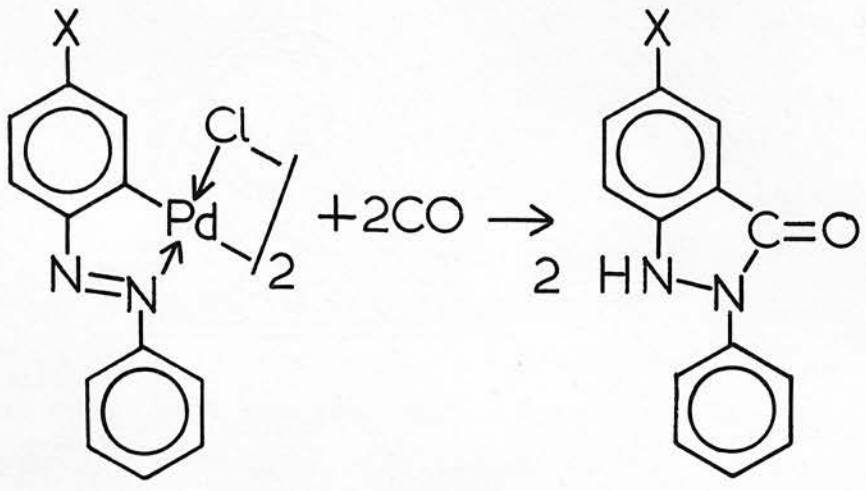


(14)

In an attempt to use Heck's method of treating palladium complexes with metal carbonylates, as a possible route to iron complexes, Pauson[18] found no expected transfer of the azo-ligand to iron, but, in fact, transfer to another palladium atom was observed, resulting in the formation of the novel, neutral bis(2-phenylazophenyl)-palladium (II) complexes (41). The same complexes were recently obtained in better yield by Sokolov and his coworkers,[20] from the metal-exchange reaction of bis(2-phenylazophenyl)mercury complexes with the dibenzylideneacetone complex of zerovalent palladium.

Earlier, Cross[30] had reported that ortho-mercurated azobenzene derivatives react with palladium chloride to give quantitative yields of the metal-exchanged products (42). By treatment of the bis (2-phenylazophenyl)mercury complex with the phosphine complex, $(R_3P)_2PdCl_2$, the trans-$(R_3P)_2PdCl(C_6H_4N_2Ph)$ complex (38), was obtained. An exchange reaction of the same mercury complex with nickelocene, afforded high yields of the complex (12), first described by Kleiman and Dubeck,[6] and another reaction involving the (2-phenylazophenyl) mercuric iodide complex and pentacarbonyl-manganese chloride gave a high yield of the metal-exchanged complex (27). These reactions are summarised in Fig. (ii).

One metal-exchange reaction involving rhodium has been reported[29] in which the reaction of dimeric dicarbonylrhodium



(43) (44)

$X = H, CH_3, OCH_3$

dichloride with Cope's palladated azobenzene complex (14) gave the rhodium chloride-bridged dimer (15).

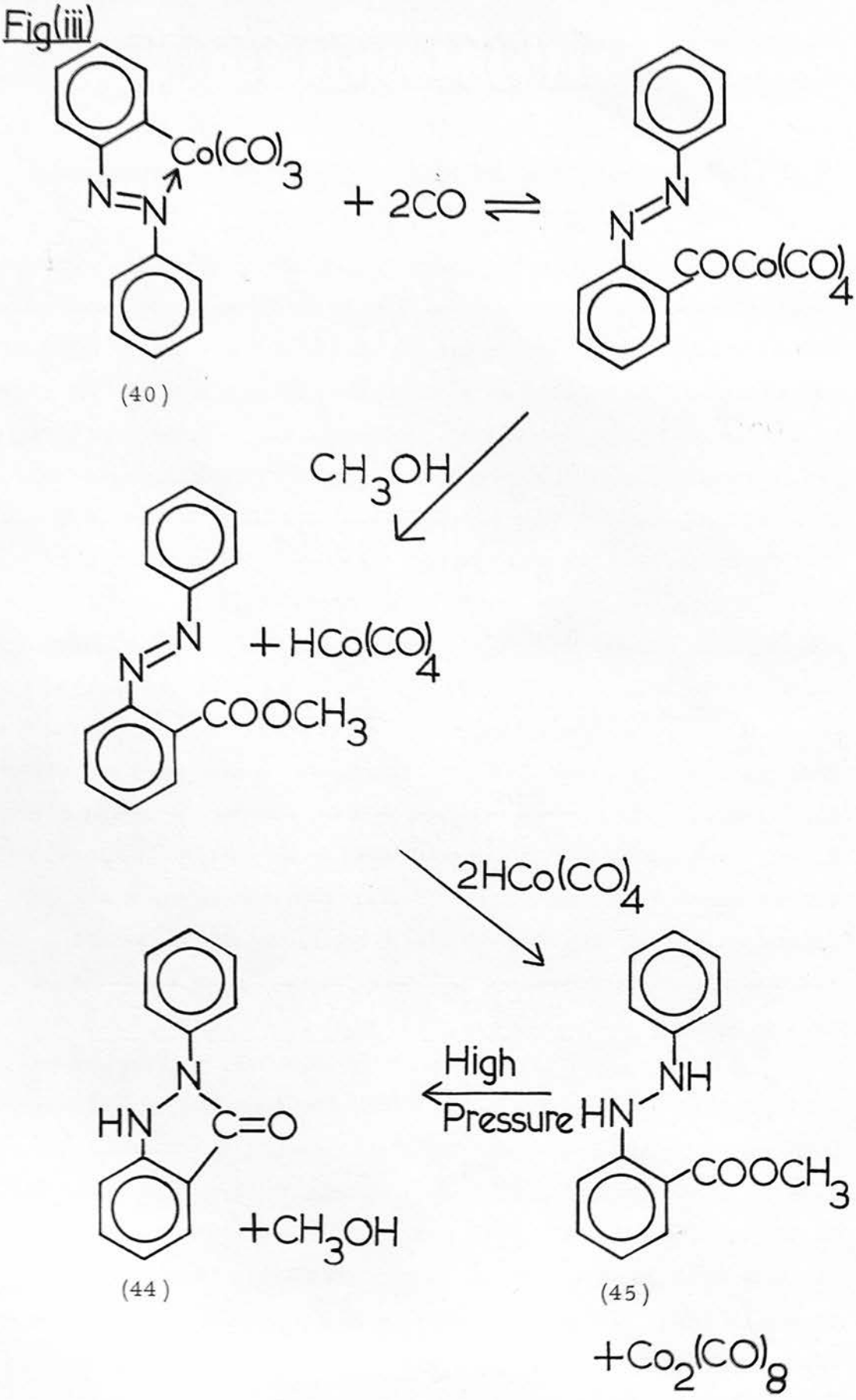
(3) Reactions involving Replacement of Metal by Non-Metallic Atoms or Groups

The simplest reactions of cyclometallated complexes involving replacement of the metal by non-metallic atoms or groups are those involving replacement with hydrogen via lithium aluminium hydride degradation. These reactions were carried out initially, with a view to proving that ortho-metallation had occurred. Studies[2] involving the deuteride, $LiAlD_4$, showed that ortho-deuterioazobenzene was invariably the product obtained from such reactions thus confirming that the complexes degraded had in fact been ortho-metallated.

Fahey[31] reported that azobenzene was halogenated by chlorine and bromine selectively ortho- to the azo-group, when its solutions were treated with the respective halogen in the presence of a palladium (II) catalyst. Fahey suggested that the specificity for ortho-halogenation was due to interaction of the halogen with a carbon-metal sigma-bonded intermediate, di-μ-halobis(2-phenylazophenyl) dipalladium (II). Intermediates such as this were isolated from reaction mixtures and characterised using far infrared spectroscopy and ligand exchange reactions. Thus, in these reactions, the metal of the initially formed cyclometallated intermediate had been replaced by a non-metallic halogen atom.

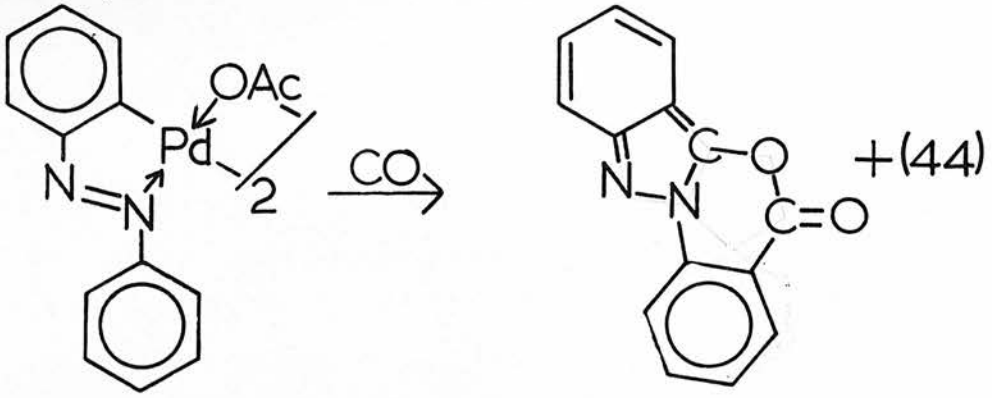
A great deal of interest has surrounded the carbonylation reactions of cyclopalladated azobenzene complexes, since Takahashi[22] first reported these reactions and their potential in organic synthesis. 4-Substituted azobenzene-palladium complexes (43) were carbonylated in aqueous ethanol at 150 atm. pressure to give the indazolone derivatives (44) in good yield. These reactions presumably involved initial insertion of a carbonyl group into the carbon-palladium sigma-bond, followed by displacement of palladium from nitrogen, to give the cyclised products.

Fig(iii)


Co(CO)3
N=N
+ 2CO ⇌
N=N
COCo(CO)4
(40)
CH3OH
N=N
+ HCo(CO)4
COOCH3
2HCo(CO)4
High
Pressure
NH
HN
HN
C=O
COOCH3
+CH3OH
(44)
(45)
+Co2(CO)8

Indazolones had previously been obtained by Horiie,[32] in 1960, from the octacarbonyldicobalt-catalysed carbonylation of azobenzenes, at high pressures. In the light of Takahashi's findings, Heck[13] suggested that this catalysed reaction might have involved ortho-metallated azobenzene intermediates and he further investigated this possibility by preparing an ortho-metallated azobenzene-cobalt complex (40), as described earlier, and treating it with carbon monoxide under conditions similar to those originally employed by Horiie. By this method, 2-(methoxycarbonyl) hydrazobenzene (45) was obtained, which under high pressures cyclised to the indazolone. Heck suggested the scheme summarised in Fig. (iii) to explain the reaction.

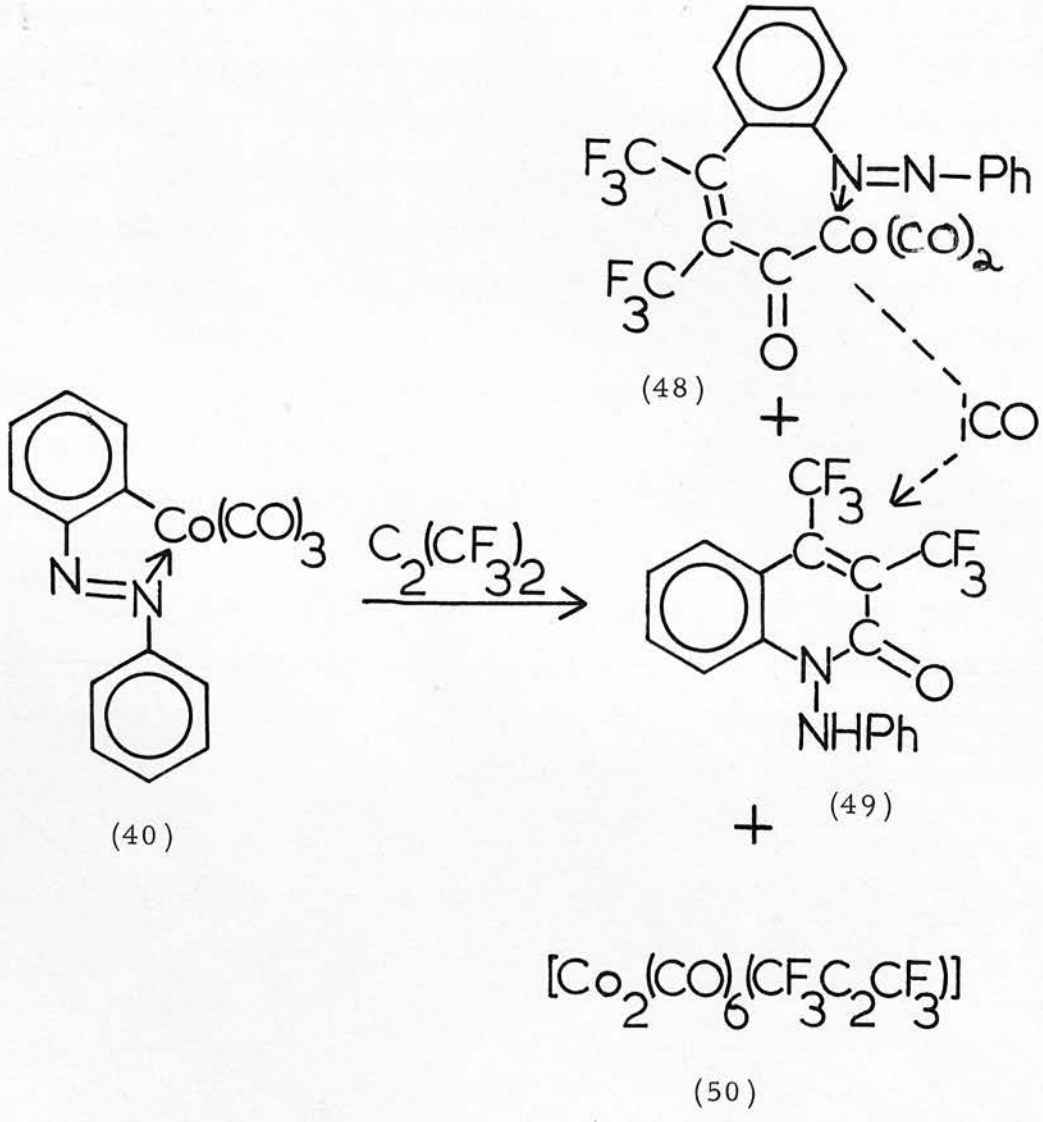
More recent research carried out by Heck[33] on the carbonylation of ortho-palladated complexes of azobenzene, and other types of nitrogen-donor ligand complexes of palladium, has extended the scope of the carbonylation reaction. Carbonylation of di-μ-acetato-bis (2-phenylazophenyl) dipalladium (II) (46) in xylene at 100°C under one atmosphere of carbon monoxide gave the heterocyclic lactone (47) in addition to the indazolone (44). Further suggestions concerning the mechanism of such reactions were made.



(46) (47)

As earlier described, Ustynyuk[8] obtained the pseudo-azulene, 4-phenyl-4H-cyclopenta[c]cinnoline (13), from the cyclopentadienyl-nickel complex (12). This reaction involves replacement of the metal by a cyclopentadienyl ring and dehydrogenative cyclisation. Cross[34] later obtained the same product from the analogous palladium complex (8) by heating in a sublimation apparatus.

Fig(iv)

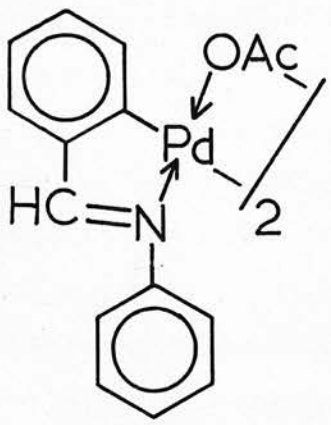

F3C
C
N=N–Ph
C
Co(CO)2
F3C
C
O
(48)
+
CO
Co(CO)3
N=N
C2(CF3)2
CF3
C
C
CF3
C
N
O
NHPh
(49)
(40)
+
[Co2(CO)6(CF3C2CF3)]
(50)

In the reactions studied by Ustynyuk, Cross, and by Heck in which either a carbonyl group or the double bond of the cyclopentadienyl ring was formally inserted between the azo function and the ortho-carbon of the aryl group, only organic products were obtained. The proposed organometallic intermediates were not isolated. Bruce,[35] however, has recently reported the insertion of a formal three-carbon unit, $[CO + C_2(CF_3)_2]$, into the carbon-cobalt σ-bond of (2-phenylazophenyl) tricarbonylcobalt (40) and related complexes. The organic products were formed *via* organometallic intermediates of unusual structure, which were isolated and fully characterised. Complex (40) was treated with hexafluorobut-2-yne and the products (48), (49) and (50) were obtained. Further treatment of (48) with carbon monoxide resulted in its conversion to (49). The reactions are summarised in Fig (iv) and represent a new route to substituted quinoline-2-ones, *via* isolable organometallic intermediates.

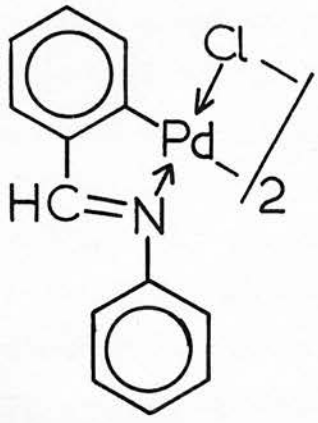
(b) Schiff's Bases as Nitrogen Donor Ligands

Schiff's bases (51) derived from aromatic aldehydes and ketones, were first shown to react with transition metals in 1965, when Pauson[15] described their reaction with nonacarbonyldi-iron. In contrast to azobenzene, these compounds yielded ortho-metallated products (52). A crystallographic study[36] of the para-toluidine derivative, ($R'=p\text{-}CH_3C_6H_4$; X=H; $Y=CH_2$), was carried out and the compound was shown to possess a non-planar five-membered ring, containing the σ-bonded iron. Another tricarbonyliron grouping was bonded to one face of the ring and the methylene group was evidently bent away from the second iron. The methylene group was formed from the azomethine carbon of the Schiff's base, apparently by transfer of an ortho-hydrogen from the aromatic ring.

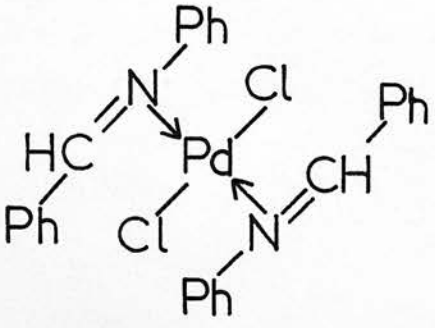
Although cyclometallation reactions of Schiff's bases have not been studied to the same extent as those of azobenzene and its derivatives, nevertheless, a variety of Schiff's base transition-



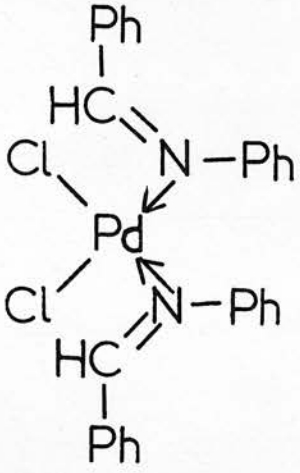
NaCl →



(54) (53)



(56)



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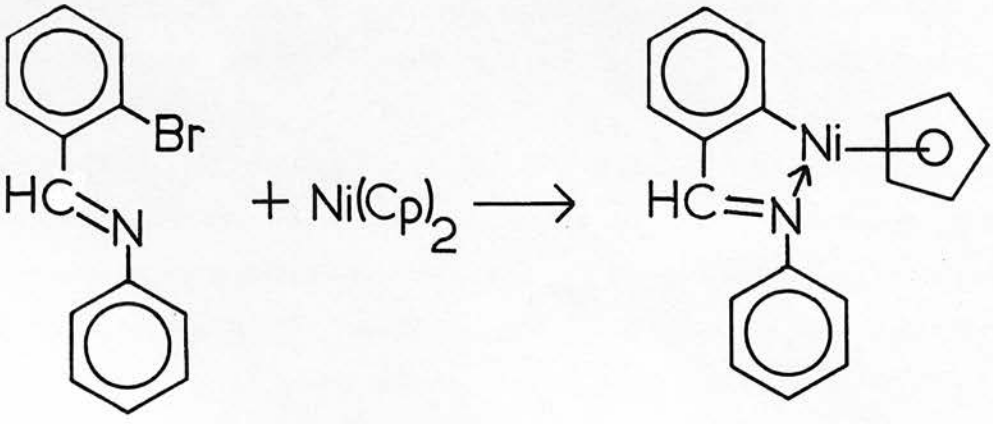
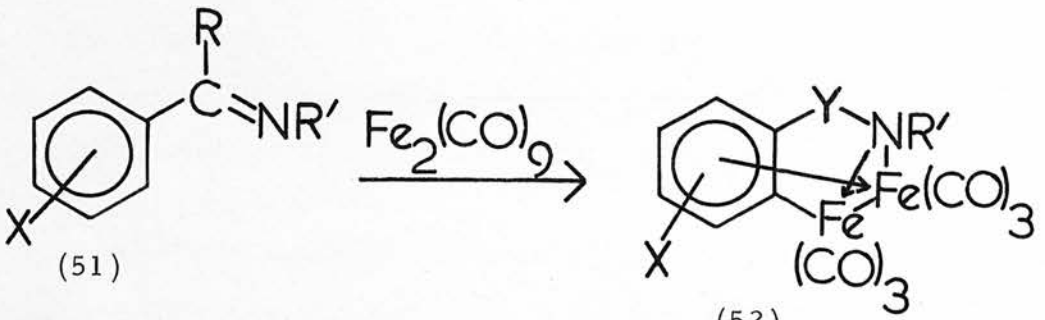


(57)



(51) (52)

R = H, Me, Ph, R'= Me, Ph Y = CHR

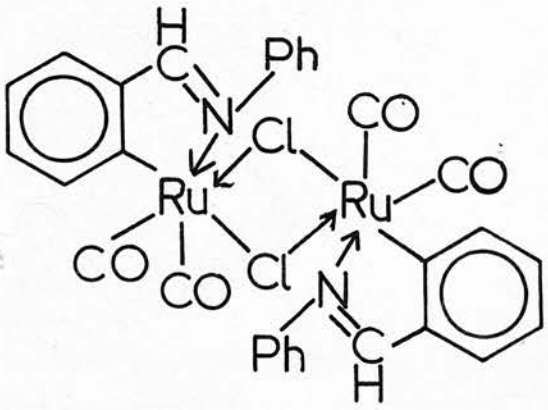
metal complexes have been reported following Pauson's initial discovery.

A number of compounds of group VIII metals, namely palladium, nickel, rhodium and ruthenium, and of the group VII metals, manganese and rhenium, were observed to react with Schiff's bases, affording cyclometallated complexes.

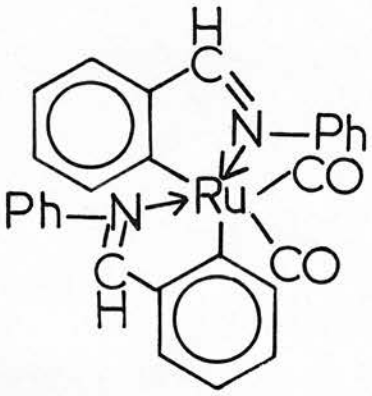
Of the metals of the nickel sub-group, palladium has been the most frequently studied. Molnar and Orchin[37] reported that bis(benzonitrile)palladium dichloride reacted with a considerable number of Schiff's bases to form ortho-palladated complexes of type (53). However, a number of authors[38, 39, 40] later questioned Molnar and Orchin's work, among them Onoue and Moritani. On repeating Molnar and Orchin's work, Onoue and Moritani found[39] that the reaction of bis(benzonitrile) palladium dichloride with N-benzylideneaniline, in refluxing methanol, yielded dichlorodianiline palladium (II) (69%), and dichlorobis(N-phenylbenzaldimine) palladium (II) (6% yield), but no cyclometallated products were formed. They, and others,[40] concluded that the aniline complex was formed <u>via</u> hydrolysis of the N-benzylideneaniline ligand co-ordinated to palladium, as similar metal-assisted cleavage reactions had been reported previously.

Onoue and Moritani went on to report the preparation of palladium acetate-Schiff's base complexes of type (54), which could be converted to the <u>ortho</u>-metallated halogen-bridged complexes, (53).

Lewis later investigated[40] the reactions of N-benzylidene-

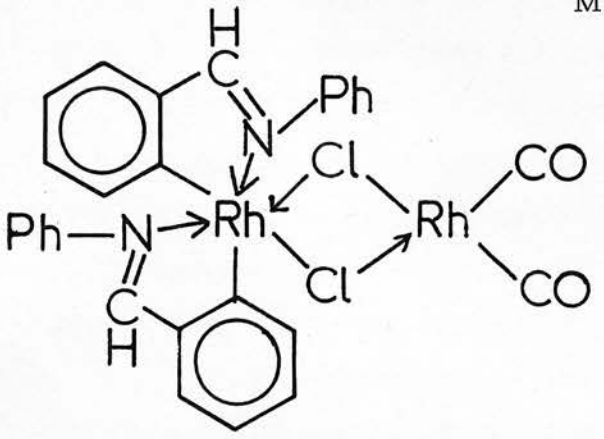


(58)=

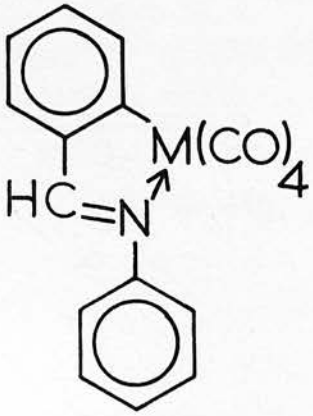


(59)

(60) Ph is replaced by Me

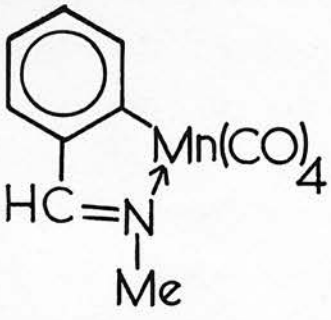


(61)



(62), M = Mn

(63), M = Re



(64)

aniline and related ligands with several palladium (II) species under different conditions, but reported only the bis(benzylideneaniline) palladium dichloride *cis* and *trans* isomers, (55) and (56). No *ortho*-metallated products were obtained.

Only one example of a cyclometallated nickel-Schiff's base complex has been reported. Ustynyuk[41] and his co-workers obtained the complex (57) from the reaction of 2-bromobenzylideneaniline with nickelocene, a process analogous to the formation of the product, (12) from 2-chloroazobenzene and nickelocene.

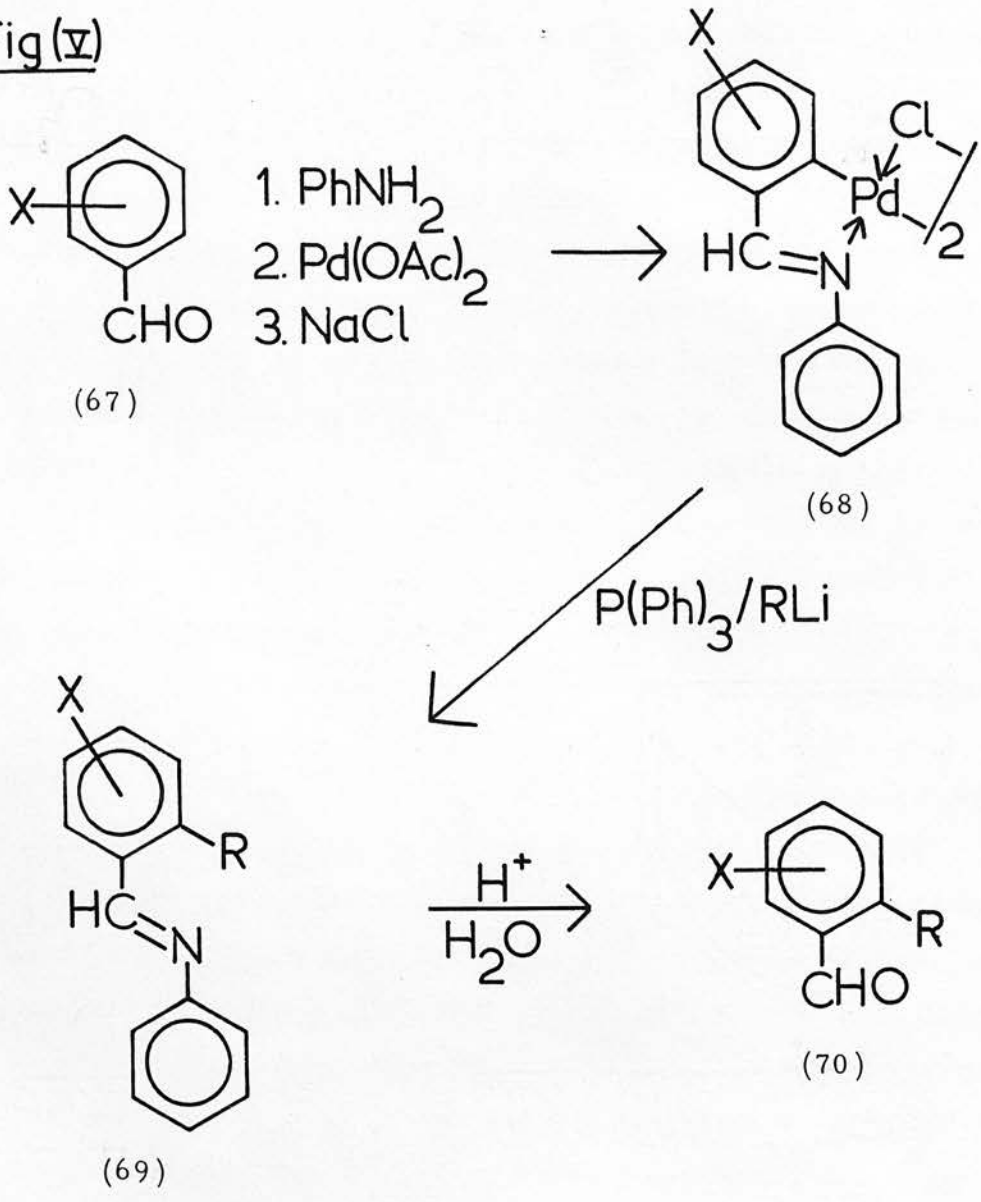
Cyclometallated ruthenium complexes were obtained by Bruce[42] and his co-workers, in reactions of the Schiff's bases, benzylideneaniline and benzylidenemethylamine with both dimeric tricarbonylruthenium dichloride and dodecacarbonyltriruthenium.

With tricarbonylruthenium dichloride only a small yield of the benzylidenemethylamine complex, (58), was obtained, this product being analogous to the azobenzene complex, (21). With dodecacarbonyltriruthenium, however, good yields of the cyclometallated complexes (59) and (60) were obtained.

The reaction of dimeric dicarbonylrhodium chloride with the same ligands afforded only one cyclometallated complex, (61). This derivative of benzylideneaniline was similar to the azobenzene complex (16), but the two ligands attached to the rhodium (III) atom, in this case, are in different environments; one metal-carbon σ-bond was *trans* to chlorine, and the second *trans* to nitrogen, as shown. Benzylidenemethylamine reacted to give only the product, $RhL(CO)_2Cl$, in which the ligand was coordinated *via* the nitrogen atom only.

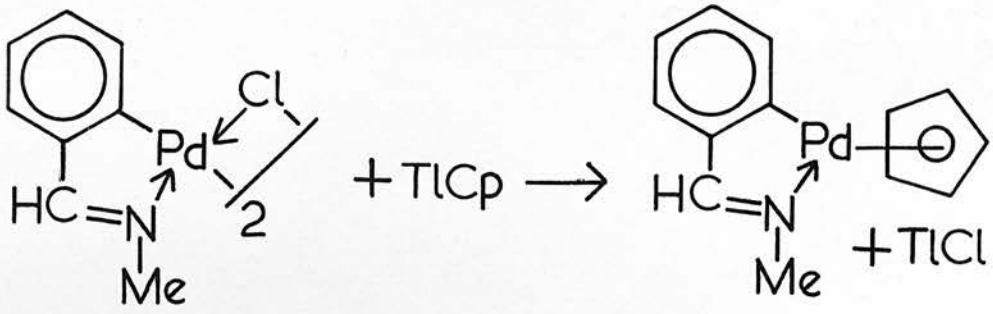
The use of methylpentacarbonyl complexes of manganese and rhenium, which had yielded cyclometallated azobenzene complexes, was also applied to Schiff's bases.[42] Benzylideneaniline afforded fair yields of the cyclometallated complexes (62) and (63) and benzylidenemethylamine reacted with methylpentacarbonyl manganese to give another (64). The crystal structure of (62) was determined[43] and confirmed the cyclometallated structure.

Fig (V)


X
CHO
1. PhNH2
2. Pd(OAc)2
3. NaCl
(67)
X
Cl
Pd
2
HC=N
(68)
P(Ph)3/RLi
X
R
HC=N
(69)
H+
H2O
X
R
CHO
(70)

Reactions of Cyclometallated Schiff's Base Complexes

No comprehensive study of the ligand exchange reactions of Schiff's base cyclometallated complexes has been reported to date, but a few examples of such reactions have been described. The reaction of the benzylidenemethylamine complex (65) with thallium cyclopentadienide afforded the monomeric cyclopentadienyl complex (66).[42] No ligand exchanged product was observed, however, with the corresponding benzylideneaniline complex (53). The previously mentioned metathetical exchange reactions of the Schiff's base-palladium acetate complexes with sodium halide in aqueous acetone are further examples of ligand exchange.[39]

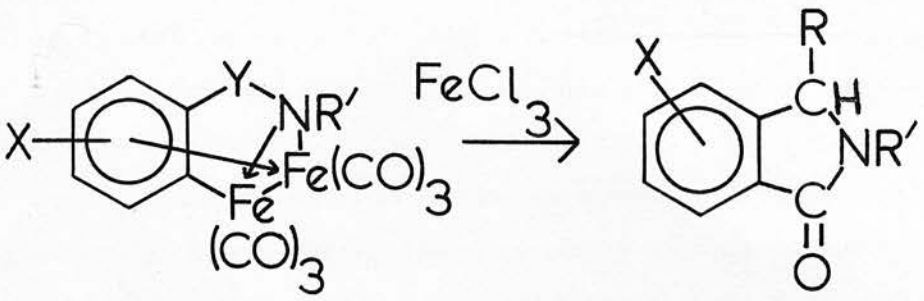


(65) (66)

Metal exchange reactions have not been reported to date and the most frequently studied reactions of these complexes are those involving replacement of the metal by non-metallic groups.

Murahashi[44] and his co-workers reported the reaction of a number of Schiff's base-palladium halide dimers with alkyl-lithiums and Grignard reagents. These reactions, described in more detail below, provided a useful synthesis of benzaldehydes.

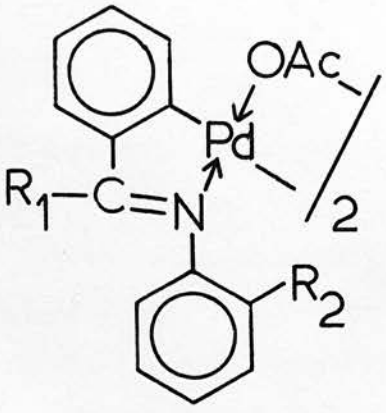
A series of substituted Schiff's bases were initially obtained from the appropriate aromatic aldehydes (67) and these were converted into the ortho-metallated, halogen-bridged dimers (68), using the method of Onoue and Moritani. The dimers were then treated with either alkyl-lithium or Grignard reagents, in the presence of triphenylphosphine, to give good yields of the ortho-alkyl substituted Schiff's bases (69). Subsequent hydrolysis afforded the appropriately substituted aromatic aldehyde (70). These reactions involving the

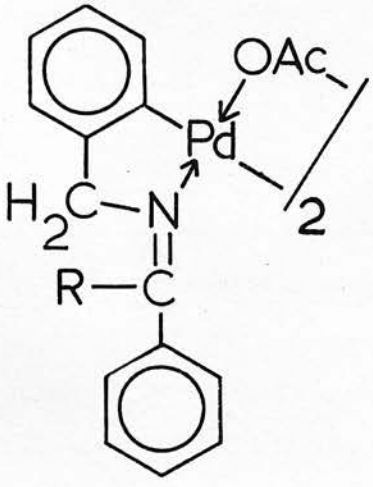


(52) (71)

Y = CHR
R = H, Me, Ph

R' = Me, Ph

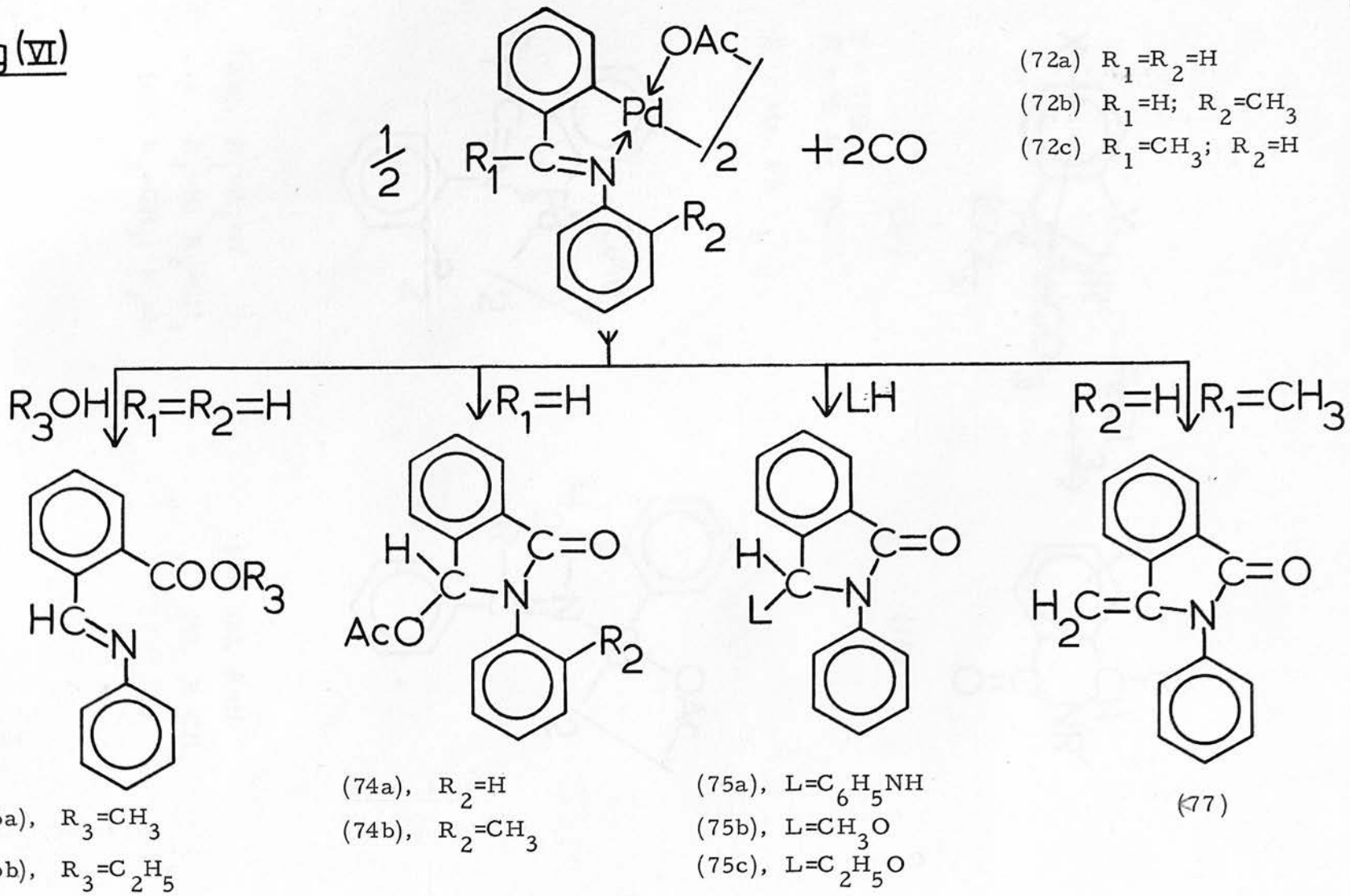




72(a), $R_1=R_2=H$
(b), $R_1=H$; $R_2=CH_3$
(c), $R_1=CH_3$; $R_2=H$

(73) (a), R=H
(b), $R=CH_3$

Fig (VI)



(72a) $R_1=R_2=H$

(72b) $R_1=H$; $R_2=CH_3$

(72c) $R_1=CH_3$; $R_2=H$

(76a), $R_3=CH_3$

(76b), $R_3=C_2H_5$

(74a), $R_2=H$

(74b), $R_2=CH_3$

(75a), $L=C_6H_5NH$

(75b), $L=CH_3O$

(75c), $L=C_2H_5O$

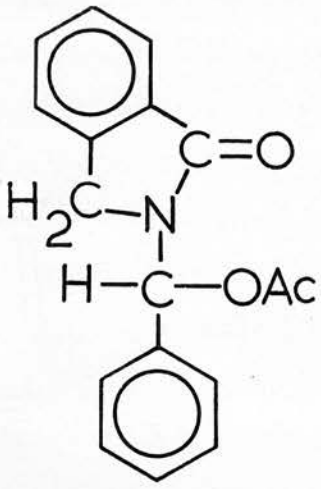
(77)

replacement of a metal in a cyclometallated complex by an alkyl group are summarised in Fig. (v).

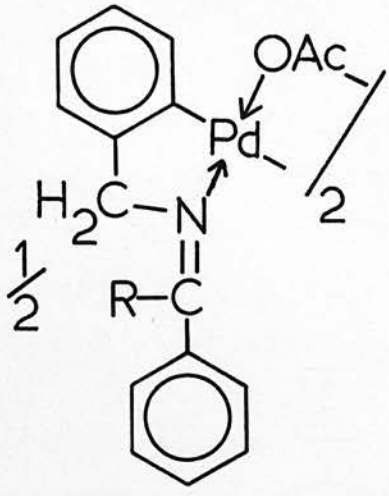
Prior to Pauson's work,[15,46] Schiff's bases were known to yield dihydroisoindolones[45] by reaction with carbon monoxide at high pressures in the presence of octacarbonyl dicobalt which acted as a catalyst. Pauson[46] showed that the same products (71) could be obtained by ferric chloride degradation of the ortho-metallated iron complexes (52). In the ferric chloride reaction iron was replaced by a carbonyl group to give the heterocyclic products. As in the case of cobalt-catalysed carbonylation of azobenzene, ortho-metallated cobalt complexes of the Schiff's bases were suggested as intermediates in the catalysed reactions.

Much later, Heck,[33] in his work on the carbonylation of cyclometallated complexes, prepared a number of ortho-palladated Schiff's base complexes and investigated their carbonylation reactions in detail. A variety of heterocyclic products was obtained and possible mechanistic pathways were discussed. The known N-phenyl Schiff's base complexes (72) and novel complexes of N-benzyl Schiff's bases (73) were prepared.

From the carbonylation reactions of these complexes, products were obtained analogous to those obtained from the carbonylation of the structurally related azobenzene complexes. In contrast, however, while the tendency for azobenzene to react at both aromatic rings complicated the reaction, carbonylations of the Schiff's base complexes (72a-c) were more straightforward. The benzylidene-aniline-palladium acetate complex (72a) was carbonylated readily in xylene at 100°C with one atmosphere of carbon monoxide, forming only one product, 3-acetoxy-2-phenyldihydroisoindolone (74a). The ortho-methyl derivative (72b) reacted to give the analogous product (74b). Carbonylation of complex (72a) in the presence of nucleophiles led to incorporation of the nucleophiles in the final products (75a-c) and also, when alcohols were the nucleophiles, to the formation of esters (76a and b) as by-products. The methyl derivative (72c) was

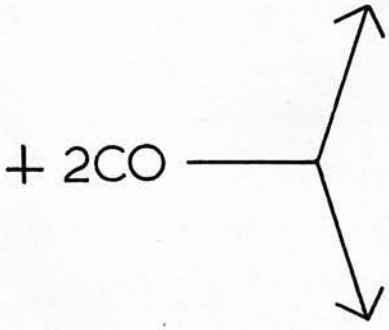


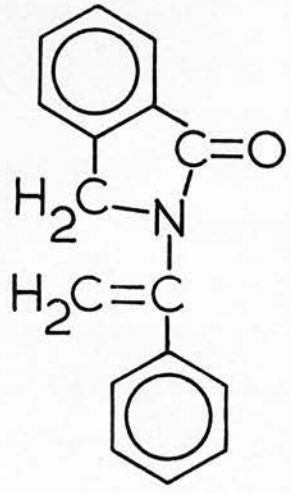
(78)



(73a) R=H

(73b) R=CH_3





(79)

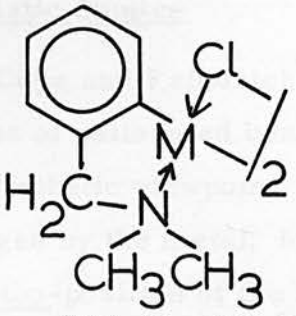
carbonylated in xylene at 100°C to form exclusively the olefinic product (77) rather than the tertiary acetate. These reactions are summarised in Fig. (vi).

Schiff's base complexes of the type (73a and b) were shown to undergo carbonylation in xylene to form cyclic products (78) and (79).

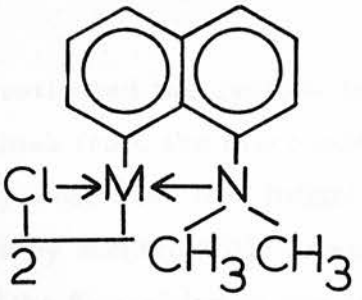
(c) Amines as Nitrogen Donor Ligands

Amines have frequently been used as nitrogen donor ligands in cyclometallation reactions, benzylamines being the type of amines most extensively investigated.

Cope and Friedrich[47] first examined the reactions of primary, secondary and tertiary benzylamines with both palladium and platinum chlorides. Facile cyclometallation reactions were observed for the tertiary N, N-dimethylbenzylamines and the related N, N-dimethyl-1-naphthylamine, to give the complexes (80) and (81) respectively. Primary and secondary amines, however, were found to be unreactive towards cyclometallation.



(80) M = Pd or Pt

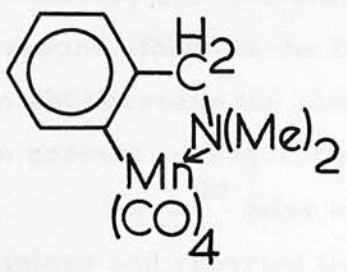


(81) M = Pd or Pt

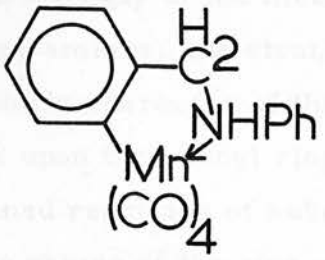
As with the other types of nitrogen donor ligands reviewed, cyclometallation reactions of benzylamines were not confined solely to palladium and platinum. However, the benzylamine ligand was shown[48] to be more limited in the scope of its cyclometallation reactions than azobenzenes and Schiff's bases, being unreactive towards iron, ruthenium and rhodium.

A successful metallation was achieved[48] by reaction of N, N-dimethylbenzylamine with methylpentacarbonylmanganese, affording the complex (82), and the secondary, N-phenylbenzylamine reacted

to a lesser extent giving low yields of the complex (83). A



(82)



(83)

crystallographic study of (82) confirmed[49] the cyclometallated structure and showed that the five-membered metallocycle was distinctly buckled as a result of the tetrahedral configuration about the nitrogen atom and the adjacent benzylic methylene group. The secondary amine was further investigated[48] with other transition metals but no other cyclometallated complexes were obtained.

Thus cyclometallation reactions of benzylamines are at present limited to palladium, platinum and manganese, the palladium complexes being the most extensively studied.

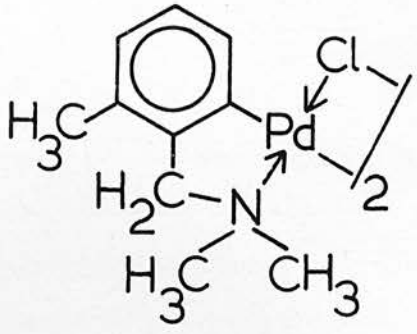
Mechanistic Studies

Cope and Friedrich[47] investigated the cyclometallation reactions of palladated benzylamines from the mechanistic as well as the synthetic viewpoint. They suggested that initial coordination of nitrogen by the metal, followed by electrophilic attack of the metal at an ortho-position of the ring, [the 8-position in the case of (81)], might account for the mode of formation of these complexes. Apparently, favourable entropy factors for electrophilic attack by the coordinated palladium via a five-membered ring transition state, were also necessary to facilitate aromatic substitution. No carbon-metal bonded products were obtained from the deactivated p-nitro-N, N-dimethylbenzylamine, or from N, N-dimethyl-2-phenylethylamines and -3-phenylpropylamines, which would have had to react via six and seven-membered ring transition states, respectively.

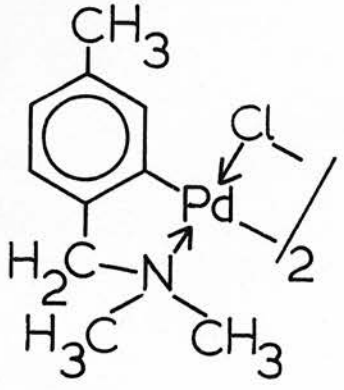
The reason for the inertness of primary and secondary amines

towards cyclopalladation was unclear, and it was suggested that since they coordinated more strongly to the metal for steric reasons, than did the tertiary amines, the stronger coordination might decrease the electrophilic character of the metal sufficiently to prevent subsequent attack upon the phenyl ring.

Lewis[40] later examined reactions of substituted benzylamines and reported that the nature of the ring substituents affected the course of the cyclopalladation reaction. N, N, 2- and N, N, 4-trimethylbenzylamines, both slightly activated towards electrophilic attack at the ortho-position of the aromatic ring, reacted to give cyclometallated complexes (84) and (85) with sodium tetrachloropalladate. The reaction of the highly hindered N, N, 3, 5-



(84)



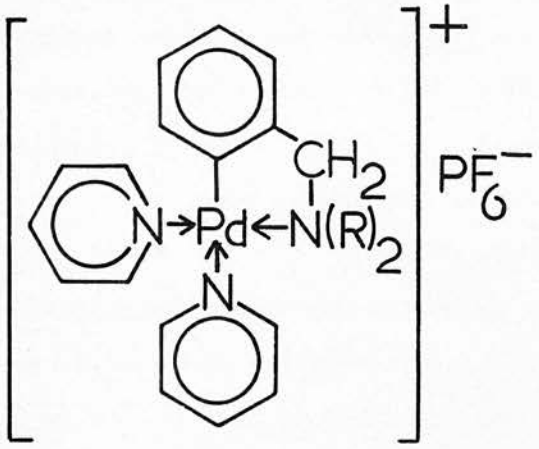
(85)

tetramethylbenzylamine, however, yielded only a nitrogen-coordinated complex with no carbon-palladium bonds. This behaviour contrasted with that of the similarly hindered, but more highly activated, N, N-dimethyl-3, 5-dimethoxybenzylamine, which had previously been reported to form a cyclopalladated complex, by Cope and Friedrich.[47]

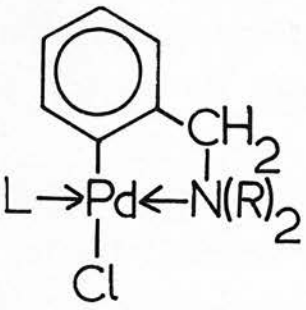
Trofimenko[50] varied the R group in the benzylamines, $C_6H_5NR_2$ (R=Me, Et, Pr), and found that the course of the reaction was not significantly altered.

Reactions of Cyclometallated Benzylamines

All the reports concerning the reactions of these complexes

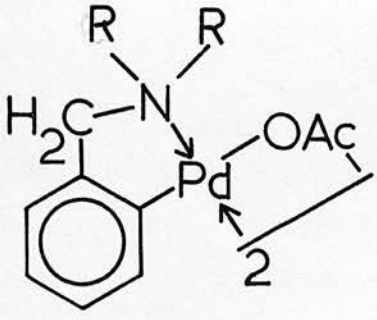


(88)



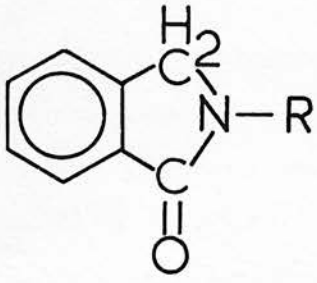
(87)

L = pyridine



(89a), R=CH_3

(89b), R=C_2H_5

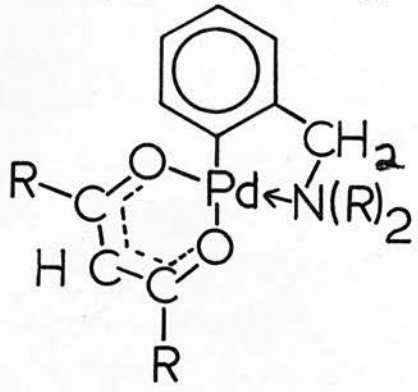


(90a), R=CH_3

(90b), R=C_2H_5

have involved the reactions of the palladium compounds.

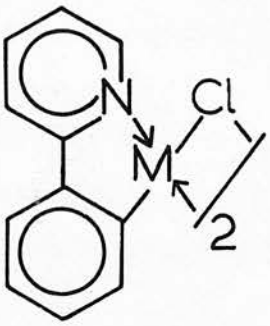
Characterisation of the halogen-bridged dimeric complexes of type (80) was achieved both directly and by conversion to monomeric derivatives *via* ligand-exchange reactions. Uninegative bidentate ligands such as acetylacetonate, 1, 3-ketoiminate or tropolonate ions were employed[50] to afford more easily characterised derivatives such as (86). Another type of ligand exchange



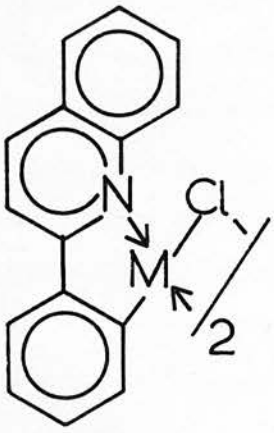
(86)

reagent, found useful for determining the presence of cyclometallated ligands, was pyridine.[50] When dimers of the type (80) reacted with pyridine in organic solvents, insoluble monosubstitution products of the type (87) were obtained. However, when the reaction was carried out in water, the bis(pyridine) cations (88) were readily obtained and isolated as hexafluorophosphate salts. The formation of these cations was found to be of value in distinguishing chemically between compounds of type (80) and, for example, bis(benzylamine) palladium dichloride, which had no carbon-palladium bonds. Under these conditions pyridine displaced the simply coordinated benzylamine ligand but not the carbon-bonded ligand in (80). Thus, by way of the ligand exchange reaction with pyridine, the presence of a cyclometallated ligand could be validated or invalidated on the evidence obtained.

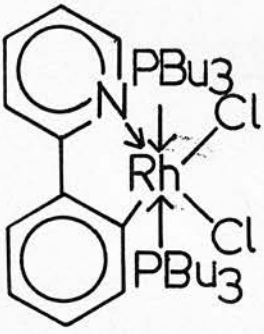
Metal-exchange reactions of benzylamine complexes have not been reported to date and only one, recently reported, metal-replacement reaction is known, that involving the replacement of palladium with a carbonyl group *via* the carbonylation reactions of



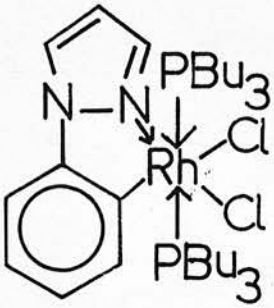
(91) M = Pd or Pt



(92) M = Pd or Pt



(93)



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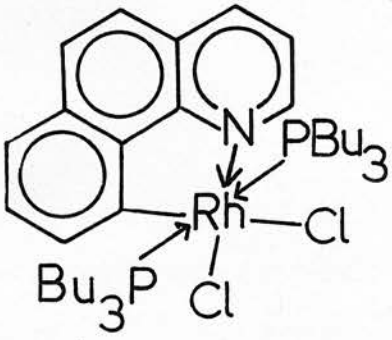

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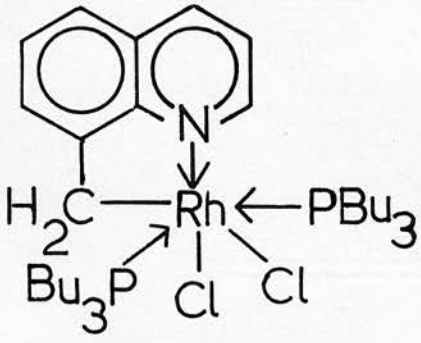
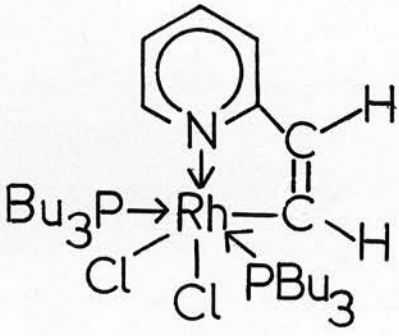


(96)



(97)

benzylamine-palladium acetate complexes.

The palladium acetate-tertiary benzylamine complexes (89a and b) were carbonylated by Heck,[33] in the same manner as were azobenzene and Schiff's base complexes, to afford mixtures of products, from which the heterocyclic dihydroisoindolones (90a and b) were separated. Cyclisation, in this instance, is accompanied by loss of one of the alkyl groups.

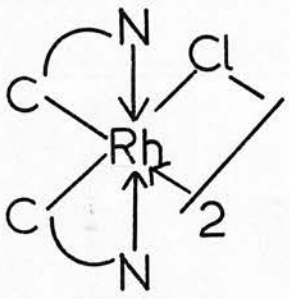
(d) Phenyl-Substituted Nitrogen Heterocycles as Nitrogen Donor Ligands

A number of examples of cyclometallation reactions involving phenyl-substituted heterocyclic ligands have been reported. The complexes obtained involved ligands such as 2-phenylpyridine,[51, 52, 53, 54, 2-phenylquinoline,[51] 1-phenylpyrazole[50, 53, 54, 62] and benzo[h] quinoline.[52, 54, 55, 56, 57] In cyclometallated complexes of this type an aromatic carbon atom was metallated, while in the related reactions of 2-vinylpyridine,[53, 54, 58, 59] and 8-methyl[54, 60] or 8-ethylquinolines,[61] an olefinic or methylenic carbon was bonded to the metal.

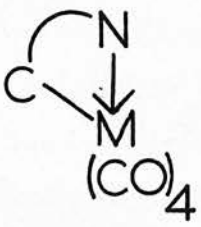
2-Phenylpyridine and 2-phenylquinoline were the first heterocyclic compounds reported[51] to undergo cyclometallation reactions and the cyclometallated compounds (91) and (92) were the products of their reactions with sodium tetrachloropalladate in methanol at room temperature.

Since these, the earliest examples, a variety of phenyl-substituted heterocyclic compounds has been cyclometallated by a number of metals other than palladium and platinum. The group VIII metals, rhodium[54, 62] and iridium,[62] the group VII metals, manganese[53] and rhenium[53] and the group VI metal, molybdenum,[63] have all been reported to give cyclometallated complexes with heterocyclic ligands.

Rhodium complexes of 2-phenylpyridine, 1-phenylpyrazole, benzo[h]quinoline, 8-methylquinoline and the related 2-vinylpyridine were reported[54] and these are exemplified by (93), (94), (95), (96) and (97) respectively. All the rhodium complexes described were

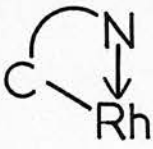


(98)

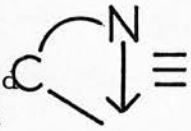


(100)

M = Mn or Re



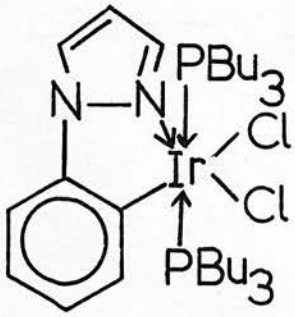
≡ A heterocyclic ligand carbon bonded to Rh
eg 2-phenylpyridine



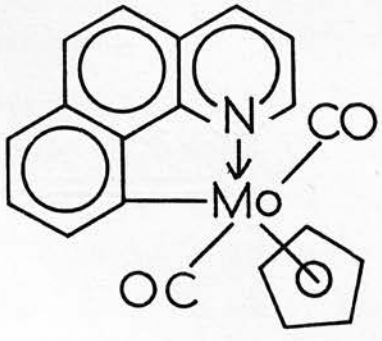
≡

2-phenylpyridine
4-phenylpyrimidine
2-phenylquinoline

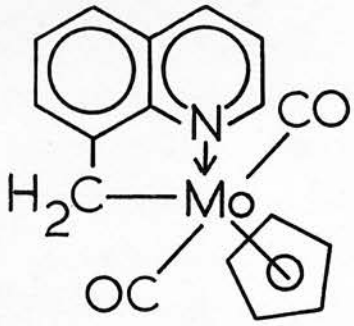
1-phenylpyrazole
1-benzo[h]quinoline
2-vinylpyridine



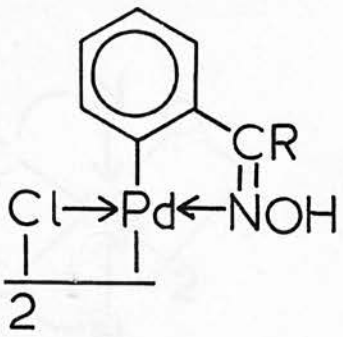
(99)



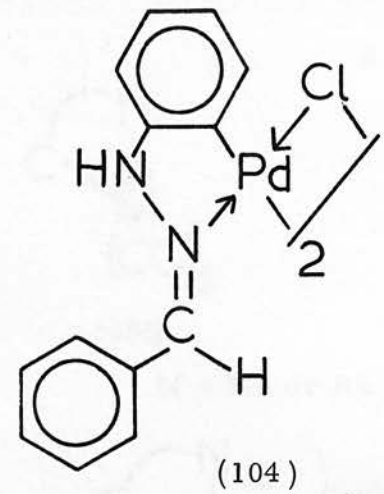
(101)



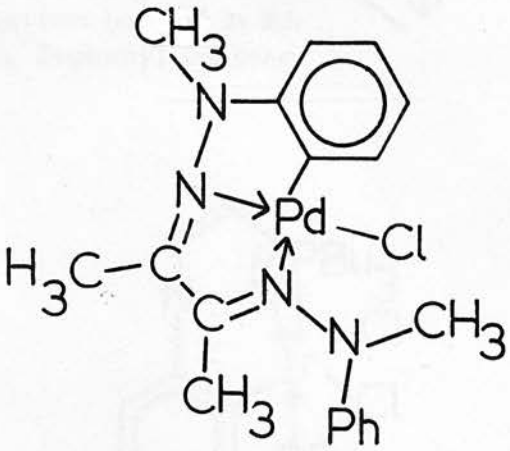
(102)



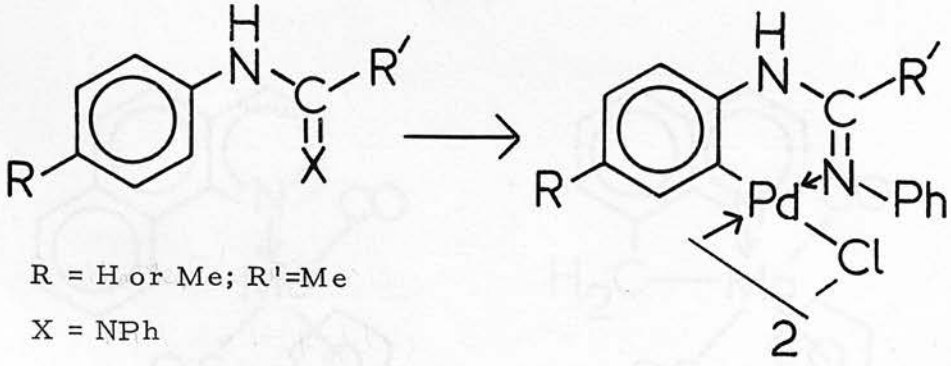
(103)



(104)



(105)



R = H or Me; R'=Me

X = NPh

(106)

obtained from the reactions of the respective ligands with hexachlorotetrakis(tri-n-butylphosphine) dirhodium (III), in refluxing xylene. These complexes, in contrast to the earlier reported[52] rhodium complexes of type (98), were mono-rhodocyclic and more easily characterised.

An example of an iridium cyclometallation product (99) was reported[62] relatively recently but no heterocyclic ligands other than 1-phenylpyrazole have yet been shown to form cyclometallated complexes with iridium.

Manganese and rhenium, via their methylpentacarbonyl derivatives, were found[53] to directly metallate a whole range of heterocyclic ligands in facile cyclometallation reactions to afford complexes of the type (100).

The group VI metal, molybdenum, was reported[63] to metallate benzo[h]quinoline and 8-methylquinoline to afford the complexes (101) and (102) respectively, both in low yield.

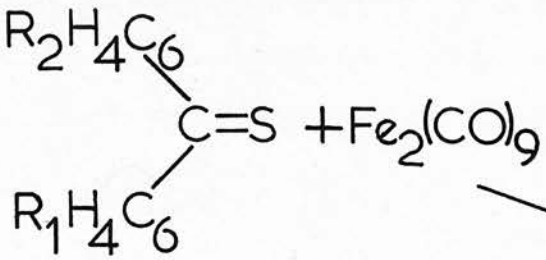
Reactions of Cyclometallated Heterocyclic Complexes

No reactions of these complexes, other than the simple ligand exchange reactions, previously discussed for the other types of nitrogen donor ligands, have been reported. Uninegative bidentate ligands, such as acetylacetonate, and donor ligands such as phosphines, pyridine and cyclopentadienyl were used in these ligand exchange reactions.

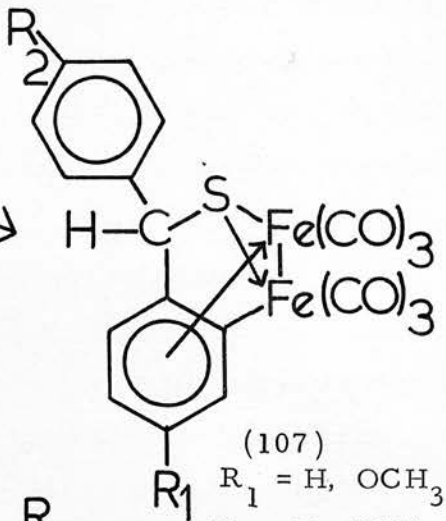
To date these complexes have not been shown to undergo reactions involving either metal exchange or replacement of the metal by non-metallic atoms or groups.

(e) Other Nitrogen Donor Ligands

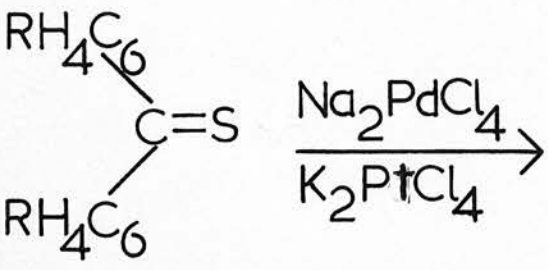
Complexes containing cyclometallated nitrogen donor ligands, other than those previously described, have been reported for derivatives of aromatic oximes,[64,65] phenylhydrazones[40] and osazones[66] (103), (104) and (105).



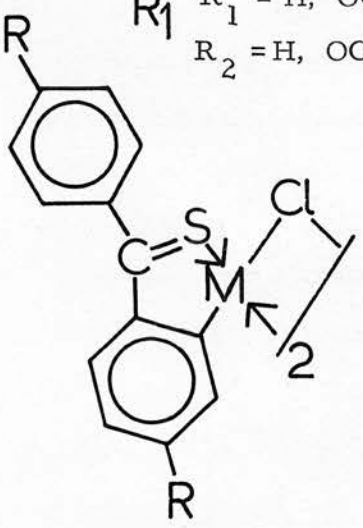
(113)



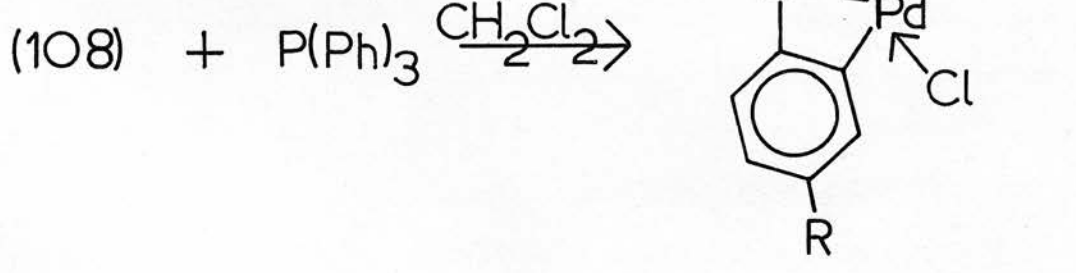
(107)
R_1 = H, OCH_3
R_2 = H, OCH_3, $N(CH_3)_2$, CF_3



(116)



(108) M = Pd R=H, OMe
(109), M = Pt



(110) R = H, OMe

A very recent publication has reported[67] the first synthesis of cyclometallated derivatives of N-arylamidines and amidines (106), containing a six-membered metallocyclic ring.

Sulphur Donor Ligands

Carbon disulphide was known to react with metal carbonyls such as nonacarbonyldi-iron[68] and octacarbonyl dicobalt,[69] to afford complexes containing metal-sulphur and, in some cases, metal-carbon bonds. This led Alper and Chan[70, 71] to investigate the reactions of the aromatic thioketone, thiobenzophenone, and its derivatives with nonacarbonyldi-iron and complexes containing metal-carbon and metal-sulphur bonds were obtained.

The cyclometallated products (107) were obtained in reasonable yield by reaction of the thiobenzophenones with the iron carbonyl in benzene at room temperature. This reaction results in reduction of the carbon-sulphur double bond and is thus clearly related to the reaction[15] of benzylideneaniline with nonacarbonyldi-iron.

Alper[3] and his co-workers also obtained cyclometallated thiobenzophenones from reactions of the sulphur ligands with sodium tetrachloropalladate and potassium tetrachloroplatinate. The palladium and platinum complexes (108) and (109) were obtained in good yield in these facile reactions, and characterised directly.

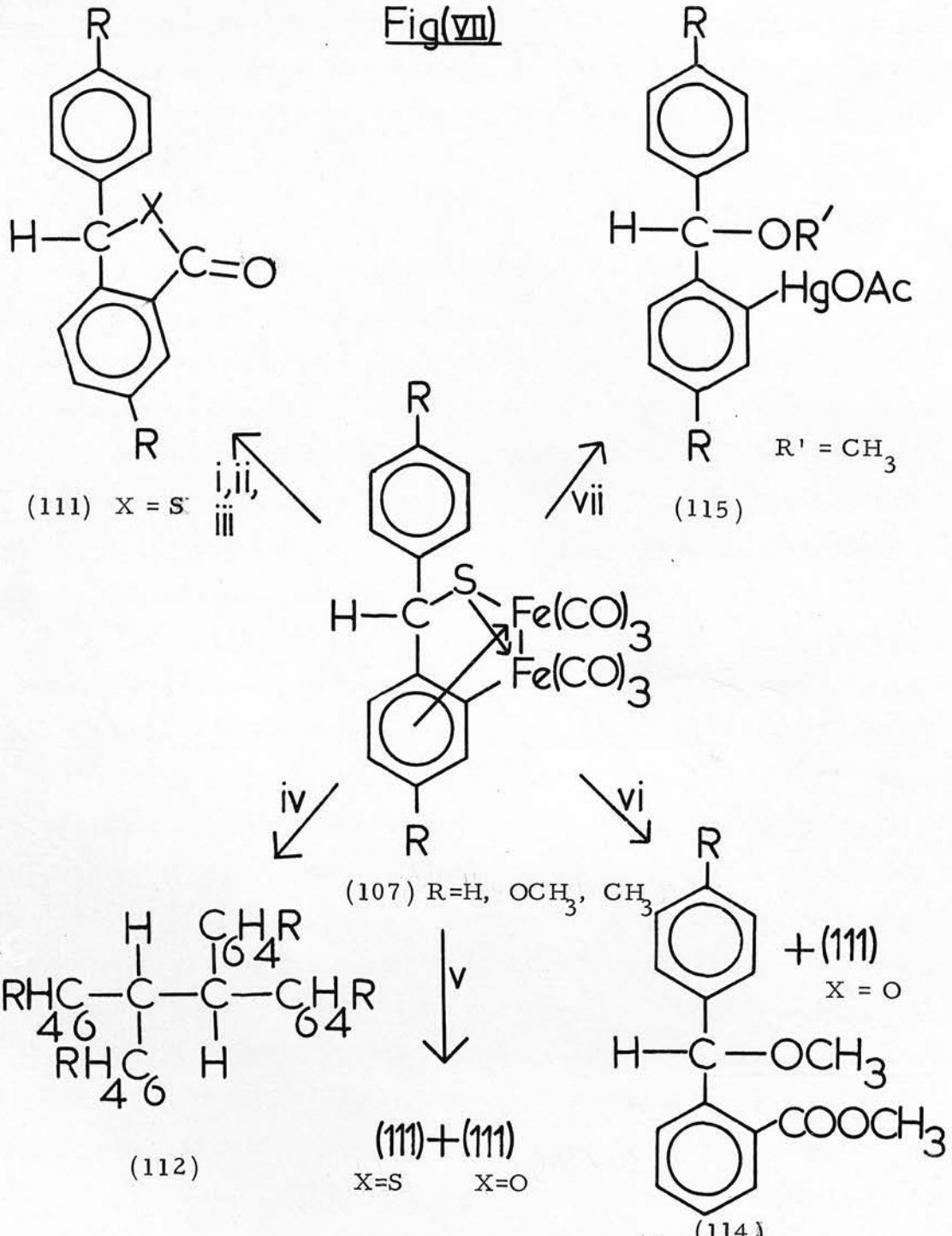
The few other sulphur donor ligands that were investigated[50] by other workers were found to be unreactive to cyclometallation and to date thiobenzophenone and its derivatives are the only sulphur donor ligands known to undergo cyclometallation.

Reactions of Cyclometallated Sulphur-Donor Ligand Complexes

The only simple ligand exchange reaction reported[3] is that of the halogen-bridged complex (108, M=Pd) which is split by triphenylphosphine to give the monomeric complex (110).

A number of reactions involving the iron carbonyl complexes (107) were reported[71, 72, 73] and these are summarised in Fig. (vii).

Fig(VII)

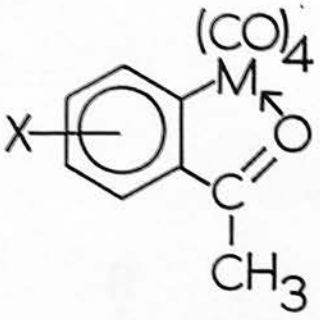


i=OH^-, MeO^-, SCN^-, N_3^-, CNBr; ii=hν or Ce^{4+}

iii=C_2H_5OH, $(C_2H_5)_2NH$, $(i\text{-}C_3H_7)_2NH$, $p\text{-}CH_3C_6H_4NH_2$, $(C_6H_5)_3P$;

iv=$K^{+-}OC(CH_3)_3$; v=$H_2O_2/ClC_6H_4CO_3H$; vi=$Hg(OOCF_3)_2$

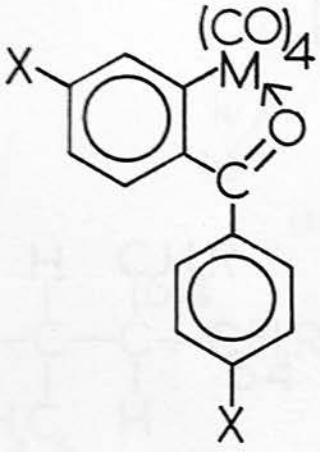
vii=$Hg(OAc)_2/CH_3OH$



(117)

X = H; M = Mn or Re

X = 3-CH_3, 4-CH_3, 5-CH_3,
3-OCH_3, 4-OCH_3, 5-OCH_3,
4-Cl; M = Mn

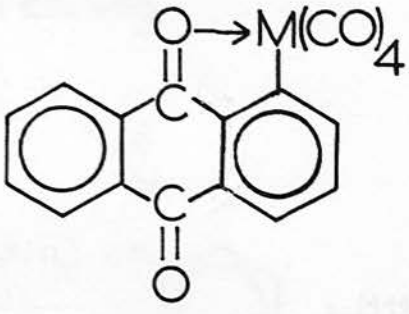


(118)

X = H; M = Mn or Re

X = CH_3, OCH_3, F, Cl;

M = Mn



(119)

M = Re

Carbonyl insertion products (111, X=S) were formed when the complexes were treated with Lewis bases, cerium(IV)salts, or cyanogen bromide. Photolysis of the complexes also yielded the same products.

The reaction of the iron complexes with potassium tert-butoxide in tertiary butanol resulted in the formation of the tetra-arylethane compounds (112).

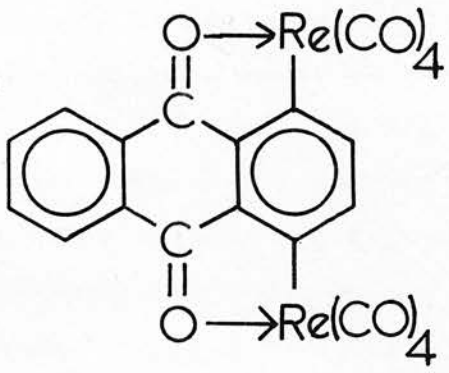
Lactones (111, X=O) and esters (114) were obtained by treatment of the iron complexes with mercuric trifluoroacetate, while mercuric acetate gave the ortho-mercurated methyl ethers (115). Treatment with the peroxidic oxidants, hydrogen peroxide or m-chloroperbenzoic acid gave mixtures of the lactones (111, X=O) and the thiolactones (111, X=S).

The carbonyl insertion, desulphurisation and metal-exchange reactions, shown in Fig.(vii), demonstrate the potential synthetic value of cyclometallated complexes containing sulphur donor ligands.

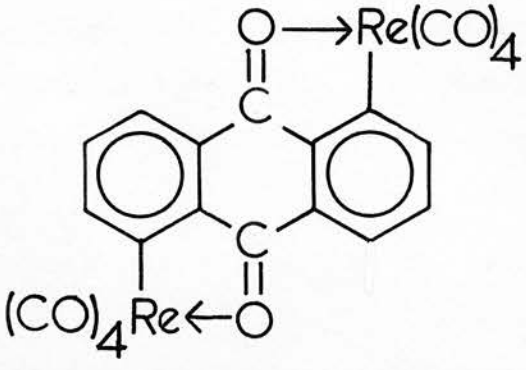
Oxygen Donor Ligands

The ortho-directing effects of oxygen functional groups in the metallation of aromatic rings by complexes of the main group metals, such as lithium[74] or thallium,[75] are well established. Similar effects in cyclometallation by complexes of the transition metals were restricted to compounds with functional groups containing nitrogen, phosphorus, or sulphur, until McKinney[4, 76] and his co-workers reported the metallation of aromatic ketones and of anthraquinone with methylpentacarbonyl-manganese or -rhenium.

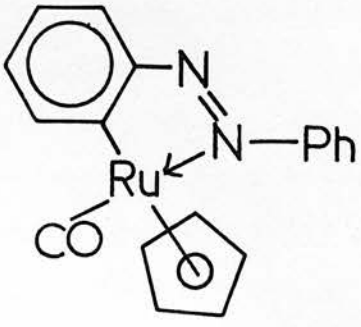
The products (117), (118) and (119) obtained, contained a tetracarbonyl-manganese or -rhenium group coordinated to the oxygen atom of the acyl group as part of a five-membered ring also containing a metal to carbon bond. A crystallographic study of the representative compound (117, X=H; M=Mn) was carried out[77] and confirmed the metallocyclic structure described.



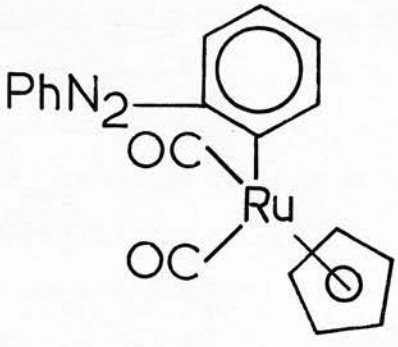
(120)



(121)



(123)



(124)

Substituent effects were observed in the metallation reactions of acetophenones. The methyl group in m-methylacetophenone directed the metal principally to a position para to itself whereas the methoxy group in m-methoxyacetophenone directed the metal principally to a position ortho- to itself.

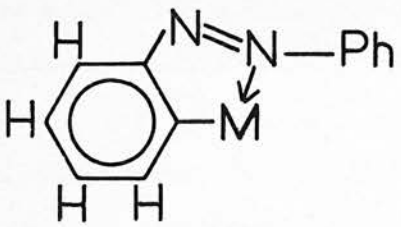
Metallation reactions of anthraquinone with methylpentacarbonylrhenium gave not only the monometallated product (119), but also the bimetallated isomers (120) and (121). Of these, the one containing both rhenium atoms substituted on the same aromatic ring seemed to be less favoured, in contrast to Trofimenko's[50] earlier observations in the cyclopalladation of aromatic diamines where facile formation of complexes with two palladium atoms bonded to the same aromatic ring was observed.

All the products obtained were characterised directly by mass, infrared and ^{1}H n.m.r. spectroscopy but, to date, no reactions of these cyclometallated complexes have been reported.

^{1}H and ^{13}C N.m.r. Studies of Cyclometallated Complexes

Bruce[17] investigated the ^{1}H n.m.r. spectra of several phenylazophenyl complexes (122) and found that, in the aromatic region, these complexes exhibit four relatively well defined resonances, together with a fifth resonance which usually partially overlaps one or two of the others. In the best resolved spectra each of the four resonances gave four- or eight-line signals, and this was consistent with the presence of an AMPX system. Double resonance experiments allowed the signals to be assigned. The signal due to the proton on the carbon atom ortho- to the metal occurred at lowest field, and the fifth, broad resonance was assigned to the phenyl group not involved in bonding to the metal.

Other features of the ^{1}H n.m.r. spectra confirmed the structures assigned, such as the spectra of the cyclopentadienyl-iron and -ruthenium complexes exhibiting singlets at 5.6τ assigned



(122)

M = $Mn(CO)_4$
$Re(CO)_4$
$Mn(CO)_3PPh_3$
$Fe(CO)(C_5H_5)$
$Ni(C_5H_5)$
$Mo(CO)_2(C_5H_5)$
$Fe(PPh_3)(C_5H_5)$

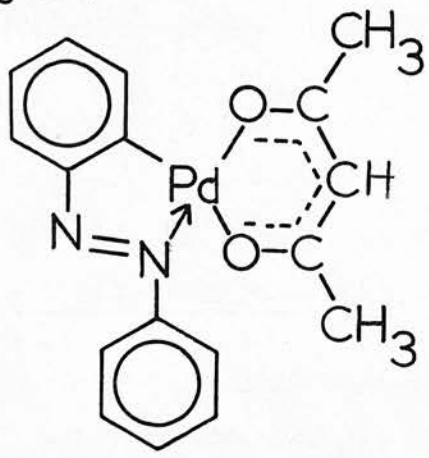
to the C_5H_5 group and the manganese phosphine complex showing further fine structure, due to phosphorus-hydrogen coupling.

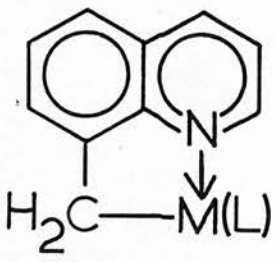
A further study by Bruce[16] and his co-workers on twelve ruthenium complexes, containing chelated phenylazophenyl ligands, was reported. Again the resonances arising from the chelating phenylazophenyl ligand occurred in the region 1.7-3.0τ, as four more or less well-resolved multiplets, together with a broad complex multiplet for the protons of the unsubstituted phenyl ring at 2.6τ. The four protons on the ortho-metallated ring formed a first order AMPX system. Theoretically each proton should have given rise to an eight-line multiplet, but, generally, somewhat broadened quartets were observed.

The differences between the chelated and the only σ-bonded ligands in (123) and (124) were shown in their respective proton n.m.r. spectra. The chelated ligand showed resonances in the usual positions, but the chemical shifts of the protons in the σ-bonded ligand were shifted upfield by ca 0.5 p.p.m.

The ^1H n.m.r. spectra of a number of Schiff's base complexes were also investigated[42] and found to show several features common to those of phenylazophenyl complexes. However, the separation of the resonances of the ortho-metallated ring was not as great, probably owing to the relative lack of shielding by the CH group as compared to the lone pair of the uncoordinated nitrogen of the phenylazophenyl ligand. As with azobenzene complexes the resonance of the unsubstituted phenyl group overlaps the other aromatic resonances.

Fig (VIII)

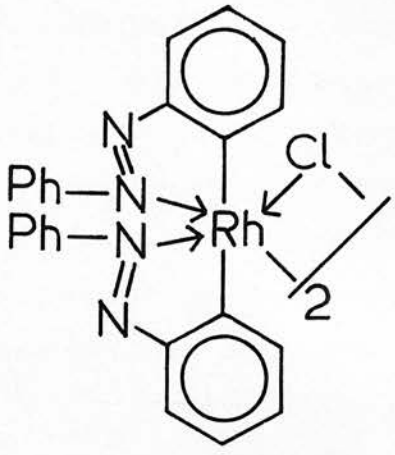


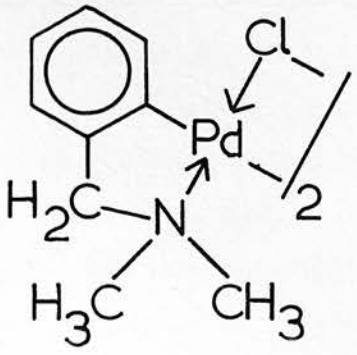


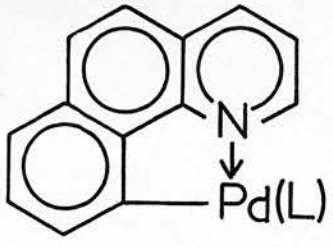
M = Pd, L = acac

M = Mo, L = $Cp(CO)_2$

M = Pt, L = (Br) (HPh_3)







L = acac or C_5H_5

McKinney[76] and his co-workers reported features similar to those of cyclometallated azobenzene[17] and Schiff's base[42] complexes, in the ^{1}H n.m.r. spectra of their oxygen donor ligand transition metal complexes; the low field signal in the aromatic region was again assigned to the proton ortho- to the metal. The oxygen donor ligand transition metal complexes were found to give well resolved aromatic resonances, and cyclometallated and uncyclometallated products could be easily distinguished by their respective ^{1}H n.m.r. spectra.

The recent development of ^{13}C spectroscopy has provided a sophisticated method of confirming that cyclometallation has occurred. Garber[63] and his co-workers recently described the ^{13}C n.m.r. spectra of a variety of cyclometallated nitrogen donor ligand transition metal complexes. The complexes studied are shown in Fig. (viii).

Although certain features of the ^{1}H n.m.r. spectra appear to be characteristic of ortho- or cyclometallated products as described, these features are not sufficiently distinctive to allow unambiguous confirmation of the presence of carbon-metal σ-bonds. Such evidence was best obtained by X-ray crystallographic study. Garber, however, using ^{13}C n.m.r. spectroscopy, showed that it can be readily determined whether or not cyclometallation has occurred via the ^{13}C n.m.r. spectrum of a given complex. The complexes shown in Fig. (viii) were examined by ^{13}C n.m.r., the total number of expected aromatic quaternary and CH carbon atom resonances being determined. This was done by comparison of the noise-decoupled and the single frequency off-resonance decoupled spectra of each complex. In this way it was established that cyclometallation of the said complexes had occurred since each exhibited one quaternary carbon resonance more and one CH resonance less than were present in the free ligand. In those cases where metal-^{13}C coupling was observed further evidence of metal-carbon σ-bond formation was obtained.

Thus both ^{1}H and ^{13}C n.m.r. spectroscopy are useful diagnostic methods, in the characterisation of cyclometallated products.

DISCUSSION

Aim of Research

The object of this research was to synthesise heterocyclic compounds which were difficult and, in some cases, impossible to prepare by existing organic routes, *via* isolable organometallic intermediates. It was intended to replace the metal in cyclometallated complexes of azobenzene, 2-phenylpyridine, 2-styrylpyridine, benzylideneaniline and quinolizine-4-thione in order to provide a source of substituted organic products which could be used for the syntheses of heterocycles. In some cases direct conversion to a heterocycle was envisaged as a possibility.

One of the main areas of interest involved the possible replacement of palladium by sulphur in cyclopalladated complexes of 2-phenylpyridine and benzylideneaniline, thus providing convenient routes to benzisothiazole and isothiazolopyridinium systems. Dr. G. Abbot, working in this department, had previously developed a purely organic route to isothiazolo[2, 3-*a*]pyridinium salts but this route was not readily capable of extension to the benzo-fused analogues which, it was hoped, might be available *via* organometallic intermediates.

Another area of particular interest concerned the sulphur donor ligand quinolizine-4-thione. Previous attempts to use this compound as a precursor in the syntheses of certain cyclazines had been frustrated by the fact that the 6-position of the ring system could not be functionalised. It seemed possible that substitution of a good leaving group for the metal in a cyclometallated complex of this ligand might lead to a suitable precursor.

It had been intended originally to investigate the metal replacement reactions of not only palladium but also nickel, iron and mercury complexes. It was also hoped to introduce other non-metallic atoms and groups in addition to sulphur. However, owing to difficulties encountered in obtaining cyclometallated complexes of other metals, our study was confined to cyclopalladated complexes. Further difficulties in achieving facile metal replacement reactions meant that

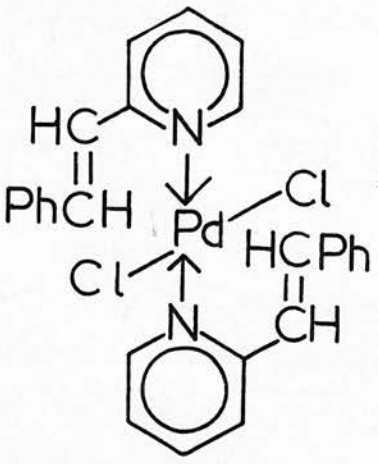
little work was done on the introduction of non-metallic atoms other than sulphur; limited studies on the introduction of phosphorus and of bromine were carried out.

1. Synthesis of Dimeric Halogen-bridged Cyclopalladated Complexes of Azobenzene, 2-Phenylpyridine, 2-Styryl-pyridine, Benzylideneaniline and Quinolizine-4-thione.

Azobenzene and 2-phenylpyridine were previously shown by Cope[2] and Kasahara[51] respectively, to undergo direct cyclo-palladation reactions on treatment with sodium tetrachloro-palladate thus giving the halogen-bridged dimeric complexes, (14) and (91), earlier described. Benzylideneaniline, on the other hand, was reported[40] to give only the cis- and trans-isomers (55) and (56) of the simple coordination complex containing no carbon-metal bonds. The cyclopalladated complex (53) was obtained indirectly, however, by Onoue and Moritani,[39] from the metathetic reaction of the corresponding acetate complex with sodium chloride. Neither 2-styrylpyridine nor the sulphur donor ligand, quinolizine-4-thione, had been previously reported to form cyclometallated complexes with transition metals.

The cyclopalladated azobenzene and 2-phenylpyridine complexes were obtained by the literature methods already described.

The benzylideneaniline complex (53) was prepared directly *via* the reaction of equimolar amounts of sodium acetate and palladium chloride with benzylideneaniline in refluxing acetic acid. The reaction produced a mixture of three products which were purified and examined. The mass spectrum of the major product showed a parent ion at m/e 644 consistent with the molecular weight of the cyclometallated halogen-bridged dimer and a satisfactory carbon, hydrogen, and nitrogen elemental analysis was obtained. Comparison of the infrared spectrum with that of an authentic sample made *via* Onoue's[39] indirect route, confirmed that the two were identical. The ^{1}H n.m.r. was not very well resolved but a singlet downfield from the other signals was assigned to the methine proton and integration against the aromatic resonances was consistent for the *ortho*-metallated benzylideneaniline complex proposed. The minor products were similar in infrared spectra



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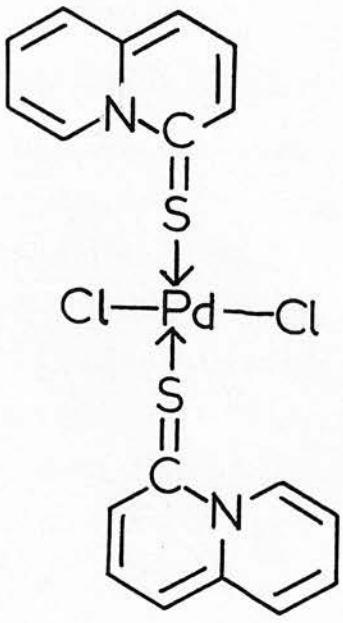
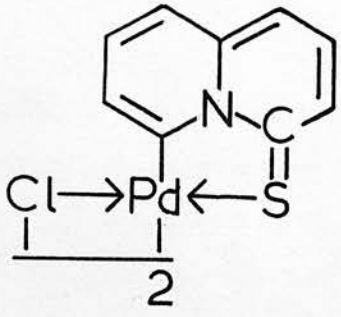


(126)



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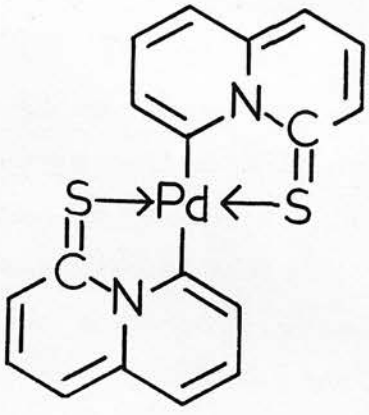


(128)

not only to each other but also to the simple coordination complexes reported by Lewis,[40] and they were assumed to be mixtures of the stereoisomeric, bis(benzylideneaniline) palladium dichlorides (55) and (56). These were not further investigated.

It was also shown that 2-phenylpyridine could be cyclopalladated by this method but yields were considerably lower than those obtained by Kasahara's[51] method.

An attempt to cyclopalladate 2-styrylpyridine with sodium tetrachloropalladate in methanol led only to the bis(styrylpyridine) palladium dichloride complex (125) and no evidence for the formation of the cyclometallated compound was obtained.

The reactions of the sulphur donor ligand, quinolizine-4-thione, with both sodium tetrachloropalladate and sodium acetate-palladium chloride, were investigated. The reaction of the thione with sodium acetate and palladium chloride gave a bright yellow solid as the major product. Elemental analysis of the compound was consistent with a non-cyclometallated structure and very close to the analysis required for the simple sulphur-metal bonded co-ordination complex (126). A ^{1}H n.m.r. spectrum of the compound, which was sparingly soluble in dimethyl sulphoxide, showed a resonance at δ10.3 which was assigned to the proton on the 6-position of the quinolizine ligand. This proton resonated at δ10.6 in the spectrum of the free ligand and thus had been shifted upfield on formation of the complex by ca 0.3 p.p.m.

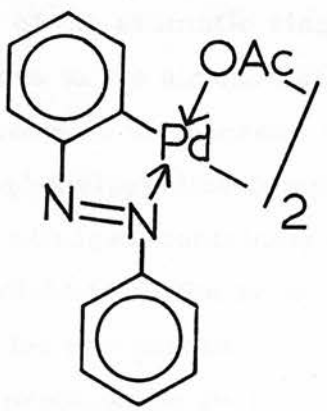
A subsequent reaction of quinolizine-4-thione with sodium tetrachloropalladate yielded a russet-brown insoluble solid product. After purification by Soxhlet-extraction with methanol, elemental analysis gave results consistent with that of the required cyclometallated complex (127). The mass spectrum showed a parent ion at m/e 426, which corresponded to the bis(quinolizine-4-thione) palladium complex (128) but this structure was discounted on the basis of the analytical data obtained. The compound was sparingly soluble in dimethyl sulphoxide and gave a very weak and poorly

resolved ^{1}H n.m.r. spectrum which, while showing no sign of the quinolizine 6-proton at low field, was not entirely satisfactory.

2. Syntheses and Attempted Syntheses of Acetate-bridged Complexes

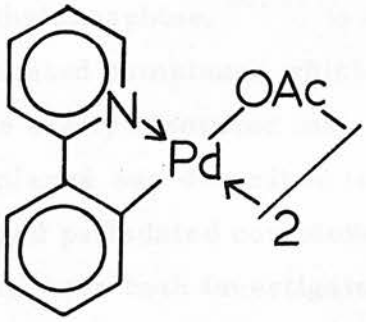
Only the di-μ-acetatobis(benzylideneaniline)dipalladium complex (54) had been reported[39] prior to this investigation.

The azobenzene-palladium acetate complex (46) was obtained in good yield by the reaction of palladium acetate with azobenzene in refluxing acetic acid. The dark red crystalline complex was soluble in organic solvents and was fully characterised by its mass, infrared and ^{1}H n.m.r. spectra together with an elemental analysis which was consistent with the proposed structure. Heck later described[33] the same compound obtained from the same reagents but in methanol instead of acetic acid. The physical and spectral properties observed by Heck compare favourably with those of our complex. The ^{1}H n.m.r. spectrum of the complex was not well-resolved in the aromatic region and did not clearly show four well-resolved resonances overlapped by a fifth broader one, as reported by Bruce[17] for a series of cyclometallated azobenzene complexes of trasition metals. This finding did however correspond to Bruce's[16] for the analogous azobenzene-ruthenium acetate complex, which had also given a poorly resolved ^{1}H n.m.r. spectrum.

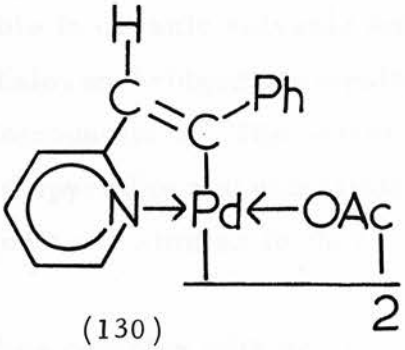


(46)

2-Phenylpyridine reacted under the same conditions to give the readily characterisable di-μ-acetatobis(2-phenylpyridine) dipalladium complex (129) in good yield. Mass spectral evidence was consistent with a dimeric structure analogous to that of the azobenzene complex and a better-resolved ^{1}H n.m.r. spectrum was obtained. In contrast to the spectra of azobenzene complexes, however, the resonance at lowest field was assigned to the *α*-pyridyl proton of the unsubstituted ring instead of to the proton ortho- to the metallated carbon atom of the phenyl ring. The *α*-pyridyl proton resonance, which was present at δ7.8, had been shifted upfield from δ8.4 in the spectrum of the free ligand.



(129)



(130)

The related ligand, 2-styrylpyridine, gave a low yield of the cyclopalladated complex (130) on reaction and work-up under similar conditions. By using silica instead of alumina for chromatographic isolation of the product, a higher yield was obtained. The ^{1}H n.m.r. spectrum was not well resolved and it was noticeable that the resonances of the aromatic rings were much closer together. This was probably due to the absence of any strongly shielding or deshielding substituents in the benzene ring which, unlike those in the azobenzene and phenylpyridine complexes, is not directly joined to the metal or to a nitrogen-containing double bond. The olefinic proton resonated upfield from the aromatic protons at δ5.40 as a singlet, integrating for one proton.

Attempts to prepare the cyclometallated quinolizine-4-thione-

palladium acetate complex were inconclusive since the products could not be identified owing to their insolubility in organic solvents.

The proton resonances in the n.m.r. spectra of the four ligands were all shifted upfield by complexing with palladium acetate. Mass spectral and elemental analytical evidence were consistent with the dimeric acetate-bridged compounds described.

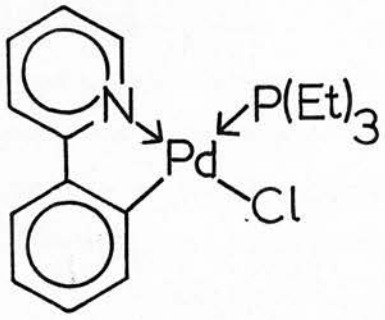
3. Conversion of the Dimeric Halide- and Acetate-bridged Complexes into Monomeric Phosphine Complexes.

Previous work on the use of bridge-splitting agents, such as triethylphosphine,[26, 27] to obtain monomeric derivatives of cyclopalladated complexes which were soluble in organic solvents and more easily identified than the initial halogen-bridged cyclopalladated complexes was described fully in the introduction. The halogen-bridged palladated complexes of 2-phenylpyridine and quinolizine-4-thione were both investigated under conditions similar to those earlier referred to.

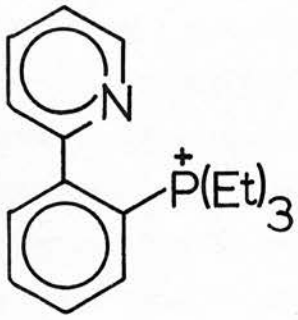
The reaction of the phenylpyridine complex with one mole of triethylphosphine in dichloromethane gave one product, a pale yellow crystalline solid. The compound was readily characterised by spectroscopic and analytical methods and identified as the monomeric triethylphosphine complex (131). An interesting feature of the mass spectrum was the presence of a very strong m/e 272 peak which corresponded to the 2-(2-pyridyl)phenylphosphonium cation (132). This compound was obviously being formed in the mass spectrometer perhaps by way of the scheme shown below.

$$[LPdP(Et)_3Cl]^{+\cdot} \longrightarrow LPEt_3^{+} + Pd(0) + Cl\cdot$$

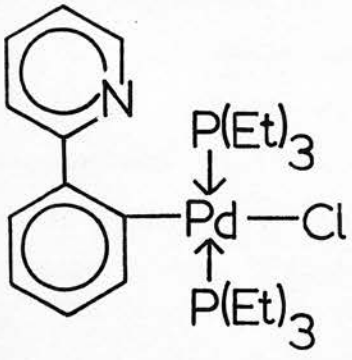
When the reaction was repeated using an excess of triethylphosphine under the same conditions, two products were obtained, one of which was identified as the mono-triethylphosphine complex



(131)



(132)



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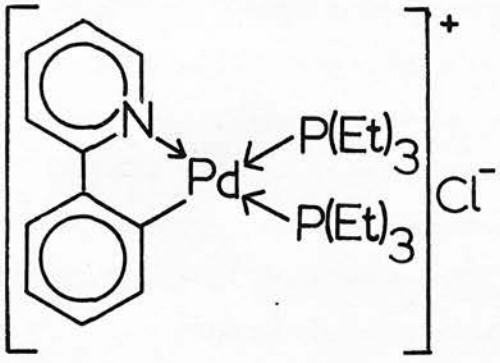
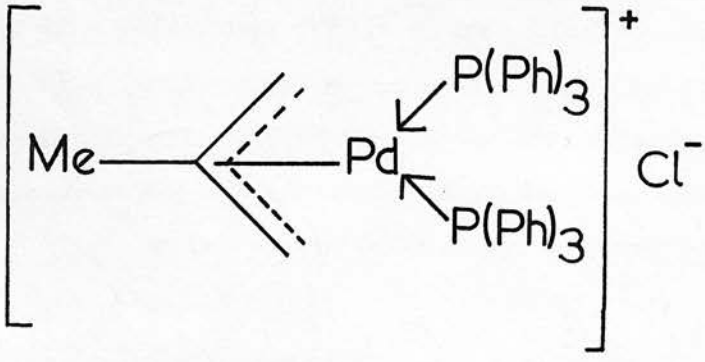


(134)



(135)

(131), previously obtained in the stoicheometric reaction. The other product, a white crystalline solid, differed in infrared spectrum and melting point. Elemental analysis gave results consistent with either the bis(phosphine) complex of type (133)* or the cationic complex (134). Similar cationic complexes of the 2-methylallyl ligand have been isolated by Powell and Shaw[78] (135).

The ^{1}H n.m.r. spectrum of the mono-triethylphosphine complex was consistent with the proposed structure, showing one aromatic proton further downfield than the others. This resonance, at δ9.5, was assigned to the α-proton of the pyridyl ring. The proton spectrum of the white crystalline solid, on the other hand, appeared to indicate a mixture of compounds. Two low field proton resonances were present and complex multiplets for the other aromatics and the aliphatic protons, all suggested that a mixture of compounds had formed in solution.

The proton resonance at lowest field corresponded to that of the α-pyridyl proton of the mono-triethylphosphine complex, at δ9.5, as earlier described. The other resonance upfield of this at δ8.7 suggested an α-pyridyl proton with no metal-nitrogen coordination.

The two α-pyridyl protons could be accounted for in two ways. In the first, a phosphine dissociation reaction might have occurred when the bis(phosphine) complex was dissolved into solution as shown below. Thus two α-pyridyl proton resonances would be observed, one for the monophosphine complex with metal-nitrogen coordination and one for the bis(phosphine) complex which lacks metal-nitrogen coordination. The other possibility is that an equilibrating mixture of the neutral and the cationic bis(phosphine)

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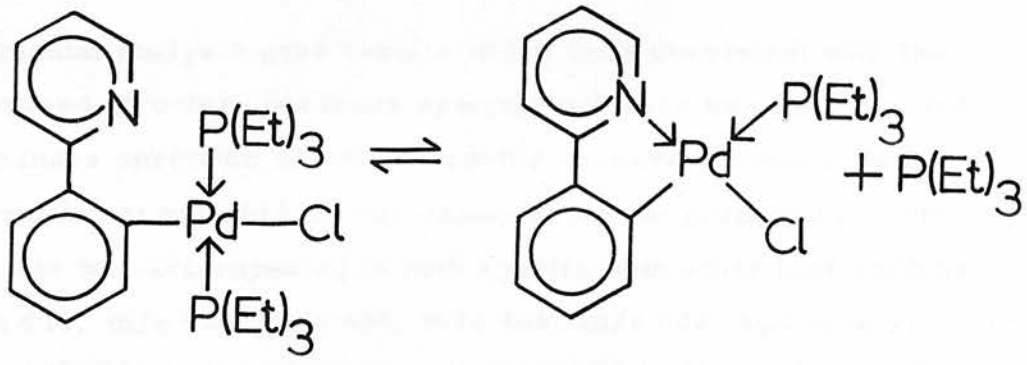
* Footnote: The geometry of the ligands in this complex and in all others, unless precisely stated to the contrary, has not been determined and the way in which these complexes are depicted is purely for convenience.



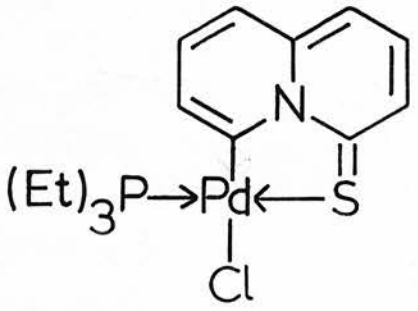
(133) (131)

complexes (133) and (134) was present in solution, again causing the features observed in the ^{1}H n.m.r. spectrum.

Recovery of the sample, which had been used for the ^{1}H n.m.r. spectrum, resulted in isolation of the monophosphine complex together with free triethylphosphine, thus suggesting that the first explanation of phosphine dissociation was more probable. The white compound was converted to the monophosphine complex simply by heating in solution, triethylphosphine being liberated, thus further illustrating the lability of the phosphine ligand.

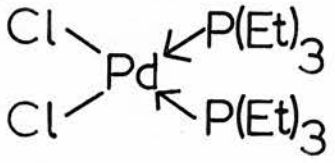
Treatment of the halogen-bridged palladated quinolizine-4-thione complex with triethylphosphine, in amount equivalent to one phosphine per palladium atom, gave two yellow crystalline compounds which were separable by chromatography but identical physically and spectroscopically. This suggested the products were isomers one with chlorine cis- to the carbon-metal bond and one with chlorine trans-. The ^{1}H n.m.r. spectra, which were identical, were consistent with the cyclometallated monophosphine structure (136). In both spectra, a proton resonance at δ8.9, downfield of the rest of the aromatic protons, was observed and this was assigned, tentatively, to the proton ortho- to the metallated 6-carbon atom of the quinolizine ring. In the spectrum of the bis(quinolizine-4-thione) palladium dichloride complex (126) detailed earlier, the proton on the 6-carbon of the ring system was observed as a singlet at δ10.3, thus suggesting the absence of the 6-proton in the phosphine complex which must therefore be metallated at the 6-position. An

elemental analysis gave results which were consistent with the proposed structure but mass spectral evidence was inconclusive. The mass spectrum of both suspected isomers showed a weak parent ion at m/e 419 as was expected for the proposed structure but this was accompanied in both spectra with other ions such as m/e 414, m/e 426, m/e 458, m/e 466, m/e 602, and m/e 512. The m/e 426 peak was consistent with the bis(quinolizine-4-thione) palladium complex earlier described (128) but this structure could be discounted on the basis of analytical and n.m.r. results. The other ions could not be assigned to any particular structure and it was assumed that decomposition of the phosphine in the mass spectrometer was occurring and that subsequent fragment-coupling was being observed, accounting for these unexplained ions.



(136)

Several attempts to repeat this reaction were made and, in every case, without success. The bis(quinolizine-4-thione) complex (126), previously described, was found to be one of the products of these reactions, the other being bis(triethylphosphine) palladium (II)dichloride (137), identified by melting point, infrared and ^{1}H n.m.r. spectroscopy. No satisfactory explanation has been found as yet to account for these anomalous observations.



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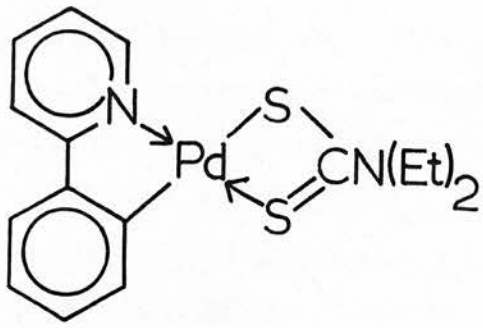
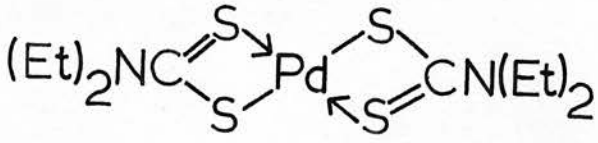
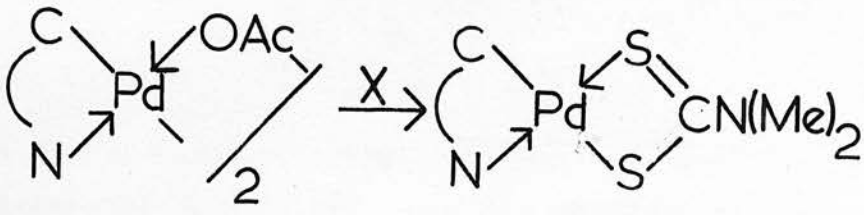


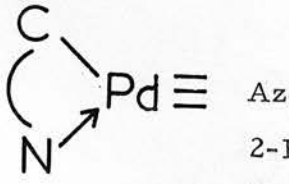
(138)



(139)



(140)



Azobenzene (140)
2-Phenylpyridine (140a)
Benzylideneaniline (140b)
2-Styrylpyridine (140c)

Cyclometallated by Palladium

$X = NEt_4^{\oplus}\ S_2CN(Me)_2^{\ominus}$

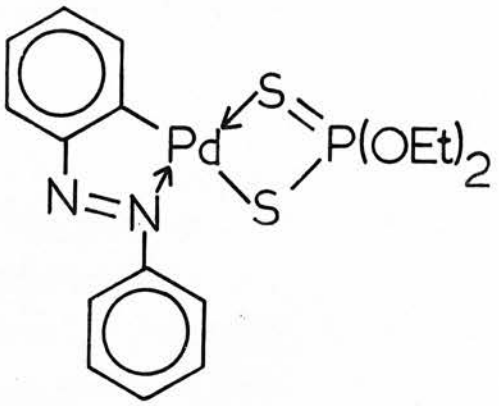
4. Synthesis of Dithiocarbamato-derivatives of Cyclo-palladated Complexes.

Attempts to make the monomeric diethyldithiocarbamato (2-phenylpyridine) palladium (II) complex (138) by reaction of the halogen-bridged dimer (91) with sodium diethyldithiocarbamate in acetone, were unsuccessful. A mixture of the desired product and bis(diethyldithiocarbamato) palladium (139) was obtained. Attempts to separate them were unsuccessful. The mass spectrum of the mixture showed the parent ions of both complexes and the ^{1}H n.m.r. spectrum showed two quartets and two triplets indicating the presence of ethyl groups in two different environments. The insolubility of the halogen-bridged complex was thought to be the main reason for the formation of the bis(dithiocarbamato) complex; the initially formed complex (138) being relatively soluble, would have a greater opportunity to react with another dithiocarbamato-ion than would the remaining insoluble dimer.

Thus it was decided to investigate the reaction of the dimeric acetate complexes, which were more soluble. In order to avoid the presence of water, which might have been the source of the proton required for regeneration of 2-phenylpyridine from its metallated complex, the hydrated sodium salt of the diethyldithio-carbamate was replaced by anhydrous tetraethylammonium dimethyldithiocarbamate and chloroform was used as the solvent in place of the less easily dried acetone. Facile exchange reactions were achieved at room temperature and the benzylideneaniline, azobenzene, styrylpyridine and phenylpyridine complexes were all isolated in good yield and fully characterised (140). Mass spectra of the complexes showed the expected parent ion masses and the ^{1}H n.m.r. spectra, which were better resolved than those of the corresponding acetate complexes, were consistent with the structures proposed. The non-equivalence of the two N-Me groups was shown by two closely grouped singlets in the region δ3.0-3.5.

The azobenzene-diethyldithiophosphato complex (141) was

prepared in the same way by reacting the corresponding acetate complex with tetraethylammonium diethyldithiophosphate.

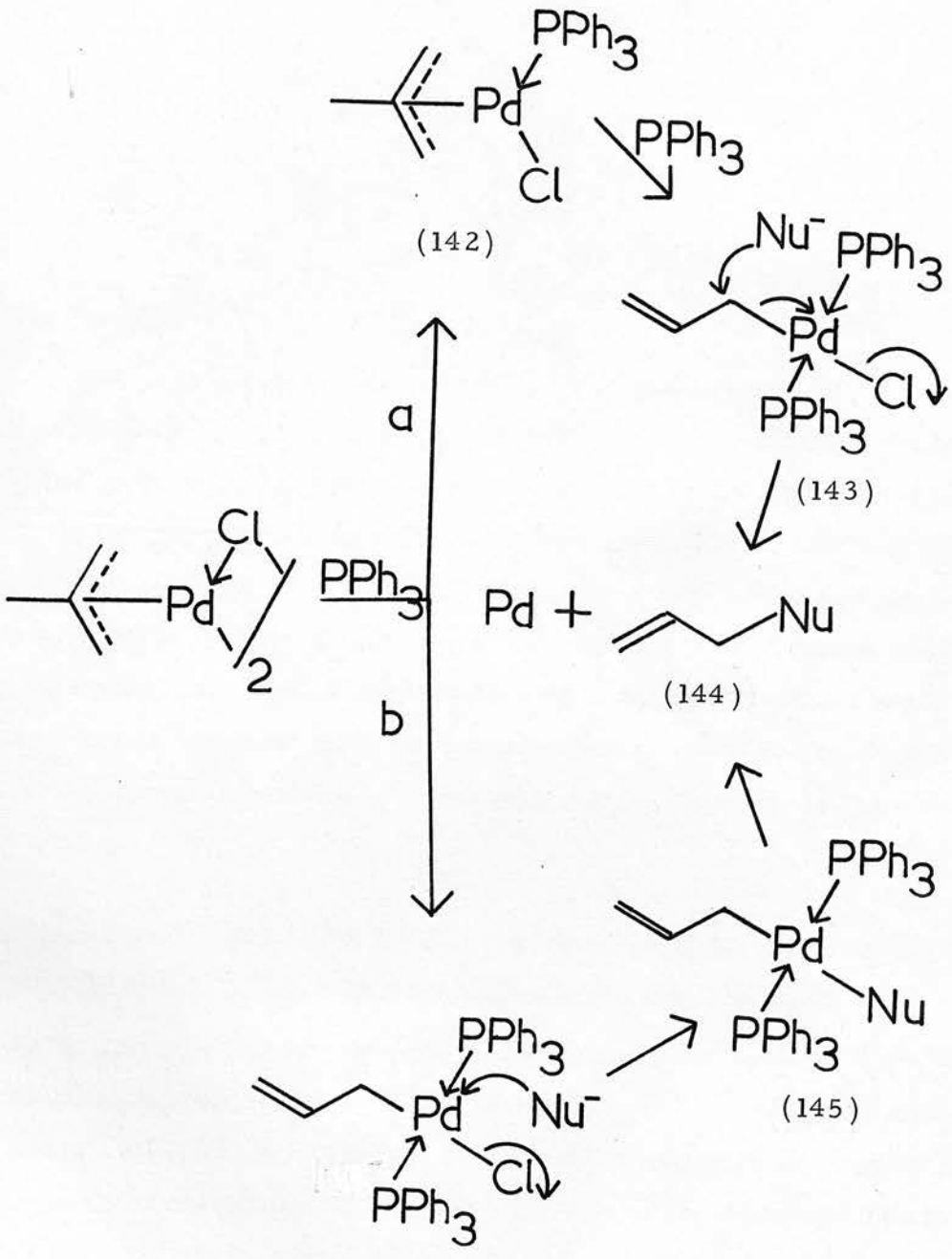


(141)

More recently it was found possible to prepare the phenylpyridine-dimethyldithiocarbamato-complex (140a) from the halogen-bridged dimer which was treated with sodium dimethyldithiocarbamate in dimethylformamide at room temperature. The yield was somewhat lower than that obtained via the acetate complex. This method, if investigated more thoroughly with other ligands, might be found a more convenient route to dithiocarbamatopalladium complexes of other nitrogen and, possibly, sulphur donor ligands, since it obviates the need to prepare palladium acetate.

5. Types of Reactions likely to be effective in the Utilisation of Cyclometallated Complexes as Synthetic Intermediates.

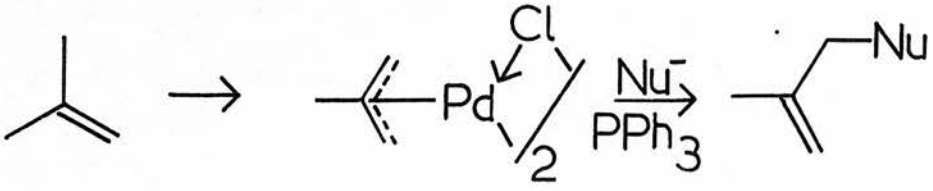
The types of reactions of organotransition-metal complexes which were considered likely to be of use in achieving the main objective of this investigation (viz. replacement of palladium by non-metallic atoms, notably sulphur) may be conveniently grouped into three main categories, depending on the type of reagent, nucleophilic, free radical, or electrophilic, involved in the displacement of the metal. It is also necessary to consider two other types of reactions common among transition metal complexes, reductive elimination and oxidative addition. One or both of these processes might be involved as a step in the overall reaction, irrespective of the type of reagent


PPh3
Pd
Cl
PPh3
(142)
Nu⁻
PPh3
Pd
Cl
PPh3
(143)
a
Cl
Pd
2
PPh3
Pd +
Nu
(144)
b
PPh3
Pd
Nu
PPh3
(145)
PPh3
Pd
Nu⁻
Cl
PPh3

initially employed. It is perhaps useful to look at some examples of these types of reaction before discussing the reactions of the cyclopalladated complexes described earlier.

In synthetic reactions involving palladium, activation of simple molecules such as hydrogen, carbon monoxide, olefins, acetylenes, aromatic compounds and other compounds having active hydrogens, has been observed to take place upon coordination. Palladium (II) has been shown to be readily reduced to the zero-valent state, oxidising coordinated molecules, and by this property, unique oxidation with palladium (II) has been possible.

An example of such activation and subsequent nucleophilic attack at a carbon-palladium bond was reported by Trost and Fullerton.[79] The reaction of a π-allyl palladium chloride dimer with diethyl malonate carbanion, in the presence of excess triphenylphosphine, gave alkylated products as shown below.

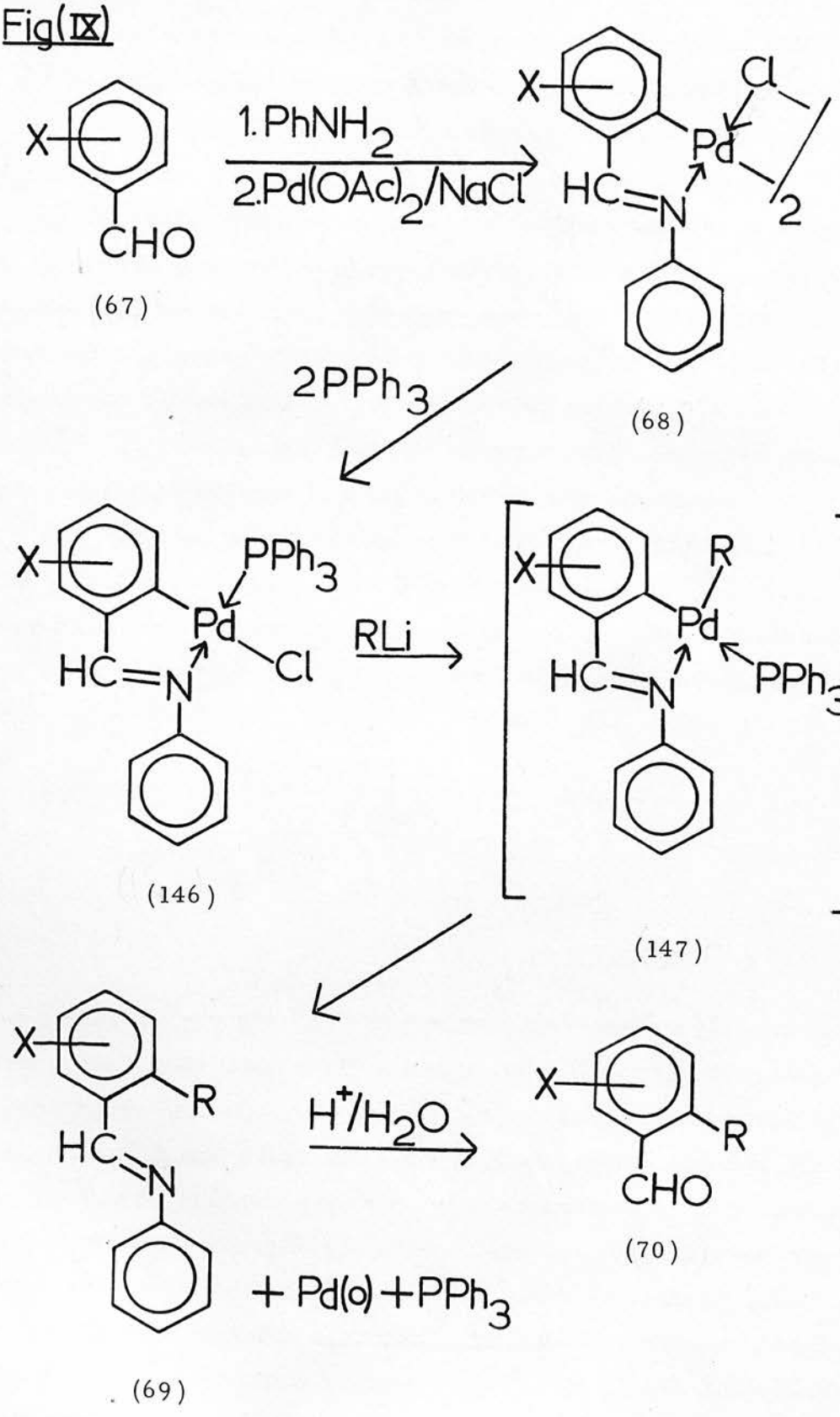


$Nu^- = {}^-CH(CO_2Et)_2$

Presumably a bridge-splitting reaction of triphenylphosphine gives the monophosphine π-allyl complex (142) which then reacts with another mole of phosphine to give the diphosphine σ-allyl complex (143). Nucleophilic attack by malonate carbanion at the metallated carbon would then produce the alkylated product (144) and palladium metal as shown in (route a). Alternatively, the carbanion might initially displace chloride giving a complex (145) containing two palladium-carbon σ-bonds, which then undergo reductive elimination (route b). Thus Trost and Fullerton's work illustrates the practicality of nucleophilic substitution reactions with organo-palladium complexes.

Another nucleophilic displacement of palladium which is

Fig(IX)



(67)

(68)

(146)

(147)

(70)

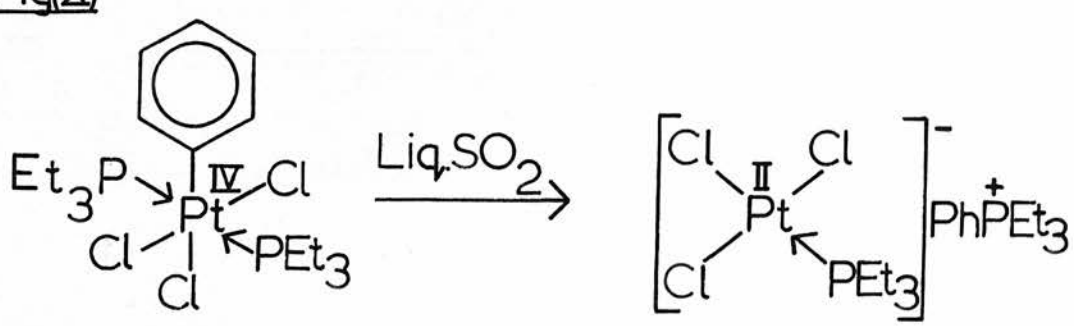
(69)

believed to involve reductive elimination is the synthesis of ortho-alkylbenzaldehydes, reported by Murahashi and co-workers[44] and detailed fully in the introduction. The reaction sequence is summarised in Fig. (IX). Schiff's bases, prepared from aromatic aldehydes, were cyclometallated by palladium acetate and the acetate-bridged products then converted to the chloride-bridged analogues. On treatment of halogen-bridged complexes with two equivalents of triphenylphosphine in the presence of an alkyllithium, the ortho-substituted Schiff's bases (69) were isolated together with palladium metal. The alkylated Schiff's bases prepared by this method were then hydrolysed to give the appropriately substituted ortho-alkylbenzaldehydes.

Murahashi suggested that addition of one mole of phosphine gave the monomeric complex (146) and that subsequent ligand exchange of alkyl for chlorine, using alkyllithium, afforded the intermediate (147) which then reductively eliminated to give palladium (o) and the ligand coupled product (69).

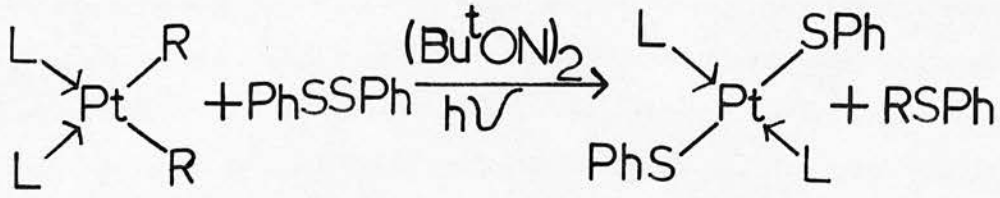
Another example of reductive elimination which is relevant to the subsequent discussion was reported by Coulson[80] and involves the conversion of a platinum (IV) species to platinum (II). On attempting to react the platinum (IV) complex (148) with sulphur dioxide, Coulson observed a novel rearrangement which is shown in Fig. (X). The product of the rearrangement was the complex salt (149) which comprised an anionic platinum (II) species and the phenyltriethylphosphonium cation. Reductive elimination in the platinum (IV) complex resulted in reduction of platinum (IV) to platinum (II) and formation of the ligand-coupled phosphonium cation.

Fig(X)



(148) (149)

Fig(XI)



(150) (151) (152)

L=PMe_2Ph;

R=Me_3SiCH_2

$$(Bu^tON)_2 \longrightarrow 2Bu^tO\cdot + N_2$$

Initiation: $PhSSPh + X\cdot \longrightarrow PhS\cdot + XSPh$

Propagation: $PhS\cdot + PtL_2R_2 \longrightarrow PtR(SPh)L_2 + R\cdot$

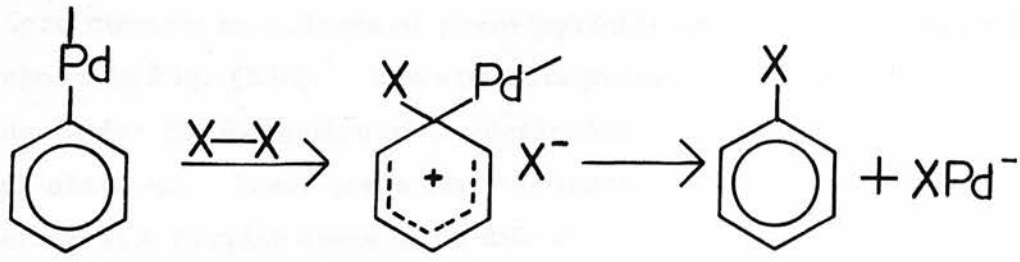
$R\cdot + PhSSPh \longrightarrow RSPh + PhS\cdot$

($X\cdot$=Me· from $Bu^tO\cdot$)

The second type of reaction to be considered involves free radical attack at carbon-transition metal bonds. One example of such a free radical displacement reaction has been reported by Lappert,[81] who observed a bimolecular homolytic substitution in the complex (150) by reaction with diphenyl disulphide in the presence of an initiator, di-t-butyl hyponitrite. The diagrammatic description of both the reaction and its mechanism is summarised in Fig. (XI). The displacement reaction was thought to occur by way of the chain reaction proposed, giving the disubstituted complex (151) and the organic product (152).

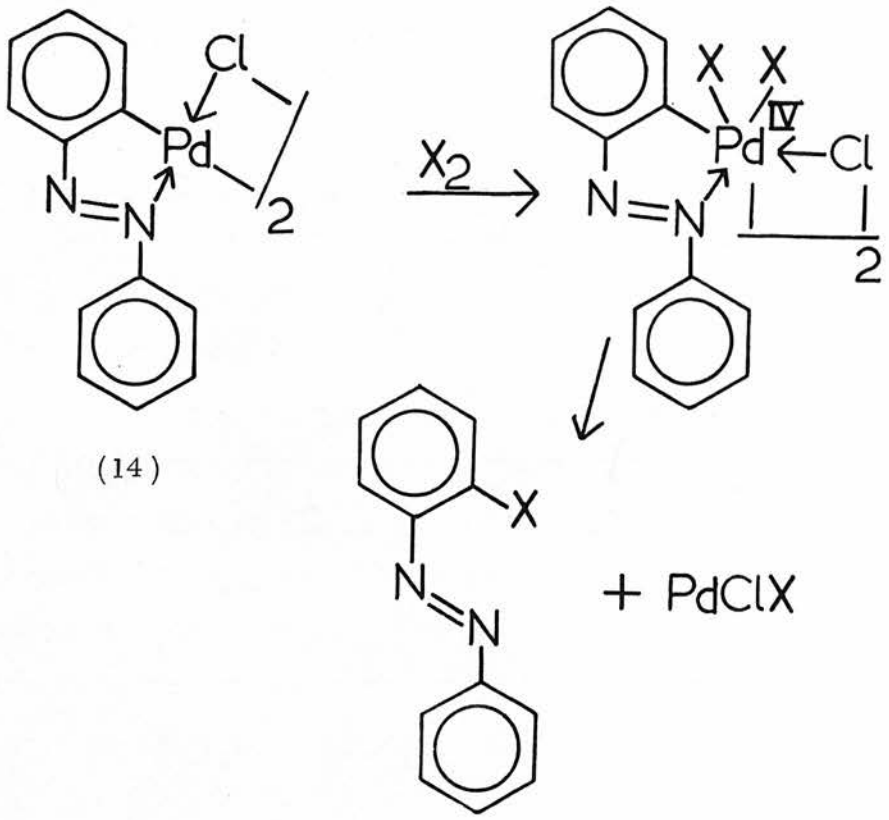
Fahey's work,[31] which was mentioned in the introduction, provides a simple example of a reaction in which a carbon-palladium σ-bond is replaced by a carbon-non-metal bond during reaction of an organometallic complex with an electrophile. In the palladium chloride catalysed halogenation of azobenzene, Fahey isolated the azobenzene-palladium halide dimers exemplified by (14) which were thought to be intermediates in the halogenation process. Reaction of the complexes with halogen gave o-halogenoazobenzenes and regenerated palladium halide catalyst.

It is possible that this reaction involves a direct attack by the electrophilic halogen molecule at the carbon atom of the carbon-metal bond as shown below.



Alternatively, the reaction may involve oxidative addition of the halogen, to give a transient palladium (IV) species, followed by reductive elimination as shown in Fig. (XII).

Fig (XII)



(14)

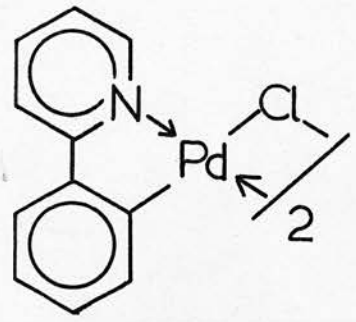
6. Reactions of Cyclopalladated Complexes

(a) Reactions involving sulphur nucleophiles

Nucleophilic displacement of palladium by benzyl mercaptide anion was attempted with both the halogen-bridged and the acetate-bridged dimeric complexes of phenylpyridine and benzylideneaniline as shown in Fig. (XIII). The attempts proved unsuccessful, no evidence for the formation of the desired product or metallic palladium being obtained. In all cases starting materials were recovered together with varying amounts of dibenzyl disulphide.

The work of Murahashi,[44] involving displacement of palladium by alkyl groups in the presence of triphenylphosphine, suggested that similar conditions might be effective in causing displacement by alkylthiolate groups. Accordingly, the halogen-bridged phenyl-pyridine complex (91) was treated with sodium benzyl mercaptide

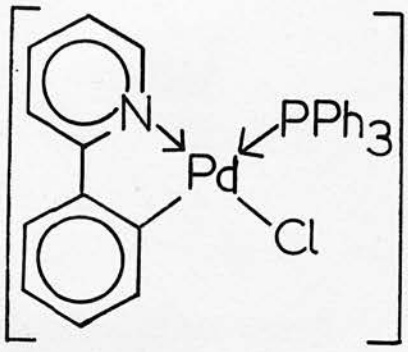
Fig (XIV)



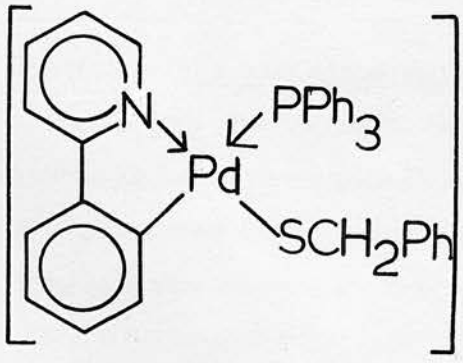
+ $NaSCH_2Ph$ + PPh_3 (xs)

(91)

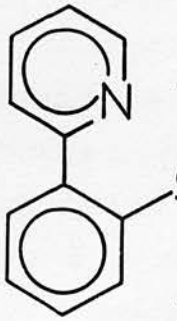
T.H.F.



(153)



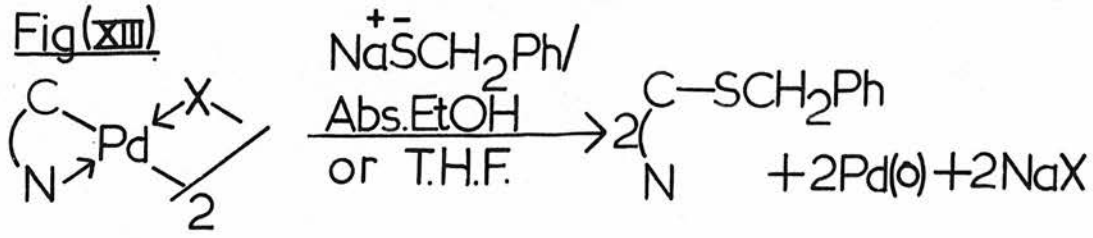
(154)

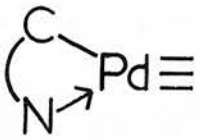


+ Pd(o) + PPh_3

(155)

Fig(XIII)





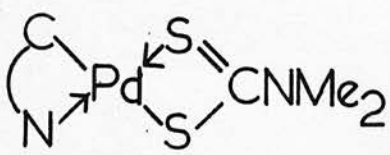
≡ Cyclopalladated phenylpyridine and benzylidene-aniline ligands

X ≡ Cl or OAc

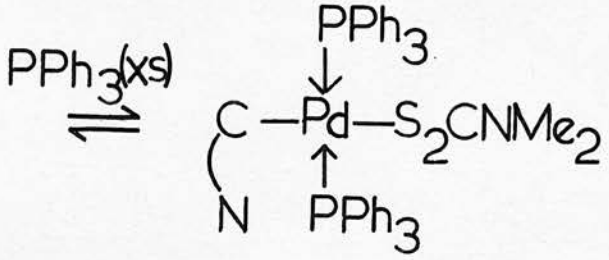
in the presence of an excess of triphenylphosphine with tetrahydrofuran as solvent. It was thought that the reaction might proceed as shown in Fig. (XIV). An initial bridge-splitting reaction of triphenylphosphine would form the complex (153) which could then undergo a ligand exchange reaction resulting in the formation of the intermediate mercaptide complex (154). It was envisaged that this complex might then undergo reductive elimination, in the same way as Murahashi's intermediate, to give the sulphide (155) together with metallic palladium and triphenylphosphine.

A mixture of four products was obtained and these were separated chromatographically and examined by mass, infrared and ^{1}H n.m.r. spectroscopy. The mass spectrum of the major product, a yellow solid, gavean ion mass at m/e 590 and one at m/e 262. These were consistent for halogen-bridged starting material and triphenylphosphine respectively. However, the solubility of the compound in organic solvents suggested that it did not contain starting material and the ^{1}H n.m.r. spectrum gave further proof. The spectrum, although not conclusive, suggested the presence of the phosphine complex (153), analogous to the triethylphosphine complex (131) discussed earlier. A low-field proton resonance at δ 9.6, which was possibly the *α*-pyridyl proton, integrated against the other proton resonances in the aromatic region to give a proton ratio consistent with that required for the proposed structure. Dissociation of triphenylphosphine and subsequent dimerisation of the metallated fragment could possibly explain the mass spectroscopic results.

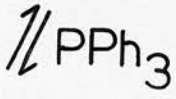
Fig(XV)

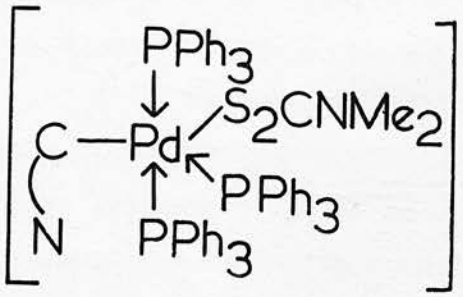


(140)

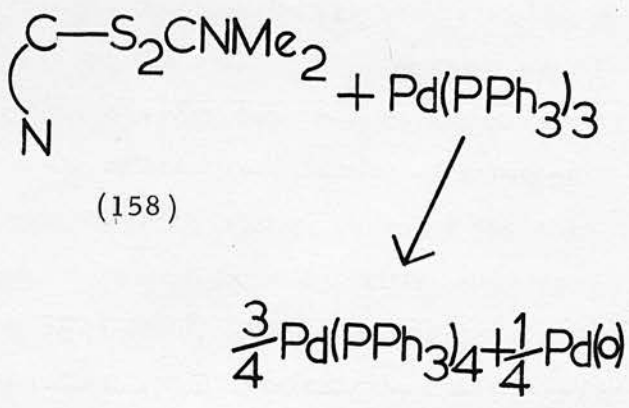


(156)

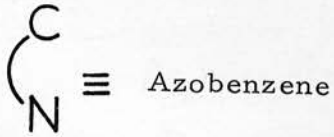


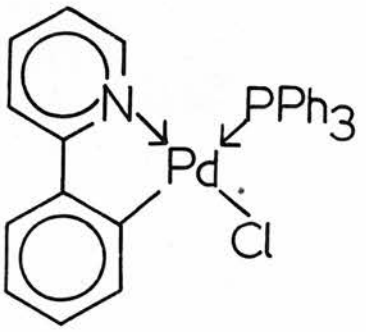


(157)



(158)





(153)

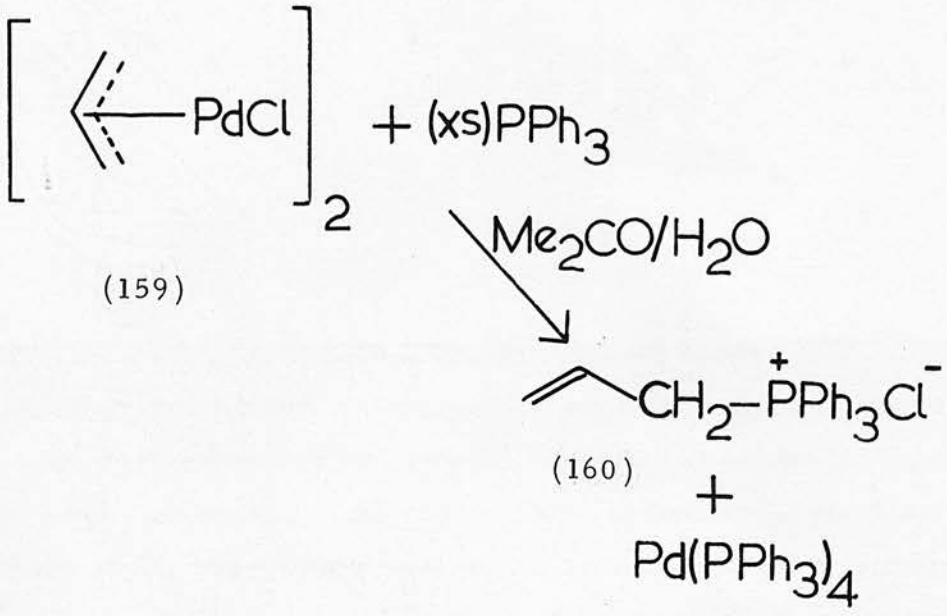
The second product, a small amount of yellow oil, gave mass and ^{1}H n.m.r. spectra consistent with a mixture of triphenylphosphine and dibenzyl disulphide while the third was tentatively identified as triphenylphosphine sulphide. The final product, a brown solid of limited solubility, could not be identified but its mass spectrum gave an ion mass at m/e 278 which was consistent with triphenylphosphine oxide. No evidence for the formation of the desired products was obtained and the reactions of sulphur nucleophiles were not further investigated.

(b) Attempted reductive eliminations in dithiocarbamato- and phosphine-complexes of cyclometallated ligands.

The dimethyldithiocarbamatoazobenzene complex (140) was treated with an excess of triphenylphosphine at 150°C both in the presence and absence of solvent. It was thought possible that two moles of phosphine might coordinate to the central palladium atom, as shown in Fig. (XV), resulting in the formation of the 16-electron complex (156) which would contain unidentate azobenzene and dithiocarbamato-ligands. Further addition of triphenylphosphine might then give an unstable eighteen electron complex (157) which might undergo reductive elimination to give ortho-(dimethyldithiocarbamato)azobenzene (158) and tris(triphenylphosphine) palladium (o). The latter would then probably disproportionate to palladium metal and tetrakis (triphenylphosphine) palladium (o).

When the reactants were fused together at 150°C, only a

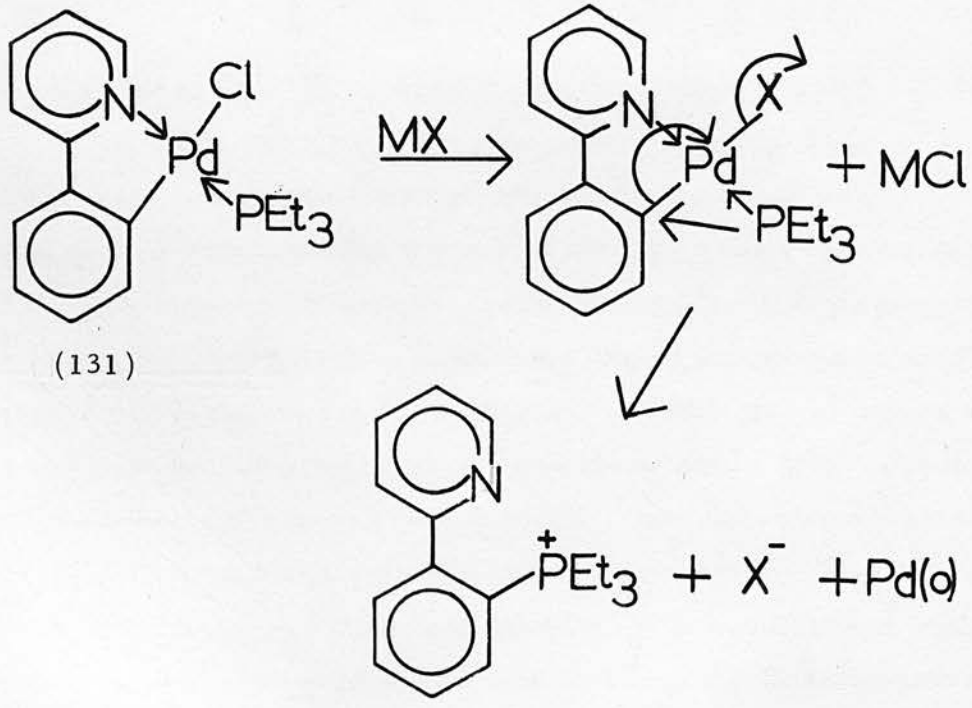
Fig (XVI)



(159)

(160)

Fig (XVII)



(131)

(132)

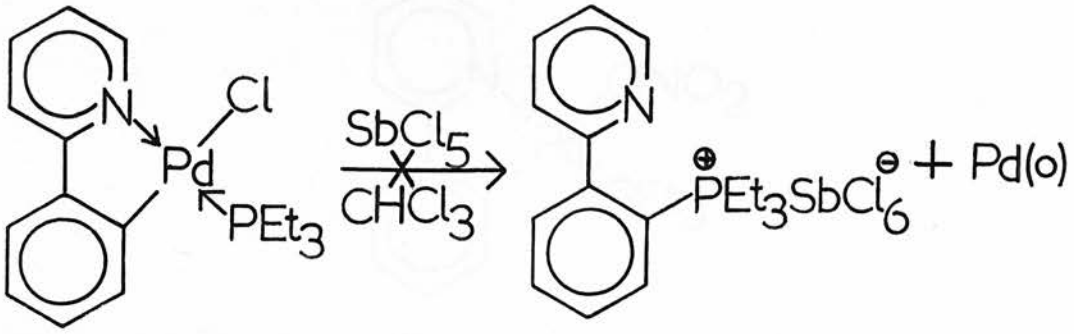
yellow crystalline solid, identified as triphenylphosphine sulphide, and starting materials were isolated, indicating that the desired reaction had not taken place. The similar attempt in refluxing diglyme showed promise in that a palladium mirror was observed after some considerable time. However, subsequent work-up resulted in the isolation of only azobenzene, triphenylphosphine sulphide and starting materials, all identified by their respective infrared spectra and melting points. There was no evidence to suggest that reductive elimination was taking place.

Powell and Shaw reported[78] the isolation of an allylphosphonium salt from the halogen-bridged allyl palladium chloride complex (159) on reaction with an excess of triphenylphosphine in aqueous acetone. This product was formed via a reductive elimination reaction which gave the ligand coupled product (160) and tetrakis (triphenylphosphine) palladium (o) as shown in Fig. (XVI).

Prompted by this knowledge and our earlier observation of the 2-(2-pyridyl)phenyltriethylphosphonium ion (132) in the mass spectrum of two different triethylphosphine complexes (131) and (133), it was decided to investigate the possibility of obtaining this cation by chemical means from the monophosphine complex (131). It was thought possible that replacing the chloride ligand with a better leaving group (X) might facilitate a reductive elimination reaction, as shown in Fig. (XVII), by making the palladium a better electron acceptor.

Initially, the complex (131) was treated with antimony pentachloride, a Lewis acid capable of coordinating with chloride ion to form the stable anion $SbCl_6^{\ominus}$. A pink solid precipitated from the reaction mixture but no palladium was formed. Spectroscopic examination of the product, which was hindered by its very low solubility, gave no indication of its composition. An attempted anion exchange reaction with perchlorate was unsuccessful and the reaction was not further investigated. The intended reaction is summarised in Fig. (XVIII).

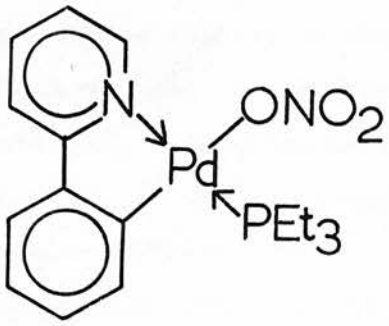
Fig.(XVIII)



Attempts were then made to obtain salts of the phosphonium cation by reactions of the phosphine complex (131) with silver nitrate, silver perchlorate and silver hexafluorophosphate in refluxing acetonitrile. No phosphonium salt could be isolated from any of these reactions but some unexpected products were obtained.

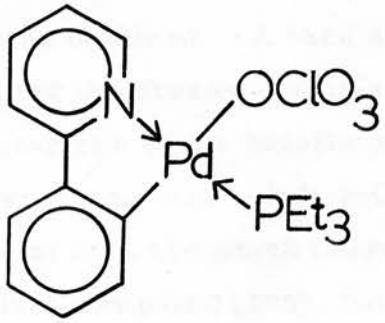
Treatment of the phosphine complex with silver nitrate gave an immediate precipitate of silver chloride and, after refluxing for a short time, work-up of the reaction mixture yielded a pale-grey crystalline solid. The mass spectrum gave a weak ion mass at m/e 440 which was consistent with the covalent structure (161); a stronger ion mass at m/e 322, which also exhibited a palladium isotope pattern, was consistent with loss of the triethylphosphine ligand from the proposed structure. Elemental analysis confirmed this structure. The ^{1}H n.m.r. spectrum, obtained in trifluoroacetic acid, was inconclusive, showing complex multiplets in both the aromatic and aliphatic region; precipitation from the sample of what may have been palladium metal was observed. The evidence suggested that the nitrate anion was not a strong enough leaving group to cause the reductive elimination process required for the formation of the phosphonium salt and that only the ligand exchanged product (161) had been formed.

Reaction of the phosphine complex with silver perchlorate, which was thought to contain a better leaving group in the form of the perchlorate anion, was carried out under similar conditions.

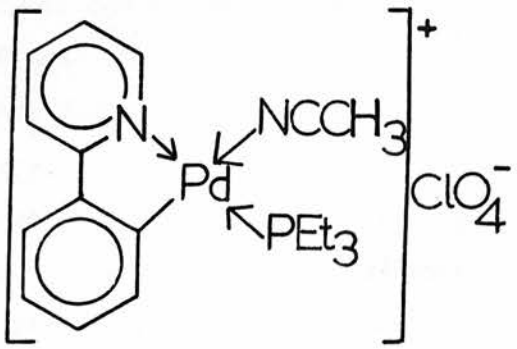


(161)

Silver chloride was again precipitated on mixing and work-up of the reaction mixture gave a grey crystalline solid. The ^{1}H n. m. r. spectrum was again inconclusive but did show a singlet at δ 2. 7 which suggested that a methyl group was present. The infrared spectrum showed a broad peak for perchlorate anion in the expected region of 1060-1100 cm^{-1}. The mass spectrum of the compound exhibited an ion mass at m/e 272, consistent with the required phosphonium cation (132) and one at m/e 477, consistent with the ligand-exchanged product (162). The compound was recrystallised and submitted for elemental analysis, the results of which were consistent with a mixture of the two compounds (162) and (163). It was concluded that solvent participation had occurred resulting in the ionic complex (163) which seemed, from the evidence, to be the major product. This accounted for the methyl singlet in the ^{1}H n. m. r. spectrum.



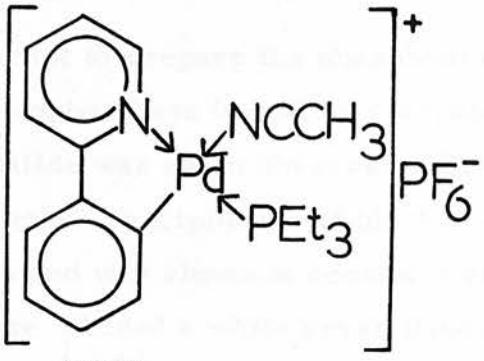
(162)



(163)

The m/e 272 peak in the mass spectrum resulted, presumably, from a process analogous to that observed in the initial chloro-complex (131).

Reaction of the complex with silver hexafluorophosphate under the same conditions was also found to be influenced by solvent participation. The dark grey crystalline product gave an infrared spectrum which indicated the presence of hexafluorophosphate by a broad stretch in the expected 840-860 cm^{-1} region. Mass and ^1H n. m. r. spectra were inconclusive, but the presence of a singlet at δ2.4 in the n. m. r. spectrum suggested that participation of solvent in the reaction was again occurring. Elemental analysis gave results close to, but not quite consistent with, those required for the ionic complex (164). The presence of a nitrile group was

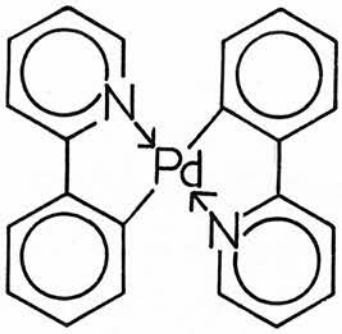


(164)

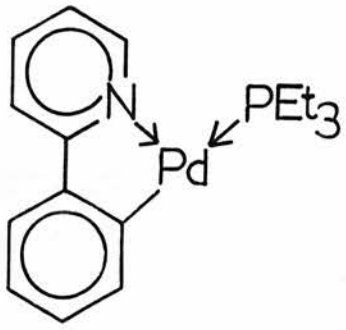
also suggested in the infrared spectra of both the perchlorate and hexafluorophosphate complexes, which showed a weak C≡N stretching band in the region 2300-2310 cm^{-1}.

The reaction with silver hexafluorophosphate was repeated using chloroform instead of acetonitrile and a green crystalline solid was obtained. A band at 1040 cm^{-1} in the infrared spectrum suggested the presence of triethylphosphine but no absorption characteristic of the hexafluorophosphate anion was present. The mass spectrum was uninformative, showing one palladium isotopic pattern at m/e 414 which corresponded to the bis(phenylpyridine) palladium compound (165), but this was discounted as a major component of the sample on the basis of analytical evidence. The compound was too insoluble for a ^1H n. m. r. spectrum to be obtained. Elemental analysis for C, H and N gave results which were close to those required for a complex containing the unit (X) together with one

additional phosphorus and four fluorine atoms. In the absence of further evidence, no acceptable structural formula can be proposed.

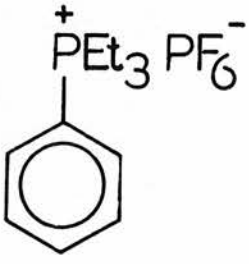


(165)



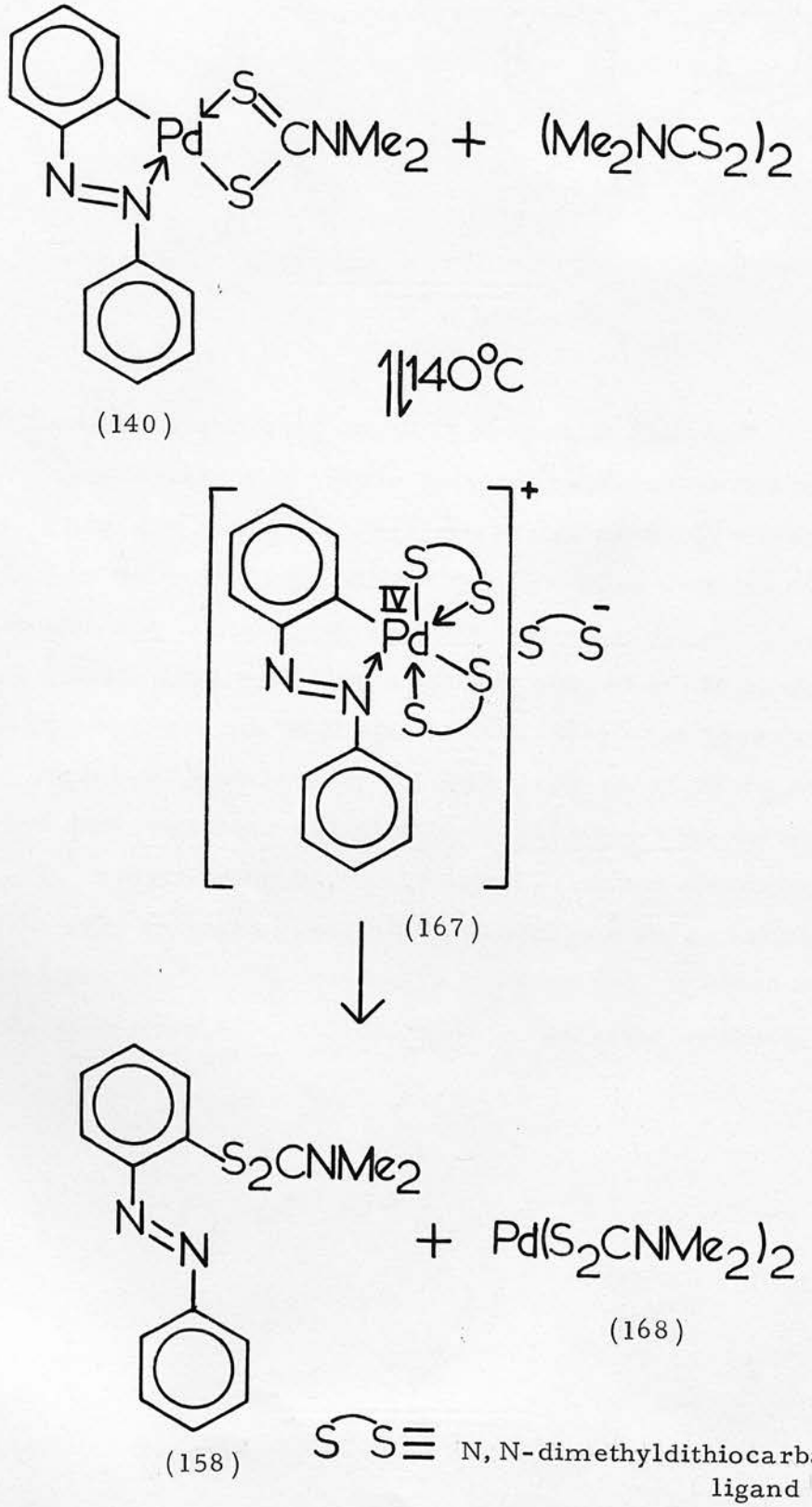
(X)

One final attempt to prepare the phosphonium salt was made using silver hexafluorophosphate in boiling chlorobenzene. Precipitation of silver halide was again observed followed by a darkening of the solution and further precipitation of black material. This was removed by filtration and was shown to contain metallic palladium. Work-up of the filtrate yielded a white crystalline solid which showed an infrared absorption characteristic of the hexafluorophosphate anion but no bands attributable to pyridyl ring vibrations. The mass spectrum gave a parent ion at m/e 195 consistent with phenyltriethylphosphonium cation. It was not possible to obtain a ^{1}H n. m. r. spectrum of the compound but elemental analysis gave results which were close to, but not quite consistent with, those required for the phosphonium salt (166). No other products were isolated and it



(166)

Fig.(XX)

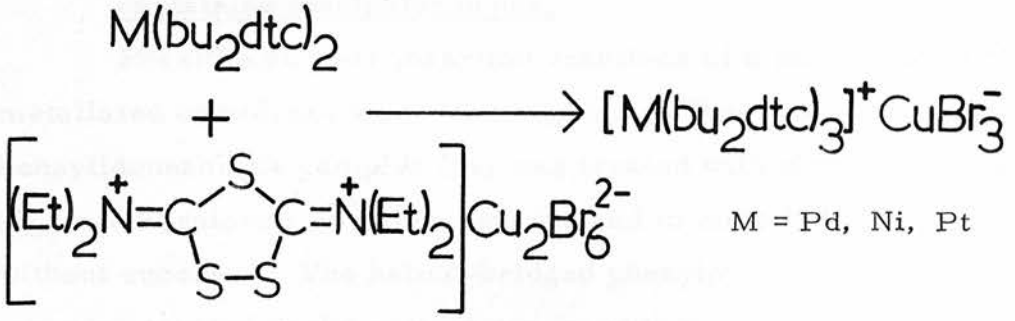

Pd
S
CNMe2
+
(Me2NCS2)2
N=N
140°C
(140)
+
S
IV
Pd
S
S
S
S
S
S
N=N
(167)
S2CNMe2
N=N
+
Pd(S2CNMe2)2
(168)
(158)
S S≡ N, N-dimethyldithiocarbamato ligand

seemed clear that thermal breakdown of the complex had occurred and that the liberated triethylphosphine had reacted with the solvent. Halogenobenzenes are normally unreactive towards nucleophilic attack but various transition metal halides are known to catalyse their reactions with phosphines to form quaternary phosphonium salts.[82]

No further attempts were made to effect reductive elimination in phosphine complexes.

The possibility of preparing an azobenzene dithiocarbamato-palladium (IV) complex, which might be susceptible to reductive elimination, was also considered. Nickel, palladium, and platinum (IV) complexes, stabilised by dithiocarbamato-ligands, had been previously reported by Willemse and Cras,[83] who had reacted the bis(diethyldithiocarbamato)metal (II) complexes with salts of the 3, 5 bis(N, N-diethyliminium)-1, 2, 4-trithiolan dication to give ionic tris(dithiocarbamato)metal (IV) complexes, as shown in Fig. (XIX) below.

Fig.(XIX)



It was envisaged that treatment of the dimethyldithiocarbamato-azobenzene complex (140) with tetramethylthiuram disulphide at 140°C, in the absence of solvent, might cause heterolytic fission of the disulphide and transfer of dithiocarbamato-cation to the central palladium, thus generating a low concentration of the palladium (IV) complex (167), as shown in Fig. (XX). Reductive elimination might then result in the formation of the ortho-substituted azobenzene (158), and bis(dimethyldithiocarbamato)palladium (II) (168).

After fusing the reactants for three hours at 140°C, the residual melt was dissolved in ether and an insoluble yellow solid was obtained. Chromatographic treatment of the remaining soluble material gave three further products which were obtained as red oils. The yellow solid was identified from its mass and infrared spectra as bis(dimethyldithiocarbamato)palladium (II). The other products were not obtained pure and could not be identified from their spectra. Neither product showed a mass spectrometric peak corresponding to the required o-(dimethyldithiocarbamato)azobenzene (158).

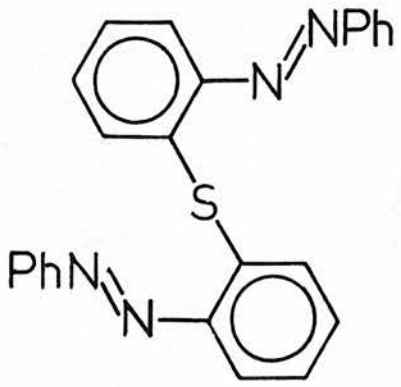
Other attempts to obtain dithiocarbamatopalladium (IV) intermediates, which might then reductively eliminate to give the desired ortho-substituted azobenzene, were made. By treatment of the dimethyldithiocarbamatoazobenzene complex (140) with powerful oxidising agents such as ceric ammonium nitrate and lead tetraacetate, it was thought that palladium (IV) species might result, but neither reaction gave evidence to suggest that this had happened.

(c) Reactions with substances, other than thiocyanogen, containing disulphide bonds.

Possible sulphur insertion reactions of a number of cyclometallated complexes were investigated. The acetate-bridged benzylideneaniline complex (54) was treated with elemental sulphur (S_8) in chloroform, in chlorobenzene and in dimethylformamide without success. The halide-bridged phenylpyridine complex (91) was also treated in the same manner, with dimethylformamide as the solvent, but no reaction was observed.

Reaction of the dimethyldithiocarbamatoazobenzene complex (140) with sulphur in dimethylformamide gave two products which were separated by chromatography. The major product, a grey-black tarry solid, was not obtained pure even after rechromatography, and could not be crystallised despite repeated attempts. The compound gave a weak and poorly resolved ^{1}H n.m.r. spectrum from which no structural conclusions could be drawn. The mass spectrum showedan ion mass at m/e 394 which corresponds to the molecular

weight of bis(2-phenylazophenyl)sulphide (169) and another at m/e 213 which was consistent with loss of one phenylazophenyl group from the proposed structure. However firm evidence to substantiate this structure was not obtained despite repetition of the reaction and further attempts to purify the product. The minor product, a brown oil, could not be identified by spectroscopic means.



(169)

An analogous reaction with the diethyldithiophosphatoazobenzene complex was similarly unsuccessful, and no characterisable products could be isolated. Treatment of the azobenzene cyclopentadienyl-nickel complex (12) with sulphur in refluxing chlorobenzene and chromatography of the reaction mixture gave seven bands. The two major bands gave azobenzene and starting material complex respectively and the others gave only trace amounts of solid and liquid materials which could not be identified.

Of all the reactions with elemental sulphur, only that of the dithiocarbamatoazobenzene complex gave any evidence of sulphur insertion in the carbon-palladium bond and, even in this case, no pure product could be isolated. The cyclometallated complexes investigated seemed to be very unreactive in this type of reaction.

The reaction with tetramethylthiuram disulphide detailed earlier in Fig. (XX) as a possible reductive elimination route to ortho-substituted organic products, could also be envisaged as a potential free radical process; homolytic fission of the disulphide and attack by dithiocarbamato-radical at the carbon atom of the carbon-palladium bond could give the same products as the reductive

Fig.(XXI)

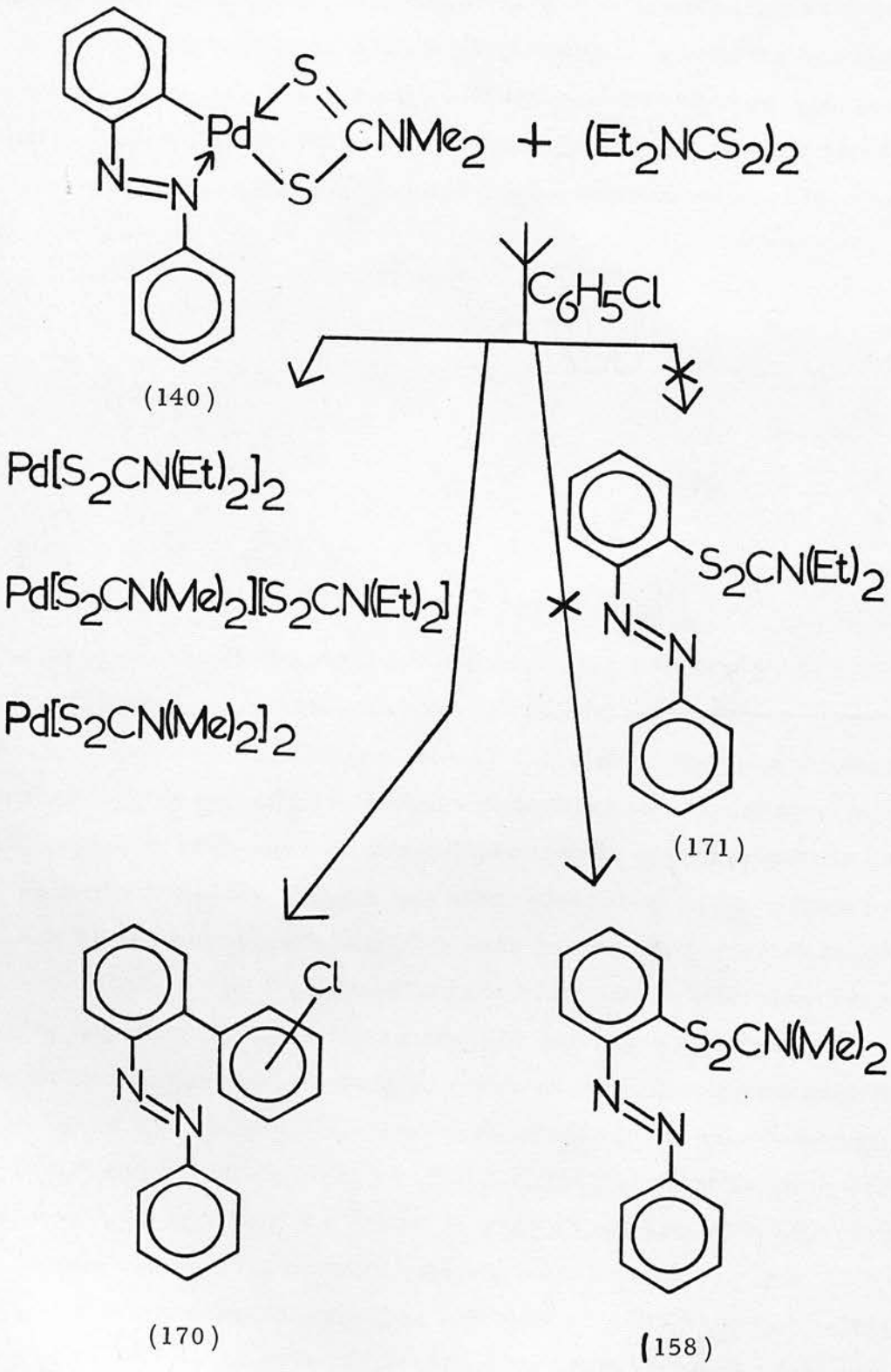
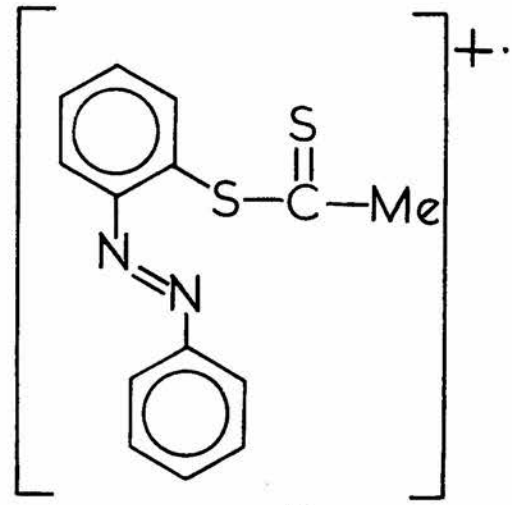
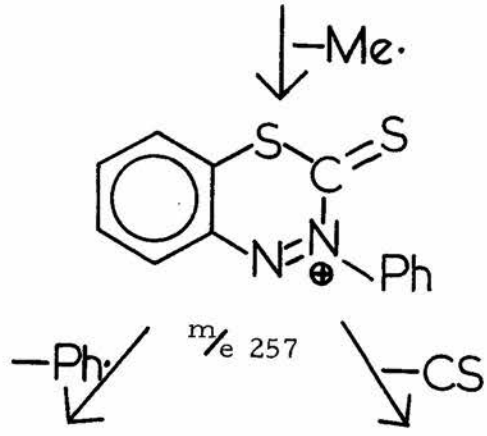
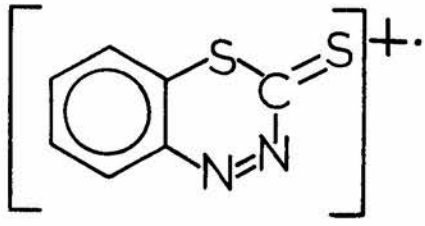

Pd
S
S
CNMe2
+ (Et2NCS2)2
N=N
C6H5Cl
(140)
Pd[S2CN(Et)2]2
Pd[S2CN(Me)2][S2CN(Et)2]
Pd[S2CN(Me)2]2
S2CN(Et)2
N=N
(171)
Cl
N=N
(170)
S2CN(Me)2
N=N
(158)

Fig.(XXII)

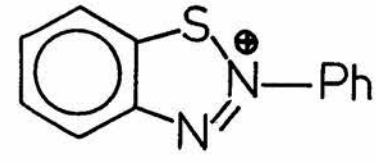


(172) m/e 272





m/e 180

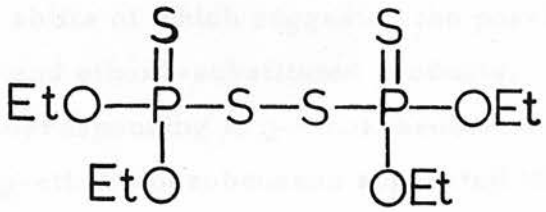


m/e 213

elimination process described.

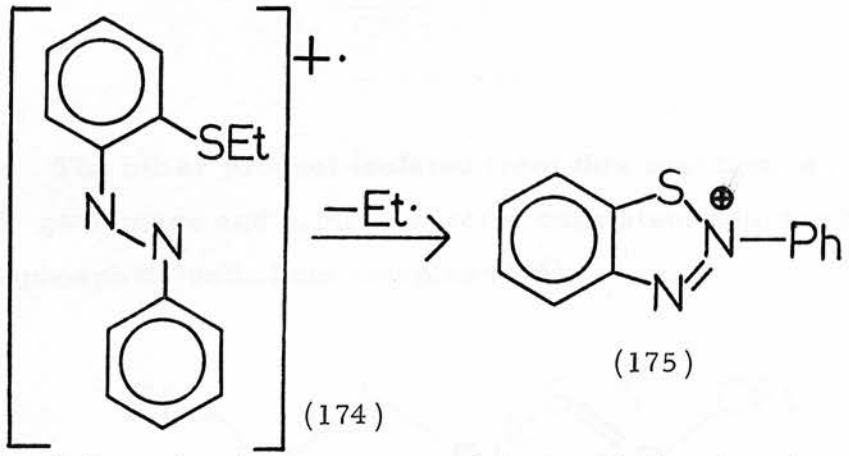
This particular reaction yielded no evidence of either process but a similar one, involving tetraethyl- instead of tetramethylthiuram disulphide and the dimethyldithiocarbamatoazobenzene complex in refluxing chlorobenzene, did suggest the possibility of free radicals reacting both with the complex and with the solvent. After twenty four hours in refluxing chlorobenzene two products were obtained, one a sparingly soluble yellow solid and the other a red oil. The mass spectrum of the solid gave three ion masses (m/e 402, 374 and 346) which were consistent with the mixture of bis(dithiocarbamato)palladium complexes shown in Fig. (XXI). The mass spectrum of the red oil also showed what appeared to be a mixture of products. A pair of peaks at m/e 294 and 292 (rel. ab. 1:3 approx.) was consistent with an o-(chlorophenyl)azobenzene (170). No substantial peaks were present at m/e values corresponding to the required products (158) and (171) but a peak at m/e 272 suggested the possible presence of the dithioacetate (172). The formation of such a compound is not easily accounted for but further ion masses at m/e 257, 213 and 180 were also observed and these could have been formed by fragmentation of the m/e 272 species as shown in Fig. (XXII). Exact mass measurements were therefore carried out on these ion masses but in all cases the results were inconsistent with the proposed elemental compositions. The ^{1}H n.m.r. spectrum of the inseparable mixture gave complex multiplets in the aromatic and aliphatic regions and was uninformative. Thus the presence in the mixture of the o-(chlorophenyl)-substituted product suggests that a free radical reaction of some kind is taking place. Such a reaction would probably involve attack on the solvent by 2-phenylazophenyl radicals and it is surprising, therefore, that neither of the expected products (158) or (171) was isolated since radical attack on disulphide bonds is known to be reasonably facile.

Reactions analogous to the foregoing were carried out using the diethyldithiophosphatoazobenzene complex (141) in the presence of bis(diethoxythiophosphoryl) disulphide (173). Reaction of the



(173)

compounds in the absence of solvent at 135°C yielded two products, one a red oil which could not be crystallised, and an oily brown solid. The mass spectrum of the red oil gave a weak ion mass at m/e 242 and a very strong one at m/e 213. The m/e 242 peak was consistent with the parent ion of o-ethylthioazobenzene (174) and m/e 213 corresponded to the ion (175) which could have resulted from loss of the ethyl group as shown below. Exact mass measure-



(174) (175)

ments of these two ions were consistent with the structures proposed.* The ^{1}H n. m. r. spectrum was inconclusive, however, showing two well-resolved ethyl triplets and two ethyl quartets,

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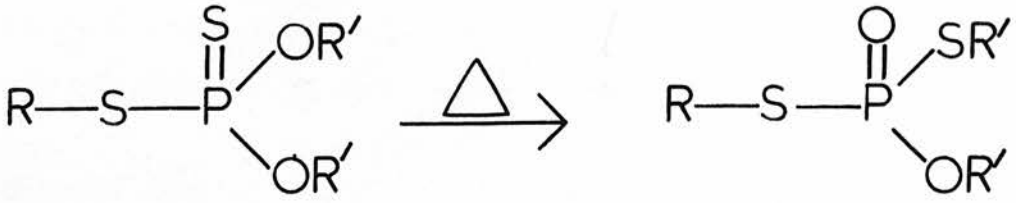
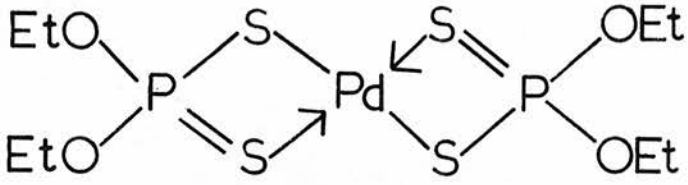
*Footnote: This result casts doubt on the validity of the exact mass measurements carried out previously for the product obtained in the reaction of the corresponding dithiocarbamato-complex. In this case the exact masses found, including the one at m/e 213 had not supported the suggested structures. However, in view of the apparent complexity of the reaction mixture and the low yields of individual products, it was not considered worthwhile to repeat the experiment.

the chemical shifts of which suggested the possibility of a mixture of ethylthio- and ethoxy-substituted products. No ion mass was present at m/e 229 corresponding to o-ethoxyazobenzene. The probable presence of o-ethylthioazobenzene suggested that, as in the corresponding reaction of the dithiocarbamato-complex, a deep-seated break-down of the sulphur-containing ligand had again taken place. The ethylthio-group is thought to originate in the O —> S alkyl migration which is known[84] to occur in dialkoxythiophosphoryl groups as shown below.



The other product isolated from this reaction, an oily brown solid, gave mass and n.m.r. spectra consistent with the bis(diethyldithiophosphato)palladium complex (176).

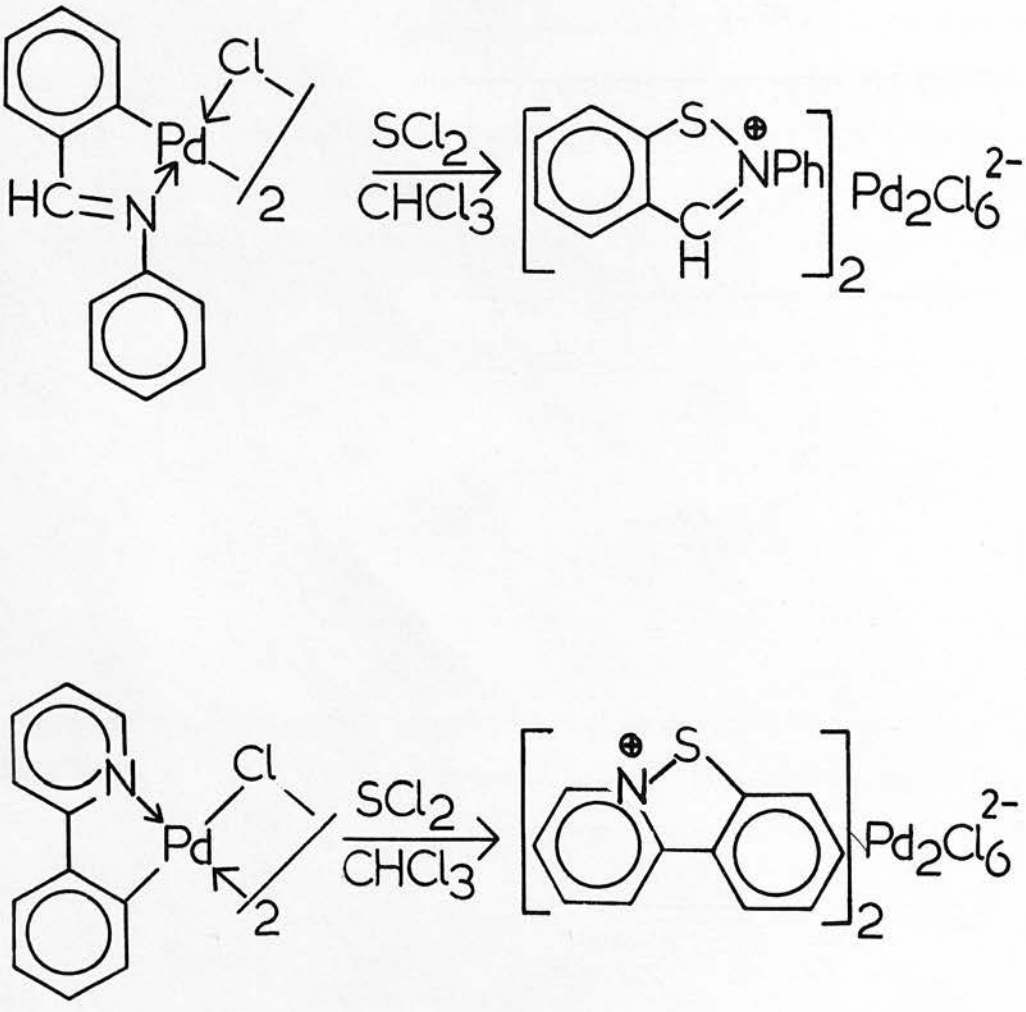


(176)

An attempt to obtain o-benzylthioazobenzene by fusion of the acetate-bridged dimeric azobenzene complex (46) with dibenzyl disulphide in the absence of solvent at 130°C was unsuccessful. A similar reaction of the disulphide with the azobenzene cyclopentadienyl nickel complex (12), which contains a more reactive metal-carbon bond than the palladium complexes, was also unsuccessful, both starting materials being recovered.

Irradiation with ultraviolet light was also investigated as a

Fig(XXIII)


Cl
Pd
HC=N
2
SCl2
CHCl3
S
NPh
C
H
2
Pd2Cl6 2-
N
Cl
Pd
2
SCl2
CHCl3
N
S
2
Pd2Cl6 2-

possible means of inducing reaction of the dithiocarbamato-complex (140) with tetramethylthiuram disulphide and of the dithiophosphato-complex (141) with the disulphide (173). In both cases, however, the starting materials remained unchanged even after prolonged irradiation.

(d) Reactions with electrophiles

Reactions of some halogen-bridged and acetate-bridged dimeric complexes with sulphur dichloride were investigated with a view to effecting an electrophilic displacement of palladium by sulphur, and creation of a sulphur-nitrogen bond, to form cationic heterocycles as shown in Fig. (XXIII).

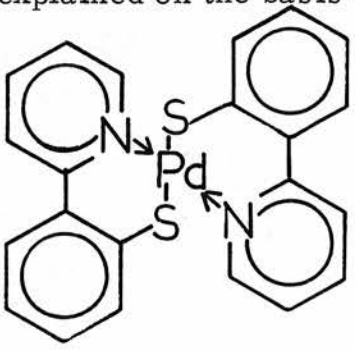
The reaction of both the halogen-bridged and the acetate-bridged benzylideneaniline complexes resulted in precipitation of pale-brown solids which were identical in both infrared spectrum and melting point. ^{1}H n.m.r. study was impossible owing to the extreme insolubility of the product. The mass spectrum of the product was complex and uninformative; it seems likely that many of the peaks were due to thermal breakdown products since strong heating was necessary in order to obtain a satisfactory ion-pressure. Elemental analysis gave results which were consistent for the molecular formula, $C_{13}H_{10}Cl_2NPdS$. In the absence of further evidence, no acceptable structural formula can be proposed. The amorphous nature of the product and its almost complete lack of solubility in a wide range of solvents seemed more in keeping with a polymeric structure than with the required heterocyclic salt. However, it was thought worthwhile to attempt a reduction with lithium aluminium hydride in the hope of obtaining o-mercapto-N-phenylbenzylamine and thus establishing that palladium had been replaced by sulphur. In the event, no identifiable product was obtained.

Reaction of sulphur dichloride under the same conditions with the halogen-bridged dimeric phenylpyridine complex (91) also yielded an amorphous, extremely insoluble, pale-brown solid which could not be characterised directly. An attempted reduction of the product

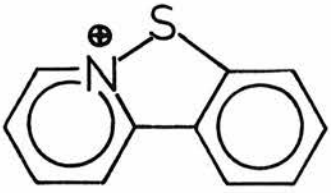
was carried out with sodium bis(2-methoxyethoxy)dihydroaluminate, a reducing agent similar to, but more soluble than, lithium aluminium hydride; again, however, no organic reduction product could be isolated. Anion exchange with perchlorate was also attempted and yielded an orange crystalline solid but the yield was extremely small and no conclusive spectral or analytical data could be obtained.

Finally, the compound, suspended in dichloromethane, was treated with a large excess of triethylphosphine. A clear red solution was obtained and two products were isolated on work-up of the reaction mixture, an orange solid in very small yield and a yellow-orange crystalline solid in larger amount.

A ^{1}H n.m.r. spectrum of the orange compound, though weak and poorly resolved, showed only aromatic resonances. The mass spectrum showed a parent ion mass at m/e 478, a weak m/e 446 and a strong m/e 186. These ion masses can all be explained on the basis of the structure (177) shown below; loss of



(177)

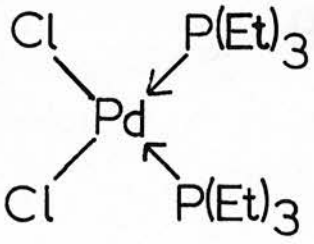


(178)

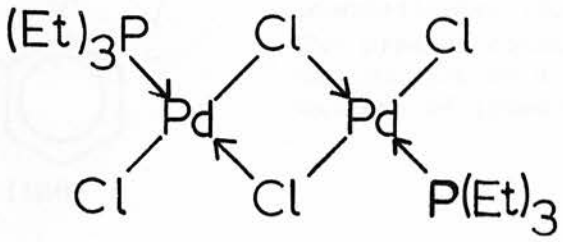
sulphur from the parent ion would explain the m/e 446 peak and the strong m/e 186 peak corresponds to the pyridoisothiazolium cation (178). Such a structure would also explain the sole presence of aromatic resonances in the ^{1}H n.m.r. spectrum of the compound. Elemental analyses of the compound, however, were not consistent with the proposed structure and thus conclusive evidence is lacking.

The major product, a yellow-orange crystalline solid, gave an infrared spectrum (650-3500 cm^{-1}) identical with that of an

authentic sample of bis(triethylphosphine) palladium dichloride. However, the melting points of the two compounds differed markedly, the authentic sample melting at 139°C and the product obtained melting at 180°C. The two were also different in colour, the authentic specimen being light yellow and the product orange-yellow. The dimeric tetrachlorobis(triethylphosphine) palladium (II), orange in colour, melts at 230°C. It seemed likely that the product obtained was in fact a mixture of the monomeric and dimeric phosphine complexes (137) and (179). The ^{1}H n.m.r. spectrum also suggested



(137)



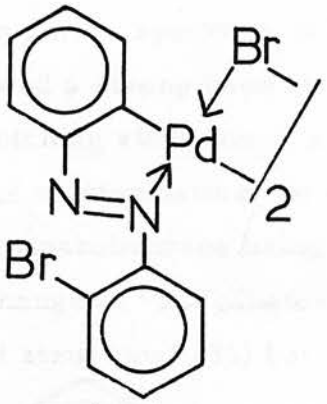
(179)

a mixture since it showed complex multiplets in the aliphatic region of the spectrum (δ0.8-2.1) consistent with those expected for a mixture of compounds containing triethylphosphine ligands in different environments. Conclusive proof, however, was not obtained as it was not thought worthwhile to attempt to separate the supposed mixture.

No firm conclusions concerning the structure of the product from the phenylpyridine complex and sulphur dichloride could be drawn from its reaction with triethylphosphine, though some of the data obtained pointed to a structure in which sulphur had been inserted into the carbon-palladium bond.

The potential of various reagents for causing electrophilic displacement of palladium was further investigated by using the acetate-bridged complex of azobenzene which is a more readily available ligand than 2-phenylpyridine. From an attempted electrophilic displacement of palladium by bromine under mild

conditions, an insoluble brick-red solid was obtained together with a red oil. The red solid, which was the major product, could not be characterised owing to its low solubility. The mass spectrum did, however, show features suggesting that the product was the dimeric complex (180). An ion cluster grouped around a strong peak at m/e 447, and showing an isotope pattern consistent with



(180)

The bromine atom may be in either the substituted or the unsubstituted ring The product obtained may in fact be a mixture of isomers.

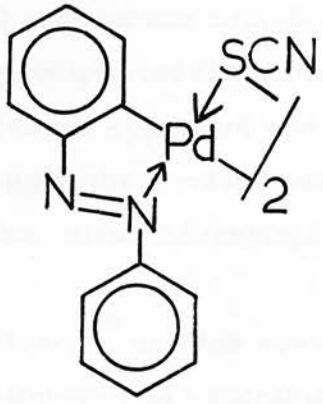
the presence of one Pd and 2 Br atoms, corresponded to the half-mass of this complex and other higher ion masses, which could not be counted, suggested that the product was dimeric.

The mass spectrum of the red oil showed ion masses with isotope patterns due to one and two Br atoms, respectively, at m/e 262, 260 and at m/e 342, 340, 338. These masses corresponded to mono- and di-bromoazobenzenes and the greater intensity of the peaks at m/e 262, 260 suggested that the monobromo-compound was the major component of the mixture. The ^{1}H n.m.r. spectrum, which showed two well resolved complex multiplets in the aromatic region very close together, differed from that of azobenzene itself.

This reaction then, was partially successful, in that some substituted azobenzene products were obtained, but the disadvantage of the reaction appeared to lie in the fact that the palladium displaced in the reaction, in the form of palladium bromide, was free to re-metallate the substituted ligand giving the major product (180) instead of the required 2-bromoazobenzene.

Having shown that the azobenzene acetato-complex (46) reacts with a halogen (bromine) at the carbon-palladium bond, it

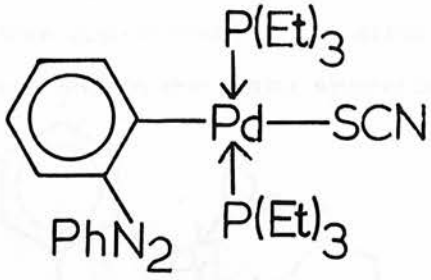
was decided to try an analogous reaction with the pseudo-halogen, thiocyanogen, in an attempt to obtain 2-thiocyanatoazobenzene. When a chloroform solution of the azobenzene acetatopalladium complex was treated with thiocyanogen at room temperature, a heavy yellow precipitate was obtained. This was collected and examined by infrared and mass spectroscopy, the compound being too insoluble for a ^{1}H n.m.r. spectrum to be obtained. The infrared spectrum showed a strong band at 2150 cm^{-1} which corresponds to the C≡N stretching vibration of a thiocyanato group. The mass spectrum was uninformative, no evidence for the formation of 2-thiocyanatoazobenzene being obtained. It seemed likely that a ligand exchange of thiocyanato- for acetato- had occurred resulting in the bridged structure (181) but, since the product could



(181)

not be recrystallised, satisfactory analytical data were not obtained. In order to obtain a monomeric derivative which would substantiate the proposed structure, the yellow compound was treated with an excess of triethylphosphine. The reaction, carried out in dichloromethane, gave a clear dark red solution and chromatography afforded one product, a purple crystalline solid. An infrared spectrum showed the presence of a thiocyanato-group (2100 cm^{-1}) but the mass spectrum, in common with those of phosphine complexes discussed earlier, was uninformative. The ^{1}H n.m.r. spectrum showed both aromatic and aliphatic resonances and the integral ratio of these was consistent with the structure (182). Elemental analysis was also consistent with this structure

and thus the proposed structure of the yellow precursor was confirmed.



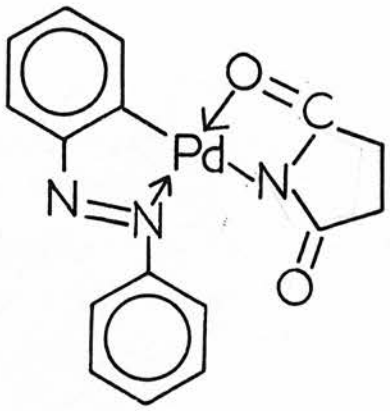
(182)

In a further attempt to promote replacement of palladium by a sulphur-containing group, trichloromethanesulphenyl chloride (Cl_3CSCl) was used as the electrophilic reagent. This reacted with the acetate-bridged azobenzene complex (46) to give a red crystalline solid which precipitated from the chloroform solution. By comparison of its infrared spectrum and melting point with those of an authentic sample the product was identified as the ligand-exchanged complex, di-μ-chlorobis[2-(phenylazo)phenyl] dipalladium (II) (14).

Recent work by Harpp[85] and his co-workers has shown that N-(alkylthio)-phthalimides and -succinimides can act as sulphenylating agents with many types of organic nucleophiles. These compounds are more stable and thus more convenient to handle than the corresponding sulphenyl halides, though they are somewhat less reactive. It seemed possible that such reagents might be suitable sources of electrophilic sulphur for reaction with cyclometallated complexes. N-(Benzylthio)succinimide was chosen for trial since it is easily prepared and contains the easily removable benzyl group.

Reaction of this compound with the azobenzene-acetato-complex was carried out in refluxing chlorobenzene and work-up of the reaction mixture afforded a dark red crystalline solid. Broad carbonyl stretching bands centred at 1725 cm^{-1} and 1700 cm^{-1} in the infrared spectrum suggested the presence of the succinimido-

group and the ^{1}H n. m. r. spectrum confirmed this, a broad singlet at δ 2. 5 being observed for the aliphatic protons of the succinimido-group. Integration showed that the ratio of aliphatic to aromatic protons was consistent for the structure (183) and a parent ion mass at m/e 385 in the mass spectrum gave further

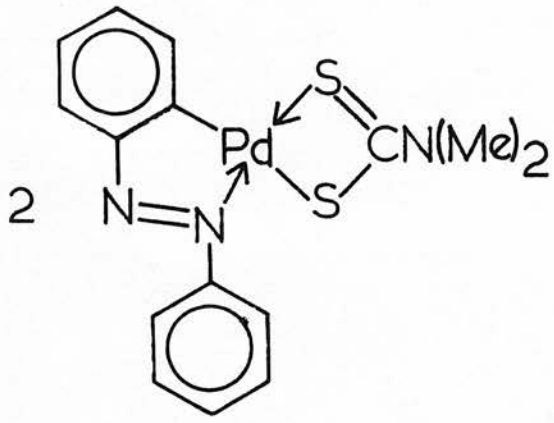


(183)

evidence. Elemental analysis of the compound gave results almost, but not quite, consistent with the proposed structure. Thus, instead of the intended electrophilic attack by the phenylmethanesulphenyl cation, displacement of the acetato-ligand by a succinimido-ligand had occurred. The benzylthio-groups were not completely accounted for though some were recovered in the form of dibenzyl disulphide.

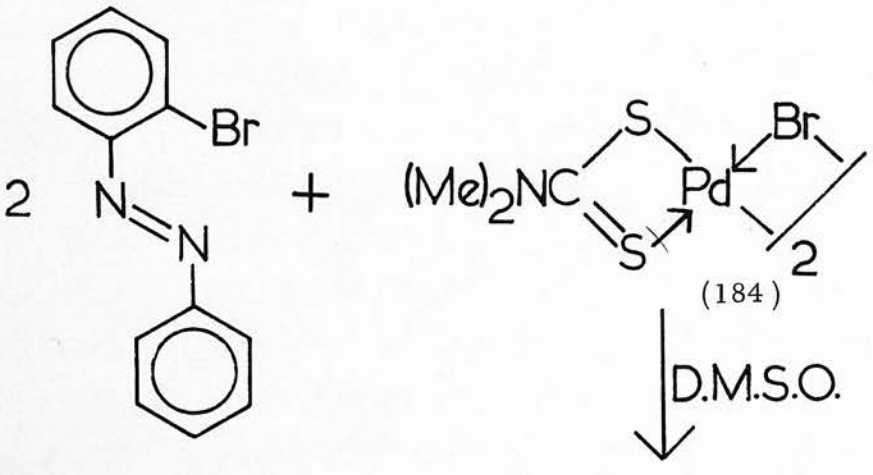
In view of the somewhat discouraging results obtained in reactions of the acetate- and halogen-bridged dimeric complexes with electrophilic reagents, it was decided to investigate some corresponding reactions of the monomeric dithiocarbamatopalladium complex of azobenzene. Treatment of this compound (140) with one equivalent of bromine under mild conditions yielded a purple solid and a red oil which was crystallised with some difficulty to give red needles.

An infrared spectrum of the purple-red solid showed a broad band in the region 1540-1580 cm^{-1} which was consistent with a metal-complexed dithiocarbamato-group but, the spectrum showed no evidence of aromatic ring vibrations. The compound was involatile in the mass spectrometer and a ^{1}H n. m. r. spectrum



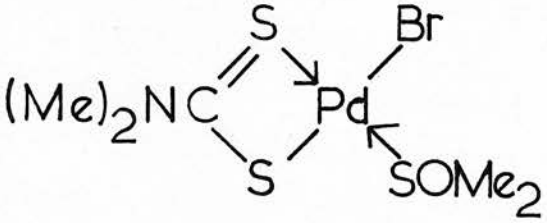
(140)

$2\,Br_2$



(184)

D.M.S.O.



(185)

in d^6-dimethyl sulphoxide merely showed two closely spaced singlets between δ3.3 and δ3.5 attributable to the N-methyl protons of a dithiocarbamato-group. Elemental analysis gave results consistent with the novel, bromide-bridged dithiocarbamato-palladium complex (184). The ^{1}H n.m.r. spectrum showed two distinct N-methyl resonances instead of the one expected for this symmetrical structure. Dimethyl sulphoxide, however, has been reported[88] to act as a bridge-splitting agent in the same way as phosphines and other Lewis bases. This would explain the presence of two N-methyl resonances instead of one since a bridge-splitting reaction would result in the formation of the monomeric derivative (185). The two methyl groups would thus be situated in different environments and give different chemical shifts in the n.m.r. spectrum.

The red crystalline product was identified as 2-bromo-azobenzene, both from analytical and spectroscopic evidence, and also by comparison of its melting point with the value reported by Belcher[86] and his co-workers. A high yield of 2-bromoazobenzene was obtained and this reaction was the first efficient replacement of palladium by a non-metallic atom or group that we had achieved.

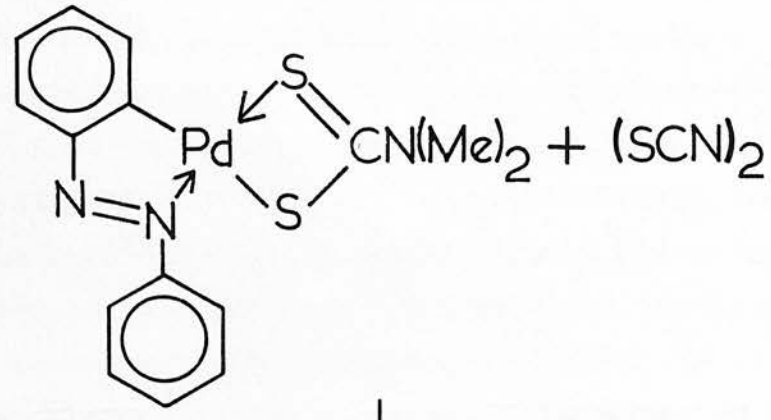
It was thought that the reaction involved either direct attack by the electrophilic halogen molecule at the carbon atom of the carbon-metal bond or oxidative addition of the halogen to give a transient palladium (IV) species, followed by a reductive elimination to give the observed products. The efficiency of the reaction was evidently due to the presence of the dithiocarbamato-ligand which remained firmly attached to the palladium, thus preventing further metallation of the 2-bromoazobenzene.

In order to extend this type of reaction to the preparation of an azobenzene containing a sulphur substituent in the ortho-position, the dithiocarbamato-complex (140) was treated with various reagents containing electrophilic sulphur. Neither trichloromethanesulphenyl chloride nor phenylmethanesulphenyl bromide gave a product of the required type (see Experimental Section) but

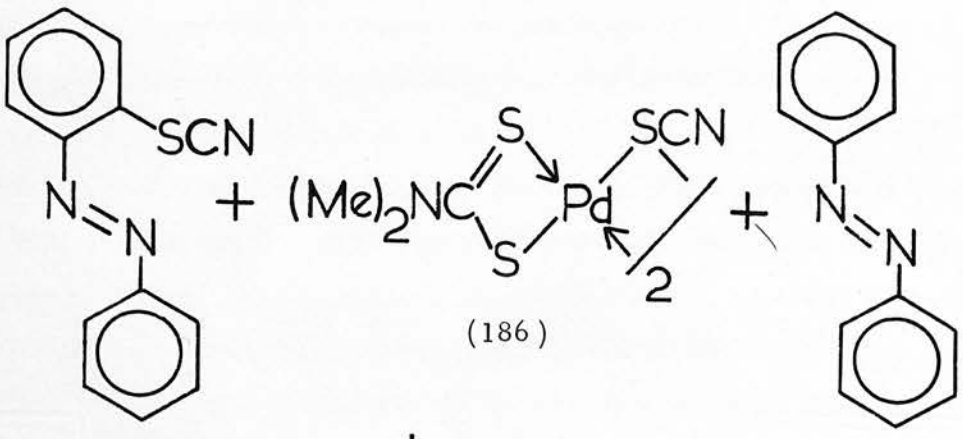
thiocyanogen behaved in the expected manner.

Treatment of the azobenzenedithiocarbamato complex (140) with one equivalent of thiocyanogen in chloroform gave three products, a yellow powdery solid and two red crystalline compounds. The yellow solid, which precipitated from the reaction mixture, gave an infrared spectrum showing a strong sharp band at 2140 cm^{-1} and a broad band in the region 1550-1570 cm^{-1}; aromatic ring absorptions were absent. The band at 2140 cm^{-1} was assigned to the C≡N stretching vibration of a thiocyanato-ligand and the broad band at 1550-1570 cm^{-1} was consistent with a metal-complexed dithiocarbamato-group. These observations suggested the thiocyanato-bridged dithiocarbamato-complex (186) as a possible structure for the yellow solid, this being analogous to the bridged compound obtained in the reaction with bromine. The mass spectrum did not show a peak corresponding to this dimeric structure but a weak peak was present at m/e 346, corresponding to bis(dimethyldithiocarbamato) palladium. The ^{1}H n. m. r. spectrum was uninformative since it showed only a single peak at δ3. 3 attributable to the N-methyl protons of a dithiocarbamato-group. The absence of a second singlet in the same region of the spectrum did not preclude the possibility of some bis(dimethyldithiocarbamato) palladium being present as a minor component of the yellow solid, since this compound is known to be extremely insoluble and might have been removed when the solution was filtered before measuring the n. m. r. spectrum. Elemental analysis of the yellow product gave results consistent with a mixture consisting mainly of the proposed thiocyanato-bridged dimer (186) together with a smaller amount of the bis(dithiocarbamato) palladium. Of the two red crystalline products, the minor one was identified, from its infrared spectrum and melting point, as azobenzene. The major of the two products showed a very weak infrared absorption at 2150 cm^{-1} consistent with the presence of a thiocyanato-group and its mass spectrum showed a parent ion mass (m/e 239) corresponding to <u>ortho</u>-thiocyanatoazobenzene (187). The ^{1}H n. m. r. spectrum of the compound showed two complex multiplets close

Fig (XXIV)



(140)



(186)

(187)

+

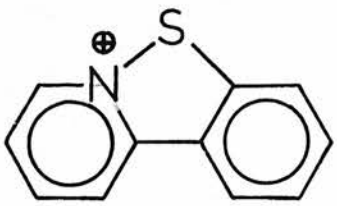
$Pd[S_2CN(Me)_2]_2$

together in the aromatic region and was generally similar to that of o-bromoazobenzene. Elemental analysis further confirmed the identity of the compound and comparison with an authentic specimen prepared by a previously reported[87] method showed the two to be identical. The reaction and the products obtained are shown in Fig. (XXIV).

In view of this successful synthesis of ortho-thiocyanatoazobenzene, similar reactions of thiocyanogen with dithiocarbamato-complexes of other ligands were carried out in order to investigate the generality of the method.

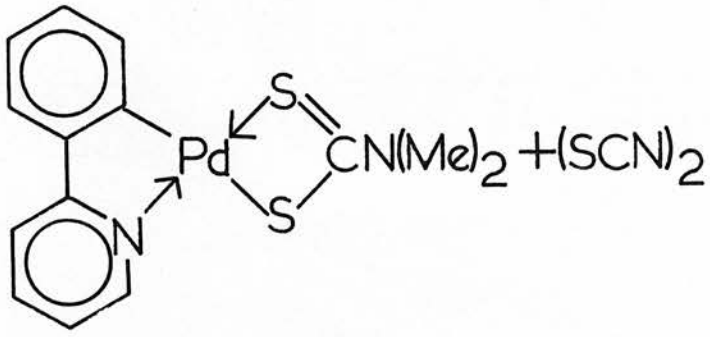
The 2-phenylpyridine complex (140a) was treated with thiocyanogen under the same conditions as had been used for the azobenzene complex. In this case only two products were obtained, one a pale yellow powdery solid and the other a white crystalline compound. The pale yellow solid showed the same infrared and mass spectra, and had the same melting point as the yellow product from the corresponding reaction of the azobenzene complex; it was thus identified as a mixture consisting mainly of the thiocyanato-bridged complex (186) with a smaller amount of bis(dimethyldithiocarbamato) palladium.

The white crystalline solid was readily characterised as 2-(2-thiocyanatophenyl)pyridine (188). A sharp peak in the infrared spectrum at 2150 cm^{-1} showed the presence of the thiocyanato-group and a strong parent ion mass at m/e 212 in the mass spectrum corresponded to that expected for the proposed compound. A strong fragment ion mass at m/e 186 was consistent with the isothiazolo-pyridinium cation (178). A ^{1}H n.m.r. spectrum of the compound

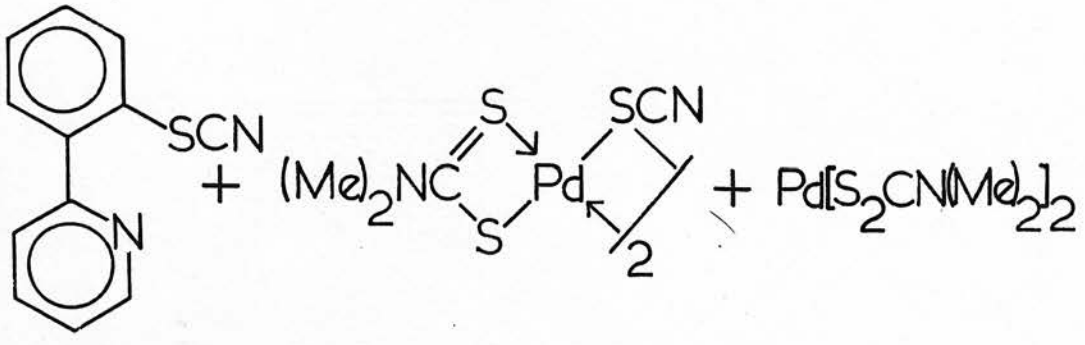


(178)

Fig.(XXV)



(140a)



(188)

(186)

showed three relatively well-resolved resonances in the aromatic region, one of which was at significantly lower field (δ8.6) than the others. As expected, replacement of the metal resulted in a general downfield shift of the aromatic proton resonances. In view of the spin-spin splitting no attempt was made to assign signals other than the one at δ8.6 which had 1/7 the intensity of the remaining signals and was assigned to H-6 of the pyridyl ring. A satisfactory elemental analysis of the compound was obtained. The reaction and its products are summarised in Fig. (XXV).

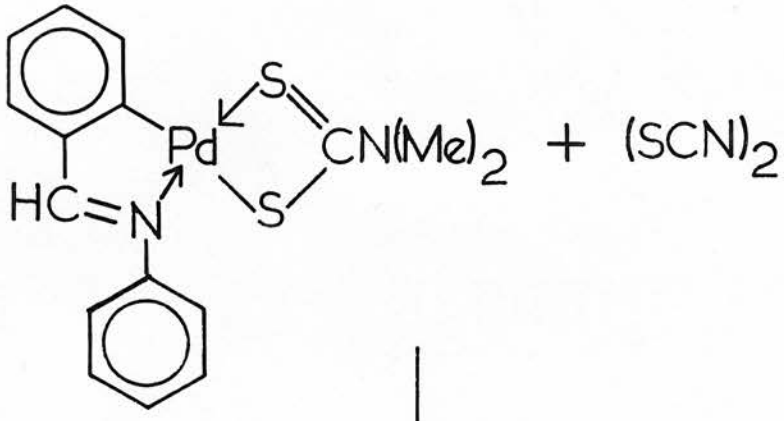
A fair yield (50%) was obtained in the reaction of the phenylpyridine complex with one equivalent of thiocyanogen and repetition of the experiment using an excess of the reagent did not significantly improve upon it.

The reactions of the benzylideneaniline and styrylpyridine dimethyldithiocarbamatopalladium complexes (140b) and (140c) with thiocyanogen each gave two products, one a yellow solid of limited solubility and the other an oil. The pale yellow solids obtained in both reactions were very similar both to each other and to the sparingly soluble products obtained in the analogous reactions of the azobenzene and phenylpyridine complexes.

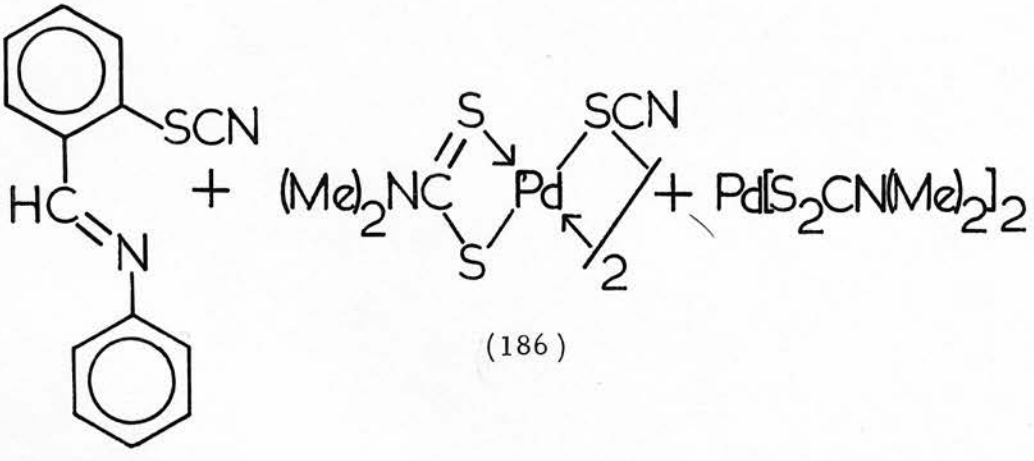
The oil, yellow in colour, obtained from the reaction of the benzylideneaniline complex was not crystallised despite several attempts and appeared to decompose on standing in air for more than a short period of time. The mass and n.m.r. spectra of the compound were consistent with those expected for ortho-thiocyanatobenzylideneaniline (191). The mass spectrum showed strong ion masses at m/e 238 and m/e 212 consistent with the parent ion (189) and with the benzisothiazolium cation (190), respectively, as shown below.

In the absence of a crystalline sample for elemental analysis, an exact mass measurement was carried out for m/e 238 and the results confirmed the expected elemental composition. A ^{1}H n.m.r. spectrum of the oil showed one resonance at lower field (δ8.5) than the other aromatic ones which were closely grouped in a broad

Fig.(XXVI)

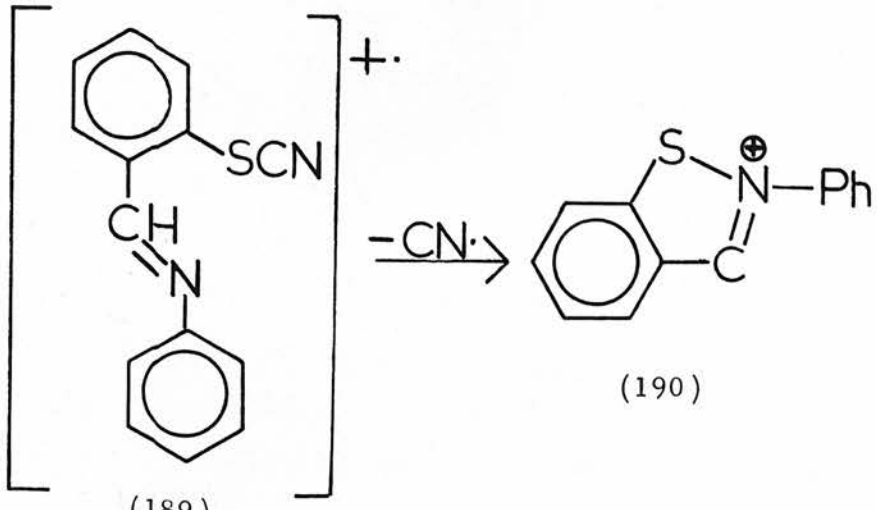


(140b)



(191)

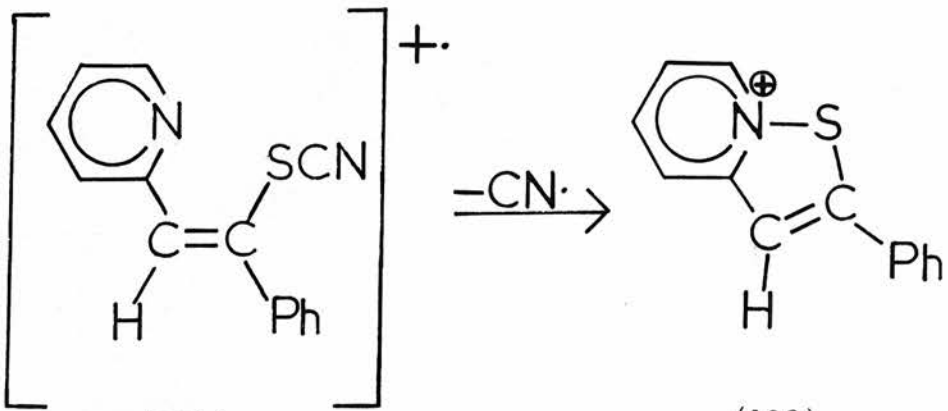
(186)



(189) (190)

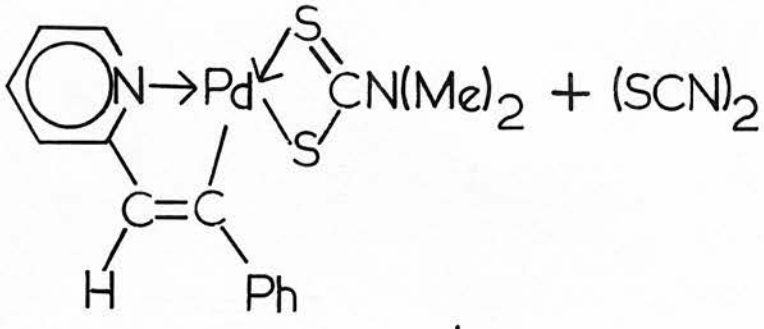
multiplet (δ8.5-8.0). The singlet at low field had 1/9 the intensity of the multiplet and was assigned to the methine proton. Owing to the complexity of the other closely grouped resonances, further proton assignment was not possible. The overall reaction and the products obtained are summarised in Fig. (XXVI).

The pale yellow oil obtained from the reaction of the styrylpyridine complex was also reluctant to crystallise, though a small amount of slightly sticky white solid was obtained from one attempt. There was sufficient only for a melting point determination, an infrared spectrum and a mass spectrum. A ^{1}H n.m.r. spectrum was obtained using the purified oil. As with the oil obtained from the previous reaction, this compound appeared to decompose when left in air. The infrared spectrum gave a sharp nitrile stretching band at 2150 cm^{-1} and the mass spectrum gave strong ion masses at m/e 238 and m/e 212, consistent with the proposed structures shown below. Exact mass measurement of the peak at m/e 212 gave results in agreement with the elemental composition

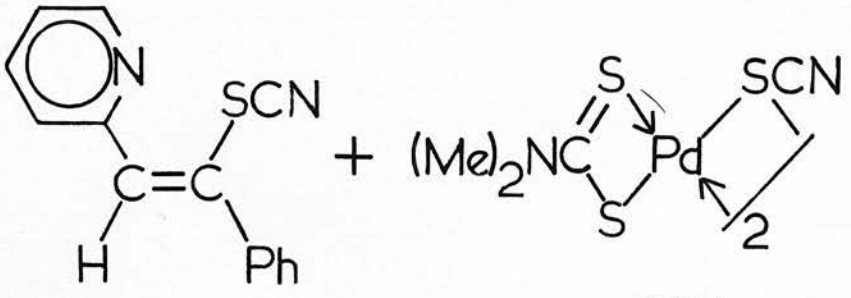


(193) (192)

Fig(XXVII)



(140c)



(194)

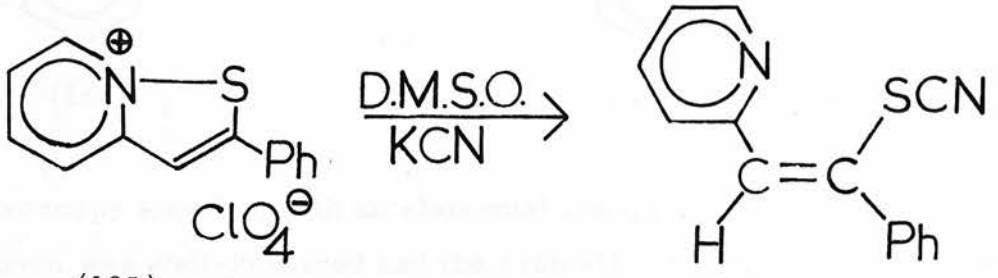
(186)

+

$Pd[S_2CN(Me)_2]_2$

of the cation (192) but the result for the m/e 238 ion, believed to be due to the parent ion of 2-(2-phenyl-2-thiocyanatovinyl) pyridine (193), was just outwith the permissible error margin. The ^1H n.m.r. spectrum of the compound was in agreement with structure (194) and showed a singlet at δ6.8 and a multiplet at δ8.5-8.7 which both integrated for one proton and a closely grouped set of aromatic resonances in the region δ7.0-7.8, which integrated for eight protons. The high-field singlet was assigned to the olefinic proton and the low-field multiplet to the H-6 of the pyridyl ring. The reaction and products are shown in Fig. (XXVII).

In order to confirm the identity of the thiocyanato-stilbazole (194), a specimen of this compound was synthesised by treatment of 2-phenylisothiazolo-[2, 3-a]-pyridinium perchlorate (195) with potassium cyanide in dimethyl sulphoxide. A pale yellow oil was obtained which was crystallised with some difficulty, and the resulting solid gave a satisfactory elemental analysis. The melting point and infrared spectrum of this authentic specimen were almost



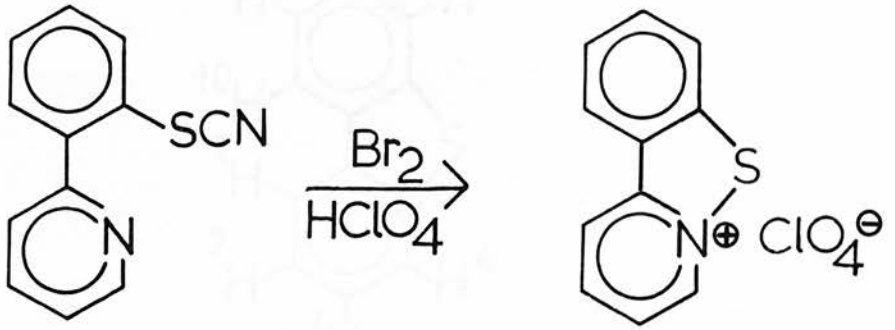
(195) (194)

identical with those of the white solid obtained via the organometallic route, minor differences being attributable to the lower purity of the latter product. The ^1H n.m.r. spectra of the two specimens were identical. The yield of thiocyanato-compound from the styrylpyridine complex, was notably lower than the yields obtained from the other three cyclometallated complexes.

Thus these reactions involving replacement of palladium in

cyclometallated complexes by treatment with thiocyanogen, were shown to be synthetically useful for the preparation of thiocyanato-derivatives of azobenzene, 2-phenylpyridine, benzylideneaniline and 2-styrylpyridine. Of the four derivatives prepared only that of azobenzene had been reported[87] prior to this investigation, the others being novel thiocyanato-derivatives. Thus this route represents a new, convenient, and efficient route to these compounds.

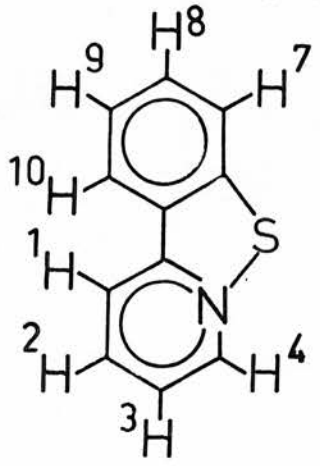
Having thus prepared a range of these compounds their potential for the syntheses of fused-ring isothiazolium salts remained to be demonstrated. 2-(2-Thiocyanatophenyl)pyridine was taken as an example and oxidised with bromine to give the novel heterocyclic product (196) which had not hitherto been prepared. The product was fully characterised by infrared and ^{1}H n.m.r.



(188) (196)

spectroscopy together with an elemental analysis. The ^{1}H n.m.r. spectrum was well-resolved and the aromatic resonances had shifted downfield markedly from those of the starting material. The spectrum showed four well-resolved resonances in the regions δ9.3-9.4, δ8.7-8.8, δ8.4-8.6 and δ7.8-8.2. These resonances integrated against each other in the approximate ratio 1:1:2:4. The doublets at δ9.3-9.4 and δ8.7-8.8 were assigned to the protons of the 4- and 1-positions of the pyridyl ring, respectively. ^{1}H n.m.r. spectra of similar systems indicated this assignment to be correct showing doublets at low field for these protons. The resonance at δ8.4-8.6, which integrated for two protons, comprised a doublet

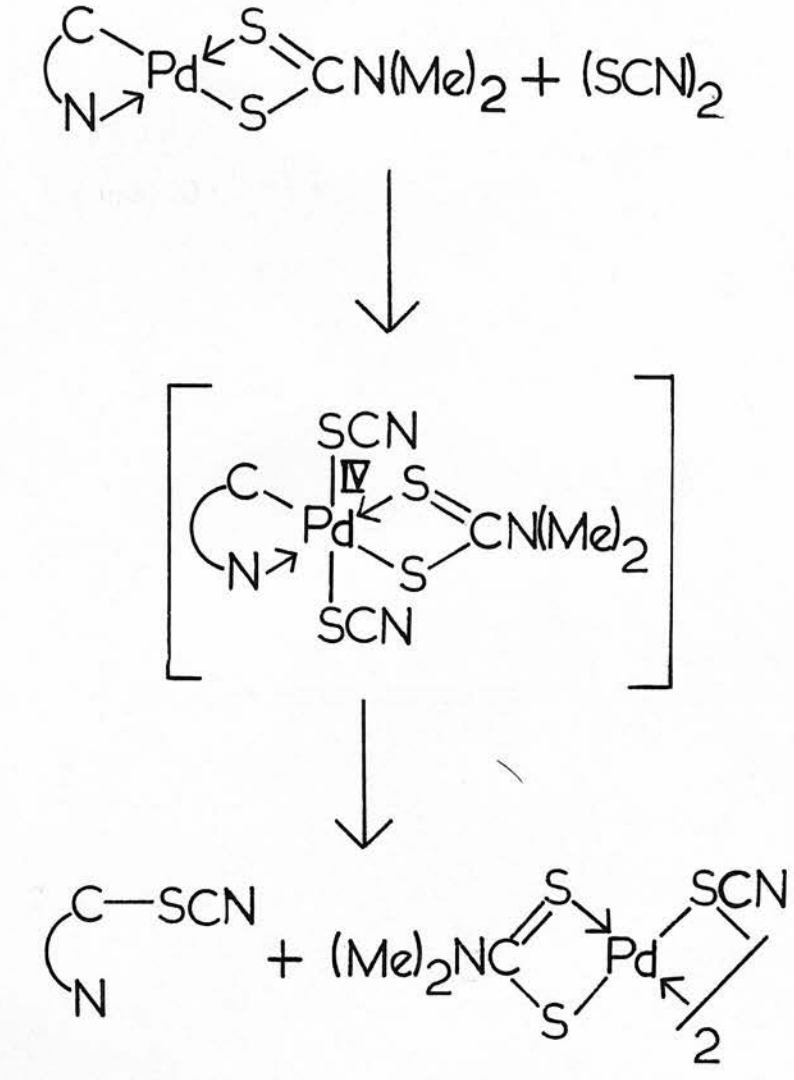
and a triplet superimposed upon one another. The triplet was assigned to the 2-H since this proton would be coupled to two ortho-protons and being para- to the nitrogen in the pyridyl ring it would be expected to resonate at low-field as a triplet. The superimposed doublet was assigned to the 10-H. This low-field doublet could be due to either the 10- or the 7-H but it was assigned to the 10-H because it seemed likely that this proton would be under not only the influence of the phenyl ring current, as in the case of the 7-H, but also, by virtue of its position, the pyridyl ring. The protons of the 3-, 7-, 8- and 9-positions could not be individually assigned due to the complexity of their resonances in the multiplet at δ7.8-8.2. The numbered ring system is shown below.



This example serves to illustrate one way in which these organic products, synthesised via organometallic intermediates, can be utilised to produce heterocyclic products which would be difficult to obtain by conventional organic routes. Time did not permit the investigation of other examples but it is confidently expected that the method will be applicable to the synthesis of other novel fused-ring isothiazolium salts and probably to fused-ring dithiolium salts by starting with cyclometallated thiones.

The two processes discussed earlier, either addition of thiocyanogen to the central metal atom of the complex followed by reductive elimination, or direct electrophilic attack of thiocyanogen at the carbon-palladium bond, are the only feasible explanations of

Fig (XXVIII)



C
N ≡ nitrogen donor ligand

the course of these reactions. Observations of the colour changes which take place during reaction suggest, in fact, that an oxidative addition might be taking place. On addition of thiocyanogen to the clear solutions of the complexes, a very dark solution resulted in each case and the dark colour persisted for an average of 5 minutes before becoming progressively lighter, at which point a precipitate became apparent. These observations support the idea of a two-stage process in which an unstable palladium (IV) complex is being rapidly formed and then slowly broken down by reductive elimination to give the final products. This process is summarised as shown in Fig. (XXVIII).

EXPERIMENTAL

General Notes

1) Melting Points

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected.

2) Elemental Analysis

Microanalyses were carried out on a Perkin-Elmer Elemental Analyser 240 by Mr. J. Grunbaum, University of Edinburgh.

3) Infrared Spectroscopy

Infrared spectra were recorded on a Unicam S. P. 200 spectrophotometer and a Perkin-Elmer S. P. 157G spectrophotometer.

4) Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectra were recorded on a Varian Associates E. M. 360 (60MHz) and a Varian Associates H. A. 100 (100 MHz) spectrometer. Chemical shifts were recorded at delta (δ) values in parts per million using tetramethylsilane as internal standard. Spectra were recorded in 10-15% weight/volume solutions, usually in deuterochloroform and in some cases d^6-dimethyl sulphoxide or trifluoroacetic acid.

5) Mass Spectroscopy

Mass spectra and exact mass measurements were obtained using an A. E. I. M. S. 902 double focussing mass spectrometer. m/e Values reported for ions containing palladium in the mass spectra of complexes refer to the principal peaks of the isotopic ion cluster, containing ^{106}Pd which is the main isotope.

6) Chromatography

Alumina for chromatography was Spence Type 'H'; x% deactivated alumina refers to Type 'H' alumina which had been

shaken for twelve hours with 5% aqueous acetic acid (x ml per 100 g alumina). Thin layer plates for preparative chromatography were prepared using Kieselgel 0.08 mm (Merck).

7) Drying of Solvents

Solvents were dried over anhydrous magnesium sulphate or molecular sieve type 4A (1/16" pellets).

Abbreviations

b. p.	boiling point
m. p.	melting point
n. m. r.	nuclear magnetic resonance
I. R.	infrared
t. l. c.	thin-layer chromatography
m. s.	mass spectrum
s	singlet
d	doublet
d. d.	doublet of doublets
t	triplet
q	quartet
m	multiplet
M^+	mass of molecular ion
m/e	mass/charge ratio

1 Synthesis of Cyclopalladated Complexes

(a) Syntheses and Attempted Syntheses of Dimeric Halogen-bridged Cyclopalladated Complexes of Azobenzene, 2-Phenylpyridine, Benzylideneaniline, 2-Styrylpyridine and Quinolizine-4-thione

Di-μ-chlorobis[2-(phenylazo)phenyl]dipalladium (II)

The method of Cope and Siekman[2] was used and, starting from 3.64 g of azobenzene, 5.9 g (92%) of the required product, m.p. 279-281°C (decomp) [lit m.p. 279-281°C (decomp)], was obtained. The identity of the product was confirmed by infrared and mass spectroscopy.

2-Phenylpyridine

The method of Evans and Allen[89] was used.

Di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II)

The method of Kasahara[51] was used and, starting from 1.55 g of 2-phenylpyridine, 2.50 g (84%) of the required product, m.p. 270°C (decomp) [lit m.p. 270°C (decomp)], was obtained. The identity of this product was confirmed by infrared, mass and ^{1}H n.m.r. spectroscopy.

Benzylideneaniline

Method as:- Vogel Part I, p. 235.

Reaction of benzylideneaniline with sodium acetate and palladium chloride

Benzylideneaniline (1.80 g) was dissolved in Analar acetic acid (50 ml), and sodium acetate (0.82 g) and palladium chloride (1.70 g) were added. The pale brown suspension was refluxed for 1 h, by which time a precipitate had formed and the reaction mixture

was dark red. Hot filtration of the reaction mixture afforded a dark green solid (product A) and this was washed with methanol and ether. On cooling, the filtrate yielded a yellow solid (product B) which was collected, washed with methanol and ether and air-dried. A further small amount of yellow solid (product C) was obtained when the residual filtrate was left to stand at room temperature overnight. Products A, B and C were purified by Soxhlet extraction into chloroform. The extract from product A was concentrated and yielded di-μ-chlorobis[2-(N-phenylformimidoyl)phenyl]-dipalladium (II) (1.10 g, 36%) as a yellow powder, m.p. 280-282°C (lit. m.p. 281-283°C).

$C_{26}H_{20}N_2Pd_2Cl_2$ requires :- C = 48.59%; H = 3.20%; N = 4.43%

found :- C = 47.68%; H = 3.22%; N = 4.38%

m/e 642 (M^+); 607; 501; 466; 321 (M^+); 286; 180.

^{1}H n.m.r. (d^6- d.m.s.o.): δ 8.45 (s, 2 methine protons), δ 8.00-6.95 (m, 18 aromatic protons).

Further confirmation of the identity of this product was obtained by comparison with an authentic sample prepared by Onoue and Moritani's method.[39]

The extract from product B was concentrated and gave bis(benzylideneaniline)palladium (II) dichloride (0.40 g, 15%) as a yellow powder, m.p. 275-280°C (decomp) [lit m.p. 275-280°C (decomp)]. Comparison of the infrared and mass spectra of this product with those of the authentic cis- and trans-isomers of bis(benzylideneaniline)palladium (II) dichloride, prepared by the method of Lewis,[40] indicated that it was a mixture of these isomers.

The extract from product C was concentrated and afforded bis(benzylideneaniline)palladium (II) dichloride (0.04 g, 1.5%) as a yellow powder, m.p. 275-280°C (decomp) [lit m.p. 275-280°C (decomp)]. Comparison of the infrared and mass spectra of this product with those of the authentic cis- and trans-isomers indicated that it was also a mixture of these isomers.

Reaction of 2-styrylpyridine with sodium tetrachloropalladate

Sodium chloride (0.58 g) and palladium chloride (0.88 g) were heated together in refluxing methanol (25 ml) until a dark-brown solution had formed. The solution was hot filtered and then added to a solution of 2-styrylpyridine (0.9 g in 10 ml MeOH). The reaction mixture was stirred overnight at room temperature and a yellow crystalline solid was deposited. The product was collected and washed with methanol and ether to yield bis(2-styrylpyridine)-palladium (II) dichloride (1.40 g) as yellow needles, m.p. 263-265°C. Infrared and mass spectroscopy indicated that the product obtained was the simple coordination complex bis(2-styrylpyridine)palladium (II) dichloride and not the required cyclopalladated complex.

4-Chloroquinolizinium perchlorate

This was prepared by the method of Dr. G. Abbot, who adapted it from that of Van Allen and Reynolds.[90]

Quinolizine-4-thione

The method of Van Allen and Reynolds[90] was used and, starting from 1.3 g of 4-chloroquinolizinium perchlorate, 0.4 g (55%) of the required product, m.p. 101-103°C (lit m.p. 104°C), was obtained. The identity of this product was confirmed by infrared and ^{1}H n.m.r. spectroscopy.

Reaction of quinolizine-4-thione with sodium acetate and palladium chloride

Quinolizine-4-thione (0.97 g) was dissolved in Analar acetic acid (50 ml), and sodium acetate (0.50 g) and palladium chloride (1.02 g) were added. The reaction mixture was refluxed for 4 h and the initial yellow colour of the mixture turned to dark red. Hot filtration of the reaction mixture afforded a brown solid thought to be unreacted starting material. Solvent was removed from the

filtrate to yield a yellow-brown solid. This was washed with chloroform and ether to remove any unreacted quinolizine-4-thione, and then Soxhlet extracted with methanol for 24 h. The extract obtained was concentrated and yielded bis(quinolizine-4-thione)-palladium (II) dichloride, (0.66 g, 25%) as a bright yellow amorphous solid, m.p. >300°C.

$C_{18}H_{14}Cl_2N_2PdS_2$ requires:- C=43.62%; H=3.01%; N=5.73%
found :- C=44.81%; H=2.91%; N=5.34%

^{1}H n.m.r. (d^6-d.m.s.o.): δ10.33 (m, H-6 of quinolizine); δ8.28-7.84 (m, other ring protons).

Mass and infrared spectra were inconclusive.

Reaction of quinolizine-4-thione with sodium tetrachloropalladate

Sodium chloride (0.36 g) and palladium chloride (0.55 g) were heated together in methanol (25 ml) until a dark brown solution had formed. The solution was then hot filtered and the filtrate cooled before being mixed with a solution of quinolizine-4-thione (0.5 g) in methanol (10 ml). On mixing, a dark-orange solid was precipitated and this persisted throughout the 3 h for which the mixture was stirred at room temperature. The orange product was collected and washed with methanol and ether. The compound was then leached with hot methanol in a Soxhlet appratus for 36 h and the residual dark-orange solid was dried. Di-μ-chlorobis(4-thiono-quinolizin-6-yl)dipalladium (II) (0.40 g, 65%) was obtained as an orange powder, m.p. >300°C.

$C_{18}H_{12}Cl_2N_2Pd_2S_2$ requires:- C=35.80%; H=1.99%; N=4.63%
found :- C=36.18%; H=2.01%; N=4.33%

The infrared, mass and ^{1}H n.m.r. spectra obtained were inconclusive owing to the involatile and insoluble nature of the product.

Note:- This reaction has since been repeated four times, each repetition affording an orange product which was not the same as that described above and probably contained unmetallated quinolizinethione ligands. No explanation can be provided for the failure

of these reactions to yield the original cyclometallated complex.

(b) Syntheses and Attempted Syntheses of Acetate-bridged Complexes.

Palladium Acetate

The method of Wilkinson et al[91] was used.

Reaction of azobenzene with palladium acetate

Azobenzene (0.91 g) was treated with palladium acetate (1.12 g) in refluxing Analar acetic acid (50 ml) for 3 h. The resultant red solution was hot filtered and cooled. Addition of an equal volume of water to the reaction mixture resulted in a dark red solid being precipitated. The aqueous suspension was extracted several times with dichloromethane and the combined extracts were then washed with a saturated solution of sodium bicarbonate to remove any acetic acid present. The combined extracts were dried over magnesium sulphate and evaporated to dryness, yielding a dark-red crystalline solid. This was taken up in the minimum of hot dichloromethane and chromatographed on 10% deactivated alumina (100 g). Two fractions were obtained (fraction A and fraction B). Fraction A, eluted with light petroleum, yielded azobenzene. Fraction B, a dark-red band on a column, was eluted with ether to give a dark-red solution which, after concentration, yielded di-μ-acetatobis[2-(phenylazo)phenyl]dipalladium (II) (1.40 g, 80%) as dark-red prisms, m.p. 208-210°C (lit m.p. 208-210°C).

$C_{28}H_{24}N_4O_4Pd_2$ requires:- C=48.51%; H=3.48%; N=8.08%

found:- C=48.63%; H=3.51%; N=7.91%

m/e 692 (M^+); 346 (1/2 M^+)

I.R. (C=O) = 1550-1570 cm^{-1}

^1H n.m.r. ($CDCl_3$): δ 8.10-6.40 (m, 18 aromatic protons); δ 2.05 (s, 6 acetate methyl protons).

Reaction of 2-phenylpyridine with palladium acetate

2-Phenylpyridine (1.55 g) was treated with palladium acetate

(2.24 g) under conditions identical with those of the preceding reaction and similar work-up afforded a yellow solid. This was taken up in the minimum of boiling chloroform and chromatographed on 10% deactivated alumina (100 g). One fraction was obtained. It consisted of a yellow band which was eluted with chloroform to give a yellow solution. Concentration of the solution gave di-μ-acetatobis[2-(2-pyridyl)phenyl]dipalladium (II) (1.92 g, 80%) as a yellow crystalline solid, m.p. 260-265°C (decomp). The compound was recrystallised from benzene-pentane to give yellow flakes.

$C_{26}H_{22}N_2O_4Pd_2$ requires:- C=48.93%; H=3.42%; N=4.40%
found:- C=48.86%; H=3.59%; N=4.28%

m/e 638 (M^+); 579; 473; 319 (1/2 M^+); 260; 154.
I.R. (C=O) = 1560-1580 cm^{-1}

^{1}H n.m.r. ($CDCl_3$): δ 7.85 (d, 2α-pyridyl protons); δ 7.45-6.35 (m, 14 aromatic protons); δ 2.25 (s, 6 acetate methyl protons).

Di-μ-acetatobis[2-(N-phenylformimidoyl)phenyl]dipalladium (II)

This compound was prepared by the method of Onoue and Moritani.[39] Benzylideneaniline (1.35 g) was treated with palladium acetate (1.68 g) to give the required product (1.64 g, 64%) as a yellow solid, m.p. 215-220°C (decomp) [lit m.p. 210-220°C (decomp)]. The identity of this compound was confirmed by infrared, mass and ^{1}H n.m.r. spectroscopy.

Reaction of 2-styrylpyridine with palladium acetate

2-Styrylpyridine (1.25 g) was treated with palladium acetate (1.57 g) in the same way as azobenzene and 2-phenylpyridine. Chromatographic isolation of the product, however, was carried out on silica gel instead of alumina. Only one fraction was isolated, consisting of a yellow band which was eluted with dichloromethane-ethanol (95:5) to give a yellow solution. Concentration of the solution gave di-μ-acetatobis[1-phenyl-2-(2-pyridyl)vinyl]dipalladium (II) (1.3 g, 60%) as a yellow solid which was recrystallised from benzene-pentane to

give yellow plates, m. p. 200-202°C.

$C_{30}H_{26}N_2O_4Pd_2$ requires:- C=52.01%; H=3.73%; N=4.02%
found :- C=51.96%; H=4.01%; N=3.71%

m/e 690 (M^+); 345 (1/2 M^+); 286; 180.

I.R. (C=O) = 1550-1570 cm^{-1}; (C=C) = 1605 cm^{-1}.

^{1}H n.m.r. ($CDCl_3$): δ7.86-6.55 (m, 18 aromatic protons); δ5.40 (s, 2 olefinic protons); δ1.59 (s, 6 acetate methyl protons).

Reaction of quinolizine-4-thione with palladium acetate

Quinolizine-4-thione (0.80 g) and palladium acetate (1.12 g) were refluxed together for 3 h in Analar acetic acid and a dark green solution resulted. Solvent was removed from the reaction mixture at the rotary evaporator and a dark-green oily residue was obtained. This was dissolved in the minimum of hot dichloromethane and chromatographed on 10% deactivated alumina (100 g). A broad yellow band separated on the column but, despite the use of several different solvents, it could not be eluted. The section of the alumina column containing the yellow band was removed and treated with boiling acetic acid. The resultant slurry was then filtered, giving a bright yellow filtrate which was reduced in volume and triturated with ether to give a flocculent yellow precipitate. This was collected and dried giving a bright yellow solid (0.6 g), m. p. 280°C (decomp). (Found: C=37.04%; H=3.33%; N=2.97%).

Infrared and mass spectroscopy were inconclusive and an elemental analysis of the product was inconsistent with that required for the acetate-bridged complex. Owing to the very low solubility of the compound it could not be studied by ^{1}H n.m.r. spectroscopy and thus remains unidentified.

(c) Syntheses of Phosphine Complexes

Reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II) with triethylphosphine

The title complex (0.59 g) was suspended in dichloromethane

(10 ml) and two mole equivalents of triethylphosphine (0. 24 g) were added. The mixture was stirred at room temperature and after a few minutes a clear red solution was obtained. The solution was stirred for a further hour and was then concentrated to give a pale yellow solid. This product was taken up in the minimum of hot dichloromethane and chromatographed on 10% deactivated alumina (50 g). One fraction was apparent as a pale yellow band, and it was eluted with dichloromethane to give a pale yellow solution. Concentration of the solution gave chloro-[2-(2-pyridyl)phenyl]triethylphosphinepalladium (II) (0. 60 g, 73%) as a pale yellow crystalline solid, m. p. 158-160°C.

$C_{17}H_{23}ClNPPd$ requires:- C=49. 40%; H=5. 56%; N=3. 39%

found :- C=49. 54%; H=5. 94%; N=3. 05%

m/e 413 (M^+); 378; 349; 320; 291; 272; 260; 154.

^1H n. m. r. ($CDCl_3$): δ 9. 60-9. 35 (m, 1 α-pyridyl proton), δ 7. 80-6. 85 (m, 7 aromatic protons), δ 2. 35-1. 70 (m, 6 CH_2-P protons), δ 1. 55-0. 75 (m, 9 methyl protons).

Reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II) with an excess of triethylphosphine

The title complex (0. 59 g) was treated with four mole equivalents of triethylphosphine (0. 47 g) under conditions identical with those of the previous reaction. The same work-up procedure was used and chromatography on 10% deactivated alumina (50 g) gave two fractions (fraction A and fraction B). Fraction A consisted of a very pale yellow band and this was eluted with ether to give a very pale yellow solution. Concentration of the solution gave chloro-[2-(2-pyridyl)phenyl]bis(triethylphosphine)palladium (II) (0. 20 g, 20%) as a white crystalline solid, m. p. 98-100°C. Recrystallisation of this product from light petroleum gave white needles.

$C_{23}H_{38}ClPdP_2$ requires:- C=51. 95%; H=7. 15%; N=2. 67%

found :- C=51. 88%; H=7. 17%; N=2. 74%

A satisfactory infrared spectrum was obtained but mass and ^{1}H n.m.r. spectra were inconclusive (see discussion).

Fraction B consisted of a pale yellow band, eluted with dichloromethane, which gave chloro-[2-(2-pyridyl)phenyl]triethylphosphinepalladium (II) (0.42 g, 50%) as a pale yellow crystalline solid, m.p. 158-160°C, identical with the product from the previous reaction.

Reaction of di-μ-chlorobis(4-thionoquinolizin-6-yl)dipalladium (II) with triethylphosphine.

The title complex (0.60 g) was suspended in dichloromethane (10 ml) and a very small excess of triethylphosphine (0.25 g) was added. After stirring the mixture for a few minutes a clear red solution was obtained and stirring was continued for 1 h. The solution was then concentrated to give a yellow solid which was taken up in the minimum of hot chloroform and chromatographed on 10% deactivated alumina (100 g). Two fractions were obtained (fraction A and fraction B) and both were yellow bands which were eluted with chloroform affording bright yellow solutions. Concentration of the solution from fraction A gave chloro-(4-thionoquinolizin-6-yl)triethylphosphinepalladium (II) (0.13 g, 15%) as a yellow crystalline solid, m.p. 173-175°C. The infrared spectrum showed strong stretching bands at 1040 cm^{-1}, 760 cm^{-1} and 730 cm^{-1} consistent with those expected for triethylphosphine but the mass spectrum, while showing a weak ion mass at m/e 419 consistent for the required product, showed other ion masses at m/e 458 and m/e 414 which were inexplicable in terms of this product.

^{1}H n.m.r. ($CDCl_3$); δ9.10- 8.70 (q, 1 proton at 7 position of quinolizine ring); δ8.0-7.25 (m, 5 ring protons); δ2.30-1.65 (m, 6 CH_2-P protons); δ1.6-0.9 (m, 9 methyl protons).
An elemental analysis of this product gave results almost, but not quite, consistent with those required.

Concentration of the solution obtained from fraction B gave a yellow crystalline solid (0.50 g, 62%) m.p. 170-171°C which gave

infrared, mass and ^{1}H n.m.r. spectra identical with those of the product from fraction A. The two products were assumed to be cis- and trans-isomers of the required product.

The products were rechromatographed and combined before being submitted for elemental analysis.

$C_{15}H_{21}ClNPdS$ requires:- C=42.92%; H=5.01%; N=3.34%
found :- C=42.90%; H=5.10%; N=3.16%

(d) Syntheses of Dithiocarbamato- and Dithiophosphato-derivatives of Cyclopalladated Complexes

Reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II) with sodium diethyldithiocarbamate

The title complex (0.30 g) and sodium diethyldithiocarbamate (0.23 g) were stirred together at room temperature in acetone (25 ml) for 24 h. The resultant cloudy yellow solution was filtered to give a yellow solid and a yellow filtrate. The yellow solid was shown to be mainly the original complex by its infrared spectrum and melting point. Concentration of the filtrate yielded an orange crystalline solid which was taken up in the minimum of hot chloroform and chromatographed on 10% deactivated alumina. The only fraction, a yellow band, was eluted with chloroform to give a yellow solution. Concentration of the solution afforded a light orange crystalline solid (0.10 g), m.p. 189-190°C. Mass and ^{1}H n.m.r. spectra showed that the product was a mixture of the required complex and bis(diethyldithiocarbamato)palladium (II). Attempts to separate the two chromatographically were unsuccessful owing to their similar retention times on alumina and silica.

Reaction of di-μ-acetatobis[2-(N-phenylformimidoyl)phenyl]dipalladium (II) with sodium diethyldithiocarbamate.

The title complex (0.35 g) and sodium diethyldithiocarbamate (0.23 g) were stirred together at room temperature in acetone (50 ml) for 24 h. A white precipitate, presumed to be sodium acetate, formed

and was collected. Concentration of the filtrate afforded a yellow solid which was dissolved in the minimum of hot chloroform and the solution was chromatographed on 10% deactivated alumina. One fraction was obtained as a yellow band and elution with chloroform afforded a yellow solution. Solvent was removed at the rotary evaporator to yield a yellow crystalline solid (0.30 g), m.p. 155-157°C. Mass and ^{1}H n.m.r. spectroscopy indicated a mixture of bis(diethyldithiocarbamato)palladium (II) and the required product. Attempts to separate the two components were again unsuccessful.

Reaction of di-μ-acetatobis[2-(2-pyridyl)phenyl]dipalladium (II) with sodium diethyldithiocarbamate

The title complex (0.32 g) was treated with sodium diethyldithiocarbamate (0.23 g) under conditions identical with those of the preceding reaction. The same work-up procedure gave a yellow crystalline solid (0.25 g), m.p. 184-186°C. Mass and ^{1}H n.m.r. spectroscopy indicated the product to be a mixture of the required complex and bis(diethyldithiocarbamato)palladium (II). Repeated attempts to separate the two components were unsuccessful.

Tetraethylammonium dimethyldithiocarbamate

Tetraethylammonium chloride (1.66 g) and sodium dimethyldithiocarbamate (1.43 g) were stirred together in absolute alcohol (25 ml) at room temperature. After ten minutes the formation of a white precipitate was apparent and this was collected. A positive test with acidified silver nitrate indicated that the white solid obtained was sodium chloride. Removal of solvent gave a pale yellow oil which, on cooling, gave a white crystalline solid (2.25 g, 94%). The compound was hygroscopic and had to be stored over calcium chloride in a vacuum-desiccator. A sample, recrystallised from ethyl acetate to give white needles, gave a ^{1}H n.m.r. spectrum consistent with that expected of the required product.

Reaction of di-μ-acetatobis[2-(phenylazo)phenyl]dipalladium (II) with tetraethylammonium dimethyldithiocarbamate

The title complex (0.86 g) was dissolved in dichloromethane (25 ml) and tetraethylammonium dimethyldithiocarbamate (0.62 g) was added. The mixture was then stirred at room temperature for 3 h. Over this period the initial dark red colour of the reaction mixture changed to dark orange. A precipitate which had formed was filtered off giving a white solid which was extremely hygroscopic and could not be isolated. This was presumed to be tetraethylammonium acetate. Concentration of the filtrate gave a dark brown solid which was dissolved in the minimum of hot dichloromethane and chromatographed on 10% deactivated alumina (50 g). One main fraction was obtained as a dark orange band and elution with dichloromethane gave a light orange solution. Concentration of the solution gave a brown solid which was recrystallised from toluene affording 2-(phenylazo)phenyl(N, N-dimethyldithiocarbamato)palladium (II) (0.7 g, 70%) as dark orange prisms, m.p. 222-224°C.

$C_{15}H_{15}N_3PdS_2$ requires:- C=44.20%; H=3.73%; N=10.29%
found:- C=44.40%; H=3.66%; N=9.98%

m/e 407 (M^+)

I.R. (R_2NCS_2) = 1530-1550 cm^{-1}

^1H n.m.r. ($CDCl_3$): δ 8.15-7.75 (m, 3 aromatic protons); δ 7.6-7.15 (m, 6 aromatic protons); δ 3.40 (s, 3N-methyl protons); δ 3.35 (s, 3N-methyl protons).

Reaction of di-μ-acetatobis[2-(2-pyridyl)phenyl]dipalladium (II) with tetraethylammonium dimethyldithiocarbamate

The title complex (0.64 g) and tetraethylammonium dimethyldithiocarbamate (0.50 g) were stirred together in dry chloroform overnight. A precipitate which had formed was collected giving a white hygroscopic solid which, as in the previous reaction, was

presumed to be tetraethylammonium acetate. The yellow filtrate was concentrated to give a bright yellow solid which was taken up in the minimum of hot chloroform and chromatographed on 10% deactivated alumina. The main fraction, a yellow band, was eluted with chloroform to give a yellow solution. Concentration of the solution yielded 2-(2-pyridyl)phenyl(N, N-dimethyldithiocarbamato)-palladium (II) (0.7 g, 80%) as a yellow crystalline solid, m.p. 259-261°C. Golden yellow prisms were obtained when the compound was recrystallised from toluene.

$C_{14}H_{14}N_2PdS_2$ requires:- C=44.21%; H=3.68%; N=7.36%
found :- C=44.58%; H=3.74%; N=7.21%

m/e 380 (M^+); 154

I.R. (R_2NCS_2) = 1520-1540 cm^{-1}

^1H n.m.r. ($CDCl_3$): δ8.50-8.30 (d, 1α-pyridyl proton); δ7.85-7.40 (m, 3 aromatic protons); δ7.30-6.85 (m, 4 aromatic protons); δ3.45 (s, 3N-methyl protons); δ3.35 (s, 3N-methyl protons).

Reaction of di-μ-acetatobis[2-(N-phenylformimidoyl)phenyl]di-palladium (II) with tetraethylammonium dimethyldithiocarbamate

The title complex (1.04 g) was treated with tetraethylammonium dimethyldithiocarbamate (0.75 g) under conditions identical with those of the preceding reactions. The same work-up procedure afforded a yellow solid which was recrystallised from toluene to give 2-(N-phenylformimidoyl)phenyl(N, N-dimethyldithiocarbamato)palladium (II) (1.08 g, 81%) as light yellow plates, m.p. 222-223°C (decomp).

$C_{16}H_{16}N_2PdS_2$ requires:- C=47.30%; H=3.94%; N=6.90%
found :- C=47.71%; H=3.96%; N=6.79%

m/e 406 (M^+); 180

I.R. (R_2NCS_2) = 1520-1550 cm^{-1}

^1H n.m.r. ($CDCl_3$): δ8.20 (s, 1 methine proton); δ7.55-6.95 (m, 9 aromatic protons); δ3.35 (s, 3N-methyl protons); δ3.30 (s, 3N-methyl protons).

Reaction of di-μ-acetatobis[1-phenyl-2-(2-pyridyl)vinyl]palladium (II) with tetraethylammonium dimethyldithiocarbamate

The title complex (1.04 g) was treated with tetraethylammonium dimethyldithiocarbamate (0.75 g) as in the foregoing reactions. Similar work-up procedure gave a pale yellow solid which was recrystallised from toluene to give 1-phenyl-2-(2-pyridyl)vinyl(N, N-dimethyldithiocarbamato)palladium (II) (1.2 g, 91%) as pale yellow flakes, m.p. 192-193°C.

$C_{16}H_{16}N_2PdS_2$ requires:- C=47.29%; H=3.94%; N=6.90%

found:- C=47.24%; H=3.93%; N=6.80%

m/e 406 (M^+); 286; 180.

I.R. (R_2NCS_2) = 1520-1545 cm^{-1}

^1H n.m.r. ($CDCl_3$): δ 8.20-8.05 (d, 1α-pyridyl proton); δ 7.90-6.75 (m, 8 aromatic protons); δ 6.35 (s, 1 olefinic proton); δ 3.30 (s, 3N-methyl protons); δ 3.25 (s, 3N-methyl protons).

Tetraethylammonium O, O-diethyl dithiophosphate

O, O-Diethyl hydrogen dithiophosphate (7.44 g) was added to an aqueous ethanolic solution of sodium hydroxide (1.6 g in 25 ml H_2O/25 ml EtOH) and the mixture was stirred for 1 h. Tetraethylammonium chloride (6.6 g) was then added to the mixture which was stirred for a further 20 minutes. Solvent was then removed at the rotary evaporator yielding a white solid. This solid was then refluxed in ethyl acetate and the solution hot filtered. On cooling the filtrate, tetraethylammonium O, O-diethyl dithiophosphate (2.2 g, 20%) was obtained as white fibrous needles, m.p. 146-147°C. Infrared and ^1H n.m.r. spectra were consistent with the required product.

Reaction of di-μ-acetatobis[2-(phenylazo)phenyl]dipalladium (II) with tetraethylammonium O, O-diethyl dithiophosphate

The title complex (1.20 g) was dissolved in dichloromethane

(20 ml) and a solution of tetraethylammonium O, O-diethyl dithiophosphate (1.10 g in 10 ml $CHCl_3$) was added. The mixture was stirred for two hours and a dark yellow solution resulted. The solution was filtered giving a hygroscopic residue which was discarded and a dark yellow filtrate. Concentration of the filtrate gave a brown solid which was taken up in the minimum of hot chloroform and chromatographed on 10% deactivated alumina. A fraction comprising a dark orange band was eluted with ether to give an orange solution. Removal of solvent afforded a brown solid which, when recrystallised from toluene, gave 2-(phenylazo)phenyl-(O, O-diethyl dithiophosphato)palladium (II) (1.20 g, 75%) as orange flakes, m.p. 109-111°C. The infrared, mass and ^1H n.m.r. spectra confirmed that this was the required product.

m/e 472 (M^+)

^1H n.m.r. ($CDCl_3$): δ 8.10-7.10 (m, 9 aromatic protons) δ 4.45-3.90 (m, 4 CH_2-P protons); δ 1.60-1.25 (t, 6 methyl protons).

Reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II) with sodium dimethyldithiocarbamate.

The title complex (0.59 g) was partially dissolved in warm dimethyl formamide (25 ml) and sodium dimethyldithiocarbamate (0.34 g) was added. The mixture was stirred at room temperature for 2 h by which time it had assumed a cloudy yellow appearance. The mixture was diluted with an equal volume of water and extracted with chloroform two or three times. The combined extracts were dried over anhydrous magnesium sulphate. The drying agent was removed and the solution remaining was reduced in volume to about 5 ml. The residue was then chromatographed on 10% deactivated alumina affording one fraction, a pale yellow band. This was eluted with dichloromethane to give a yellow solution. Concentration of the eluate gave 2-(2-pyridyl)phenyl(N, N-dimethyldithiocarbamato)-palladium (II) (0.40 g, 53%) as a yellow crystalline solid, m.p. 259-261°C. Its infrared spectrum was identical with that of the sample obtained from the di-μ-acetato-complex.

2 Reactions and Attempted Reactions of Cyclopalladated Complexes

(a) Attempted Reactions involving Sulphur Nucleophiles

Attempted reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II) with sodium benzyl mercaptide.

Sodium (0.05 g) was dissolved in absolute ethanol (100 ml) and benzyl mercaptan (0.25 g) was added to the solution which was being stirred under nitrogen. The title complex (0.26 g) was then added. No apparent change in the mixture was observed after it had been refluxed for 3 h. Hot filtration of the mixture gave a yellow solid (0.20 g) which was identified, from its infrared spectrum and melting point, as the original complex. The filtrate was diluted with water and extracted twice with ether. The combined extracts were dried over anhydrous magnesium sulphate. Removal of the drying agent and concentration of the yellow solution gave dibenzyl disulphide (0.10 g) as a yellow crystalline solid, m.p. 68-70°C (lit m.p. 69°C), identified from its infrared and ^{1}H n.m.r. spectra. It was concluded that no reaction had taken place.

Attempted reaction of di-μ-chlorobis[2-(N-phenylformimidoyl)-phenyl]dipalladium (II) with sodium benzyl mercaptide

Sodium (0.05 g) was dissolved in absolute ethanol (100 ml) under nitrogen and benzyl mercaptan (0.25 g) was added. The mixture was stirred and the title complex (0.32 g) was added. The reaction was carried out under conditions identical with those of the foregoing reaction and similar work-up afforded only starting material and a small amount of dibenzyl disulphide.

Attempted reaction of di-μ-acetatobis[2-(N-phenylformimidoyl)-phenyl]dipalladium (II) with sodium benzyl mercaptide

Sodium hydride (0.02 g) and benzyl mercaptan (0.12 g) were added to dry tetrahydrofuran (50 ml) and the mixture was stirred

in a nitrogen atmosphere. After 1 h the title complex (0.35 g) was added and the reaction mixture was refluxed for 3 h, after which time a change in colour from yellow to dark orange was noticeable. The dark orange solution was then diluted with an equal volume of water and extracted with ether twice. The combined extracts were dried over anhydrous magnesium sulphate. Removal of the drying agent gave a dark yellow solution which was evaporated to dryness yielding a tarry, dark yellow oil (0.10 g). A small amount of a yellow solid (0.03 g) was obtained on trituration of the oil with acetone and light petroleum but this product could not be identified. Further extraction of the aqueous solution with methylene chloride afforded a red extract which on work-up yielded a yellow compound (0.20 g) identified as starting material. No evidence for the formation of the required product was obtained.

Attempted reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II) with sodium benzyl mercaptide in the presence of an excess of triphenylphosphine

Sodium hydride (0.07 g) and benzyl mercaptan (0.34 g) were stirred together in tetrahydrofuran (redistilled and dried with sodium hydride) (50 ml) in a nitrogen atmosphere for 1 h. A suspension of the title complex (0.65 g) and an excess of triphenylphosphine (1.01 g) in tetrahydrofuran (10 ml) was added and the mixture brought to reflux. After 3 h at reflux thin layer chromatography of a sample taken from the reaction mixture indicated the presence of three products. The mixture was hot filtered to give a yellow solid (0.40 g), m.p. 215-217°C, and a red filtrate. The mass spectrum of the solid showed ion masses at m/e 590 and 262 and the ^{1}H n.m.r. spectrum showed multiplet resonances at δ 9.65 and δ 6.80-8.00 which integrated against each other in the ratio 1:25. These features suggested that the product obtained might be chloro-[2-(2-pyridyl)phenyl](triphenylphosphine)palladium (II) (see discussion) but positive identification was not established.

The red filtrate was evaporated to dryness yielding a brown

solid. This was taken up in the minimum of hot benzene and chromatographed on 10% deactivated alumina (100 g). Three fractions were obtained, by elution with benzene, ether and methanol respectively, and these were concentrated to give products A, B and C. Product A, a pale yellow oily solid, gave mass and ^{1}H n. m. r. spectra which indicated that it was a mixture of dibenzyl disulphide and triphenylphosphine. Product B, a yellow crystalline solid (0. 002 g), m. p. 160-161°C, was identified as triphenylphosphine sulphide (lit m. p. 163°C) from its infrared and mass spectra. Product C gave a brown solid (0. 15 g) of limited solubility which was not identified but an ion mass at m/e 278 in its mass spectrum suggested that it might be triphenylphosphine oxide.

(b) Attempted Reductive Eliminations in Dithiocarbamato and Phosphine Complexes of Cyclometallated Ligands

Attempted reaction of 2-(phenylazo)phenyl(dimethyldithiocarbamato)-palladium (II) with an excess of triphenylphosphine

The title complex (0. 10 g) and triphenylphosphine (0. 26 g) were heated together in refluxing diglyme (25 ml) for 15 h. During this period the solution darkened and a palladium mirror formed on the walls of the flask. The mixture was reduced in volume (to 10 ml) and the concentrate was diluted with water (30 ml). The resultant aqueous mixture was then extracted several times with ether and the combined extracts were dried over anhydrous magnesium sulphate. The combined extracts were then concentrated giving a dark red residue which was taken up in the minimum of hot ether and chromatographed on 10% deactivated alumina (50 g). Three fractions, A, B and C, were obtained.

Fraction A, a yellow band, was eluted with light petroleum and yielded triphenylphosphine sulphide (0. 03 g), m. p. 161-163°C (lit m. p. 163°C) which was identified by its infrared, mass and ^{1}H n. m. r. spectra.

Fraction B, an orange band also eluted with light petroleum,

afforded azobenzene (0.02 g) m.p. 67-69°C (lit m.p. 68°C), identified by comparison of its infrared spectrum with that of an authentic sample.

Fraction C, a dark orange band eluted with ether, gave the original complex (0.05 g). It was concluded that partial decomposition of the starting material had occurred and that no reductive elimination had taken place.

This reaction was carried out again, using the same quantities of reagents, both in the absence of solvent at 150°C and in refluxing toluene, without success.

Attempted reaction of chloro-2-(2-pyridyl)phenyl(triethylphosphine)-palladium (II) with silver perchlorate

The title complex (0.41 g) was dissolved in refluxing acetonitrile (25 ml) and silver perchlorate (0.21 g) was added. An immediate precipitate of a white flocculent solid was formed. Thin layer chromatographic analysis of a sample taken from the reaction mixture after 3 h at reflux indicated the absence of starting material and the mixture was hot filtered, affording silver chloride as a pale grey solid. Acetonitrile solvent was then removed from the filtrate to give a grey solid which was washed with water to remove any silver perchlorate and acetonitrile. The grey solid product was then recrystallised from ethanol to give a crystalline solid (0.28 g) as off-white needles, m.p. 148-150°C. From the evidence obtained the product was thought to comprise a mixture of perchlorato-[2-(2-pyridyl)phenyl](triethylphosphine)palladium (II) and (acetonitrile)[2-(2-pyridyl)phenyl](triethylphosphine)palladium (II) perchlorate.

$C_{19}H_{26}ClN_2O_4PPd$ requires:- C=44.0%; H=5.0%; N=5.3%

$C_{17}H_{23}ClN\,O_4PPd$ requires:- C=42.8%; H=4.8%; N=2.9%

found :- C=43.9%; H=5.10%; N=4.29%

m/e 477; 378; 359; 272; 260.

I.R. (C≡N) = 2300 cm^{-1} (ClO_4^-) = 1060-1100 cm^{-1}

^{1}H n.m.r. (T.F.A.): δ 9.05-7.50 (m, aromatic protons);

δ 2.60 (s, CH_3CN protons); δ 2.45-1.15 (m, Et_3P protons). The spectrum was very poorly resolved and the integral was uninformative. Precipitation from the sample of what may have been palladium metal was observed.

This reaction was repeated using chloroform as solvent instead of acetonitrile, the scale and the procedure remaining the same. The same work-up gave a brown oil which, when triturated with chloroform-pentane, gave a green solid (0.002 g), m.p. 212-214°C, the infrared spectrum of which showed a broad perchlorate stretch at 1060-1100 cm^{-1} but the absence of pyridyl ring breathing vibrations. Since it was obvious that the product was not that required, and in view of the very low yield, the compound was not further investigated.

Reaction of chloro-2-(2-pyridyl)phenyl(triethylphosphine)palladium (II) with silver nitrate

The title complex (0.41 g) was treated with silver nitrate (0.27 g) in refluxing acetonitrile (25 ml) for 3 h. The same work-up as used in the preceding reactions afforded a pale grey solid. Recrystallisation from ethanol gave nitrato-[2-(2-pyridyl)phenyl]-(triethylphosphine)palladium (II) (0.27 g, 75%) as an off white crystalline solid, m.p. 181-183°C.

$C_{17}H_{23}N_2O_3PPd$ requires:- C=46.36%; H=5.23%; N=6.36%
found :- C=46.07%; H=5.15%; N=6.28%

m/e 440 (M^+); 378; 260; 154.
I.R. (NO_3^-) = 1425 cm^{-1}, 825 cm^{-1}.
The ^1H n.m.r. spectrum, obtained in trifluoroacetic acid, was very poorly resolved showing complex multiplets in both the aromatic and aliphatic regions and no conclusions could be drawn from it.

Reaction of chloro-2-(2-pyridyl)phenyl(triethylphosphine)palladium (II) with silver hexafluorophosphate.

(a) The title complex (0.41 g) was treated with silver hexafluorophosphate (0.35 g) in acetonitrile (25 ml). The same work-up

procedure as in the preceding reactions afforded an off-white solid. Recrystallisation of the product from ethanol yielded (acetonitrile)-[2-(2-pyridyl)phenyl](triethylphosphine)palladium (II) hexafluorophosphate (0.30 g, 70%) as off-white needles, m.p. 164-166°C.

$C_{19}H_{26}F_6N_2P_2Pd$ requires:- C=40.42%; H=4.61%; N=4.98%
found :- C=39.02%; H=4.52%; N=4.44%

I.R. ($C\equiv N$) = 2310 cm^{-1}; (PF_6^-) = 830-880 cm^{-1}.
The mass spectrum was inconclusive but the ^1H n.m.r. spectrum, (in trifluoroacetic acid), though poorly resolved, showed a methyl singlet at δ2.55 suggesting the presence of an acetonitrile ligand. Complex multiplets in both aromatic and aliphatic regions of the spectrum were also observed.

(b) This reaction was repeated using chloroform as solvent instead of acetonitrile, the scale and the procedure remaining the same. Similar work-up procedure afforded a brown oil which was dissolved in the minimum of hot ethanol and cooled to give a green crystalline solid (0.20 g), m.p. >300°C. The infrared spectrum showed the absence of the fundamental PF_6^- vibrations and indicated the possibility of a PEt_3 group being present by a strong band at 1040 cm^{-1}. The mass spectrum was inconclusive and a ^1H n.m.r. spectrum could not be obtained owing to the insoluble nature of the product. Elemental analysis gave results which corresponded fairly closely to those required for the molecular formula shown below.

$C_{17}H_{23}F_4NP_2Pd$ requires:- C=42.10%; H=4.70%; N=2.81%
found :- C=42.33%; H=5.25%; N=2.57%

(c) A final attempt was made using chlorobenzene as solvent, the scale of the reaction being unchanged. Precipitation of silver chloride occurred on mixing and after 10 minutes of reflux the mixture darkened in colour. After 1 h a dark green solution had formed and a heavy black precipitate was apparent. Hot filtration afforded a black powdery solid which was tested for metallic palladium.

A sample of the solid (0.05 g) was dissolved in aqua regia giving a reddish brown solution and a grey residual solid. This mixture was filtered and solvent was removed from the filtrate to give a brown residue. The residue was taken up in boiling water and the solution allowed to cool. A portion of the cooled solution was mixed with an aqueous solution of potassium iodide and precipitation of a black solid, palladium iodide, represented a positive test for palladium. Another portion of the solution was tested with an aqueous solution of mercuric cyanide and a white precipitate of palladium cyanide gave further confirmation of the presence of palladium metal in the original black solid precipitated from the reaction mixture.

The green filtrate obtained on hot filtration of the reaction mixture was concentrated giving a dark brown oil. The oil was dissolved in hot ethanol and the resultant brown suspension was filtered through Celite to give a red filtrate. Concentration of the filtrate gave a light red oil which was again dissolved in hot ethanol and the resultant solution filtered through Celite. The filtrate was then dropped into ether affording a light-coloured precipitate which was collected as a white crystalline solid (0.10 g), m.p. 113-115°C. Infrared and mass spectroscopy indicated that the product might be phenyltriethylphosphonium hexafluorophosphate. A suitable ^{1}H n.m.r. spectrum was not obtained.

$C_{12}H_{20}F_6P_2$ requires:- C=43.50%; H=6.04%

found:- C=40.71%; H=5.52%

m/e 195 ($PhPEt_3^{\oplus}$)

I.R. (PF_6^-) = 840-860 cm^{-1} (pyridyl ring breathing vibrations absent). Attempts to improve the analytical results were not made since the product obtained was not that required. It appeared that decomposition of starting material had occurred and that solvent interaction with the decomposition products accounted for the experimental observations.

Reaction of chloro-2-(2-pyridyl)phenyl(triethylphosphine)palladium (II) with antimony pentachloride

The title complex (0.41 g) was dissolved in dichloromethane (50 ml) and antimony pentachloride (0.29 g) was added. The mixture was brought to reflux and after 30 minutes a pale flocculent precipitate was observed. Hot filtration of the mixture afforded a pink solid (0.35 g), m.p. 199-200°C, and a yellow filtrate. The solid product was insoluble and involatile and could not be identified by spectroscopic methods. Concentration of the filtrate gave an orange solid (0.10 g) which from its infrared and mass spectra appeared to be a mixture of starting materials.

A portion of the pink solid (0.20 g) was dissolved with difficulty in aqueous acetone (15 ml). An anion exchange column was then constructed using Dowex 1-X4 resin (50-100 mesh) (50 g). The resin, supplied in the chloride form, was treated with a solution of sodium perchlorate in distilled water to convert it into the perchlorate form. The effluent was tested for sodium chloride with acidified silver nitrate solution until the tests proved negative and the resin was then washed with distilled water. The aqueous acetone solution of the pink product was then applied to the column. A dark brown effluent was obtained and concentration of the solution gave a brown oil which could not be identified by spectroscopic means. No further fractions were obtained.

Attempted reaction of 2-(2-phenylazo)phenyl(dimethyldithiocarbamato)-palladium (II) with ceric ammonium nitrate

The title palladium complex (0.41 g) was stirred at room temperature for 48 h with ceric ammonium nitrate (0.55 g) in dimethoxyethane (25 ml). After this time no significant change in the appearance of the reaction mixture was apparent and t.l.c. of a sample taken from the reaction mixture indicated the presence of starting material. No evidence for the required product (o-dimethyldithiocarbamatoazobenzene) was obtained.

Attempted reaction of 2-(2-phenylazo)phenyl(dimethyldithiocarbamato)-palladium (II) with lead tetra-acetate

The title palladium complex (0.31 g) was treated with lead tetra-acetate (0.33 g) in dry benzene (50 ml) and the mixture stirred for 5 h at room temperature. The reaction was monitored by t.l.c. analysis of samples taken from the mixture every 30 minutes. After 1 h the reaction mixture had darkened somewhat and t.l.c. analysis indicated the presence of a mobile product running ahead of starting material on the chromatographic plate. Little change was apparent in the samples analysed thereafter and, after 5 h, the reaction mixture was filtered giving a negligible amount of an unidentified pale yellow solid and a dark orange filtrate. The filtrate was reduced in volume and the concentrate chromatographed on 10% deactivated alumina (50 g). Two main fractions were obtained; the first, a yellow band, was eluted with ether to give a dark yellow solution; the second, a brown band was also eluted with ether and gave a dark orange solution. Concentration of the first fraction gave a red oil, t.l.c. analysis of which indicated a mixture of products. Preparative t.l.c. of the oil yielded three bands from which the products were recovered by extraction with ether. Two of the products were obtained in negligible amounts but the other one a red oil (0.04 g) was identified by mass and n.m.r. spectroscopy as 2-acetatoazobenzene.

m/e 240 (M^+); 181

^{1}H n.m.r. ($CDCl_3$): δ7.85-7.55 (m, 3 aromatic protons); δ7.50-7.00 (m, 6 aromatic protons); δ 2.25 (s, 3 methyl protons).

Concentration of the second fraction from the alumina column gave a dark orange solid identified as the original complex by its infrared spectrum and melting point. No evidence for the required product was obtained.

Attempted reaction of 2-(2-phenylazo)phenyl(diethyldithiophosphato)-palladium (II) with lead tetra-acetate

The title palladium complex (0.47 g) was treated with lead

tetra-acetate (0.44 g) in dry benzene (50 ml). The mixture was stirred at room temperature for 24 h. but t.l.c. analysis after this period indicated that both starting materials were still present and that no reaction had taken place.

(c) Attempted Reactions of Cyclopalladated Complexes with Substances, other than Thiocyanogen, Containing Disulphide Bonds.

Attempted reaction of di-μ-acetatobis[2-(N-phenylformimidoyl)-phenyl]dipalladium (II) with elemental sulphur

The title complex (0.50 g) was treated with sulphur (0.05 g) in chloroform (50 ml) at reflux for 3 h. T.l.c. analysis of samples taken from the reaction mixture throughout this period indicated that no reaction had taken place and unchanged starting materials were recovered on work-up of the reaction mixture.

The reaction was attempted in different solvents, dimethylformamide and chlorobenzene but in both cases starting materials were recovered and no reaction was observed.

Attempted reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium-(II) with elemental sulphur

The title complex (0.50 g) was treated with sulphur (0.05 g) in chloroform (50 ml) at reflux for 3 h. T.l.c. analysis of samples taken from the reaction mixture throughout this period indicated that no reaction had taken place and unchanged starting materials were recovered on work-up of the reaction mixture.

The reaction was attempted in different solvents, dimethylformamide and chlorobenzene but in both cases starting materials were recovered and no reaction was observed.

Attempted reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II) with elemental sulphur

The title complex (0.50 g) was treated with sulphur (0.05 g)

in dimethylformamide (50 ml) at reflux for 3 h. T.l.c. analysis of samples taken from the reaction mixture indicated that no reaction had taken place and the mixture was not further investigated.

Attempted reaction of 2-(phenylazo)phenyl(dimethyldithiocarbamato)-palladium (II) with elemental sulphur

The title complex (0.56 g) was treated with sulphur (0.04 g) in refluxing dimethylformamide (25 ml). The reaction mixture, initially orange in colour, darkened considerably after 30 minutes at reflux. T.l.c. analysis indicated the formation of two new products and the absence of starting material. The mixture was heated at reflux for a further 2 h and then hot filtered to give a small amount of a black solid and a dark orange filtrate. Removal of solvent from the filtrate by distillation gave a black residue. The residue was heated in benzene (10 ml) and filtered, giving some more black solid and a dark orange solution which was then chromatographed on 10% deactivated alumina. Two main fractions were obtained: the first fraction comprised a broad greenish-yellow band and was eluted with light petroleum to give a dark yellow solution; the second fraction, a purple band, was eluted with ether to give a pale purple solution. Concentration of the second fraction gave a negligible amount of an oil. The solution obtained from the first fraction was concentrated and gave an oily black residue which showed two spots running closely together when analysed by t.l.c. The residue was then taken up in the minimum of benzene and re-chromatographed on 10% deactivated alumina. Two fractions were obtained and both were eluted with light petroleum to give yellow and dark grey solutions. Concentration of the yellow solution gave a small amount of a brown oil which could not be identified. The grey solution was evaporated to dryness and yielded a tarry black solid. The product was dried at the oil pump for 3 h and a black glassy solid (0.10 g), m.p. 128-130^{o}C, was obtained. An infrared spectrum of the compound was inconclusive and a ^{1}H n.m.r. spectrum

showed only a very weak, poorly resolved multiplet in the aromatic region. The mass spectrum showed a parent ion mass at m/e 394 which corresponds to that required for (2-phenylazophenyl)sulphide. No further evidence as to the identity of this product could be obtained.

Repetition of the reaction afforded no characterisable products.

Reaction of 2-(phenylazo)phenyl(O, O-diethyl dithiophosphato)-palladium (II) with elemental sulphur

The title complex (0.47 g) was treated with sulphur (0.03 g) in dimethylformamide (25 ml) under conditions identical with those of the preceding reaction. Similar work-up of the reaction mixture afforded no characterisable products and the reaction was not further investigated.

Reaction of (h^5-cyclopentadienyl)[2-(phenylazo)phenyl]nickel (II) with elemental sulphur

The title complex (0.25 g) was dissolved in chlorobenzene (25 ml) and sulphur (0.04 g) was added. The mixture was stirred at reflux for 24 h by which time a t.l.c. analysis indicated the presence of several products. Solvent was then removed from the mixture giving a dark brown residue which was taken up in the minimum of hot dichloromethane. The resultant solution was chromatographed on 10% deactivated alumina. Several fractions were obtained, the main ones being an orange band which was eluted with light petroleum giving an orange solution, and a dark blue band which was eluted with ether to give a dark blue solution. Concentration of these two solutions gave starting materials (sulphur and nickel complex, respectively) identified by infrared spectra and melting points. Work-up of the other fractions gave negligible amounts of oils which could not be identified. No evidence for the presence of the required product was obtained and in view of the complexity of the reaction, it was not thought worthwhile to

investigate further the possibility of sulphur insertion with the nickel complex.

Reaction of 2-(phenylazo)phenyl(dimethyldithiocarbamato)palladium (II) with tetraethylthiuram disulphide

The title complex (0. 20 g) was dissolved in chlorobenzene (25 ml) and tetraethylthiuram disulphide (0. 15 g) was added. The mixture was heated at reflux for 24 h by which time it had darkened considerably and t.l.c. analysis indicated the formation of a new product. Chlorobenzene was evaporated off, the orange residue was dissolved in the minimum of hot dichloromethane and the resultant solution was chromatographed on 10% deactivated alumina. Two fractions were obtained: the first, an orange band, was eluted with ether to give a dark orange solution; the second, a yellow band, was eluted with methylene chloride giving a yellow solution.

Concentration of the solution from the first fraction gave a red oily solid which could not be crystallised despite several attempts. A ^{1}H n.m.r. spectrum of the oil was poorly resolved and contaminated with aliphatic solvent residues which could not be entirely removed. The spectrum showed broad multiplets in the aromatic region consistent with those expected for a non-metallated azobenzene nucleus and broad multiplets in the aliphatic region consistent with N-ethyl proton resonances. A mass spectrum of the product gave ion masses at m/e 294, 292, 272, 257, 213, 180 and 152. The ion masses at m/e 294 and 292 showed relative abundances typical of the chlorine isotopes and corresponded to the parent ion of o-(chlorophenyl)azobenzene. The peaks at m/e 272, 257, 213, 180 and 152 were all examined by exact mass measurement but the results obtained did not confirm the suspected elemental compositions (see discussion).

$C_{14}H_{12}N_2S_2$	requires:-	272. 044
	found:-	272. 129
$C_{13}H_9NS_2$	requires:-	257. 021
	found:-	257. 107

$C_{12}H_9N_2S$	requires:-	213.049
	found :-	213.037
$C_{12}H_8N_2$	requires:-	180.069
	found :-	180.081
$C_{12}H_8$	requires:-	152.062
	found :-	152.062

The mixture was found to be inseparable and was not further investigated.

Concentration of the solution from the second fraction gave a yellow solid (0.12 g), m.p. 245-250°C. The product was identified from its infrared, mass and ^{1}H n.m.r. spectra as a mixture of bis(diethyldithiocarbamato)palladium (II), (dimethyldithiocarbamato)-(diethyldithiocarbamato)palladium (II), and bis(dimethyldithiocarbamato)palladium (II).

m/e 402, 374; 346

I.R. (R_2NCS_2) = 1510-1530 cm^{-1}

^{1}H n.m.r. ($CDCl_3$): δ3.90-3.50 (q, methylene protons); δ1.35-1.10 (t, methyl protons). No N-Me proton resonances were observed and their absence is explained in the discussion.

Reaction of 2-(phenylazo)phenyl(dimethyldithiocarbamato)palladium (II) with tetramethylthiuram disulphide

The title complex (0.20 g) was treated with tetramethylthiuram disulphide (0.18 g) at 140°C in the absence of solvent. The reaction was monitored by t.l.c. which, after 4 h, indicated the presence of a new product and the absence of starting material. The dark orange melt was then heated in benzene (10 ml) for a few minutes and the yellow cloudy mixture was hot filtered giving some yellow solid and a yellow filtrate. The yellow solid was identified by infrared and mass spectroscopy as bis(dimethyldithiocarbamato)palladium (II) and the filtrate was evaporated giving a red oil which, from a t.l.c. analysis, appeared to be a mixture of three products. The oil was dissolved in a little benzene and preparative thin layer chromatography

was used to separate the components of the mixture. Using carbon tetrachloride as eluting solvent three fractions were obtained and these, after extraction of the products with ether, yielded three red oils. The oils were examined by mass and ^{1}H n. m. r. spectroscopy but they could not be identified. No evidence for the required product was found.

Preparation of bis(diethoxythiophosphoryl)disulphide

O, O-Diethyl hydrogen dithiophosphate (9. 30 g) was added to aqueous sodium hydroxide (2. 0 g in 50 ml H_2O) and the mixture was stirred at room temperature for 30 minutes. Iodine (6. 35 g), dissolved in aqueous potassium iodide, was slowly added to the mixture. The reaction mixture became cloudy but remained colourless until the last drop of iodine was added, whereupon, a faint yellow colour, due to a slight excess of iodine, persisted. The mixture was extracted several times with ether and the combined extracts were dried over anhydrous magnesium sulphate. Solvent was removed from the extracts to give a brown oil which was taken up in the minimum of ether and the resultant solution was chromatographed on 10% deactivated alumina in ether. One fraction, a yellow band, was obtained and this gave a pale yellow oil (7. 3 g, 50%), which was identified as the required product by infrared, mass and ^{1}H n. m. r. spectroscopy.

Reaction of 2-phenylazophenyl(O, O-diethyl dithiophosphato)palladium (II) with bis(diethoxythiophosphoryl) disulphide

The title complex (0. 47 g) was treated with bis(diethoxydithiophosphoryl) disulphide (0. 37 g) at 135-140°C for 3 h in the absence of solvent. T. l. c. analysis after 3 h indicated the presence of two products. The oily mixture was dissolved in the minimum of hot benzene and chromatographed on 10% deactivated alumina. One broad yellow fraction was obtained and this was eluted with benzene to give a yellow solution. T. l. c. of a sample taken from the solution indicated that three products were present. The

solution was reduced in volume and the residue was chromatographed by preparative thin layer chromatography on silica using carbon tetrachloride as solvent. Three bands were obtained and these were collected and extracted with ether to give three products, (i) a red oil (0.10 g), (ii) a yellow oil (negligible quantity) and (iii) a brown solid (0.05 g).

The brown solid obtained was identified from its mass and ^{1}H n.m.r. spectra as bis(diethyl dithiophosphato)palladium (II).

The red oil could not be crystallised despite several attempts. The mass spectrum of the product showed a parent ion at m/e 242, and another ion at m/e 213.

$C_{14}H_{14}N_2S$	requires:-	242.087
	found:-	242.087
$C_{12}H_9N_2S$	requires:-	213.048
	found:-	213.048

^{1}H n.m.r. ($CDCl_3$): δ 8.10-7.85 (m, aromatic protons); δ 7.80-7.00 (m, aromatic protons); δ 3.70-3.30 (q, methylene protons); δ 3.25-2.90 (q, methylene protons); δ 1.6-1.10 (2t, methyl protons).

From the evidence obtained it was thought that the oil might contain o-ethylthioazobenzene (see discussion). This reaction was also attempted in toluene and diglyme without success.

Irradiation of 2-phenylazophenyl(dimethyldithiocarbamato)palladium (II) in the presence of tetramethylthiuram disulphide

The title complex (0.20 g) was dissolved in benzene (100 ml) and tetramethylthiuram disulphide (0.12 g) was added. The mixture was then irradiated for 48 h. T.l.c. analyses of samples taken from the reaction mixture during this time indicated that no reaction had taken place. Subsequent removal of solvent and chromatography of the residue afforded unchanged starting material.

Irradiation of 2-phenylazophenyl(diethyl dithiophosphato)palladium (II) in the presence of bis(diethoxythiophosphoryl) disulphide

The title complex (0.59 g) was dissolved in benzene (100 ml) and the solution was irradiated in the presence of bis(diethoxythiophosphoryl) disulphide (0.46 g) for 7 h. Regular t.l.c. analyses were carried out but after 7 h no change was observed and the reaction was not further investigated.

Reaction of di-μ-acetatobis[2-phenylazophenyl]dipalladium (II) with dibenzyl disulphide

The title complex (0.35 g) was treated with dibenzyl disulphide (0.25 g) at 120°C in the absence of solvent for 4 h. Work-up of the reaction by column chromatography afforded unchanged starting materials, no reaction having taken place.

Preparation of (h^5-cyclopentadienyl)[2-phenylazophenyl]nickel (II)

The method of Kleiman and Dubeck[6] was used and, starting from 3 g of nickelocene, 1.35 g (28%) of the required product, m.p. 115°C (lit m.p. 115°C), was obtained. The identity of the product was confirmed by infrared, mass and ^{1}H n.m.r. spectroscopy.

Reaction of (h^5-cyclopentadienyl)[2-phenylazophenyl]nickel (II) with dibenzyl disulphide

The title complex (0.31 g) was heated with dibenzyl disulphide (0.25 g) at 140°C in the absence of solvent for 6 h. T.l.c. analysis at this time indicated that no reaction had taken place. Chromatography of the mixture afforded unchanged starting materials identified by melting points and infrared spectra.

(d) Reactions with Electrophiles

Reaction of di-μ-chlorobis[2-(N-phenylformimidoyl)phenyl]di-palladium (II) with sulphur dichloride

The title complex (0.5 g) was suspended in dry chloroform (50 ml) and sulphur dichloride (0.3 ml≡ 0.18 g) was added. The mixture was heated to reflux and a deep red solution formed which quickly became clouded. Within a few minutes of reflux the clouded red solution turned to a pale-brown colour and a heavy brown precipitate was observed. The mixture was refluxed for 1 h and then hot filtered affording a pale-brown solid which was washed with chloroform and ether and then dried at the oil pump. The pale brown product (0.45 g), m.p. 210-212°C was involatile and extremely insoluble in organic solvents precluding the use of mass and ^{1}H n.m.r. spectroscopy to identify it. The infrared spectrum of the compound showed the presence of an aromatic structure. The product was leached for 24 h with boiling methanol in a Soxhlet apparatus, dried in a drying pistol, and analysed for C, H and N. The results obtained were not consistent for the required product but corresponded to the empirical formula shown below.

$C_{13}H_{10}Cl_2NPdS$	requires:-	C=40.20%;	H=2.57%; N=3.60%
	found:-	C=40.23%;	H=2.53%; N=3.47%

Reaction of di-μ-acetatobis[2-(N-phenylformimidoyl)phenyl]di-palladium (II) with sulphur dichloride

The title complex (0.25 g) was treated with sulphur dichloride (0.3 ml≡ 0.18 g) under conditions identical with those of the preceding reaction. On addition of sulphur dichloride the reaction mixture became dark red and after a few minutes at reflux a heavy brown precipitate was formed. The clouded brown reaction mixture was refluxed for a further 30 minutes and then hot filtered to give a pale-

brown solid which was washed with chloroform and ether. The pale-brown product (0.20 g), m.p. 210-212°C, seemed to be identical with the product obtained in the preceding reaction from a comparison of the respective infrared spectra. Again, the product could not be identified by mass or ^{1}H n.m.r. spectroscopy owing to its involatile and insoluble nature. An elemental analysis of the product was carried out but the results were inconsistent with those required for the desired product and they were also different from those obtained for the product of the previous reaction. (Found: C=45.49%; H=2.83%; N=4.00%).

Attempted reaction of the pale-brown product with lithium aluminium hydride

The unknown product (0.23 g) was treated with a suspension of lithium aluminium hydride (0.03 g) in tetrahydrofuran (50 ml) under a nitrogen atmosphere. The mixture was brought to reflux, by which time it had turned black, and refluxing was continued for 2 h. Hot filtration of the reaction mixture then afforded a black powder (0.20 g), m.p. >300°C. After addition of water to the filtrate, either extraction yielded a negligible amount of a yellow solid. The black powder was insoluble and could not be identified.

Reaction of di-μ-chlorobis[2-(2-pyridyl)phenyl]dipalladium (II) with sulphur dichloride

The title complex (1.53 g) was treated with sulphur dichloride (1.0 ml 0.51 g) in refluxing chloroform (50 ml) and after 5 minutes a cloudy yellow suspension had formed. The mixture was refluxed for a further 30 minutes and then hot filtered to give a pale-brown solid (1.56 g), m.p. 240°C (decomp). [This substance is referred to below as the "unknown product"]. Infrared and mass spectroscopy gave no indication of the identity of the product and a ^{1}H n.m.r. spectrum could not be obtained owing to the extreme insolubility of the product. Elemental analysis gave results which were

inconsistent with those required for the desired product. (Found: C=39.71%; H=2.45%; N=4.22%).

Attempted reaction of the "unknown product" with sodium bis-(2-methoxyethoxy)dihydroaluminate

The "unknown product" (0.67 g) was suspended in dry benzene (50 ml) in a nitrogen atmosphere and sodium bis(2-methoxyethoxy)dihydroaluminate (0.1 ml) was added. The reaction mixture darkened considerably on mixing and was black by the time the mixture had been brought to reflux. Refluxing was continued for 4 h, by which time, a faint yellow spot incompatible with starting materials could be detected by t.l.c. The reaction mixture was hot-filtered, affording a black solid and a yellow filtrate. Concentration of the filtrate gave a negligible amount of a yellow solid which was insufficient for spectroscopic study.

Attempted reaction of the "unknown product" with perchloric acid

The product (1.56 g) was treated with an aqueous solution of perchloric acid (excess). The mixture was refluxed for 15 minutes and became brick red. Hot filtration afforded a reddish brown solid and an orange filtrate. The filtrate was extracted several times with dichloromethane and the combined extracts were dried over anhydrous magnesium sulphate. The solution was then reduced in volume at the rotary evaporator and the concentrate was dropped into ether (10 ml). A light orange precipitate which formed was collected to give an orange crystalline solid (0.02 g), m.p. 185-186^{o}C. The infrared spectrum of the product indicated the presence of perchlorate ion by a broad stretch at 1060-1100 cm^{-1} but the mass and ^{1}H n.m.r. spectra obtained were uninformative. Elemental analysis gave results which were inconsistent with those required for the desired product (Found: C=37.16%; H=2.31%; N=3.69%). Thus, the product remains unidentified.

Reaction of the "unknown product" with triethylphosphine

The solid (0.20 g) was suspended in dichloromethane (10 ml) and triethylphosphine (0.71 g) was added, whereupon the mixture became clear and red. The red solution was stirred for 1 h and then reduced in volume and chromatographed on 10% deactivated alumina. Two fractions were obtained by elution with ether and chloroform, respectively. The solution from the first fraction afforded an orange solid (0.04 g), m.p. 178-180°C. It was thought possible that this might be bis[2-(2-pyridyl)phenylthio]-palladium (II) on the basis of its mass spectrum (see discussion).

$C_{22}H_{16}PdS_2$ requires:- C=55.23%; H=3.35%; N=5.86%

found :- C=53.69%; H=3.74%; N=5.39%

These inconsistent results could not be improved upon despite repetition of the reaction and a further analysis.

m/e 478; 186.

^{1}H n.m.r. ($CDCl_3$): δ8.40-8.20 (m, 1 α-pyridyl proton); δ 7.95-7.55 (m, 3 aromatic protons); δ 7.45-6.90 (m, 4 aromatic protons).

The solution obtained from the second fraction afforded an orange crystalline solid (0.12 g), m.p. 179-181°C, when evaporated to dryness. A ^{1}H n.m.r. spectrum of the compound showed two complex multiplets in the aliphatic region consistent with the aliphatic resonances expected of a triethylphosphine group but no aromatic resonances were present. The infrared spectrum was identical with that of an authentic sample of bis(triethylphosphine)-palladium (II) dichloride but the melting point of the product obtained is higher than that of the authentic sample (lit m.p. 139°C). The product obtained was recrystallised from ethanol to give orange prisms m.p. 179-181°C and it was thought likely that it consisted of a mixture of bis(triethylphosphine)palladium (II) dichloride and the dimeric tetrachlorobis(triethylphosphine)dipalladium (II) (lit m.p. 230°C) which was reported to be orange, (see discussion).

I.R. ν_{max} = 1250, 1060, 765, 730 cm^{-1} (consistent for PEt_3 vibrations). ^{1}H n.m.r. ($CDCl_3$): δ2.1-0.8 (m, methylene and

methyl protons of triethylphosphine groups).

Reaction of 2-phenylazophenyl(dimethyldithiocarbamato)palladium (II) with bromine

The title complex (0.41 g) was dissolved in chloroform (50 ml) and treated with a solution of bromine (0.16 g in 5 ml $CHCl_3$). An immediate dark red precipitate was observed and this persisted throughout a 3 h reflux of the mixture. Hot filtration of the mixture afforded a brick red solid which was washed with chloroform and ether. The product obtained was identified as di-μ-bromobis(dimethyldithiocarbamato)dipalladium (II) (0.45 g, 75%), m.p. >300°C. The mass spectrum was inconclusive but other spectroscopic evidence and elemental analysis confirmed the identity of the product.

I.R. (R_2NCS_2) = 1550-1570 cm^{-1}

^1H n.m.r. (d^6-d.m.s.o.): δ 3.45 (s, N-methyl protons); δ 3.30 (s, N-methyl protons); δ 2.6 (m, methyl protons). See discussion.

$C_6H_{12}Br_2Pd_2S_4$ requires:- C=11.76%; H=1.96%; N=4.57%

found :- C=11.70%; H=1.87%; N=4.38%

The filtrate was reduced in volume and chromatographed on 10% deactivated alumina (50 g). One fraction was obtained as a yellow band and this was eluted with ether to give an orange solution. Concentration of the solution afforded an oily red solid which, when crystallised from light petroleum, gave 2-bromoazobenzene (0.20 g, 80%) as orange prisms, m.p. 36°C (lit m.p. 36°C).

m/e 262; 260 (M^+)

^1H n.m.r. ($CDCl_3$): δ 8.05-7.85 (m, 2 aromatic protons); δ 7.80-7.00 (m, 7 aromatic protons).

Reaction of di-μ-acetatobis[2-phenylazophenyl]dipalladium (II) with bromine

A solution of the title complex (0.69 g in 50 ml $CHCl_3$) was treated with a solution of bromine (0.32 g in 5 ml $CHCl_3$) and the

mixture was heated at reflux for 3 h, during which time, a dark red precipitate appeared. The mixture was then left to stand at room temperature overnight and subsequent filtration afforded a red-brown solid (0.50 g), m.p. 280-290°C (decomp). A ^{1}H n.m.r. spectrum could not be obtained owing to the insolubility of the product which was tentatively identified as di-μ-bromobis[bromo-(2-phenylazophenyl)]dipalladium (II) on the basis of the mass spectrum which showed m/e 449, 447, 445 corresponding to the half-mass of the proposed compound.

The orange filtrate was concentrated and the residue taken up in the minimum of hot chloroform. Chromatography of this solution on 10% deactivated alumina (50 g) gave two fractions, a yellow band and a dark yellow band, eluted with light petroleum and chloroform respectively.

Concentration of the solution obtained from the first fraction gave a red oil which could not be crystallised. The mass spectrum showed strong ion masses at m/e 262 and 260, and weak ones at m/e 342, 340 and 338 which suggested that the oil was a mixture of mono- and dibromoazobenzenes. A ^{1}H n.m.r. spectrum of the oil also indicated a mixture of these products, showing resonances in the aromatic region which were more complex than those observed in the spectrum of 2-bromoazobenzene. Attempts to separate the products chromatographically were unsuccessful.

The solution obtained from the second fraction was concentrated and gave the starting material, di-μ-acetatobis(2-phenylazophenyl)dipalladium (II) identified by its melting point and infrared spectrum.

Preparation of N-(benzylthio)succinimide

The method of Büchel and Conte[92] was used and, starting from 3.0 g of N-bromosuccinimide, 3.0 g (80%) of the required product, m.p. 166-168°C (lit m.p. 165-166°C), was obtained. The identity of this product was confirmed by infrared and ^{1}H n.m.r. spectroscopy.

Reaction of di-μ-acetatobis(2-phenylazophenyl)dipalladium (II) with N-(benzylthio)succinimide

The title complex (0. 20 g) was dissolved in refluxing chlorobenzene (25 ml) and N-(benzylthio)succinimide (0. 26 g) was added. The mixture was heated at reflux for 10 h by which time t. l. c. analysis indicated the presence of two new products. The reaction mixture was hot filtered giving only a dark red solution and this was concentrated at the rotary evaporator. The dark red residue obtained was taken up in the minimum of hot chloroform and chromatographed on 10% deactivated alumina. Two main fractions were obtained: the first, a pale yellow band, was eluted with chloroform and gave only a trace amount of a yellow solid; the second fraction, a deep red band, was eluted with the same solvent to give a dark red solution. Concentration of the solution gave (2-phenylazophenyl)(succinimido)palladium (II) (0. 16 g, 70%) as dark red flakes, m. p. 280-290°C (decomp).

$C_{16}H_{13}N_3O_2Pd$ requires:- C=49. 80%; H=3. 41%; N=10. 89%
found :- C=49. 23%; H=3. 35%; N=10. 49%

m/e 385 (M^+)
I. R. (C=O) = 1725 cm^{-1} and 1700 cm^{-1}
^{1}H n. m. r. ($CDCl_3$): δ7. 65-7. 50 (d, 1 aromatic proton); δ7. 25-6. 45 (m, 7 aromatic protons); δ6. 15-5. 95 (d, 1 aromatic proton); δ 2. 50 (s, 4 methylene protons).

Preparation of phenylmethanesulphenyl bromide

The method of Emde[93] was used in which the sulphenyl bromide is prepared in solution and not isolated owing to its instability in air. The solution of the required product was used immediately in the reactions in which it was employed. Emde reported quantitative yields of the required product and quantities of it hereafter recorded are based upon such yields.

Reaction of 2-phenylazophenyl(dimethyldithiocarbamato)palladium (II) with phenylmethanesulphenyl bromide

The title complex (0.41 g) was stirred in dry benzene (20 ml) and treated with a freshly prepared benzene solution of phenylmethanesulphenyl bromide (0.20 g in 20 ml). The mixture was stirred at room temperature for 1 h without any visible reaction being observed and then heated at reflux for 1 h. During this period a dark orange precipitate formed and this was collected as a dark orange solid (0.10 g), m.p. 260°C (decomp), [Product A]. Concentration of the filtrate resulted in more orange solid being precipitated from the solution and this was also collected (0.12 g), m.p. 250°C (decomp), [Product B]. The soluble residue was chromatographed on 10% deactivated alumina (50 g) and a single dark orange band was the only fraction obtained. Elution of the band with light petroleum and concentration of the eluate yielded a small amount of an orange solid (0.05 g), m.p. 60-61°C, [Product C]. Rechromatography of the mother liquor from product C, eluting with light petroleum, afforded a red oil which crystallised from light petroleum to give an orange solid (0.10 g), m.p. 36°C [Product D].

From infrared, mass and n.m.r. spectroscopy, product A was thought to be a mixture of di-μ-bromobis(dimethyldithiocarbamato)-dipalladium (II) and bis(dimethyldithiocarbamato)palladium (II); product B appeared to be a mixture of starting complex and bis-(dimethyldithiocarbamato)palladium (II); product C was identified as dibenzyl disulphide by spectroscopic evidence and melting point; product D was identified by its melting point and spectroscopic data as 2-bromoazobenzene. No evidence for the formation of the desired product was found. It was thought that the failure of the reaction might be due to a disproportionation reaction of the sulphenyl bromide.

Reaction of di-μ-acetatobis[2-phenylazophenyl]dipalladium (II) with trichloromethanesulphenyl chloride

The title complex (0.69 g) was dissolved in chloroform (50 ml)

and treated with trichloromethanesulphenyl chloride (0.37 g). The mixture was heated at reflux for 1 h and then left to stir at room temperature for a further 48 h. At this point, a strong red precipitate, which had formed, was collected and washed with chloroform and ether. Work-up of the filtrate by chromatography afforded only negligible amounts of two yellow oils which were discarded. The bright red crystalline solid was identified as di-μ-chlorobis[2-phenylazophenyl]dipalladium (II) by infrared and mass spectroscopy. The yield of this product was 0.5 g (80%).

Reaction of 2-phenylazophenyl(dimethyldithiocarbamato)palladium (II) with trichloromethanesulphenyl chloride

The title complex (0.41 g) was dissolved in chloroform (25 ml) and treated with trichloromethanesulphenyl chloride (0.19 g). The reaction mixture was heated at reflux for 2 h. by which time the initial orange colour had changed to light yellow and a flocculent precipitate had formed. This was collected as a yellow solid and was identified by its infrared and mass spectra as bis(dimethyldithiocarbamato)palladium (II). The filtrate was concentrated and chromatographed on 10% deactivated alumina. The main fraction was eluted with light petroleum to give a red solution which, when concentrated, gave a red oil. This was crystallised from light petroleum to give azobenzene (0.05 g), m.p. 66-67°C (lit m.p. 69°C). The identity of this product was confirmed by its infrared spectrum. The mother liquor was concentrated and gave a red oil which could not be crystallised but had the odour of the starting material trichloromethanesulphenyl chloride. A mass spectrum of this oil showed a weak ion mass at m/e 330 (main peak of isotopic cluster) which was consistent with o-trichloromethylthioazobenzene but a ^{1}H n.m.r. spectrum was inconclusive and the oil could not be purified sufficiently to warrant further investigation.

Preparation of thiocyanogen[94]

Solutions of thiocyanogen were obtained by treatment of lead

(II) thiocyanate with bromine and were used without delay in subsequent reactions. It was assumed that yields were quantitative.

Reaction of di-μ-acetatobis[2-phenylazophenyl]dipalladium (II) with thiocyanogen

The title complex (0.69 g) was dissolved in chloroform (25 ml) and the solution was cooled to 5-10°C in an ice-bath. It was then treated with a cold solution of thiocyanogen (0.23 g in 10 ml $CHCl_3$). On mixing, a bright yellow precipitate was formed and this persisted throughout the 4 h for which the mixture was stirred. Filtration of the mixture gave a bright yellow solid (0.55 g), m.p. 290°C (decomp). Removal of solvent from the filtrate gave a negligible amount of a yellow solid. It was thought likely that a ligand-exchange reaction had occurred giving the thiocyanato-bridged complex, di-μ-thiocyanatobis[2-phenylazophenyl]dipalladium (II). The infrared spectrum showed a C≡N stretching band at 2150 cm^{-1} but a mass spectrum obtained was uninformative. A ^1H n.m.r. spectrum of the compound could not be obtained owing to its low solubility in organic solvents and elemental analysis gave results which were in poor agreement with those required for the proposed compound.

$C_{26}N_{18}N_6S_2Pd_2$ requires:- C=45.2%; H=2.6%; N=12.2%

found :- C=41.13%; H=2.35%; N=11.80%

Reaction of the foregoing product with triethylphosphine

The yellow solid (0.40 g) was suspended in dichloromethane (10 ml) and triethylphosphine (0.94 g) was added. A clear red solution resulted and, after 30 minutes stirring at room temperature, the mixture was evaporated to dryness at the rotary evaporator to give a purple solid. This was taken up in the minimum of dichloromethane and the resultant solution was chromatographed on 10% deactivated alumina (50 g). Elution with light petroleum removed excess of triethylphosphine and a second, dark red, band was eluted

with ether to give a red solution. Concentration of the solution gave 2-phenylazophenyl(thiocyanato)bis(triethylphosphine)palladium (II) (0.45 g, 80%) as dark red prisms, m.p. 165-167°C.

$C_{25}H_{39}N_3P_2PdS$ requires:- C=51.63%; H=6.71%; N=7.22%

found:- C=51.39%; H=6.55%; N=7.16%

I.R. (C≡N) = 2150 cm^{-1}

^1H n.m.r. ($CDCl_3$): δ8.15-7.90 (m, 2 aromatic protons); δ7.75-7.30 (m, 5 aromatic protons); δ7.25-6.95 (m, 2 aromatic protons); δ1.70-0.60 (m, 30 aliphatic protons).

The mass spectrum was uninformative.

Reaction of 2-phenylazophenyl(dimethyldithiocarbamato)palladium (II) with thiocyanogen

The title complex (0.41 g) was dissolved in dry chloroform (25 ml) and a solution of thiocyanogen (0.12 g in 10 ml $CHCl_3$) was added. The orange solution turned deep red initially but, after stirring for about 10 minutes, the colour began to fade and a precipitate began to form. The reaction mixture was left to stir at room temperature overnight. T.l.c. after this period indicated the absence of starting material and the presence of a new product. The mixture was filtered yielding a yellow solid [product A] and a yellow filtrate. When the filtrate was reduced in volume a little more yellow solid was precipitated from the solution and this was collected [product B]. The chloroform-soluble portion was then chromatographed on 10% deactivated alumina. Two fractions were obtained: the first fraction, a yellow band, was eluted with light petroleum to give an orange solution which yielded an orange solid [product C]; the second fraction, an orange band, was eluted with ether to give an orange solution which yielded a second orange solid [product D].

Products A and B were found to be much the same in infrared spectra and melting point (262-264°C with prior decomposition) and were assumed to be the same compound. Both spectra showed

strong C≡N stretching bands at 2150 cm^{-1} and broad dithiocarbamate bands at 1550-1570 cm^{-1}. The mass spectrum of the combined solids gave a parent ion at m/e 346 which corresponds to that required for bis(dimethyldithiocarbamato)palladium (II). The ^{1}H n.m.r. spectrum obtained was very weak owing to the insoluble nature of the product and was inconclusive. The product could not be completely characterised but, from the evidence obtained, it was thought likely that it was a mixture of bis(dimethyldithiocarbamato)palladium (II) and di-μ-thiocyanatobis(dimethyldithiocarbamato)dipalladium (II). The yield of these combined yellow products was 0.25 g.

Product C, azobenzene (0.01 g), was identified by its melting point (66-67°C), (lit m.p. 69°C), and its infrared spectrum.

The final product [D] was recrystallised from light petroleum to give 2-thiocyanatoazobenzene (0.10 g, 42%) as orange needles, m.p. 97-99°C (lit m.p. 99°C), infrared and ^{1}H n.m.r. spectra identical with those of an authentic specimen, mixed m.p. undepressed.

$C_{13}H_9NS$ requires:- C=65.27%; H=3.76%; N=17.57%
found :- C=65.41%; H=3.91%; N=17.36%

m/e 239 (M^+); 213

$C_{13}H_9N_3S$ requires:- M=239.052
found :- M=239.051

$C_{12}H_9N_2S$ requires :- M=213.049
found :- M=213.049

I.R. (C≡N) = 2145 cm^{-1} (v. weak).

^{1}H n.m.r. ($CDCl_3$): δ 8.15-7.65 (m, 4 aromatic protons); δ 7.60-7.10 (m, 5 aromatic protons).

Preparation of 2-thiocyanatoazobenzene

An authentic sample was prepared by the method of Burawoy.[87] Starting from 0.45 g of azobenzene-2-sulphenyl bromide, 0.4 g (75%) of the required product, m.p. 98-99°C (lit m.p. 98-99°C) (lit m.p.

99°C), was obtained.

Reaction of 2-(2-pyridyl)phenyl(dimethyldithiocarbamato)palladium (II) with thiocyanogen

The title complex (0.5 g) was dissolved in dry chloroform (25 ml) and a freshly prepared sample of thiocyanogen (0.15 g in 5 ml $CHCl_3$) was added. The course of the reaction after mixing the reagents ran parallel to that described for the analogous reaction of the azobenzene complex; the mixture at first darkened considerably and then, as a precipitate formed, it became much lighter in colour. After 2 h a yellow precipitate was apparent and this was collected as a pale yellow solid [product A]. The filtrate was evaporated to dryness and the yellow residue was taken up in the minimum of hot chloroform and chromatographed on 10% deactivated alumina (50 g). A barely perceptible band was eluted with ether and evaporation of the eluate gave a pale yellow oil which crystallised on cooling. N-Pentane was added and the product was filtered off as a white crystalline solid [product B]. A second fraction, eluted with chloroform, gave the starting complex (0.01 g), identified by melting point and infrared spectrum.

An infrared spectrum of product A was very similar to that of the insoluble yellow product obtained in the analogous reaction of the azobenzene complex, showing C≡N and dithiocarbamate bands at 2150 cm^{-1} and 1550-1570 cm^{-1} respectively. A mass spectrum showed an ion mass at m/e 346 corresponding to bis(dimethyldithiocarbamato)palladium (II). The product was tentatively identified as a mixture of bis(dimethyldithiocarbamato)palladium (II) and di-μ-thiocyanatobis(dimethyldithiocarbamato)dipalladium (II) (see discussion).

Product B was identified as 2-(2-thiocyanatophenyl)pyridine (0.10 g, 50%), a white crystalline solid, m.p. 102-103°C.

$C_{12}H_8N_2S$ requires:- C=67.92%; H=3.77%; N=13.20%
found:- C=67.93%; H=3.77%; N=13.24%

m/e 212 (M^+); 186
I.R. (C≡N) = 2150 cm^{-1}

^{1}H n.m.r. ($CDCl_3$): δ 8.70-8.50 (d.d., 1 α-pyridyl proton); δ 8.02-7.55 (m, 4 aromatic protons); δ 7.50-7.10 (m, 3 aromatic protons).

Reaction of [2-(N-phenylformimidoyl)phenyl](dimethyldithiocarbamato)palladium (II) with thiocyanogen

The title complex (0.55 g) was dissolved in dry chloroform (20 ml) and treated with a freshly prepared solution of thiocyanogen (0.30 g XS in 10 ml $CHCl_3$) under the same conditions as the preceding reaction. The solution turned dark red on mixing and, after 15 minutes stirring at room temperature, became a cloudy brown colour. After 30 minutes a yellow precipitate had formed and the mixture was bright yellow. Stirring was continued for a further 90 minutes and then the solution was filtered giving a yellow solid [product A] (0.40 g).

Concentration of the filtrate gave a yellow residue which was taken up in the minimum of hot chloroform and chromatographed on 10% deactivated alumina. Elution with ether yielded one fraction as a pale yellow oil [product B].

Product A gave a melting point [261-264°C (decomp)], infrared and mass spectrum identical with those of product A in the preceding reaction. By warming a sample of the product in hexadeuteriodimethyl sulphoxide a solution was obtained and this enabled a ^{1}H n.m.r. spectrum to be run. Apart from minor peaks indicating traces of aliphatic and aromatic impurities, the only signal was a singlet at δ3.3. This observation is referred to in detail in the discussion. Elemental analysis gave results which suggested that this product might be a mixture of bis(dimethyldithiocarbamato)-palladium (II) and di-μ-thiocyanatobis(dimethyldithiocarbamato)-dipalladium (II). (Found: C=22.25%; H=2.47%; N=10.47%).

Product B, a yellow oil, could not be crystallised despite several attempts. It was identified as the required product 2-(N-phenylformimidoyl)phenylthiocyanate (0.10 g, 48%) from its mass

and n.m.r. spectra.

m/e 238 (M^+); 212.

$C_{14}H_{10}N_2S$ requires M=238.056

found M=238.055

^{1}H n.m.r. ($CDCl_3$): δ 8.70-8.50 (m, 1 methine proton); δ 8.0-6.6 (m, 9 aromatic protons).

This product turned dark brown when left standing in air for more than a short period of time.

Reaction of [1-phenyl-2-(2-pyridyl)vinyl](dimethyldithiocarbamato)-palladium (II) with thiocyanogen

The title complex (0.50 g) was dissolved in dry chloroform (25 ml) and the solution was stirred at room temperature. A freshly prepared solution of thiocyanogen (0.30 g XS in 10 ml $CDCl_3$) was added and the mixture became very dark red. After 10 minutes the mixture began to become lighter and a red oily solid was deposited on the sides of the flask. Stirring was continued for a further 30 minutes by which time a yellow precipitate had formed and the mixture was pale yellow. The mixture was left to stand at room temperature overnight. Filtration after this period afforded a yellow solid (0.4 g), m.p. 260-262°C, an intractable red tar was left in the flask. It was thought possible that this residue contained some excess thiocyanogen which had polymerised but it could not be identified. The pale yellow filtrate was reduced in volume and chromatographed on 10% deactivated alumina (50 g). A single fraction was eluted with ether and gave a yellow semi-solid material which gave a small amount of a sticky white solid when a solution in ethanol was cooled in solid CO_2. This solid product was sufficient only for examination by melting point, infrared and mass spectroscopy; a ^{1}H n.m.r. spectrum was obtained using the product in the form of an oil.

The insoluble yellow solid gave an infrared spectrum which showed a broad C≡N stretch at 2080-2120 cm^{-1} and a very broad

dithiocarbamate band at 1540-1560 cm^{-1}. The presence also of bands at 1590 cm^{-1} and 1615 cm^{-1} (C=C and C=N) suggested that some starting material might be present in the yellow product. The mass spectrum confirmed this showing a weak m/e 406 peak. An ion mass at m/e 346 also indicated the presence of bis(dimethyldithiocarbamato)palladium (II). From the evidence obtained it seemed likely that the solid was a mixture of bis(dimethyldithiocarbamato)palladium (II), starting material and di-μ-thiocyanato-bis(dimethyldithiocarbamato)dipalladium (II).

The yellow oil (0.07 g, 30%) which partially crystallised in the form of a white solid (0.01 g), m.p. 49-50°C, was identified as 2-(2-phenyl-2-thiocyanatovinyl)pyridine.

m/e 238 (M^+); 212; 180.

$C_{14}H_{10}N_2S$ requires M=238.056

found M=238.054

$C_{13}H_{10}NS$ requires M=212.053

found M=212.053

The discrepancy in the experimental figure for m/e 238 is somewhat higher than the permissible error but the good agreement for m/e 212 casts some doubt on the reliability of measurement in the former case.

I.R. (C≡N) = 2150 cm^{-1}; (C=C) = 1585 cm^{-1}; (C=N) = 1605 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 8.70-8.60 (d.d. 1 α-pyridyl proton); δ 7.75-7.65 (m, 1 aromatic proton); δ 7.60-7.05 (m, 8 aromatic protons); δ 6.80 (s, 1 olefinic proton). The product appeared to decompose on standing in air if left for more than a short period.

Preparation of 2-(2-phenyl-2-thiocyanatovinyl)pyridine

2-Phenylisothiazolo-[2, 3-a]-pyridinium perchlorate[95] (0.5 g) was dissolved in dimethyl sulphoxide (10 ml) and potassium cyanide (0.10 g) was added. The resultant pale red solution was

stirred at room temperature for 1 h and a pale yellow solution was obtained. The mixture was poured into water (20 ml) and extracted with ether three times (3 x 50 ml). The combined yellow extracts were dried over anhydrous magnesium sulphate and then evaporated to dryness affording a yellow oil. The oil was crystallised from ethanol with a little difficulty yielding 2(2-phenyl-2-thiocyanatovinyl)pyridine (0.25 g, 67%) as white needles, m.p. 50-51°C.

$C_{14}H_9N_2S$ requires:- C=70.59%; H=4.20%; N=11.76%

found:- C=70.89%; H=4.30%; N=11.81%

m/e 238 (M^+); 212.

I.R. (C≡N) = 2150 cm^{-1}; (C=C) = 1585 cm^{-1}; (C=N) = 1605 cm^{-1}.

^{1}H n.m.r. ($CDCl_3$): δ 8.70-8.60 (d.d., 1 α-pyridyl proton); δ 7.75-7.65 (m, 1 aromatic proton); δ 7.60-7.05 (m, 8 aromatic protons); δ 6.80 (s, 1 olefinic proton). This spectrum was identical with that obtained in the previous reaction confirming the identity of the product in that reaction.

Reaction of 2-(2-thiocyanatophenyl)pyridine with bromine and perchloric acid

A solution of the thiocyanate (0.15 g) in absolute ethanol (20 ml) was treated with bromine (0.13 g in 2 ml abs EtOH) to give a light yellow solution. The solution was heated under reflux for 30 minutes during which time it became colourless. Solvent was removed from the solution yielding a white solid which was dissolved in ethanolic perchloric acid (1 ml 70% $HClO_4$ in 15 ml abs EtOH). The mixture was heated at reflux for 10 minutes and hot filtered giving a colourless filtrate. The filtrate was cooled in solid CO_2 and the white solid which crystallised was collected, washed with several portions of ether and air dried to give [1, 2]benzothiazolo-[2, 3-a]pyridinium perchlorate (0.10 g, 51%) as white needles m.p. 168-169°C.

$C_{11}H_8ClNO_4S$ requires:- C=46.31%; H=2.80%; N=4.91%

found:- C=46.16%; H=2.68%; N=4.67%

The mass spectrum was uninformative as is not uncommon with perchlorate salts generally.

I.R. (C=N) = 1620 cm^{-1}; (ClO_4^-) = 1060-1100 cm^{-1}

^1H n.m.r. (T.F.A.): δ 9.40-9.30 (d, 1 α-pyridyl proton); δ 8.85-8.75 (d, 1 pyridyl proton); δ 8.60-8.40 (m, 2 aromatic protons); δ 8.20-7.80 (m, 4 aromatic protons).

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