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CYCLOMETALLATED COMPOUNDS

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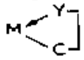
CONTENTS

A. INTRODUCTION

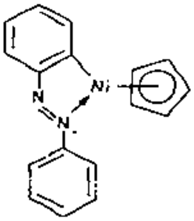
Recently, there has been some considerable interest shown in a new class of organometallic compounds of the "cyclometallated" type. These are so called because they contain the ring system  with a coordination bond between a transition metal "M" and a Group V (N, P, As) or Group VI (O, S) donor atom "Y", and a covalent metal—carbon bond. The M—C bond is formed by intramolecular rupture of a C—H bond from an M←Y coordination complex, thus

where "X" is a halogen or alkyl group. This method of formation of the M—C σ bond is more convenient than the classical approach using organomagnesium or organolithium reagents. Their formation by the cyclometallation reaction, together with their potential catalytic properties, has prompted the current interest in these compounds. The study of these complexes is rapidly increasing; it is therefore our purpose to complete and develop the general articles alrėady known [1—3] with the following review.

B. CYCLOMETALLATED COMPOUNDS IN WHICH Y = NITROGEN

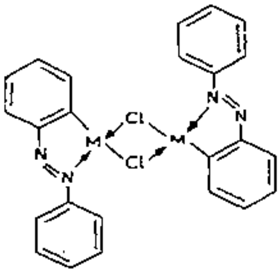
(i) M = Ni, Pd, Pt

In 1963, Kleinmann and Dubeck [4] reported the first cyclometallated compound formed by the reaction of azobenzene on nickelocene (I)



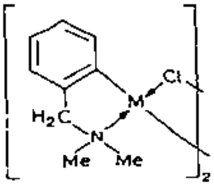
(I)

This compound was found to be monomeric, soluble in organic solvents, and stable in air. Azobenzene has been extensively employed in the formation of other metal—aryl σ bonds. Thus, with platinum and palladium chlorides Cope and Siekman [5] described the dimer (II)



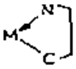
M = Pd, Pt (II)

and the analogues formed from N,N-dimethylbenzylamine (II) [6].



M = Pd, Pt (III)

Using the ligands $C_6H_5(CH_2)_mNH_n(CH_3)_{2-n}$ (m = 0—3; n = 0—2) Cope and Friedrich [6] determined the conditions for a donor nitrogen atom ligand to perform the cyclometallation reaction. These were found to be:

(1) The  *ring must contain 5 atoms*

Where the ligands L have m = 0, 2, 3; n = 0 which could give a 4, 6 or 7-

membered ring by substitution of an ortho-hydrogen of the phenyl group, only the compounds of type ML_2Cl_2 (where L is only coordinated by the nitrogen to the metal) were obtained.

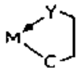
(2) The nitrogen atom must be tertiary

Benzylamine and N-monoalkylbenzylamine (n = 1 or 2) also only form ML_2Cl_2 compounds.

(3) The carbon atom must be substituted by electrophilic attack

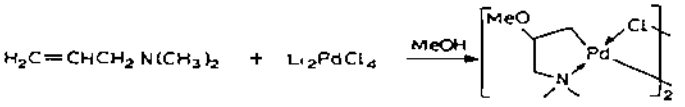
The para nitro-N,N-dimethylbenzylamine (in which the carbon atom ortho to the CH_2—$N(CH_3)_2$ group is deactivated) yields a compound containing only a coordinated amine group, where no M—C σ bond is formed. There appear to be no exceptions to the first "rule". To the second, it would be more true to say that the nitrogen atom coordinated to the metal must be sterically hindered, since Table 1 contains two compounds not containing tertiary nitrogen (triphenylmethylamine and N-methyltriphenylmethylamine). For the third "rule", nucleophilic attack can take place on the carbon atom when the metal is other than platinum or palladium.

All the compounds listed in Tables 1 and 2 are obtained after substitution of a hydrogen atom of the ligand by the metal. Other compounds of the type



exist, but they are not formed by the cyclometallation reaction.

Cope et al. [27] reported reaction (IV)



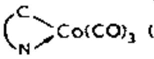
(IV)

In this case, the Pd—C bond is formed by the addition of OMe and Pd across the double bond. Another such example [90] is discussed below.

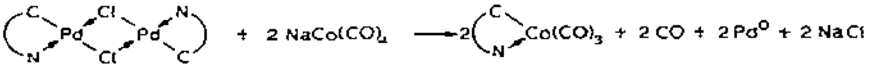
(ii) Compounds with other transition metals

Table 3 lists some of the known cyclometallated compounds formed from transition metals other than Ni, Pd, Pt. We have not mentioned in this table the very numerous complexes which may be obtained from those here cited by reactions such as nucleophilic substitutions or halide bridge cleavage. Examples of these reactions are given on page 346.

The compound



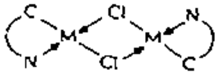
(C—N = azobenzene) was not formed by the action of azobenzene on $Co_2(CO)_8$ but rather by the reaction (V) [31]



(V)

Thus, there has been a transfer of azobenzene from the palladium to the

TABLE 1

Nitrogen donor ligands giving compounds of the type  (M = Pt, Pd)

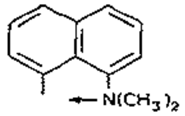
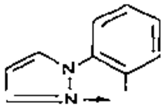
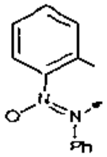
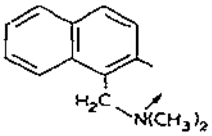
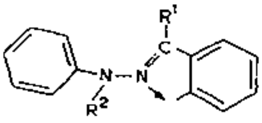
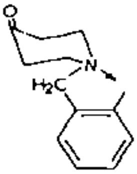
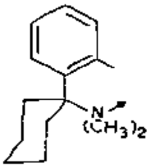
Ligands [a]		M	Reference
	N,N-dimethyl α-naphthylamine	Pd	[6]
	1-phenylpyrazole	Pd	[7]
	azoxybenzene	Pd	[8]
	N,N-dimethyl α-naphthylmethylamine	Pd	[9]
	R^1=Ph, Me, H; R^2 = H benzophenone-acetophenone-benzaldehyde-phenylhydrazones	Pd	[9,10]
	R^1 = Me; R^2 = Ph, Me acetophenone-diphenylhydrazone acetophenone-N methyl, N phenylhydrazone	Pd	[10]
	N-benzyl-4-piperidinone	Pd	[9]
	N,N-dimethyl-1-phenyl cyclohexylamine	Pd	[9]

TABLE 1 (continued)

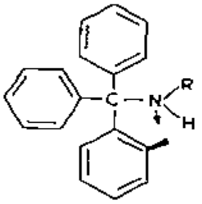
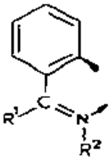
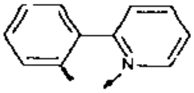
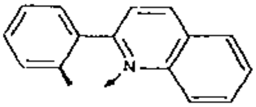
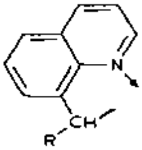
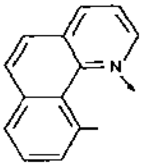
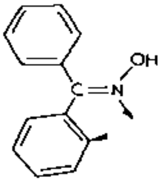
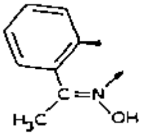
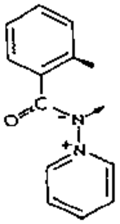
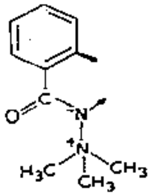
Ligands [a]		M	Reference
	R = H, Me N-methyltriphenylmethylamine or triphenylmethylamine	Pd	[9]
	SCHIFF'S bases	Pd	
	$R^1 = H$; $R^2 = C_6H_5$		[11]
	$R^1 = H, CH_3, C_6H_5$; $R^2 = CH_3, C_6H_5$		[12]
	2-phenyl pyridine	Pd	[13]
	2-phenyl quinoline	Pd	[13]
	R = H, Me		
	8-methyl quinoline	Pd, Pt	[14]
	8-ethyl quinoline	Pd	[15]
	benzo(h)quinoline	Pd, Pt	[14,9]
	benzophenone oxime	Pd	[16]
	acetophenone oxime	Pd	[16]

TABLE 1 (continued)

Ligands [a]		M	Reference
	N-(1-pyridinio)benzamidate	Pd	[17,18]
	N-(trimethylamino)benzamidate	Pd	[18]

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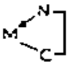
[a] Substituted phenyls are not included in this table.

TABLE 2

Other cyclometallated compounds containing the  ring (M = Ni, Pd, Pt) [a]

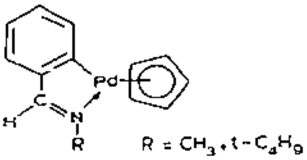
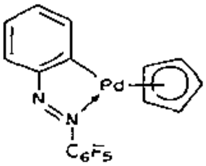
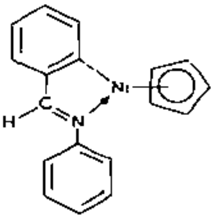
Ligand	Complex	Reference
benzylidene alkylamine		[7,19]
2,3,4,5,6-pentafluoro-azobenzene		[20]
benzylidene aniline		[21]

TABLE 2 (continued)

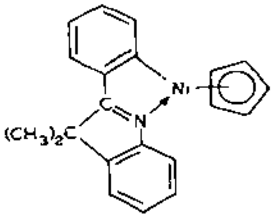
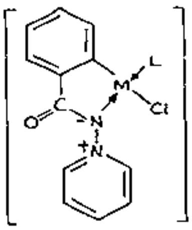
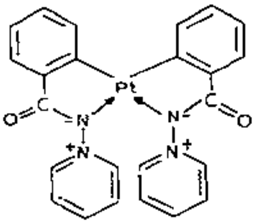
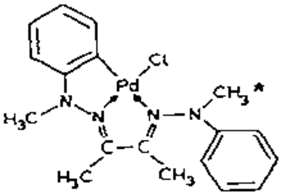
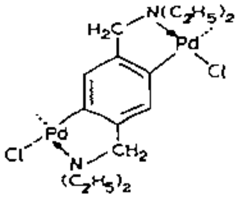
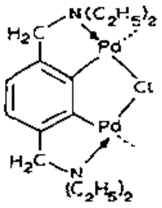
Ligand	Complex	Reference
3,3-dimethyl-2-phenylindoleamine		[21]
N-(1-pyridinio)benzamidate (L)	 2 H_2O M = Pt, Pd	[18]
		[18]
diacetyl-bis-(N-methyl,N-phenyl) hydrazone		[22]
N,N,N′,N′-tetraethyl α,α′-diamino,p-xylene	 	[7]

TABLE 2 (continued)

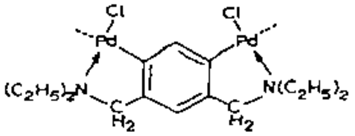
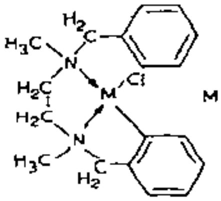
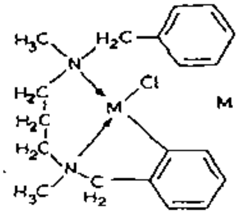
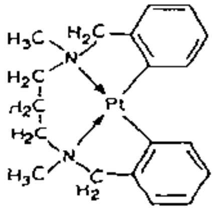
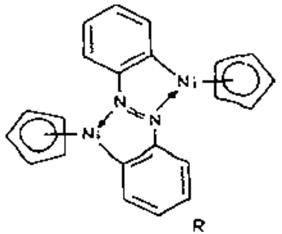
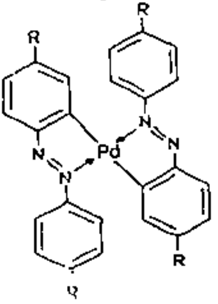
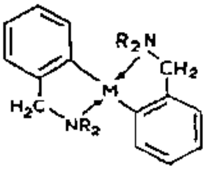
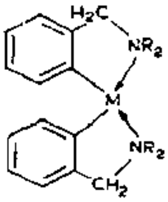
Ligand	Complex	Reference
N,N,N′,N′-tetraethyl α,α′-diamino m-xylene		[7]
N,N′-dibenzyl N,N′-dimethyl-1,2 diaminoethane	 M = Pd, Pt	[23]
N,N′-dibenzyl N,N′-dimethyl-1,3 diaminopropane	 M = Pd, Pt	[23]
		[23]
azobenzene		[24]
	R = CH_3, OCH_3 ** 	[25]

TABLE 2 (continued)

Ligand	Complex	Reference
N,N-dialkylbenzylamine ***	 R = CH_3, C_2H_5 M = Ni, Pd, Pt	[26,7]
	 R = CH_3, C_2H_5 M = Pd, Pt	[26]

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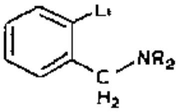
[a] Monomers derived from Table 1 compounds by bridge breaking are not listed.

* The X-ray crystallographic structure is reported.

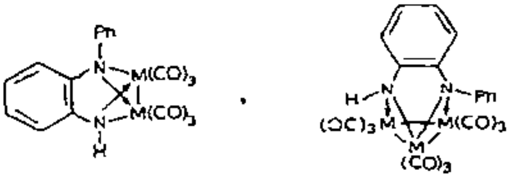
** Obtained from the dimers $(Pd(C—N)Cl)_2$ in the presence of $Fe(CO)_4^{2-}$.

*** Prepared from 

cobalt, the latter passing from oxidation state —1 (in $Co(CO)_4^-$) to +1 (in the cyclometallated compound), whilst the palladium (II) is reduced to the free metal state O.

The manganese and rhenium analogues may also be prepared in this manner, but may alternatively be synthesised from azobenzene and $M_2(CO)_{10}$ or $CH_3M(CO)_5$ (M = Mn, Re).

The action of the ligands which verify the condition above, described by Cope on transition metals, often results in the formation of complexes in which the ligands have undergone modification. For example, azobenzene with $Fe_2(CO)_9$ or $M_3(CO)_{12}$ (M = Fe, Ru) gives orthosemidine complexes (VI) [25,37]



M = Fe, Ru (VI)

TABLE 3

Cyclometallated complexes with a nitrogen donor ligand (M ≠ Pt, Pd, Ni)

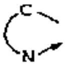
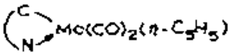
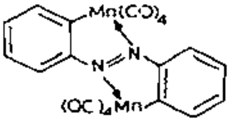
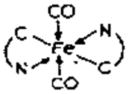
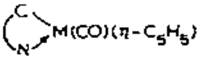
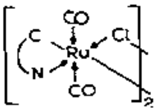
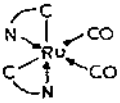
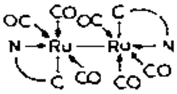
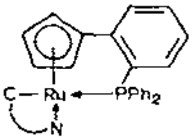
Complexes		Ref.
	azobenzene 8-methylquinoline benzo(h)quinoline	[28] [29] [30]
 M = Mn, Re	azobenzene benzo(h)quinoline benzilidene aniline (M=Mn) * benzilidene methylamine N,N-dimethylbenzylamine (M=Mn) * 2,3,4,5,6-pentafluoroazobenzene 2H nonafluoroazobenzene	[28,31] [30] [19,32,33] [19] [34] [20]
	azobenzene	[35]
	4,4-dimethoxyazobenzene	[25]
 M = Fe, Ru	azobenzene	[28]
	azobenzene	[36]
	benzylidene aniline benzylidene methylamine benzo(h)quinoline	[19] [19] [30]
	azobenzene	[37]
	decafluoroazobenzene *	[38]

TABLE 3 (continued)

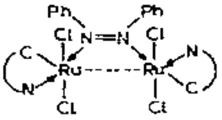
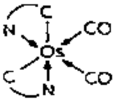
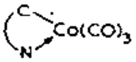
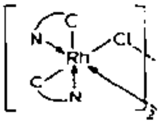
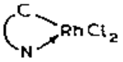
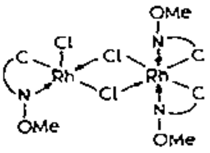
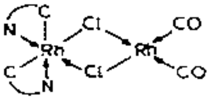
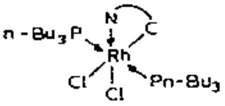
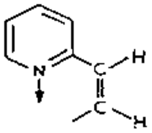
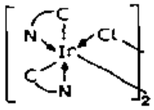
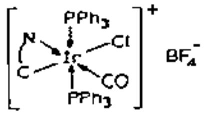
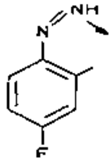
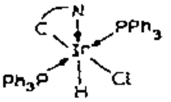
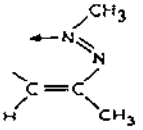
Complexes		Ref.
	azobenzene	[39]
	benzo(h)quinoline	[30]
 (a)	azobenzene	[31]
	azobenzene benzo-, aceto-, propio and n-butyro phenone oximes 2-phenylpyridine benzo(h)quinoline 1-phenylpyrazole	[40,41] [42] [43] [43] [44]
 (b)	8-methylquinoline	[45]
	O-methylbenzophenone oxime O-methyl p-tertiobutylacetophenone oxime	[42]
	azobenzene * benzylidene-aniline benzo(h)quinoline 2,3,4,5,6-pentafluoroazobenzene	[40,41,46] [19,40] [30] [20]
	2-vinylpyridine 	[47]
$[Rh(C{-}N)_2(H_2O)_2]Cl$	N-(1-pyridinio)benzamidate	[18]
$[Ir(C{-}N)_2(H_2O)Cl]$, 3 H_2O	N-(1-pyridinio)benzamidate	[18]
	1-phenylpyrazole	[44]

TABLE 3 (continued)

Complexes		Ref.
	(4-fluorophenyl)-di-imide * 	[48]
	azobenzene benzylidene methylamine benzylidene aniline 2-methylazo propene 	[49,50] [50]

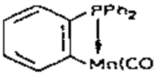
(a) See text for synthesis.
(b) Unknown stereochemistry.
* The X-ray crystallographic structure is reported.

Azobenzene is also rearranged to orthosemidine when reacting with cobalt [51], rhodium [52] and molybdenum [28] complexes. With $RhCl_3$ and $(Rh(CO)_2Cl)_2$, the N=N bond is broken, and the aniline complexes $((PhNH_2)_2RhCl_3)_n$ and $(PhNH_2)Rh(CO)_2Cl$ respectively are isolated. The C=N bond of benzylidene aniline (PhCH=NPh) is broken in the presence of palladium, platinum (II) or rhodium (III) salts, yielding free benzaldehyde and aniline—metal complexes [9,53]. The mechanism is, as yet, unclear.

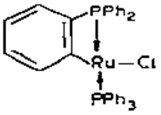
C. CYCLOMETALLATED COMPOUNDS IN WHICH Y = PHOSPHORUS

(i) Phosphines

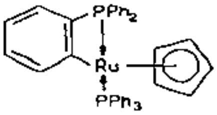
In the case of phosphines, the Cope rules for ligands of donor nitrogen are not applicable, since 4 atom rings are found. There are several compounds of this type of triphenylphosphine with manganese, ruthenium, rhodium, iridium and platinum (VII)



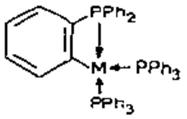
[54]



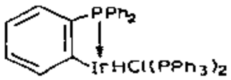
[55]



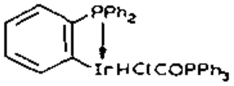
[56]



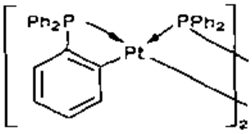
M = Rh [57]
M = Ir [58]



[59] (VII)

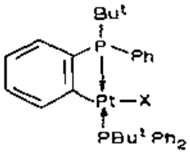


[60]

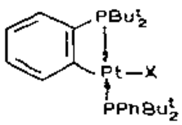


[61]

Shaw and co-workers [62] have demonstrated that phosphines hindered by t-butyl groups are required for the cyclometallation reaction with platinum, for example (VIII), (IX)



(VIII)

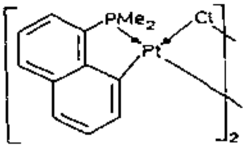


(IX)

X = Cl, Br, I

In such compounds the 4 atom ring is very strained, and in case (VIII) where X = NO_2, the P—Pt—C angle is 68° [2], and CO is easily inserted in the M—C bond [1]. In fact, a 5 atom ring is formed preferentially, as with 1-dimethyl naphthylphosphine (L) (X).

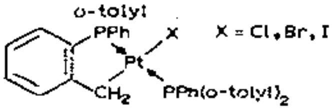
$RuCl(P-C)(CO)L_2$
$OsCl_2(P-C)L_2$
$Os(P-C)_2(CO)L$
} [64]



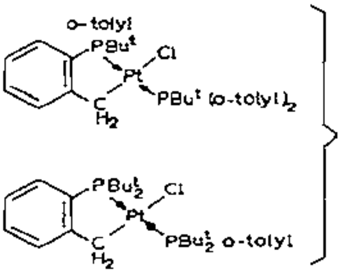
[63] and (X)

$RhCl_2(P-C)L_2$
$IrCl_2(P-C)L_2$
$IrCl(P-C)_2L$
$Ir(P-C)_3$
} [65]

When the phenyl ring is α alkyl substituted, a five atom ring is formed, the metal being linked to the alkyl group as follows (XI)

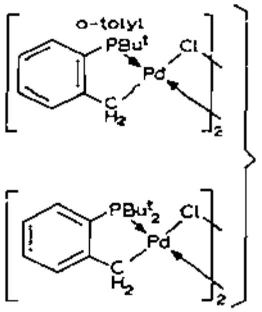


[62]

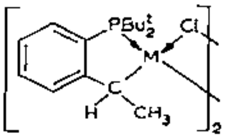


[66]

(XI)

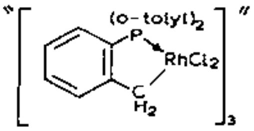


[67]



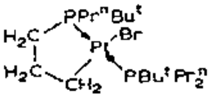
[68]

M = Pt, Pd



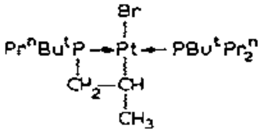
[69]

or with dipropyl-tert-butylphosphine (XII) [62]



(XII)

With the latter compound, Shaw and co-workers have isolated a further 4-membered ring (XIII) [62]

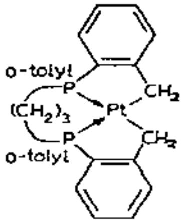


$$Pr^nBu^tP \rightarrow \overset{Br}{\underset{CH}{Pt}} \leftarrow PBu^tPr^n_2$$

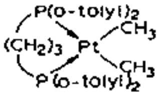
(XIII)

The tendency for a hindered phosphine to give a cyclometallated ring is so strong that platinum complexes were isolated with two cyclometallated phosphines (XIV)

when $P{-}C = \begin{cases} PBu^t_2\ (o\text{-tolyl}) \\ PBu^t\ (o\text{-tolyl})_2 \end{cases}$ [66] (XIV)

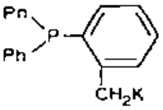
The analogous compound (XV)  was formed by the pyrolysis

(XV)

of (XVI)  with the evolution of methane [23].

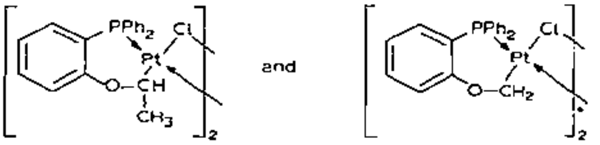
(XVI)

There are reports [70] of analogous compounds formed with nickel, palladium or platinum and phosphine previously metallated by potassium (XVII)



(XVII)

With 2-alkoxy phenylphosphine it is possible to isolate cyclometallated compounds containing 6 atom rings (XVIII) [71]



(XVIII)

(ii) Triphenylphosphite

Table 4 lists the known cyclometallated compounds of triphenylphosphite and group VIII metals.

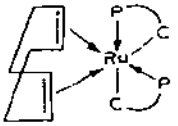
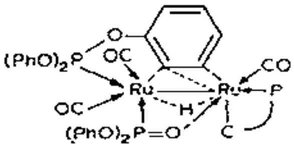
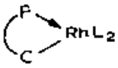
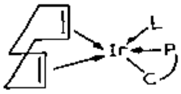
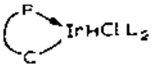
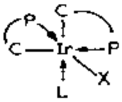
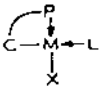
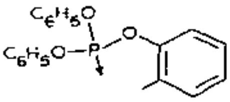
As in the case of the phosphines, it appears that the C—H bond is activated via an oxidative addition on the metal followed by the reductive elimination of HX. The appearance of a Pt^{IV} intermediate may explain why more platinum than palladium compounds are known, the latter being more difficult to oxidise.

D. CYCLOMETALLATED COMPOUNDS IN WHICH Y = ARSENIC, OXYGEN OR SULPHUR

Several attempts have been made at cyclometallation with benzyldimethylarsine [9], methylthio-benzyl [7,9], phenylthiobenzyl [87] and Pd^{II} salts, but only PdL_2Cl_2 compounds resulted.

TABLE 4

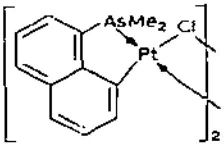
Cyclometallated compounds of triphenylphosphite *

Complexes	Ref.	Complexes		Ref.
	[72,73]			[74]
(a) 	[75]	Ru(CO)$_2$(P—C)$_2$		[76]
OsL$_2$(P—C)$_2$, Os(P—C)LPPh$_3$(CO)H	[77]			
	[78]			[79]
	[80—82]		(a) X = H, Cl	[82—84]
Ir(P—C)$_3$	[82]		M = Pt, Pd X = Cl, Br, I	[85,86]
L = P(OPh)$_3$		P—C = 		

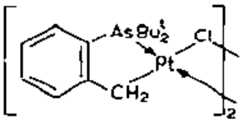
* (a) The X-ray crystallographic structure is reported.

(i) Arsines

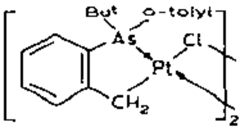
Only the following arsenic-donor ligand cyclometallated compounds have been reported (XIX)



[63]



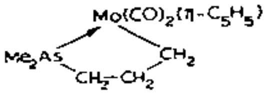
and



[88] (XIX)

These "hindered" arsines cyclometallate in a similar, but slower, manner to their phosphine analogues.

Dehalogenation of (η-C_5H_5)Mo(CO)$_2$I {Cl(CH_2)$_3$AsMe_2} by sodium amalgam yields (XX) [89]

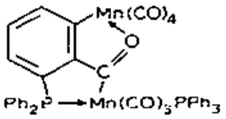


(XX)

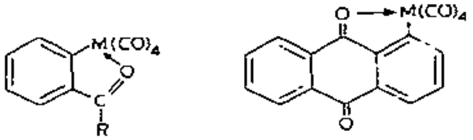
Nyholm and co-workers [90] have isolated a cyclometallated compound whose ligand contained an arsenic donor atom. It was formed by addition across a double bond, similar to the case of NN-dimethylalkylamine discussed above.

(ii) Ligands with oxygen and sulphur donors

Few examples of this type of compound are known (XXI)



[91]

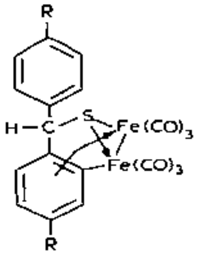


M = Mn, Re

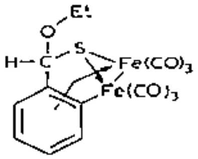
R = Me, Ph

[92]

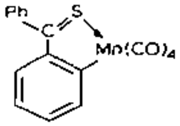
(XXI)



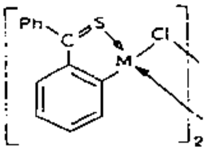
[93]



[94]



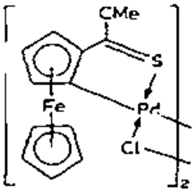
[95]



[96]

M = Pd, Pt

Recently, Alper [97] reported the first cyclometallated compound to contain a metallated carbon atom from a cyclopentadienyl moiety, synthesized from thiopivaloylferrocene and sodium tetrachloropalladite (XXII)

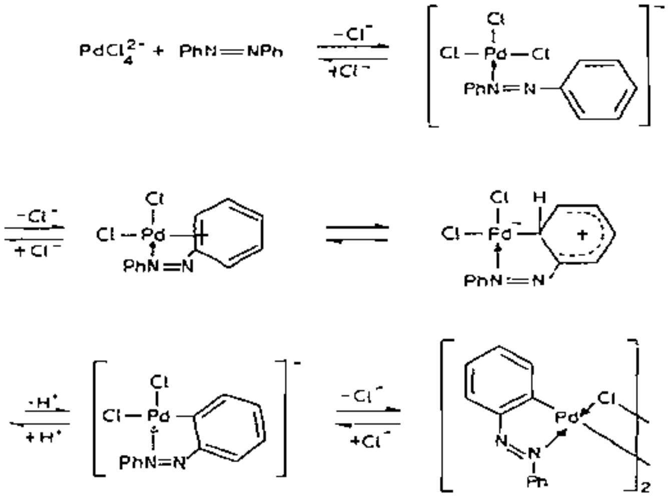


(XXII)

E. MECHANISM OF CYCLOMETALLATION

The pathway of the cyclometallation reaction depends on the nature of the atom Y.

When the ligand contains nitrogen as a donor atom, and the metal is palladium or platinum, the reaction is by way of an electrophilic substitution of the metal on the carbon. For paramonosubstituted azobenzene, the metal binds to the substituted ring in the order of ease: $OCH_3 > CH_3 > H > Cl$ [98]. For the methoxy moiety, the most electron donating, only the substituted ring is attacked by the metal, whereas in the case of the chloride the unsubstituted ring is preferentially attacked. Parshall [1] has proposed the following mechanism for cyclopalladation with azobenzene (XXIII)



(XXIII)

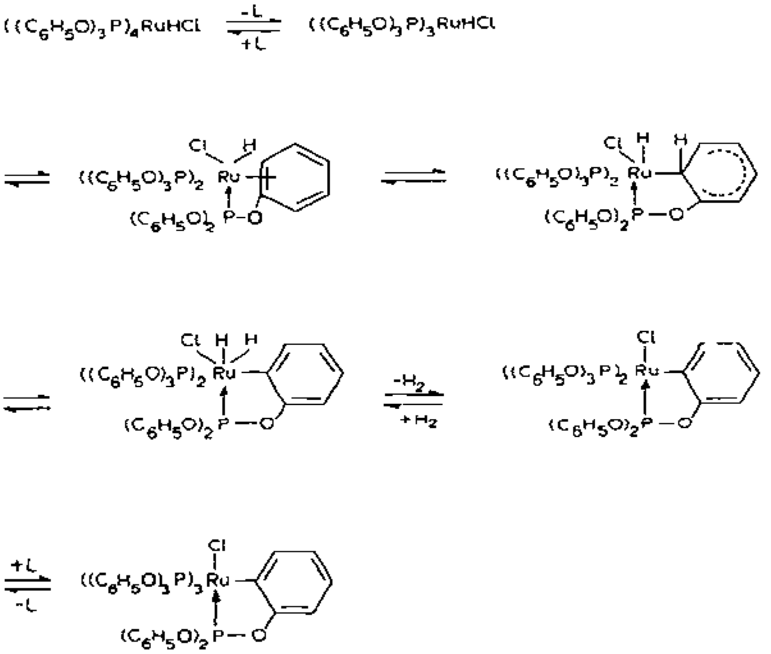
The reaction proceeds with the evolution of hydrogen chloride, and hence is often accelerated by the addition of a base to the medium, although there are exceptions here, like: (C_6H_5Pz). In this case it appears that acid is necessary to replace one of the ligands (by protonation) from $Pd(C_6H_5Pz)_2Cl_2$ to $[(C_6H_5Pz)PdCl_2]$ which forms the required dimer [7].

Stone and co-workers [99] have shown that, for certain electron-rich metals, it is more convenient to postulate a mechanism in which the first step is a nucleophilic attack of the metal on the aromatic ring.

In meta fluoroazobenzene the ortho position of the substituted ring is the most deactivated and least susceptible to electrophilic attack. It is this carbon atom which binds to the manganese atom when the ligand reacts with methyl manganese pentacarbonyl. (With palladium, Stone and co-workers have demonstrated the preferential attack on the ortho carbon atom of the unsubstituted ring, this being the most favourable to electrophilic attack.)

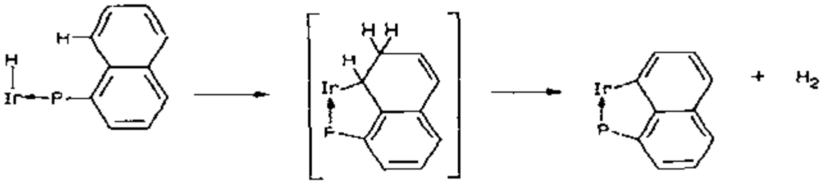
Most of the examples discussed so far are formed by the substitution of a hydrogen atom by the metal, although several cases are known in which a halogen atom on a carbon atom is substituted. Orthochloroazobenzene [100] and nickelocene form the complex of Kleinmann and Dubeck [4] by this method, and cycloruthenated complexes are formed by the breaking of a C—F bond of decafluoroazobenzene [38] (Table 3). These examples also illustrate the nucleophilic attack of the metal on the aromatic ring.

The mechanism of formation of complexes containing a donor phosphorus ligand is somewhat different. The key step is an oxidative addition on the metal, followed by a reductive elimination. Parshall [1] postulates the following pathway for the ruthenium cyclometallation of triphenylphosphite (XXIV)



(XXIV)

A different mechanism is proposed by Duff and Shaw [65] for the hexacoordinated iridium (III) compounds where oxidative addition cannot occur. The iridium is here an electrophile (XXV)



(XXV)

It is thus evident that the more the donor atom Y is hindered, the more the cyclometallation is favoured. If the substituents on this atom are small, there is a large rotational entropy, and rotation about the M—Y bond is possible. When the ligands are bulky, no rotation can occur and the rotational entropy is low [2].

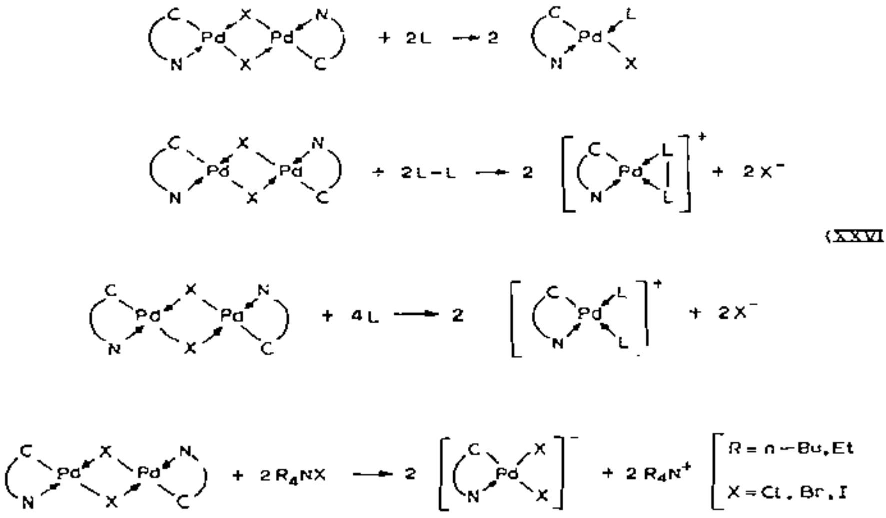
F. CHEMICAL REACTIONS OF CYCLOMETALLATED COMPOUNDS

These compounds have some interesting properties because of different types of bonds, which may further react.

(i) Reactivities of the metal—halogen and metal—Y bonds

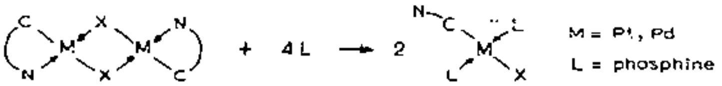
In the case of the metal—halogen bond, several examples of breaking of the halogen bridges in dimers by neutral ligands (CO, pyridine, phosphine, diphosphine, ethylene diamine) or anionic ligands (thiocyanate, acetyl acetonate, halides) are known.

For example (XXVI) [3,7,9,101—104]



(XXVI)

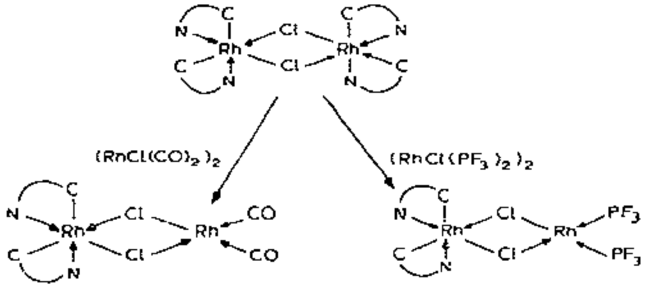
It is also possible to cleave the coordination bond N→Pd (XXVII) [12,101, 103,105,106]



(XXVII)

A similar reaction is reported [36] for the dimer (Ru(C—N)(CO)$_2$Cl)$_2$ where the reaction with NaC$_5$H$_5$ and TlC$_5$H$_5$ gives η-C$_5$H$_5$Ru(C—N)(CO) and η-C$_5$H$_5$Ru(C—N)(CO)$_2$ respectively. The cyclopentadiene anion breaks the chlorine bridges, substitutes a chlorine atom and a CO in the first case, and displaces the N→Ru bond in the latter, so that the azobenzene is only bonded to the metal by a Ru—C bond.

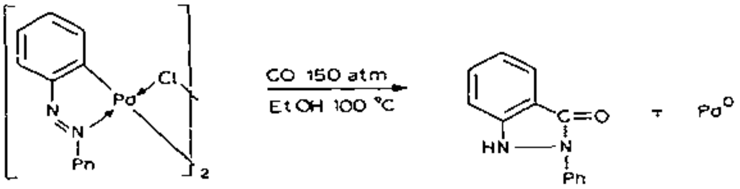
The complex (Rh(C—N)$_2$Cl)$_2$ where C—N = azobenzene undergoes an unusual reaction [40,107] with a dimer of rhodium (I), yielding the asymmetric dimer (XXVIII)



(XXVIII)

(ii) Reactivity of the metal—carbon bond

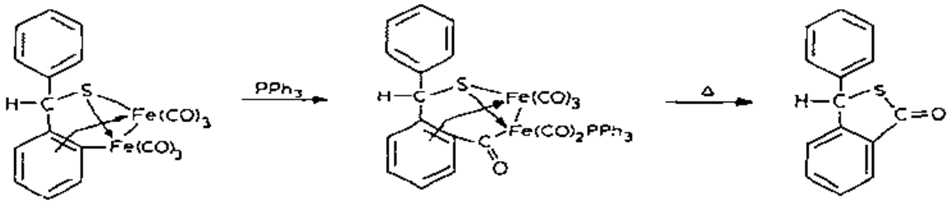
The lability of the metal—carbon bond may be of interest in organic synthesis. For example, one of the first known reactions of cyclometallated compounds was the formation of indazolone from an azobenzene cyclopallatated compound (XXIX) [98]



(XXIX)

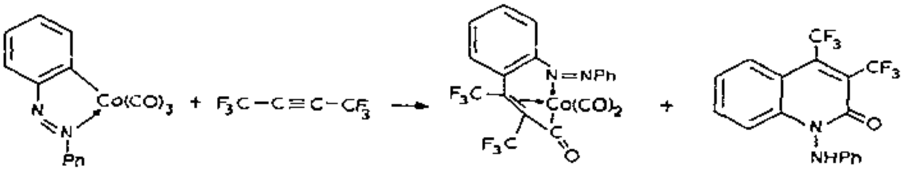
The indazolone obtained was probably formed by the insertion of CO in the C—Pd bond, followed by breaking of the N→Pd bond. Before this reaction using cyclometallated compounds, indazolone had been synthesized from azobenzene in the presence of Co$_2$(CO)$_8$ [108], probably by way of a cyclocobaltated intermediate [31].

Alper and Chan [93], and Alper et al. [109] have reported a similar reaction involving donor sulphur ligands and have isolated an intermediate compound in which the carbonyl is inserted in the C—M bond (XXX)



(XXX)

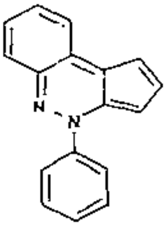
Stone and co-workers [110] obtained a substituted N-anilinoquinolone and a π-acryloyl complex of cobalt from the reaction of hexafluorobut-2-yne on phenylazophenyl-2C,N cobalt tricarbonyl (XXXI).



(XXXI)

Here, there has been an insertion of the alkyne and the carbonyl into the cobalt—phenyl bond.

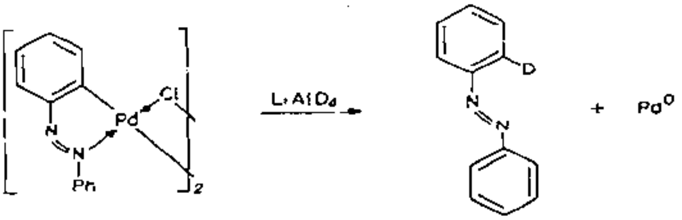
Ortho-chloroazobenzene reacts with η-$C_5H_5Ni(PhN{=}NC_6H_4)$ to yield 4-4H-phenylcyclopental[c]-cinnoline (XXXII) [100]



(XXXII)

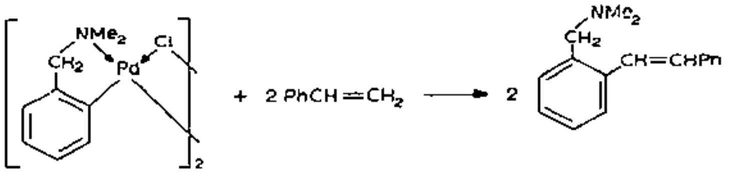
by virtue of the condensation of the complexed azobenzene with the cyclopentadienyl group. A metal—carbon bond, where the carbon belongs to an aromatic ring, may also be used in the synthesis of disubstituted ortho phenyls. Fahey [111] has described the chlorination of azobenzene in the presence of $PdCl_2$, and reports the product as being a mixture of 2-chloro-(12%), 2,6-dichloro-(22%), 2,2′-dichloro-(30%), 2,6,2′-trichloro-(33%) and 2,6,2′,6′-tetrachloro-(3%)-azobenzene.

It is also possible to cleave the metal—carbon bond reductively with $LiAlD_4$ to yield an ortho-deuterated aromatic ring (XXXIII) [5]



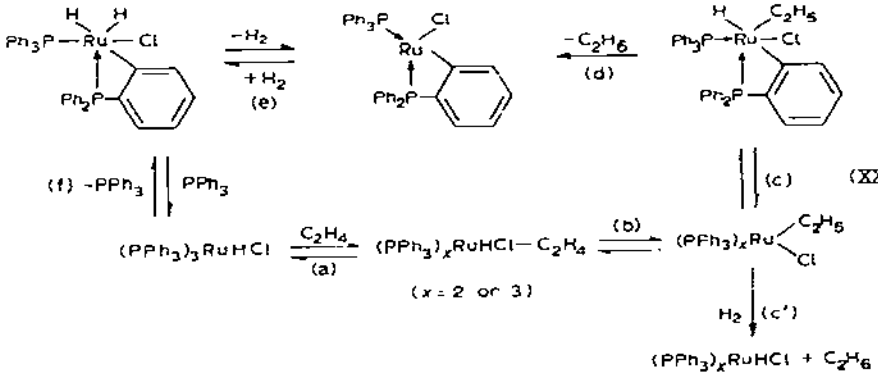
(XXXIII)

Similarly, an aromatic ring may be substituted at the ortho position by a vinylic group (XXXIV) [112]



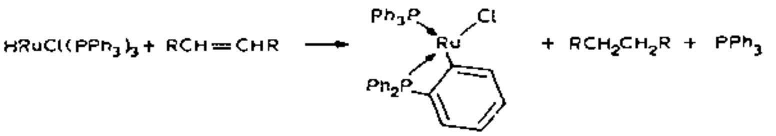
(XXXIV)

Furthermore, in the case of olefin hydrogenation, the existence of similar cyclometallated complexes has been proposed to explain the catalytic reaction mechanism [1,113]. The following catalytic cycle using a ruthenium complex may be postulated (XXXV)



(XXXV)

Step (XXXV) (b), in the presence of hydrogen, would liberate ethane and regenerate $(PPh_3)_xRuHCl$ (XXXV) (c'). Ethane may equally be liberated in the absence of hydrogen assuming the cyclometallation of a phenyl group of a phosphine (oxidative addition) followed by the release of ethane (reductive elimination). Hence the hydrogen would serve only to regenerate the departing $(PPh_3)_3RuHCl$. An analogous scheme has been proposed for the hydride complexes of cobalt with triphenylphosphite [114]. Recently, the following reaction under stoichiometric conditions has been determined (XXXVI) [55]:



(XXXVI)

It was reported that the departing compound $HRuCl(PPh_3)_3$ may be regenerated by the action of hydrogen followed by triphenylphosphine on the cycloruthenium compound.

REFERENCES

1 G.W. Parshall, Accounts Chem. Res., 3 (1970) 139.
2 F.R. Hartley, The Chemistry of platinum and palladium, Applied Science Publishers, London, 1973, p. 149.
3 A.J. Carty, Organometal. Chem. Rev. Sect. A, 7 (1972) 191.
4 J.P. Kleinmann and M. Dubeck, J. Amer. Chem. Soc., 85 (1963) 1544.
5 A.C. Cope and R.W. Siekman, J. Amer. Chem. Soc., 87 (1965) 3272.
6 A.C. Cope and E.C. Friedrich, J. Amer. Chem. Soc., 90 (1968) 909.
7 S. Trofimenko, Inorg. Chem., 12 (1973) 1215.
8 A.L. Balch and D. Petridis, Inorg. Chem., 8 (1969) 2247.
9 B.N. Cockburn, D.V. Howe, T. Keating, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton, (1973) 404.
10 P. Braunstein, J. Dehand and M. Pfeffer, Inorg. Nucl. Chem. Lett., 10 (1974) 521.
11 S.P. Molnar and M. Orchin, J. Organometal. Chem., 16 (1969) 169.
12 H. Onoue and I. Moritani, J. Organometal. Chem., 43 (1972) 431.
13 A. Kasahara, Bull. Chem. Soc. Jap., 41 (1968) 1272.
14 G.E. Hartwell, R.V. Lawrence and M.J. Smas, J. Chem. Soc., Chem. Commun., (1970) 912.
15 V.I. Sokolov, T.A. Sorokina, L.L. Troitskaya, L.I. Solovieva and O.A. Reutov, J. Organometal. Chem., 36 (1972) 369.
16 H. Onoue, K. Minami and N. Nakagawa, Bull. Chem. Soc. Jap., 43 (1970) 3480.
17 S.A. Dias, A.W. Downs and W.R. Whinnie, Inorg. Nucl. Chem. Lett., 10 (1974) 233.
18 S.A. Dias, A.W. Downs and W.R. Whinnie, J. Chem. Soc., Dalton, (1975) 162.
19 R.L. Bennet, M.I. Bruce, B.L. Goodall, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc., Dalton, (1972) 1787.
20 M.I. Bruce, B.L. Goodall, G.L. Sheppard and F.G.A. Stone, J. Chem. Soc., Dalton, (1975) 591.
21 Y.A. Ustynyuk, V.A. Chertov and I.V. Barinov, J. Organometal. Chem., 19 (1971) C53.
22 G. Bombieri, L. Caglioti, L. Cattalini, E. Forsellini, F. Gasparini, R. Graziani and P.A. Vigato, J. Chem. Soc., Chem. Commun., (1971) 1415.
23 M.G. Clerici, B.L. Shaw and B. Weeks, J. Chem. Soc., Chem. Commun., (1973) 516.
24 I.V. Barinov, T.I. Voyevodskaya and Y.A. Barinov, J. Organometal. Chem., 30 (1971) C28.
25 M.M. Bagga, W.T. Flannigan, G.R. Knox and P.L. Pauson, J. Chem. Soc., C, (1969) 1534.
26 G. Longoni, P. Fantucci, P. Chini and F. Canziani, J. Organometal. Chem., 39 (1972) 413.
27 A.C. Cope, J.M. Kliegman and E.C. Friedrich, J. Amer. Chem. Soc., 89 (1967) 287.
28 M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc., A, (1970) 3204.
29 A.R. Garber, P.E. Garrow, G.E. Hartwell, M.J. Smas, J.R. Wilkinson and L.J. Todd, J. Organometal. Chem., 86 (1975) 219.
30 M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Organometal. Chem., 60 (1973) 343.
31 R.F. Heck, J. Amer. Chem. Soc., 90 (1968) 313.
32 M.I. Bruce, B.L. Goodall, F.G.A. Stone, R.J. Doedens and R.G. Little, J. Chem. Soc., Chem. Commun., (1971) 1525.
33 R.G. Little and R.J. Doedens, Inorg. Chem., 12 (1973) 840.
34 R.G. Little and R.J. Doedens, Inorg. Chem., 12 (1973) 844.
35 R.L. Bennet, M.I. Bruce, B.L. Goodall and F.G.A. Stone, Aust. J. Chem., 27 (1974) 2131.
36 M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc., A, (1971) 2820.
37 M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, J. Organometal. Chem., 31 (1971) 275.
38 M.I. Bruce, R.C.F. Gardner, B.L. Goodall and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1974) 187.
39 J.D. Gilbert, D. Rose and G. Wilkinson, J. Chem. Soc., A, (1970) 2766.

40 M.I. Bruce, B.L. Goodall, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1971) 661.
41 M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, J. Organometal. Chem., 40 (1972) 393.
42 H. Onoue and I. Moritani, J. Organometal. Chem., 44 (1972) 189.
43 M. Nonoyama and K. Yamasaki, Inorg. Nucl. Chem. Lett., 7 (1971) 943.
44 M. Nonoyama, J. Organometal. Chem., 86 (1975) 263.
45 M. Nonoyama, J. Organometal. Chem., 74 (1974) 115.
46 R.J. Hoare and O.S. Mills, J. Chem. Soc., Dalton, (1972) 2141.
47 R.J. Foot and B.T. Heaton, J. Chem. Soc., Chem. Commun., (1973) 838.
48 F.W.B. Einstein, A.B. Gilchrist, G.W. Rayner-Canham and D. Sutton, J. Amer. Chem. Soc., 94 (1972) 645.
49 M.I. Bruce, B.L. Goodall, F.G.A. Stone and B.J. Thomson, Aust. J. Chem., 27 (1974) 2135.
50 J.F. van Baar, K. Vrieze and D.J. Stufkens, J. Organometal. Chem., 85 (1975) 249.
51 T. Joh, N. Hagihara and S. Murahashi, Bull. Chem. Soc. Jap., 40 (1967) 661.
52 T. Joh, N. Hagihara and S. Murahashi, J. Chem. Soc. Jap., 88 (1967) 786.
53 I. Jardine and F.J. McQuillin, Tetrahedron Lett., 6 (1972) 459.
54 R. Howmeier, B. Deubzer and D.H. Kaesz, J. Amer. Chem. Soc., 93 (1971) 536.
55 B.R. James, L.D. Markham and D.K.W. Wang, J. Chem. Soc., Chem. Commun., (1974) 439.
56 M.I. Bruce, R.C.F. Gardner and F.G.A. Stone, J. Organometal. Chem., 40 (1972) C39.
57 W. Keim, J. Organometal. Chem., 14 (1968) 179.
58 B. Longato, F. Morandini and S. Bresadola, J. Organometal. Chem., 88 (1975) C7.
59 M.A. Bennet and D.L. Milner, J. Amer. Chem. Soc., 91 (1969) 6983.
60 J.S. Valentine, J. Chem. Soc., Chem. Commun., (1973) 857.
61 F. Glockling, T. McBride, R.J.I. Pollock, J. Chem. Soc., Chem. Commun., (1973) 650.
62 A.J. Cheney, B.E. Mann, B.L. Shaw and R.M. Slade, J. Chem. Soc., A, (1971) 3833.
63 J.M. Duff, B.E. Mann, B.L. Shaw and B. Turtle, J. Chem. Soc., Dalton, (1974) 139.
64 P.G. Douglas and B.L. Shaw, J. Chem. Soc., Dalton, (1973) 2078.
65 J.M. Duff and B.L. Shaw, J. Chem. Soc., Dalton, (1972) 2219.
66 A.J. Cheney and B.L. Shaw, J. Chem. Soc., Dalton, (1972) 754.
67 A.J. Cheney and B.L. Shaw, J. Chem. Soc., Dalton, (1972) 860.
68 D.G. Gill, B.E. Mann and B.L. Shaw, J. Chem. Soc., Dalton, (1973) 270.
69 M.A. Bennett and P.A. Longstaff, J. Amer. Chem. Soc., 91 (1969) 6266.
70 G. Longoni, P. Chini, F. Canziani and P. Fantucci, J. Chem. Soc., Chem. Commun., (1971) 470.
71 C.E. Jones, B.L. Shaw and B.L. Turtle, J. Chem. Soc., Dalton, (1974) 992.
72 W.H. Knoth and R.A. Schunn, J. Amer. Chem. Soc., 91 (1969) 2400.
73 J.J. Levison and S.D. Robinson, J. Chem. Soc., A, (1970) 639.
74 J.J. Hough and E. Singleton, J. Chem. Soc., Chem. Commun., (1972) 371.
75 M.I. Bruce, J. Howard, I.W. Nowell, G. Shaw and P. Woodward, J. Chem. Soc., Chem. Commun., (1972) 1041.
76 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton, (1973) 1667.
77 E.W. Ainsgough, T.A. James and S.D. Robinson, J. Chem. Soc., Dalton, (1974) 2384.
78 E.K. Barefield and G.W. Parshall, Inorg. Chem., 11 (1972) 964.
79 L.M. Haines and E.S. Singleton, J. Organometal. Chem., 25 (1970) C83.
80 E.W. Ainsgough and S.D. Robinson, J. Chem. Soc., Chem. Commun., (1970) 863.
81 M.A. Bennett and R. Charles, Aust. J. Chem., 24 (1971) 427.
82 E.W. Ainsgough, S.D. Robinson and J.J. Levison, J. Chem. Soc., A, (1971) 3413.
83 J.M. Guss and R. Mason, J. Chem. Soc., Chem. Commun., (1971) 58.
84 J.M. Guss and R. Mason, J. Chem. Soc., Dalton, (1972) 2193.
85 E.W. Ainsgough and S.D. Robinson, J. Chem. Soc., Chem. Commun., (1971) 130.
86 N. Ahmad, E.W. Ainsgough, T.A. James and S.D. Robinson, J. Chem. Soc., Dalton, (1973) 1151.

87 Y. Takahashi, A. Tokuda, S. Sakai and Y. Ishii, J. Organometal. Chem., 35 (1972) 415.
88 B.L. Shaw and R.E. Stainbank, J. Chem. Soc., Dalton, (1973) 2394.
89 K.P. Wainwright and S.B. Wild, J. Chem. Soc., Chem. Commun., (1972) 571.
90 M.A. Bennett, K. Hoskins, W.R. Kneen, R.S. Nyholm, R. Mason, P.B. Hitchcock, G.B. Robertson and A.D.C. Towl, J. Amer. Chem. Soc., 93 (1971) 4592.
91 R.J. McKinney, B.T. Huie, C.B. Knobler and H.D. Kaesz, J. Amer. Chem. Soc., 95 (1973) 633.
92 R.J. McKinney, G. Firestein and H.D. Kaesz, J. Amer. Chem. Soc., 95 (1973) 7910.
93 H. Alper and A.S.K. Chan, J. Amer. Chem. Soc., 95 (1973) 4905.
94 H. Alper and A.S.K. Chan, J. Chem. Soc., Chem. Commun., (1973) 724.
95 H. Alper, J. Organometal. Chem., 73 (1974) 359.
96 H. Alper, J. Organometal. Chem., 61 (1973) C62.
97 H. Alper, J. Organometal. Chem., 80 (1974) C29.
98 H. Takahashi and J. Tsuji, J. Organometal. Chem., 10 (1967) 511.
99 M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1973) 558.
100 Yu.A. Ustynyuk and I.V. Barinov, J. Organometal. Chem., 23 (1970) 551.
101 B. Crociani, T. Boschi, R. Pietropaolo and U. Belluco, J. Chem. Soc., A, (1970) 531.
102 H. Onoue, K. Nagakawa and I. Moritani, J. Organometal. Chem., 35 (1972) 217.
103 J. Dehand, M. Pfeffer and M. Zinsius, Inorg. Chim. Acta, 13 (1975) 229.
104 P. Braunstein, J. Dehand and M. Pfeffer, Inorg. Nucl. Chem. Lett., 10 (1974) 581.
105 D.L. Weaver, Inorg. Chem., 9 (1970) 2250.
106 R.J. Cross and N.H. Tennent, J. Chem. Soc., Dalton, (1974) 1445.
107 M. Kooti and J.F. Nixon, J. Organometal. Chem., 63 (1973) 415.
108 S. Horiie and S. Murahashi, Bull. Chem. Soc. Jap., 33 (1960) 247.
109 H. Alper, W.C. Root and A.S.K. Chan, J. Organometal. Chem., 71 (1974) C14.
110 M.I. Bruce, B.L. Goodall, A.D. Redhouse and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1972) 1228.
111 D.R. Fahey, J. Organometal. Chem., 27 (1971) 283.
112 J. Tsuji, Accounts Chem. Res., 2 (1969) 151.
113 R.A. Schunn, 155th National Congress of the American Chemical Society, San Francisco, California, April 1968.
114 R.A. Schunn, Inorg. Chem., 11 (1970) 2567.