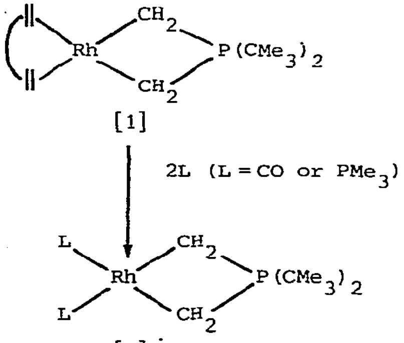
COBALT, RHODIUM, AND IRIDIUM
ANNUAL SURVEY COVERING THE YEAR 1978

RAYMOND D. W. KEMMITT
Department of Chemistry, The University, Leicester, LE1 7RH (Great Britain)

CONTENTS

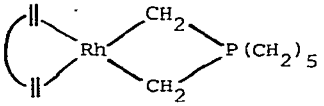
Metal carbon σ-bonded compounds

Treatment of $[RhCl(cod)]_2$ with the phosphorus ylides $(Me_3C)_2P(Me)=CH_2$ and $(CH_2)_5P(Me)=CH_2$ gives the mononuclear compounds [1] and [2] respectively. The cyclo-octa-1,5-diene ligand in [1] can be displaced by either carbon monoxide or



[1]

[3]



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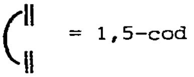
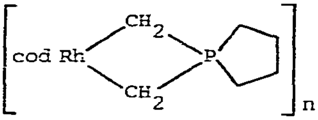
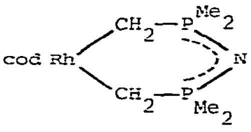


trimethylphosphine to give the compounds [3]. A rhodium σ-carbon bonded compound [4] may also be obtained from the reaction of $(CH_2)_4PMe_2^+Cl^-$ with $[RhCl(cod)]_2$ but this compound is insoluble and is probably polymeric. The double ylide

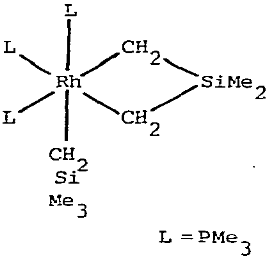


[4]

$Me_3P{=}N{-}P(Me){=}CH_2$ and $[RhCl(cod)]_2$ give a very stable chelate ylide compound [5] (ref. 1). A metallacyclic compound [6] also results from the reaction of the

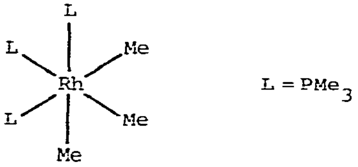


[5]

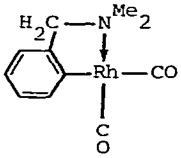


[6]

binuclear rhodium acetate $Rh_2(OAc)_4$ with PMe_3 and $Mg(CH_2SiMe_3)_2$. However, $Rh_2(OAc)_4$ reacts with $MgMe_2$ in the presence of PMe_3 to give the trismethyl compound [7] (ref. 2).

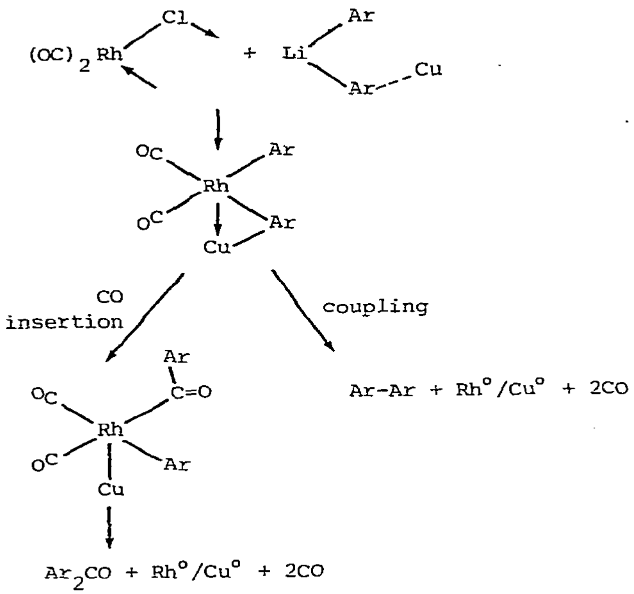


[7]



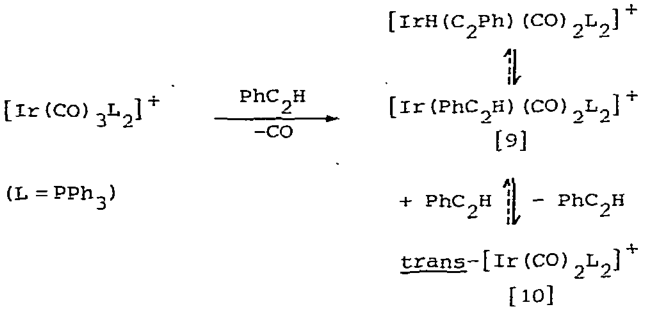
[8]

A novel rhodium-phenyl compound [8] has been obtained from the reaction $(2\text{-}Me_2NCH_2C_6H_4)M_2Li_2$ (M = Cu or Au) with $[Rh_2Cl_2(CO)_4]$, and it appears that these IB metallithium compounds are excellent arylating agents for rhodium(I). The reaction of $(x\text{-tolyl})_4M_2Li_2$ (x = 2, M = Cu; x = 4, M = Cu or Au) with $[Rh_2Cl_2(CO)_4]$ under an atmosphere of carbon monoxide results in the formation of ditolyl ketone and ditolyl in 69%, 92% and 31% and 4% yield, respectively. The proposed mechanism is outlined in Scheme 1 (ref. 3).



SCHEME 1

The reaction of phenylacetylene with $[Ir(CO)_3(PEt_3)_2][BPh_4]$ is known to give $[IrH(C_2Ph)(CO)_2(PEt_3)_2][BPh_4]$. However, with $[Ir(CO)_3(PPh_3)_2][PF_6]$ an equilibrium is set up between $[IrH(C_2Ph)(CO)_2(PPh_3)_2][PF_6]$ [9], and *trans*-$[Ir(CO)_2(PPh_3)_2][PF_6]$, [10], (Scheme 2). However, if a mixture of excess phenylacetylene and excess



SCHEME 2

triethylamine is added to a solution of $[Ir(CO)_3(PPh_3)_2][PF_6]$ in acetone the hydrido-species is deprotonated and the acetylide $[Ir(C_2Ph)(CO)_2(PPh_3)_2]$ precipitates. This acetylide readily loses carbon monoxide to give $[Ir(C_2Ph)(CO)(PPh_3)_2]$ which undergoes addition reactions readily with a wide variety of reagents. In some cases attack is observed only at the metal atom, e.g. SO_2, $HgCl_2$, H_2, O_2, CF_3CO_2H, $MeCO_2H$, $C_2(CO_2Me)_2$, MeI, or $C_2(CN)_4$. However, with HCl, HBr, HI, Cl_2, Br_2, or I_2 attack is observed both at the metal and at the acetylene linkage. The reaction of nitrosonium hexafluorophosphate with $[Ir(C_2Ph)(CO)(PPh_3)_2]$ gives a new species in solution which may be $[Ir(C_2Ph)(NO)(PPh_3)_2][PF_6]$ (ref. 4).

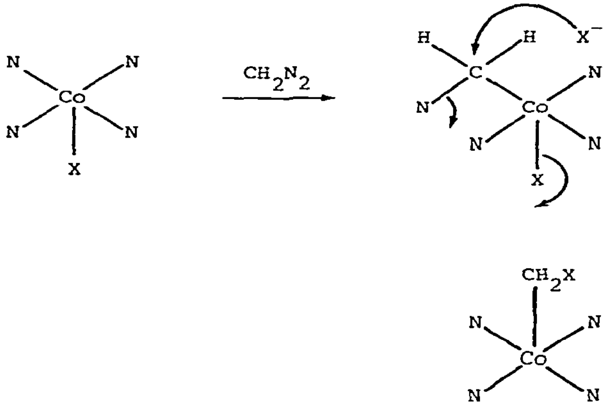
Bis(pentachlorophenyl)thallium(III) chloride and the corresponding pentafluorophenyl compound have been used to obtain pentahalophenyl-rhodium and -iridium compounds. Thus $(C_6Cl_5)_2TlCl$ reacts with trans-$[RhCl(CO)(PPh_3)_2]$ to give trans-$[Rh(C_6Cl_5)(CO)(PPh_3)_2]$ as outlined in Scheme 3.

$$\begin{array}{c}
(C_6Cl_5)_2TlCl + \underline{\text{trans}}\text{-}[RhCl(CO)L_2] \\
\downarrow \\
RhCl(C_6Cl_5)_2(CO)L_2 + TlCl \\
\downarrow \\
\underline{\text{trans}}\text{-}Rh(C_6Cl_5)(CO)L_2 + \underline{\text{cis}}\text{-}[RhCl(CO)L_2] \\
\\
(L = PPh_3)
\end{array}$$

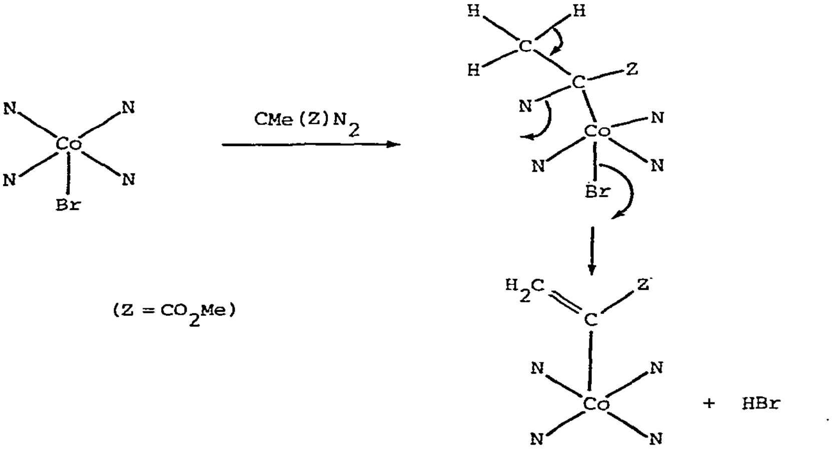
SCHEME 3

In boiling ethanol trans-$[Rh(C_6Cl_5)(CO)(PPh_3)_2]$ isomerises to the cis-form (ref. 5). Similar reactions of $(C_6F_5)_2TlBr$ with trans-$[MCl(CO)(PPh_3)_2]$ give $[MCl(C_6F_5)_2(CO)(PPh_3)_2]$, (M = Rh or Ir), the rhodium product decomposing thermally to $[Rh(C_6F_5)(CO)(PPh_3)_2]$. The hydrides, $[MH(CO)(PPh_3)_3]$, react with $(C_6F_5)_2TlCl$ to give $[M(C_6F_5)(CO)(PPh_3)_2]$ which can also be obtained from trans-$[MCl(CO)(PPh_3)_2]$ and $(C_6F_5)_2TlOH$ (ref. 6). The pentafluorophenyl compounds $[M(C_6F_5)(CO)(PPh_3)_2]$ undergo oxidative addition reactions with halogens to give $[MX_2(C_6F_5)(CO)(PPh_3)_2]$, (X = Cl, Br, or I). However, if the halogen is in excess, the pentafluorophenyl group is cleaved from the rhodium to give $[RhX_3(CO)(PPh_3)_2]$. Addition of ethanol to a chloroform solution of $[RhBr_2(C_6F_5)(CO)(PPh_3)_2]$ gives the bridged carbonyl compound $[RhBr(C_6F_5)(\mu\text{-}CO)(PPh_3)]_2$ (ref. 7). Some aryl-rhodium compounds have also been obtained by decarboxylation of the appropriate carboxylate compound. Thus reaction of trans-$[RhCl(CO)(PPh_3)_2]$ with some thallium(I) polyfluorobenzoates TlO_2CR in pyridine at room temperature ($R = C_6F_5$) or on heating ($R = C_6F_5$, p-HC_6F_5, or m-HC_6F_4) results in decarboxylation to give the compounds trans-$[RhR(CO)(PPh_3)_2]$. Similarly trans-$[Rh(O_2CC_6Cl_5)(CO)(PPh_3)_2]$ affords trans-$[Rh(C_6Cl_5)(CO)(PPh_3)_2]$ (ref. 8).

Treatment of cobalt(III) porphyrins of the type [CoX(TPP)], (X = Cl, Br, or I) or [CoBr(OEP)] (TTP = tetraphenylporphyrin, OEP = octaethylporphyrin) with diazomethane affords the halomethyl compounds [Co(CH$_2$X)(TPP)] or [Co(CH$_2$Br)(OEP)] respectively. These reactions are considered to proceed *via* a pathway involving insertion of a carbene moiety into a cobalt-nitrogen bond (Scheme 4). However, with diazoalkanes of the type CMe(CO$_2$Me)N$_2$ vinyl-cobalt compounds are formed (Scheme 5) (ref. 9). Some organocobalt(III) derivatives have also been prepared by direct aerial oxidation of tetraphenylporphinatocobalt(II) in solutions containing acetone, acetophenone, and malononitrile. The compounds isolated have the stoichiometry [CoCH$_2$COCH$_3$(TPP)], CoCH$_2$COPh(TPP), and [Co{CH(CN)$_2$}(TPP)] respectively. The acetonyl compound has been

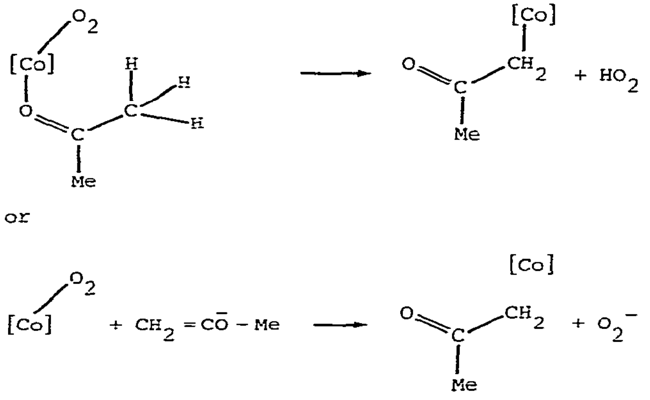


SCHEME 4



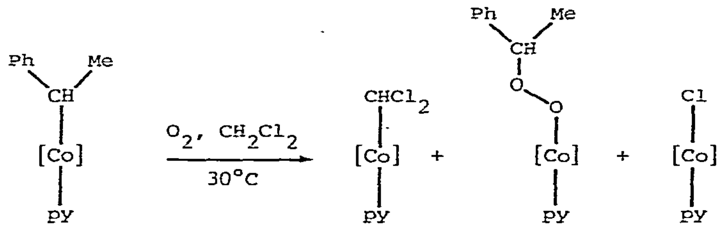
SCHEME 5

the subject of a single crystal X-ray study (ref. 10). An acetonylcobalt(III) compound has also been obtained from N,N′-ethylenebis(3-fluorosalicylideniminato)-cobalt(II) and acetone in the presence of dioxygen. This acetonyl complex has also been characterised by X-ray studies. The formation of this acetonyl complex is believed to involve transfer of hydrogen from acetone to a co-ordinated dioxygen intermediate, similar to the mechanism of hydrogen transfer in adenoxylcobalamin-dependent rearrangements. This step could be preceded by co-ordination of the acetone to the cobalt, thus bringing the C-H bond close to the cobalt, (Scheme 6). Alternatively the reaction may involve the enolate form of acetone, (Scheme 6) (ref. 11).



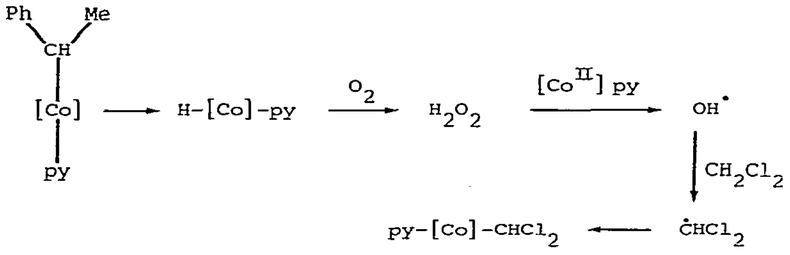
SCHEME 6

In enzyme reactions of the coenzyme (5′-deoxy-5′-adenosylcobalamin) Co-C homolysis, hydrogen transfer to and from 5′-C of the ligand, and possibly formation of a new cobalt-carbon bonded intermediate, are thought to be involved. A model system which has close similarities to these three reactions has been described and is outlined in Scheme 7. In the absence of oxygen the alkylperoxy species is not



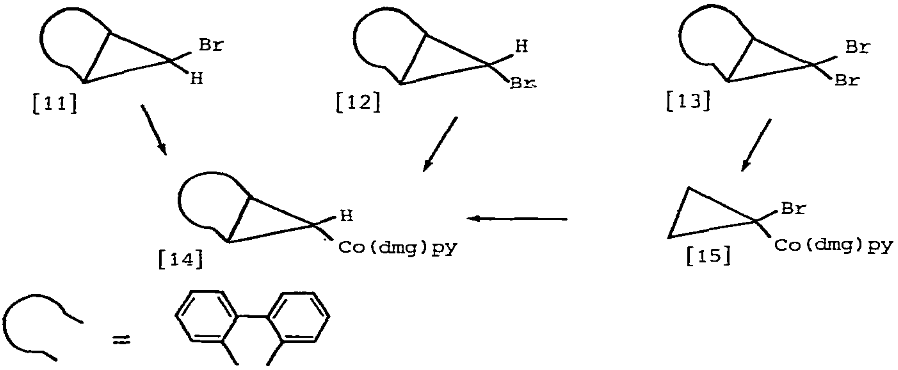
SCHEME 7

formed and the principal products are chloro(pyridine)cobaloxime and chloromethyl-(pyridine)cobaloxime. The formation of the chloromethylcobaloxime compound, formed via hydrogen abstraction from solvent, is very similar to the corresponding step in the enzyme reaction. In the present study the hydrogen abstracting species appears to be hydroxyl (Scheme 8) (ref. 11a).

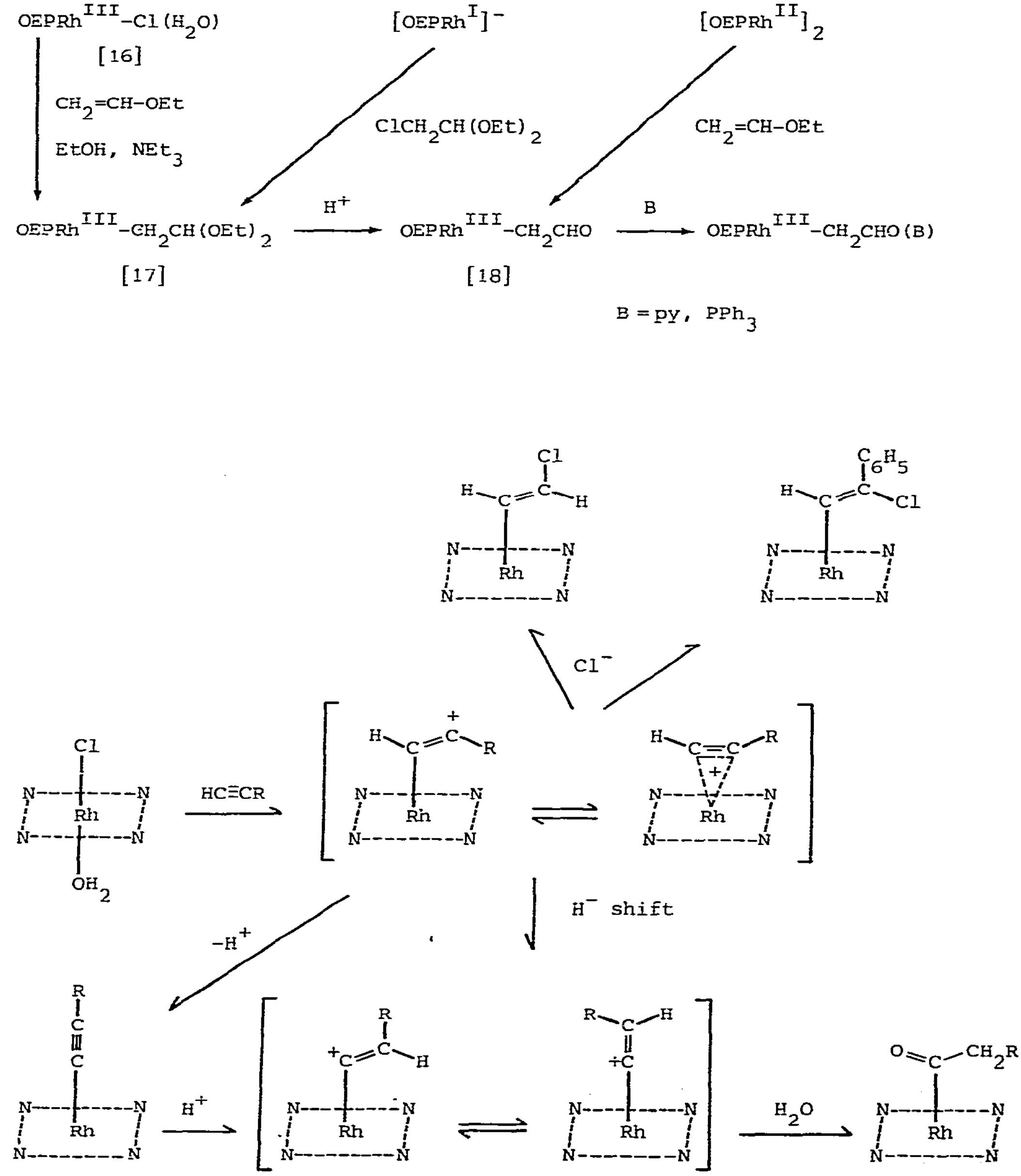


SCHEME 8

Although cobalt substituted cyclopropanes could be of importance in coenzyme B_{12}-catalysed rearrangements there have been no reports, until recently, on this type of compound. However, reaction of [12] with cobal(I)oxime gives the cobaloxime derivative [14]. Formulation of this product with the exo structure is consistent with the observation that the endo isomer [11] cannot be substituted with cobal(I)oxime. The cobaloxime [14] can also be obtained along with the bromine containing cobaloxime [15], from the dibromo derivative [13]. These reactions are considered to proceed via homolysis of the carbon-bromine bond, the observed retention of configuration at the carbon being a consequence of the shielding by the dihydrophenanthrene moiety (ref. 12). Displacement of bromine from carbon by a cobalt(I) species also occurs in the catalytic and stereoselective conversion of cis- and trans-β- and α- bromostyrenes into unsaturated nitriles by the pentacyanocobalt-



(I) ion (ref. 13). These reactions proceed via intermediate σ-styryl-cobalt(III) and η^2-cinnamonitrile-cobalt(I) cyano-complexes and reactions of chloro(aquo)rhodium(III) octaethylporphyrin, [RhCl(OEP)(H_2O)], [16], with ethyl vinyl ether and electron rich acetylenes are also considered to occur via intermediate π-complexes (Scheme 9).

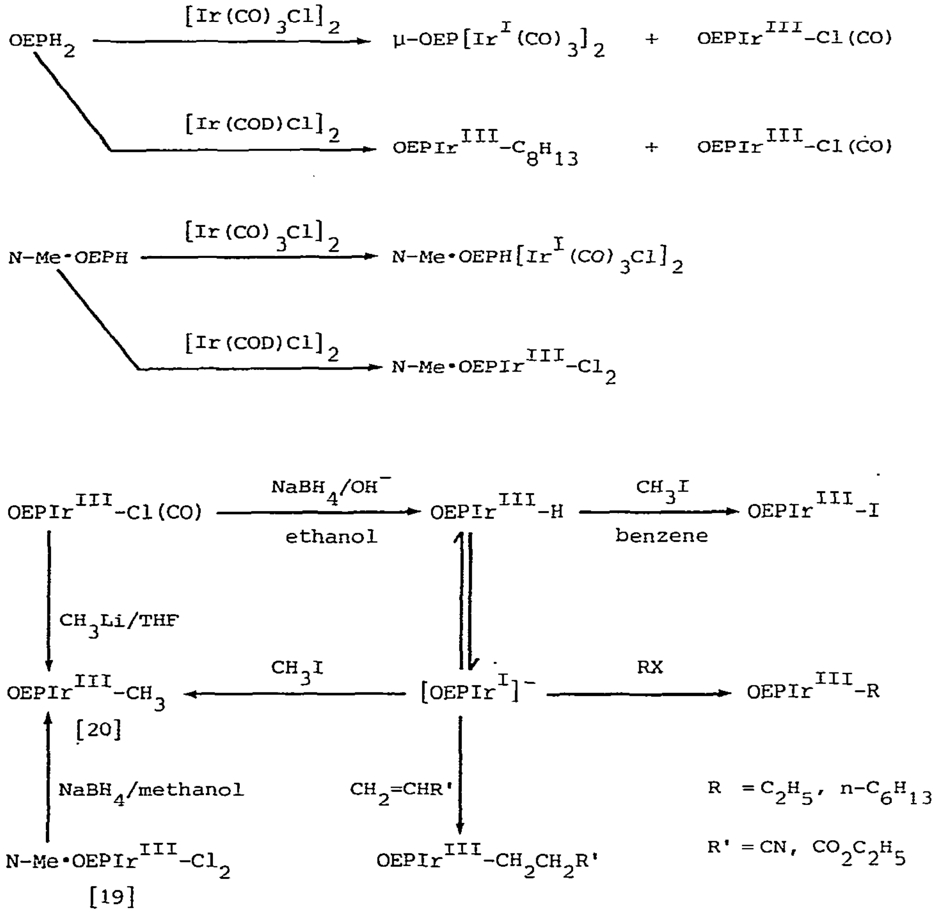


SCHEME 9

R = C_6H_5, n-C_4H_9, $(CH_2)_3OH$

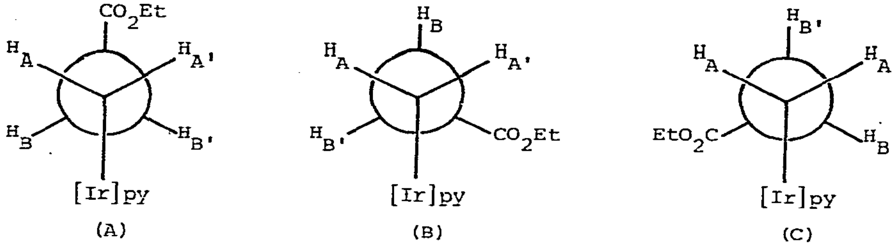
The complex [17] is readily hydrolysed to form the formylmethyl complex [18]. These reactions of [RhCl(OEP)(H_2O)] with electron-rich olefins and acetylenes take place very rapidly as compared with those of cobalt(III) complexes (ref. 14).

Some new iridium porphyrin complexes have been prepared and hydrido- and organo-iridium(III) OEP complexes have been obtained by various methods, (Scheme 10).



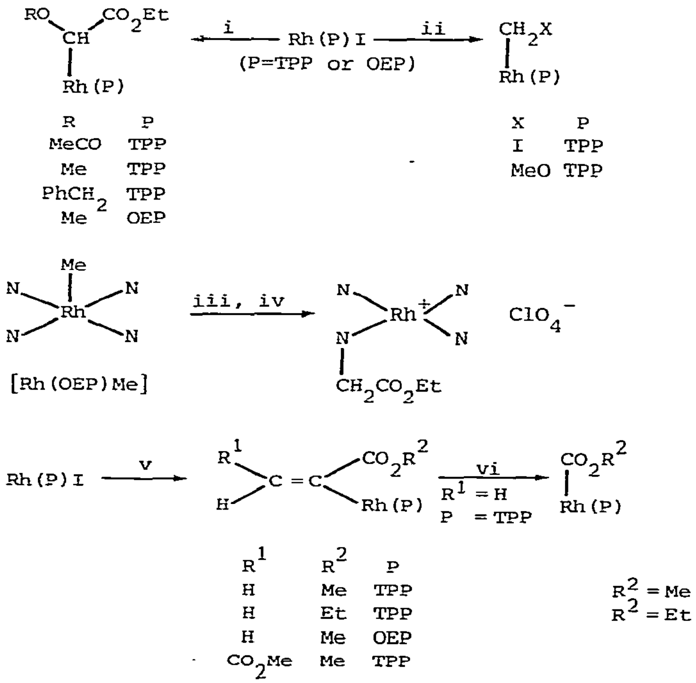
SCHEME 10

Treatment of [$IrCl_2$(N-Me•OEP)] with $NaBH_4$ in ethanol results in methyl migration from nitrogen to iridium to give [IrMe(OEP)], [20]. This reaction seems to be initiated by the reduction of [19] to an iridium(I) complex followed by an intramolecular oxidative-addition of the N-Me bond to the iridium(I). ^1H n.m.r. studies on the β-ethoxycarbonylethyliridium complex [21] reveal that the trans-isomer (A) is preferable to the gauche isomers (B) and (C) upon co-ordination of pyridine since the co-



[21]

ordinated pyridine causes a shortening of the iridium-carbon bond and an increase in the steric interaction between the ethoxycarbonyl group and the porphyrin ligand (ref. 15). Reactions of rhodium(III) porphyrins with diazoalkanes also lead to metal-alkylated products. However, in contrast to the corresponding cobalt(III) series catalytic decomposition of the reagents and fragmentation of primary olefinic products to give Rh(CO_2R) porphyrins are observed, (Scheme 11) (ref. 16).



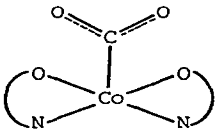
i, N_2CHCO_2Et, ROH; ii, CH_2N_2, MeOH; iii, N_2CHCO_2Et, $MeCO_2H$; iv, $NaClO_4$; v, $R^1CH_2C(N_2)CO_2R^2$; vi, excess of reagent v. TPP = Tetraphenylporphyrin; OEP = Octaethylporphyrin.

SCHEME 11

Reduction of N,N′-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), or a substituted Co(salen), with alkali metals (M) produces a bifunctional complex, Co(salen)M, in which both the basic cobalt(I) and the alkali cation are held by the same ligand. Many of these complexes form adducts with carbon dioxide and the X-ray structure of a reversible carbon dioxide carrier based on these systems has been determined. Thus a deep green solution of [Co(^{n}Pr-salen)K] in tetrahydrofuran reacts with carbon dioxide at room temperature to give deep-red crystals of [22]. The geometry about the cobalt, shown in [23], is nearly square pyramidal, and the

$$[\mathrm{Co}(^n\mathrm{Pr\text{-}salen})\mathrm{K}] + \mathrm{CO_2} \xrightleftharpoons{\mathrm{THF}} [\mathrm{Co}(^n\mathrm{Pr\text{-}salen})\mathrm{KCO_2(THF)}]$$

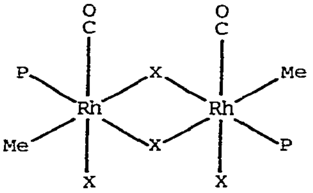
[22]



[23]

Co-C distance is similar to those found in alkyl derivatives of [Co(salen)] (ref. 17).

Oxidative-addition reactions of carbon-halogen bonds to a number of d^8 complexes of the cobalt triad have given a variety of compounds containing metal-carbon bonds. Thus the binuclear complexes $[\mathrm{RhCl(CO)(PR_3)}]_2$ undergo oxidative-addition reactions with methyl halides to give the complexes $[\mathrm{RhClXMe(CO)(PR_3)}]_2$, (X = Cl or Br). The crystal structure of $[\mathrm{RhClBrMe(CO)(PPhMe_2)}]_2$, [24], has been determined but due to



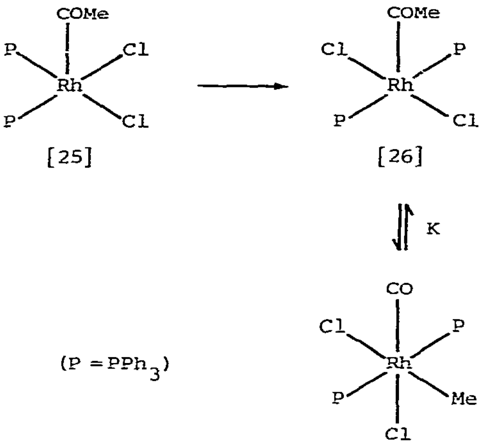
P = $\mathrm{PPhMe_2}$, X = Cl, Br,
structure disordered.

[24]

disorder differentiation between chlorine and bromine could not be made. In solution cis-migration of the methyl group occurs leading to acetyl complexes and in the case of methyl iodide it has been shown that the equilibrium

$$[\mathrm{RhClIMe(CO)(PR_3)}]_2 \rightleftharpoons [\mathrm{RhClI(COMe)(PR_3)(solvent)}]_2$$

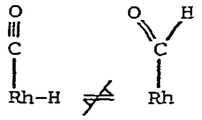
occurs in solution. Carbonylation reactions shift this equilibrium to give the carbonyls $[\mathrm{RhClI(COMe)(CO)(PR_3)}]_2$ which can also be obtained by the oxidative-addition of acyl halides to the complexes $[RhCl(CO)(PR_3)]_2$ (ref. 18). The addition of acetyl chloride to $[RhCl(PPh_3)_3]$ gives initially a rather unstable acetyl complex [25] which



[25] [26] [27]

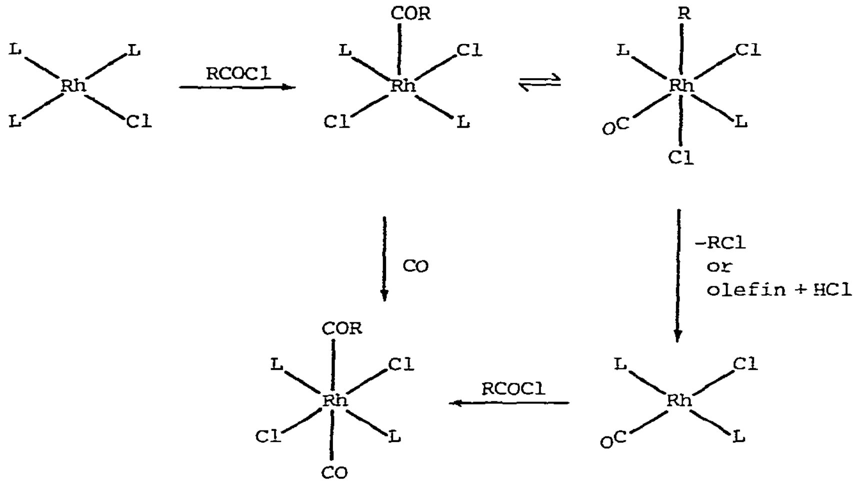
(P = PPh_3)

isomerises at room temperature, first to a second acetyl isomer [26] and then to a six-co-ordinate methyl isomer [27]. The equilibrium constant, K, for the methyl system is 0.29 ± 0.02 while for the corresponding phenethyl complex it is ca. 0.06. However, octahedral isomers of the ethyl, n-propyl, and benzyl systems could not be detected. Studies on the complexes $[RhHCl_2(CO)(PPh_3)_2]$, $[Rh(CH_2Cl)Cl_2(CO)(PPh_3)_2]$ and $[RhCl_3(CO)(PPh_3)_2]$ also indicate that acyl species are not formed with these systems and hence values of K for these complexes must be greater than ca. 40. Thus there is no apparent correlation between the steric requirements of the alkyl (or R group in general) and the magnitude of K and it is not clear why the phenethyl complex provides such a contrast to the other alkyl complexes. The stability of the hydride complex $[RhHCl_2(CO)(PPh_3)_2]$ with respect to isomerisation to the formyl complex e.g.



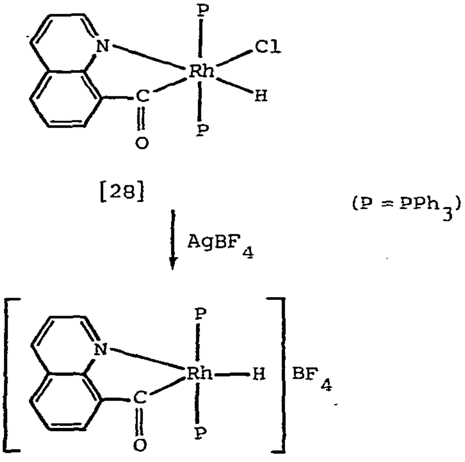
is a consequence of the hydridocarbonyl species being the thermodynamically preferred species (ref. 19).

The decarbonylation of aldehydes and acyl halides by planar d^8 metal complexes such as $[RhCl(PPh_3)_3]$ is a potentially useful process in organic synthesis. It is based on a sequence of reactions at the metal involving oxidative-addition at the metal atom of the acyl halide or aldehyde, alkyl or aryl migration from the acyl group, and reductive elimination of alkyl or aryl halide or hydride, or of olefin and hydrogen halide or hydrogen as illustrated in Scheme 12. Although such inter-



SCHEME 12

mediates have been isolated from reactions involving acyl halides no intermediates hitherto have been isolated from $[RhCl(PPh_3)_3]$-promoted aldehyde decarbonylation reactions. However, it has now been reported that addition of the aldehyde 8-quinolinecarboxaldehyde to $[RhCl(PPh_3)_3]$ gives a precipitate of [28] which in

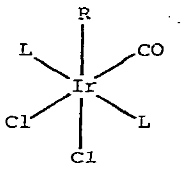


[28]

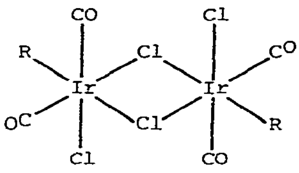
($P = PPh_3$)

[29]

refluxing xylene gives quantitative yields of quinoline and trans-$[RhCl(CO)(PPh_3)_2]$. Addition of $AgBF_4$ to [28] gives the five-co-ordinate hydride [29] but this does not undergo decarbonylation at room temperature because the intermediate alkyl would be part of a strained four-membered-ring chelate. Treatment of a tetrahydrofuran suspension of [29] with excess oct-1-ene and 8-quinolinecarboxaldehyde at 50°C gives 8-quinolinyl n-octyl ketone. Reaction with the co-ordinatively saturated [28] gives no hydroacylation product under these conditions (ref. 20). The decarbonylation of aldehydes using $[RhCl(PPh_3)_3]$ cannot be made sufficiently catalytic at useful temperatures since trans-$[RhCl(CO)(PPh_3)_2]$ which is formed in the reactions does not lose carbon monoxide and the active species $[RhCl(PPh_3)_2]$ cannot be regenerated thermally or photochemically. However, using cationic rhodium(I) complexes containing chelating diphosphine ligands, e.g. $[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$ and $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)_2]Cl$ catalytic decarbonylation of aldehydes can be achieved. A key feature of these catalysts is that they bind CO less strongly than trans-$[RhCl(CO)(PPh_3)_2]$ due to decreased Rh-CO π-back-bonding (ref. 21). Studies on the oxidative-addition reactions of isomeric pairs of normal and α-branched acyl halides RCOCl [$R = (CH_2)_2Me$ or $CHMe_2$, $(CH_2)_3Me$ or CHMeEt, $(CH_2)_4Me$ or $CHEt_2$, and CH_2CH_2Ph or CHMePh] to $[IrCl(PPh_3)_3]$ reveal that the same n-alkyliridium(III) complexes [30] are formed, [$R = (CH_2)_2Me$, $(CH_2)_3Me$, $(CH_2)_4Me$ and CH_2CH_2Ph] respectively. The α-branched acyl chlorides give $[IrCl(CO)(PPh_3)_2]$ and $[IrHCl_2(PPh_3)_3]$ as by-products. It is suggested that an initially formed secondary-alkyl complex undergoes rapid β-hydrogen migration to form an olefin hydride which can either re-form the sterically more favourable n-alkyl or can decompose irreversibly to $[IrCl(CO)(PPh_3)_2]$, olefin, and HCl. In agreement with this suggestion, n-butanoyl chloride and 2-methylpropanoyl chloride add to the sterically less crowded cyclo-octene complex $[IrCl(CO)(C_8H_{14})_2]_2$ to give respectively dimeric n- and isopropyliridium(III) complexes [31; $R = (CH_2)_2Me$, $CHMe_2$] which interconvert in hot benzene to give an approximately 3:2 mixture of n and iso complexes. A comparison of the reactions of $[IrCl(PPh_3)_3]$ and $[RhCl(PPh_3)_3]$ with straight-chain acyl halides reveals that the reactions are basically similar. However, compared with their rhodium analogues, the initially formed iridium(III) acyls re-arrange more rapidly to the six-co-ordinate alkyls and the latter do not undergo reductive elimination to $[MCl(CO)(PPh_3)_2]$ as readily. The



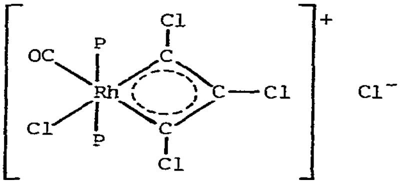
[30]



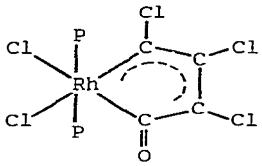
[31]

equilibrium between sec- and n-alkyl in the complexes [30] favours the n-alkyl more than is the case in the complexes [31]. The position of equilibrium is determined by the direction of addition of hydrogen to olefin in the presumed olefin hydride intermediate, a factor which is responsible for the formation of straight-chain or branched aldehydes in hydroformylation reactions. Since replacement of CO by a tertiary phosphine can reduce the acidity of the hydride species, the hydride becomes more hydridic, and it hence becomes more likely to add an olefin in the anti-Markownikoff sense. Further, a bulky phosphine can exert a steric effect especially if the two phosphines are trans to each other and cis to the hydride. Models show that there is steric hindrance between a secondary alkyl group R in structure [25] and the aromatic rings of the triphenylphosphine ligands. Hence the preference for a n-alkyl group (ref. 22).

The reaction of C_3Cl_4 with trans-$[RhCl(CO)(PMe_2Ph)_2]$ under anhydrous conditions gives a mixture of the two complexes [32] and [33]. These two complexes are hygroscopic and difficult to separate and upon attempted recrystallisation from methanol the complex [34] is formed which has been characterised by a single crystal X-ray study. The complex [34] is considered to be formed via a metal-assisted cleavage of a C-C bond of an in situ generated methoxycyclopropene, (Scheme 13). The intermediate (B) can be isolated by treating trans-$[RhCl(CO)(PMe_2Ph)_2]$ with C_3Cl_4 in a small amount of methanol. Intermediate (C) can be obtained directly by carrying out the reaction in rigorously dried methanol (ref. 23).

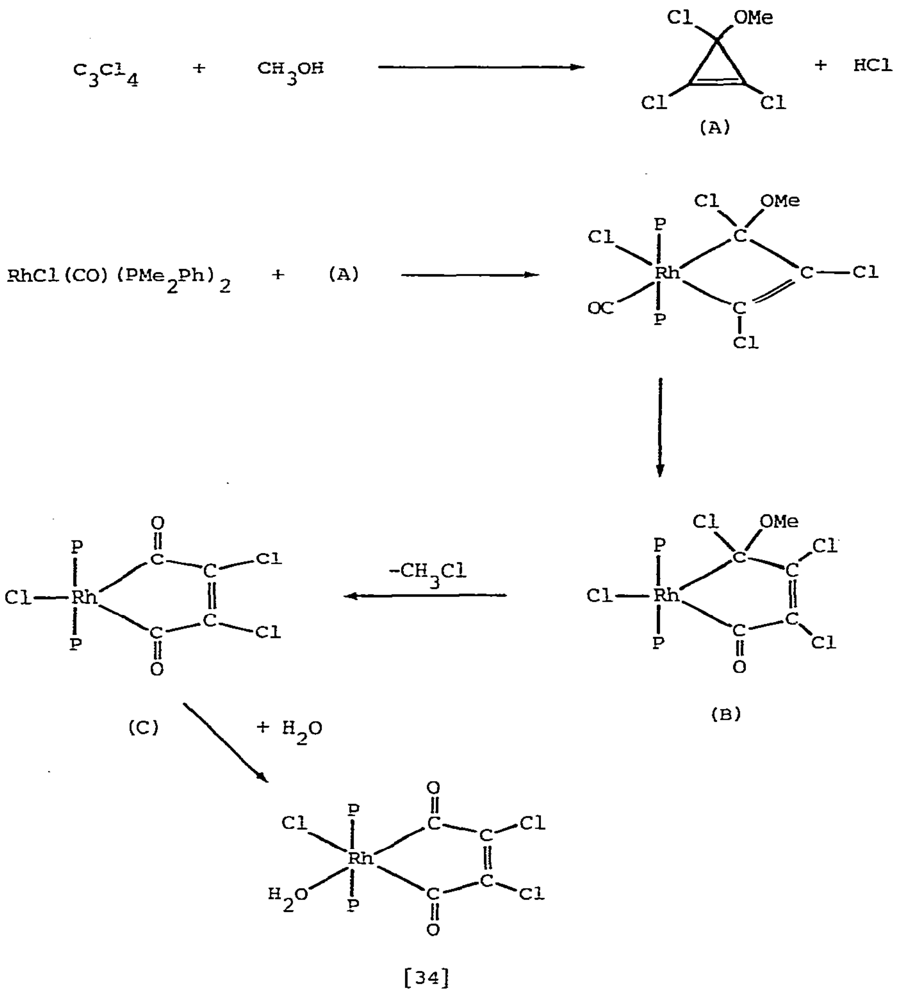


[32]

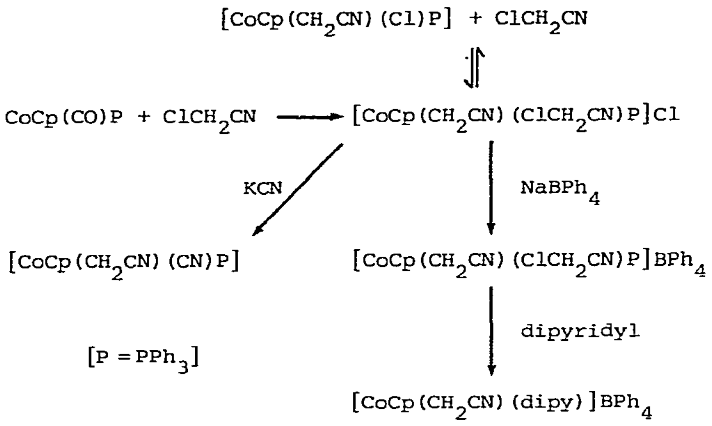


[33]

Various cationic cobalt-carbon bonded complexes have also been obtained by oxidative-addition reactions of carbon halogen bonds to cobalt(I) complexes of the $[CoCpL_2]$. Thus treatment of $[CoCp(CO)_2]$ with $ClCH_2CN$ gives an insoluble brown solid believed to be $[CoCp(CH_2CN)(ClCH_2CN)_2]Cl$. The reactions of $ClCH_2CN$ with $[CoCp(CO)(PPh_3)]$ are summarised in Scheme 14 (ref. 24). The strongly nucleophilic complexes $[CoCpL_2]$, ($L = PMe_3$, PMe_2Ph, or $PMePh_2$) react with HX or MeI to give the cations $[CoCpHL_2]^+$ and $[CoCpMeL_2]^+$ respectively which contain very stable Co-H and Co-Me bonds. The compounds $[CoCpEt(PMe_3)_2]I$ and $[CoCp(COR)(PMe_3)_2]PF_6$, ($R = Me$ or Ph) have also been obtained. The complex $[CoCpH(PMe_3)_2]BF_4$ reacts with excess HBF_4 in propionic anhydride at higher temperatures to give $[CoCp(PMe_3)_3][BF_4]_2$ [35]. An intermediate in this reaction, containing co-ordinated propionic anhydride, can be

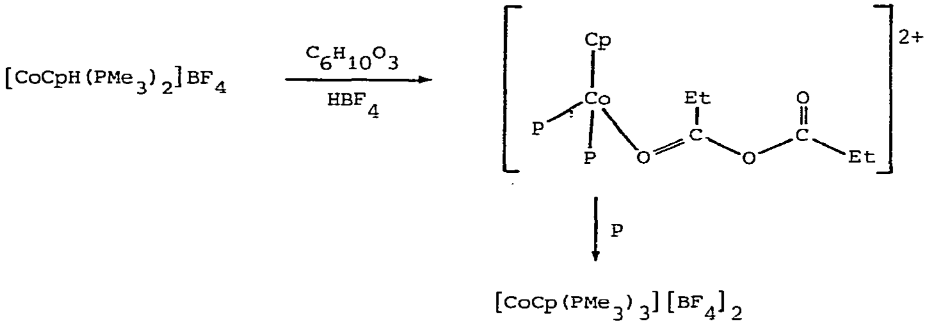

C3Cl4
+
CH3OH
Cl
OMe
Cl
Cl
+ HCl
(A)
RhCl(CO)(PMe2Ph)2
+
(A)
P
Cl
Rh
OC
P
C
C
C
Cl
Cl
Cl
OMe
Cl
-CH3Cl
(B)
(C)
+ H2O
H2O
O
[34]

SCHEME 13



SCHEME 14

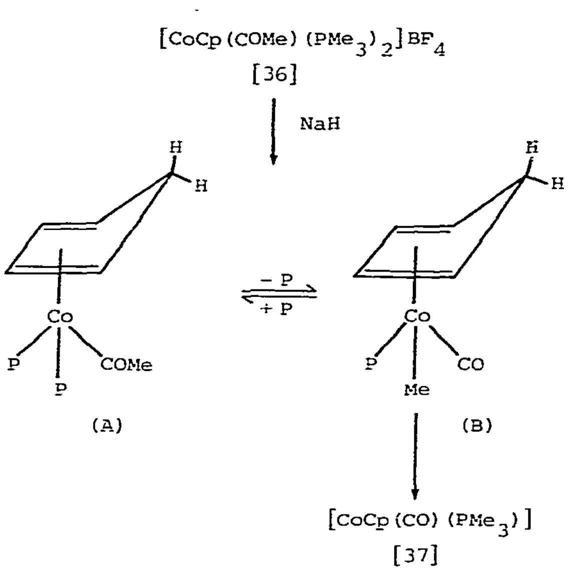
isolated, (Scheme 15), (ref. 25). The cationic acyls $[CoCp(COR)(PMe_3)_2]PF_6$, (R = Me, Ph, p-$MeOC_6H_4$, p-MeC_6H_4, m-MeC_6H_4, or 3,5-$(MeO)_2C_6H_3$) are inert to strong acids such as trifluoroacetic acid and this suggests that they are not polarised in the sense $M^{\delta+}$-$COR^{\delta-}$ Support for this proposal comes from the observation that



[35]

SCHEME 15

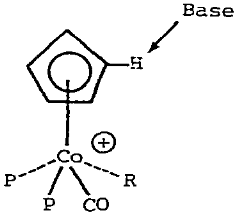
$[CoCp(COMe)(PMe_3)_2]PF_6$, [36], reacts with the nucleophile sodium hydride to give [37], the η^4-cyclopentadiene compounds (A) and (B) being proposed intermediates in this reaction (Scheme 16). The reaction of [36] with phenyllithium gives $[Co(\eta^5\text{-}C_5H_4Ph)(CO)(PMe_3)]$. The reversibility of the process (A)$\rightleftharpoons$(B) is confirmed by the result of the reaction of [36] with NaH in the presence of PEt_3 which gives $[CoCp(CO)PEt_3]$ in addition to [37]. Treatment of the salts $[CoCp(COR)(PMe_3)_2]PF_6$, (R = aryl), with base, for example 1,5-diazabicyclo[5.4.0]undec-5-ene in tetrahydrofuran or acetone gives the monocarbonyls [38] quantitatively. The mechanism of this



SCHEME 16

$$[CoCp(COR)P_2]PF_6 + Base \longrightarrow [Co(RC_5H_4)(P)(CO)] + P + [H\,Base]\,PF_6 \qquad [P = PMe_3] \qquad [38]$$

reaction is considered to proceed via interaction of the base with a proton of the ring to give an "acid-base adduct" which forms a transition state (C) possibly with an η^3-cyclopentadienyl ligand. Subsequent fast migration of the aryl group R to the



$[P = PMe_3]$

(C)

ring and elimination of $H\,Base^+$ and of PMe_3 gives the product. Reaction of $[CoCp(COMe)(PMe_3)_2]PF_6$ with NaOH gives the methyl compound $[CoCp(Me)(PMe_3)_2]PF_6$ and this reaction also proceeds via a transition state similar to (C). Initial attack at the metal or acyl carbon atom occurs only on reaction of $[CoCp(COMe)(PMe_3)_2]PF_6$ with methyllithium, the sole metal containing product being $[CoCp(PMe_3)_2]$, (ref. 26). Reductive elimination reactions also occur upon protonation of the complexes $[CoMe\{P(OR)_3\}_4]$. Kinetic studies have shown that reductive elimination of methane from the presumed intermediate $[CoMeH\{P(OMe)_3\}_4]^+$ obtained by protonation of $[CoMe\{P(OMe)_3\}_4]$ and by methylation of $[CoH\{P(OMe)_3\}_4]$ is at least three orders of magnitude greater than reductive-elimination of hydrogen from $[CoH_2\{P(OMe)_3\}_4]^+$. All attempts to isolate $[CoMe_2\{P(OMe)_3\}_4]^+$ from reactions of $[CoMe\{P(OMe)_3\}_4]$ with $MeSO_3CF_3$ or $Me_3O^+PF_6^-$ have been unsuccessful due to facile elimination of methane. A dimethylcobalt cation formed could decompose to give methane by an α-hydrogen elimination, however, attempts to determine the ultimate fate of the cobalt complex have failed. Key intermediates in the reductive-elimination of hydrogen and of methane in the CoH_2^+ and $CoMeH^+$ systems are the tetrahedral $[Co\{P(OMe)_3\}_4]^+$ species (ref. 27).

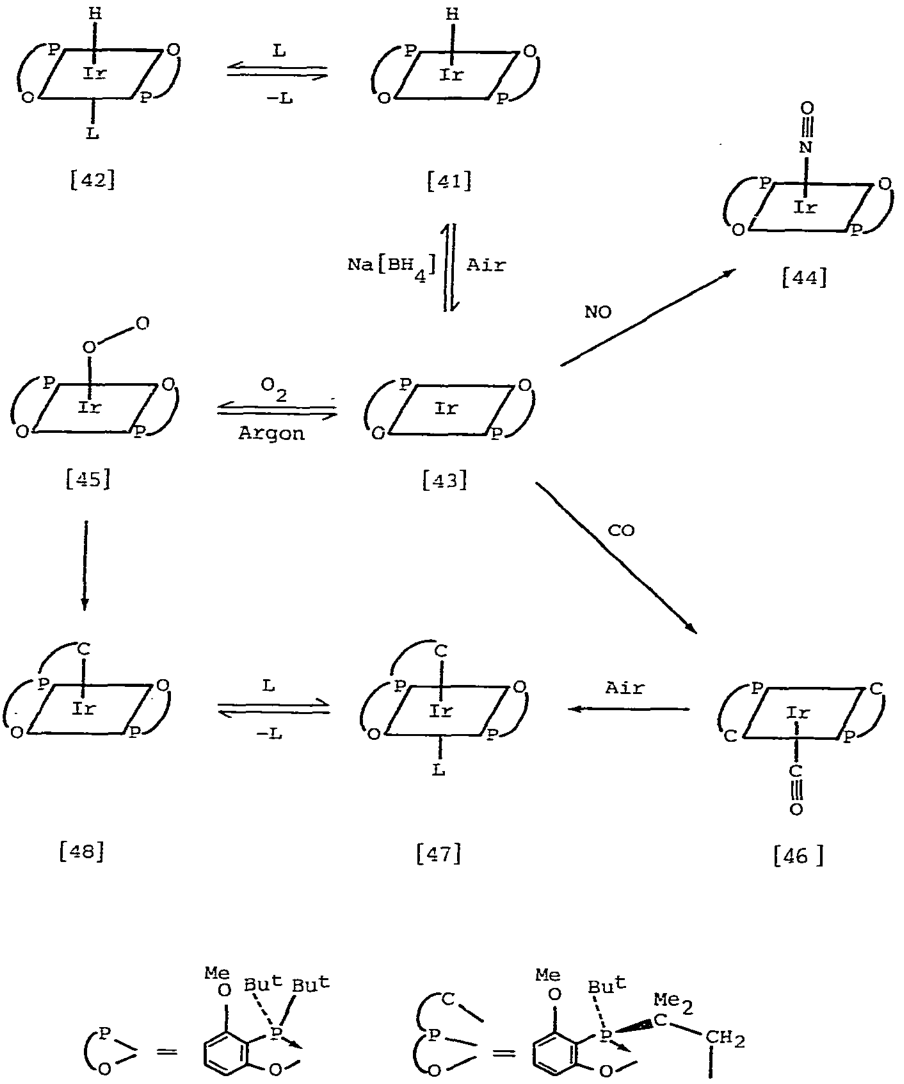
The rate of reaction of methanol with $[Co(COMe)(CO)_4]$ is accelerated 400-fold by addition of pyridine. Infrared studies indicate that $[pyCOMe]^+[Co(CO)_4]^-$ is formed which rapidly reacts with methanol to give AcOMe (ref. 28).

The five co-ordinate complexes [CoBr(L)] (L = 39, 40) react with stoichiometric amount of the appropriate organo lithium reagent to give the compounds [CoR(L)], (R = Me or Ph). These organo cobalt complexes are low spin d^8 compounds and a trigonal-bipyramidal geometry is assigned to the cobalt. The five-co-ordinate cobalt(II) d^7 compound $[CoBr(np_3)]BPh_4$ reacts with Grignard reagents to give the low-spin d^7 compounds $[CoR(np_3)]BPh_4$ (R = Me or CH_2Ph). The methyl derivative reacts with carbon monoxide to give $[Co(COMe)(np_3)]BPh_4$ which is the first acyl compound of cobalt(II) to be reported. The benzyl compound, however, reacts with carbon monoxide to give $[Co(CO)(np_3)]BPh_4$ (ref. 29).

$(Ph_2PCH_2CH_2)_3N$
(np_3)
[39]

$(Ph_2PCH_2CH_2)_3P$
(PP_3)
[40]

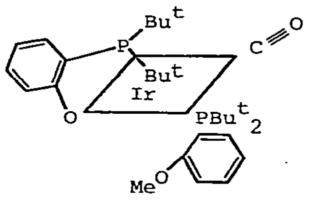
Reactions of bulky phosphines and phosphites with various iridium complexes continue to lead to cyclometallated compounds which contain iridium-carbon σ-bonds. Thus the phosphine $PBu^t_2\{C_6H_3(OMe)_2\text{-}2,6\}$ reacts with iridium trichloride in propan-2-ol to give the five co-ordinate hydride [41] which can be converted by air into the paramagnetic iridium(II) complex [43]. The purple hydride [41] picks up small ligands L such as pyridine or carbon monoxide reversibly to give the colourless adducts [42] and other reactions of these complexes are outlined in Scheme 17. The dioxygen adduct [45] is formulated with an end-on bonded dioxygen since molecular models suggest that the very bulky t-butyl groups will prevent side-on or π-bonded



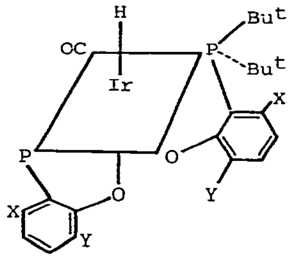
SCHEME 17

dioxygen. The analogous iridium(II) complex $[Ir\{OC_6H_4(PBu^t{}_2-2)\}_2]$ does not show reversible uptake of dioxygen and it appears that the additional methoxy-groups in [43] increase the stability of the dioxygen adduct relative to the four-co-ordinate iridium(II) complex. A benzene solution of [43] when exposed to the air for 14 hours gives a C-metallated complex [48] and the methyl isocyanide adduct (47; L = MeNC) has been characterised by a single crystal X-ray study. Treatment of iridium carbonyl chloride solutions with $PBu^t{}_2(C_6H_4OMe-2)$ is known to give the iridium(I) complex [49].

However, $PBu^t_2[C_6H_3(OMe)_2\text{-}2,6]$ gives the carbonyl hydride [50]. This complex is much more stable than its isomer of configuration (42; L = CO). A complex of configuration (50; X = H, Y = OMe) can be obtained using the ligand $PBu^t_2[C_6H_3(OMe)_2\text{-}2,3]$. The action of $PBu^t_2[C_6H_3(OMe)_2\text{-}2,3]$ on iridium trichloride in boiling propan-2-ol gives a purple compound which could not be purified but probably contains a hydride of configuration [41] (ref. 30). The reactions of tri-o-tolyl phosphite with $[IrCl(cod)]_2$



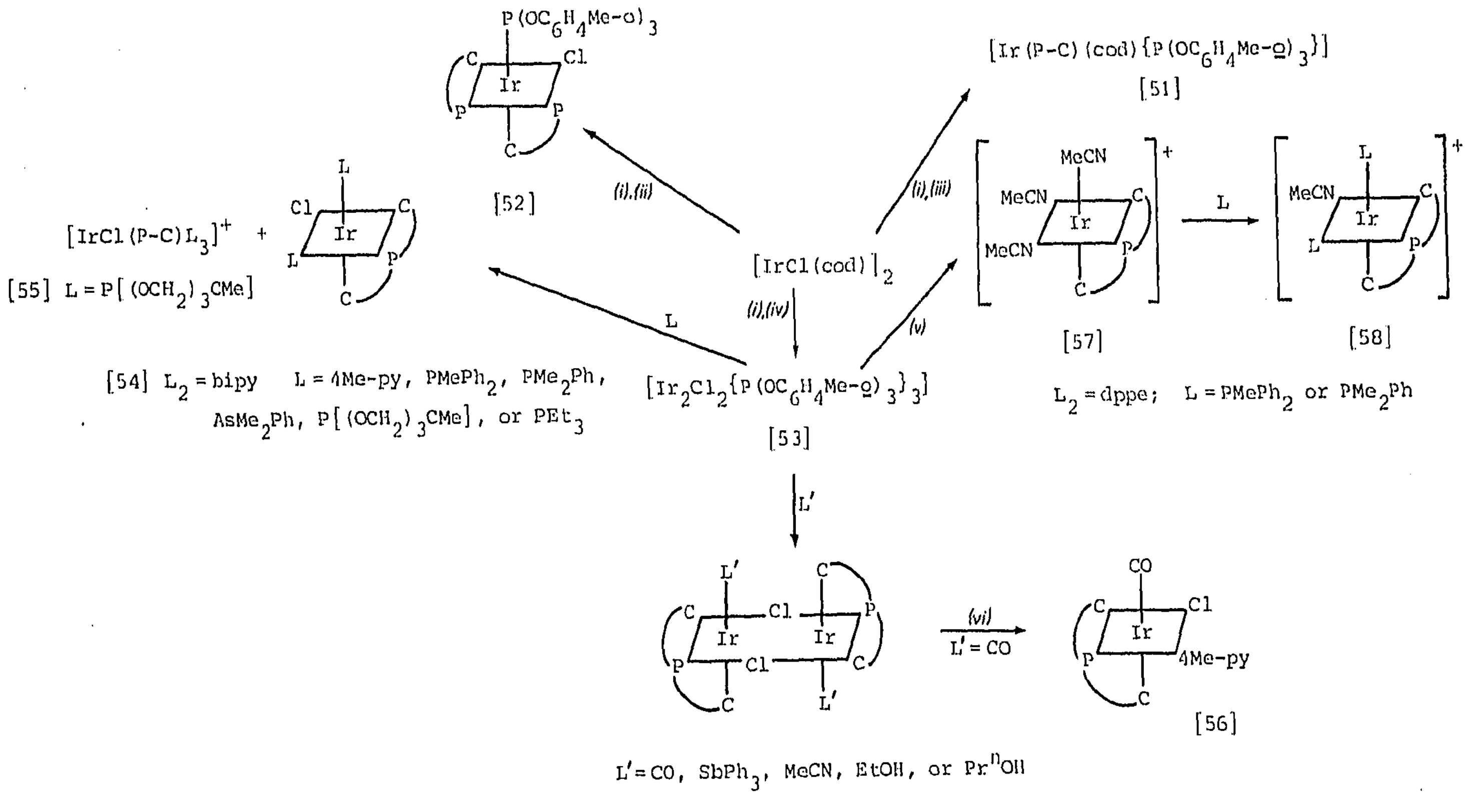
[49]



[50]

in various solvents lead to cationic monometallated and neutral and cationic dimetallated iridium(III) complexes (Scheme 18) and the structure of (54; L = 4Me-py) has been determined crystallographically (ref. 31). Treatment of [51] with a series of neutral donor ligands L [L = $PMePh_2$, PMe_2Ph, PMe_3, and $P(OCH_2)_3CMe$] leads to displacement of the tri-o-tolyl phosphite ligand but the cyclo-octa-1,5-diene ligand is not displaced. The crystal structure of the complex $[\overline{Ir\{P(OC}_6H_3Me)(OC_6H_4Me)_2\}(cod)\text{-}\{P(OCH_2)_3CMe\}]$ has been determined. The cyclo-octa-1,5-diene ligand is bonded axial-equatorial but it is not clear why the diene in [51] is not displaced by neutral donor ligands (ref. 32).

Two of the mechanisms proposed for the cyclometallation reactions of metal-triaryl phosphite systems are (i) electrophilic substitution of a proton at the carbon centre by the metal and (ii) oxidative-addition of a ligand C-H unit to the metal. Evidence for the electrophilic displacement mechanism has been obtained from a study of the reactions of acids with some cyclometallated iridium phosphite complexes. Thus the formation of [IrH(P-C)(cod)L]X, [P-C = $P(OC_6H_3Me\text{-}\underline{o})(OC_6H_4Me\text{-}\underline{o})_2$, L = PMe_2Ph or tri-o-tolyl phosphite] from [Ir(P-C)(cod)L] and HX, (X = ClO_4, PF_6 or BF_4) occurs <u>via</u> a mechanism involving direct proton attack at the metallated carbon for ring opening, followed by electrophilic displacement of a proton from an <u>ortho</u> - C-H by a preformed iridium(III) hydride in the ring closing step (ref. 33). The cyclometallated ring in iridium triaryl phosphite complexes undergoes complete aromatic substitution upon treatment of the complexes with chlorine in benzene. Thus treatment of $[IrCl_2(P\text{-}C)L]_2$ [L = PMe_3 or PMe_2Ph; P-C = $P(OC_6H_3Me\text{-}\underline{o})(OC_6H_4Me\text{-}\underline{o})$] with chlorine gives $[IrCl_2\{P(OC_6Cl_3Me\text{-}\underline{o})(OC_6H_4Me\text{-}\underline{o})_2\}L]_2$. The crystal structure of $[IrCl_2\{P(OC_6Cl_3Me\text{-}\underline{o})\text{-}$



Reaction of $[IrCl(cod)]_2$ with $P(OC_6H_4Me\text{-}o)_3$; P-C = $P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2$, P-C$_2$ = $P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)$ *(i)* $P(OC_6H_4Me\text{-}o)_3$; *(ii)* Refluxing Me_2CO; *(iii)* EtOH; *(iv)* Refluxing xylene; *(v)* MeCN-EtOH; *(vi)* 4Me-py

SCHEME 18

$(OC_6H_4Me\text{-}\underline{o})_2\}(py)(PMe_3)]$ has been determined by X-ray crystallography. It is not clear at the present whether these reactions occur <u>via</u> radical or electrophilic attack. Excess Bu^tOCl and $[IrCl_2(P\text{-}C)(PMe_3)]_2$ gives only the monosubstituted complex $[IrCl_2\{P(OC_6H_2ClMe\text{-}\underline{o})(OC_6H_4Me\text{-}\underline{o})_2(PMe_3)]_2$ whereas $MeSO_3CF_3$, $NOPF_6$, and HY ($Y = ClO_4$ or PF_6) give only the triply-halogen bridged cation $[L(P\text{-}C)IrCl_3Ir(P\text{-}C)L]^+$, (ref. 34). Treatment of the <u>ortho</u>-substituted tolyl, xylyl, and mesityl complexes $[Ir(Me_nC_6H_{5-n})\text{-}(CO)L_2]$, ($Me_nC_6H_{5-n} = 2\text{-}MeC_6H_4$, $2,3\text{-}Me_2C_6H_3$; $2,4\text{-}Me_2C_6H_3$; $2,5\text{-}Me_2C_6H_3$; $2,6\text{-}Me_2C_6H_3$; $2,4,6\text{-}Me_3C_6H_2$; $L = PR_3$) with $P(OR)_3$ results in the formation of the cyclometallated complexes of the type <u>fac</u>-$[\overline{IrH(2\text{-}CH_2C}_6H_{5-n}Me_{n-1})\{P(OR)_3\}]$ [$2\text{-}CH_2C_6H_{5-n}Me_{n-1} = 2\text{-}CH_2C_6H_4$; $2\text{-}CH_2C_6H_3Me\text{-}3$; $2\text{-}CH_2C_6H_3Me\text{-}4$; $2\text{-}CH_2C_6H_3Me\text{-}5$; $2\text{-}CH_2C_6H_3Me\text{-}6$; $2\text{-}CH_2C_6H_2Me_2\text{-}4,6$; $P(OR)_3 = P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$]. Although phosphites promote these facile interactions between the C-H bonds of the <u>ortho</u>-methyl groups and the iridium, reactions of the compounds with phosphines simply result in phosphine exchange with preservation of the aryl-iridium(I) moiety (ref. 35).

The alkylation of various metals and metalloids by methylcobalamin is a reaction of environmental importance. When the demethylating agent is an electrophile such as Hg(II), Tl(III), or Pd(II) the cleavage occurs by carbanion transfer from cobalt to the attacking metal centre. The activation parameters for the transfer of the methyl group from "base on" methylcobalamin to mercury(II) chloride have been determined, the initial product being methylmercury (ref. 36). Evidence has also been presented for the alkylation of tin through reductive cobalt-carbon cleavage by a species which is generated by one equivalent oxidation of tin(II). The reaction proceeds as follows

$$\begin{array}{c} SnCl_x^{\,2-x} + \underset{(\text{"base off"})}{(Me)\text{cobalamin(III)}} + (H_2O)\text{cobalamin(III)} \\ \downarrow \\ MeSnCl_y^{\,3-y} + \underset{(\text{"base off"})}{2\ \text{cobalamin(II)}} + H_2O \end{array}$$

A similar cleavage is observed when $FeCl_3$ is substituted for aquocobalamin in the above reaction but excesses of Sn(II) and Fe(III) over methylcobalamin are necessary to achieve significant cleavage of the cobalt-carbon bond. A dramatic effect on the rate of the reaction is observed upon changing the anion in the reaction mixtures. Thus in aqueous $Na_2SO_4\text{-}H_2SO_4$ or $NaClO_4\text{-}HClO_4$ at pH 1.0, Sn(II) does not react with methyl- or ethylcobalamin. The proposed mechanism for the reaction is depicted in Scheme 19. The initial step of the mechanism is one equivalent oxidation of Sn(II) to Sn(III) and when the Sn(III) is stabilized to decomposition by the anions chloride or tartrate, cobalt-carbon bond cleavage occurs. No cleavage reaction occurs when Sn(II) is replaced by Sn(IV), (ref. 37). Cobalt-carbon and rhodium-carbon bond

$$\begin{aligned}
&\mathrm{Sn(II) + Fe(III)\ \{or\ Co(III)\}} \rightleftharpoons \mathrm{Sn(III) + Fe(II)\ \{or\ Co(II)\}}\\
&\qquad \mathrm{Sn(III) + B_{12,\,alkyl}} \longrightarrow \mathrm{alkyl\ Sn + B_{12r}}\\
&\mathrm{Sn(II) + Fe(III)\ \{or\ Co(III)\}} \longrightarrow \mathrm{Sn(IV) + Fe(II)\ \{or\ Co(II)\}}
\end{aligned}$$

SCHEME 19

cleavage also occurs upon treatment of organocobaloximes and organorhodoximes with sulphur dioxide. However, these apparent insertion reactions involve the radical-chain mechanism outlined in Scheme 20. Since the sulphur dioxide insertion reactions of organocobaloximes show remarkable similarities of initiation, rates, and regiospecificity to the oxygen insertion reactions of the same complexes it has been proposed that some oxygen insertion reactions of the cobaloximes also involve radical-chain reactions (Scheme 21), (ref. 38). An account of the reactions of electrophiles with σ-bonded organotransition-metal complexes has been published (ref. 39).

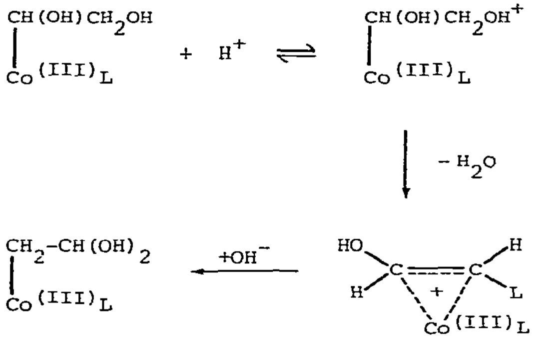
$$\begin{array}{lrcl}
\text{Initiation:} & \mathrm{RM} & \rightleftharpoons & \mathrm{R^{\bullet} + M^{\bullet}}\\
\text{Propagation:} & \mathrm{M^{\bullet} + SO_2} & \longrightarrow & \mathrm{MSO_2^{\bullet}}\\
 & \mathrm{MSO_2^{\bullet} + RM} & \longrightarrow & \mathrm{MSO_2R + M^{\bullet}}\\
\text{and/or} & \mathrm{R^{\bullet} + SO_2} & \longrightarrow & \mathrm{RSO_2^{\bullet}}\\
 & \mathrm{RSO_2^{\bullet} + RM} & \longrightarrow & \mathrm{RSO_2M + R^{\bullet}}\\
\text{Termination:} & \mathrm{MSO_2^{\bullet} + M^{\bullet}} & \longrightarrow & \mathrm{MSO_2M}\\
 & \mathrm{RSO_2^{\bullet} + M^{\bullet}} & \longrightarrow & \mathrm{RSO_2M}
\end{array}$$

SCHEME 20

$$\begin{tikzcd}
\mathrm{py(dmgH)_2Co^{\bullet} + O_2} \arrow[r] & \mathrm{py(dmgH)_2CoOO^{\bullet}} \arrow[d, "+\ \mathrm{RCo(dmgH)_2py}"] \\
 & \mathrm{py(dmgH)_2CoOOR + {}^{\bullet}Co(dmgH)_2py}
\end{tikzcd}$$

SCHEME 21

The reaction of free radicals with cobalt(II) complexes can provide a method for the formation of cobalt-carbon bonds. Thus the radicals RH (RH = $^{\bullet}CH_2OH$, $CH_3\dot{C}HOH$, $HO\dot{C}HCH_2OH$, and $\dot{C}H_2CHO$) react with a Co^{II} L complex (L = macrocyclic $Me_6[14]diene\,N_4$) to give unstable intermediate cobalt-carbon complexes $[Co^{III}L(RH)]$. The order of reactivity of various radicals with $[Co^{II}L]$ is $Me^{\bullet} > \dot{C}H_2CHO > \dot{C}H_2OH > Me\dot{C}HOH > \dot{C}HOHCH_2OH > CF_3\dot{C}HOH > Me_2\dot{C}OH > \dot{C}H_2CMe_2OH$, $\dot{C}H_2CO_2^-$. Since both electron-withdrawing groups and electron-donating groups slow down the reaction it would seem that steric hindrance is the governing factor in the formation of the cobalt-carbon bond. The mechanism of decomposition of these products depends on the nature of the aliphatic residue, RH. Thus $[Co^{(III)}L(CH_2OH)]$ decomposes by a heterolytic cleavage of the cobalt-carbon bond forming $Co^{I}L + CH_2O$. However, $[Co^{(III)}L\{CH(OH)CH_3\}]$ seems to decompose by a hydride transfer from the β-carbon yielding $[Co^{III}L(H)] + CH_3CHO$, while $[Co^{(III)}L\{CH(OH)\text{-}CH_2OH\}]$ rearranges by loss of water to give $[Co^{(III)}L(CH_2CHO)]$ which hydrolyses to $Co^{(III)}L + CH_3CHO$. This latter reaction is a model reaction to that of the diol dehydratase enzyme which contains the coenzyme B_{12}. The observation of the reaction outlined in Scheme 22 is the first direct observation of the rearrangement of ethylene glycol to acetaldehyde while it is covalently bound to a $Co^{(III)}L$ complex (ref. 40).

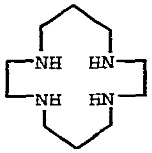


SCHEME 22

Photochemical reactions of alkyl cobalamins are known to be efficient, often straightforward reactions, with the absorption of visible light leading to homolytic cleavage of the cobalt-carbon bond to form an alkyl radical and a cobalt(II) complex. The photolysis of several alkylcobalt(III) complexes has been studied by e.s.r. and spin trapping techniques. These studies suggest that excitation of the complex is followed by expulsion of a hydrogen atom from an equatorial ligand and homolytic cleavage of the cobalt-carbon bond (ref. 41). However, studies on the photochemistry of the organocobalt complexes $[Co([14]aneN_4)(OH_2)Me]^{2+}$ and $[Co([14]tetraeneN_4)(OH_2)\text{-}Me]^{2+}$, containing the synthetic macrocyclic ligands [59] and [60] show that the only primary photoreaction observed at any wavelength for either complex is homolytic cleavage of the Co-Me bond:

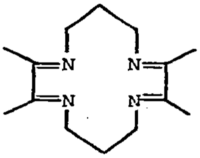
$$Co(N_4)(OH_2)Me^{2+} + h\nu \longrightarrow Co^{II}(N_4) + Me^{\bullet}$$

The principal secondary thermal reaction complicating the photochemical studies is



[14]aneN$_4$

[59]



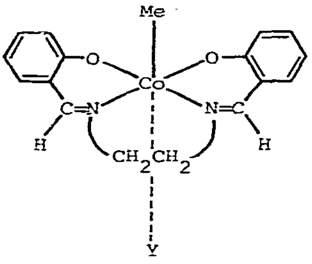
[14]tetraeneN$_4$

[60]

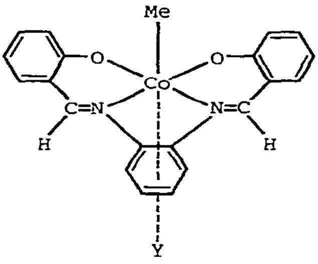
the very efficient recombination reaction:

$$\mathrm{Co^{II}(N_4) + Me^{\bullet} \xrightarrow[H_2O]{} Co(N_4)(OH_2)Me^{2+}}$$

The effect of this reaction is a reduction of the photolysis rate as $[\mathrm{Co^{II}(N_4)}]$ increases. This recombination reaction is effectively inhibited by various radical scavengers e.g. propan-2-ol or oxygen. Methane and ethane result from secondary reactions of the methyl radical. A significant proportion of the methane arises from hydrogen atom abstraction at an α-carbon atom of the ligand by the methyl radical. An orbital energy level scheme has been proposed which accommodates the weak Co-Me bond and most of the spectroscopic properties (ref. 42). An e.s.r. study of the photolysis of the methylcobalt chelates [61] and [62] has also been reported (ref. 43).



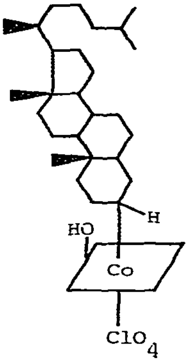
[61]



[62]

Y = H_2O, Ph_3P, py

A preliminary investigation of the electrochemical reduction of methylcobalamin and methylcobinamide has, for the first time, provided evidence for the existence of a one electron intermediate before cleavage of the cobalt-carbon bond (ref. 44). An electrochemical study of (meso-tetraphenylporphinato)cobalt(II) and -cobalt(III) complexes in alkaline medium in Me_2SO has also been reported. Dismutation of [Co(II)(TPP)] is observed and the compound [Co(CH_2SOMe)(TPP)] is formed from the solvent and [Co(III)(TPP)], (ref. 45). A chiral alkyl cobalt complex [63] has also been obtained via an electrosynthetic process and reductive cleavage of the cobalt-



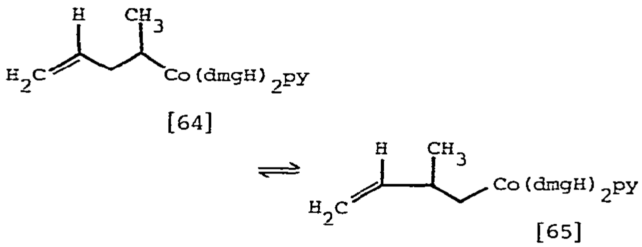
[63]

carbon bond has been shown to occur with retention of configuration at carbon (ref. 46). The observation of inversion at the carbon centre during the halogen cleavage of certain cobalt-carbon bonds has been alternatively interpreted as (a) direct electrophilic (S_E2) attack at carbon or (b) one-electron oxidation followed by nucleophilic attack of halide on the resulting radical cation. Evidence that this latter process may be a viable step in these halogen cleavage reactions is provided by the observation that nucleophilic decomposition of the organocobalt(IV) compound, 1-methylheptylbis(dimethylglyoximato)cobalt(IV) by chloride to form 2-chloro-octane occurs with inversion of configuration at the cobalt-bonded carbon (ref. 47).

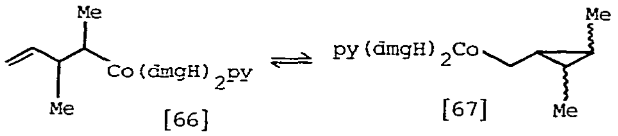
The coenzyme B_{12} catalysis of the rearrangement of methylmalonyl- to succinyl-conenzyme A and the rearrangement of methylene.glutarate to methylitaconate can be represented as follows:

$X = CH_2$; $Y = CO\ SCoA$; $Z = CO_2H$
$X = O$; $Y = SCoA$; $Z = CO_2H$

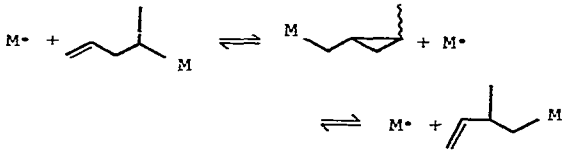
It has now been observed that [64] and [65] rearrange to an equilibrium mixture containing [64] and [65] in a ratio of ca. 1:10. Studies on this system implicate a cyclopropylcarbinyl intermediate and it has been found that the compound [66] rearranges to isomers of the corresponding cyclopropylcarbinylcobaloxime [67] via a bimolecular mechanism outlined in Scheme 23. The related B_{12} rearrangements are thus considered to proceed via homolyses of the cobalt-carbon bond of the coenzyme followed by hydrogen abstraction from C_α as outlined in Scheme 24 (ref. 48). A mechanism involving oxidative addition and reductive elimination steps has been



[64] ⇌ [65]

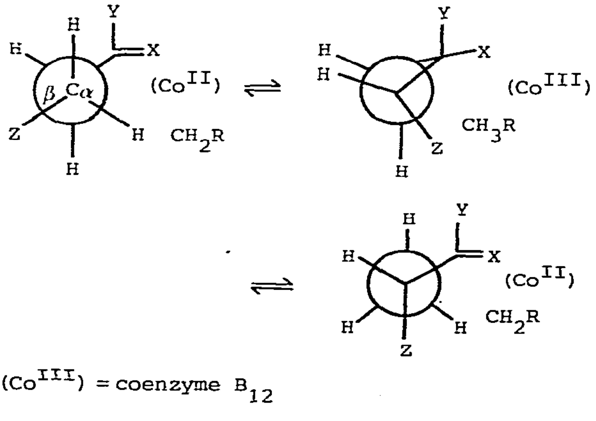


[66] ⇌ [67]



M• = $Co^{II}(dmgH)_2py$

SCHEME 23

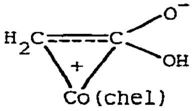


$RCH_2(Co^{III})$ = coenzyme B_{12}

SCHEME 24

suggested for the coenzyme B_{12} catalysed vicinal rearrangements (ref. 48a).

Measurement of the acidities of m- and p-carboxyphenylcobaloximes and the rate constants for the base-catalysed hydrolysis of their methyl esters shows that the aquocobaloxime moiety is a moderately electron-donating Hammett substituent which becomes more electron donating upon ionisation of its axial water ligand. The substituent effect of the cobaloxime moieties is also almost completely inductive in nature with only a minor resonance component. The pKs of the aquo and pyridine complexes of carboxymethyl- and carboxyethylcobaloxime have also been determined and in this system, the apparent inductive effect of the cobaloxime moiety is found to be dependent upon the number of methylene groups between the cobalt and the carboxyl function. The weak acidity of the carboxymethylcobalt complexes is attributed to the presence of significant σ-π conjugation in these complexes as indicated in [68] (ref. 49).

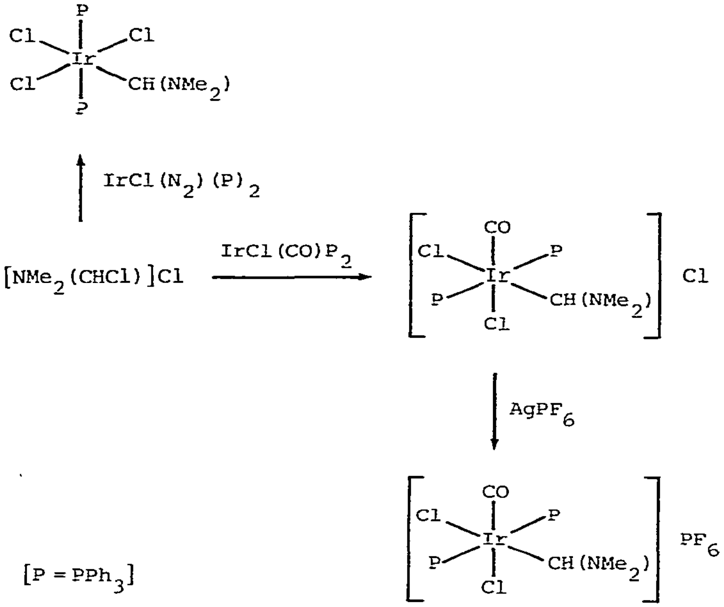


[68]

It is well established that in octahedral methylcobalamins or methylcobaloximes the methyl group exerts a bond weakening effect on the trans ligand. A kinetic investigation of the cobaloxime complexes $[CoXL(dmgH)_2]$ where X and L are anionic and neutral ligands respectively shows that the relative trans effect of the ligands X increase in the order $p\text{-}SO_2C_6H_4Me < CHBr_2 \leqslant SCPh_3 < CH_2Br < p\text{-}C_6H_4Br < p\text{-}C_6H_4OMe < Ph < p\text{-}CH_2C_6H_4CN < Me < CH_2Ph < Et$. Correlations of the observed rate constants with ^1H and ^{13}C n.m.r. shift and coupling data are consistent with ground-state bond weakening for cobaloximes with good trans activating ligands. A parameter which correlates well the rate data is the $\alpha\text{-}^{13}C$ n.m.r. chemical shift of 4-tert-butylpyridine (Bu^tpy) in $[CoX(dmgH)_2(Bu^tpy)]$ (ref. 50). The trans-influence of some anionic, neutral, and bridging ligands on the n.m.r. spectra of methyl- and fluorobenzyl-bis-(dimethylglyoximato) complexes has also been reported (ref. 51).

Metal carbene compounds

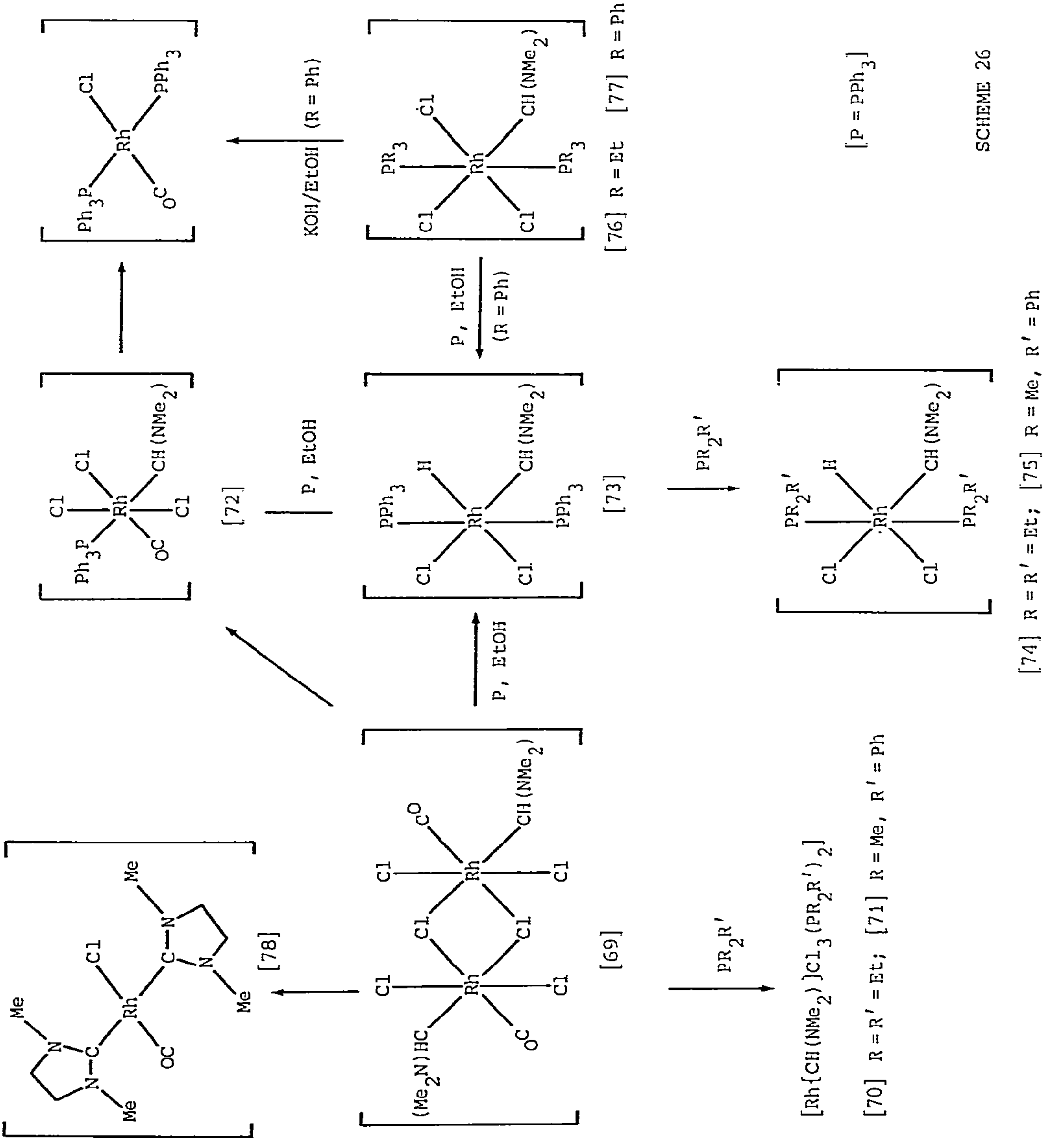
(Chloromethylene)dimethylammonium chloride $[NMe_2(CHCl)]Cl$ (or its dibromo-analogue) is a convenient source of secondary carbenemetal complexes $[M\{CH(NMe_2)\}L_n]$ (Scheme 25). In addition to these three-fragment oxidative addition reactions the secondary carbene complexes of cobalt $[CoX\{CH(NMe_2)\}(CO)_2(PPh_3)]$ can be obtained via the reaction of $[NMe_2CHX]X$ ($X = Cl$ or Br) with $Na[Co(CO)_3(PPh_3)]$, thus providing some rare examples of carbene complexes of cobalt. It appears that the presence of triphenylphosphine prevents cluster formation since $[Co(CO)_4]^-$ is known to react with



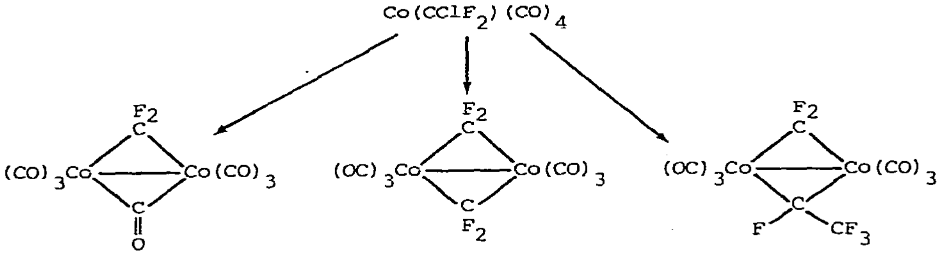
SCHEME 25

$[NMe_2(CHCl)]Cl$ to give $[Co_3(CNMe_2)(CO)_9]$. Some attempts to convert secondary carbenerhodium(III) complexes into rhodium(I) derivatives without Rh-$C_{carb.}$ bond cleavage are outlined in Scheme 26. However, the only new carbene complexes obtained are the hydrido(secondary carbene) rhodium(III) complexes [73]-[75]. The reaction of [69] with the strongly reducing electron-rich alkene $(\overline{NMeCH_2CH_2NMeC}:)_2$ gives [78] (ref. 52).

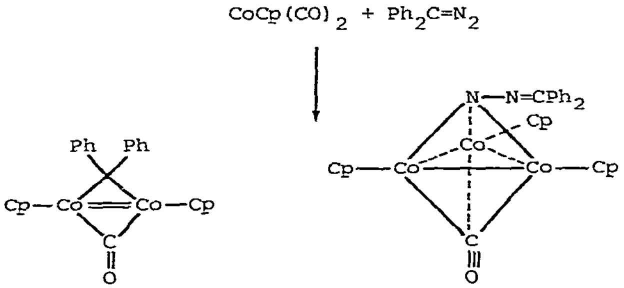
The reaction of $ClCF_2COCl$ with $Na[Co(CO)_4]$ at low temperatures gives $[Co(CClF_2)(CO)_4]$ which decomposes at normal temperatures to afford µ-difluoromethylene compounds as outlined in Scheme 27. The compound µ-difluoromethylene-µ-carbonyl-bis(tricarbonylcobalt)(Co-Co) is an intermediate in the formation of the cluster $[Co_3(CF)(CO)_9]$. $Na[Co(CO)_3(PPh_3)]$ or $Na[Co(CO)_4]$ in the presence of triphenylphosphine react with $ClCF_2COCl$ to give the stable acetyl compound $[Co(COCF_2Cl)(CO)_3(PPh_3)]$ (ref. 53). A bridged diphenylmethylene complex also results upon the low temperature photolysis of $[CoCp(CO)_2]$ with $Ph_2C=N_2$ (Scheme 28), (ref. 54). Photolysis of $[CoCp(CO)_2]$ with $RCO_2CH=N_2$ (R = Et, Me_3C) leads to a bridging alkoxycarbonylcarbene compound, (Scheme 29). The interesting irreversible carbonyl bridge opening process depicted in Scheme 29 is a first order intramolecular process (ref. 55, 56).


[78]
[69]
$\frac{1}{2}$
[72]
[73]
[76] R = Et [77] R = Ph
P, EtOH
KOH/EtOH (R = Ph)
P, EtOH (R = Ph)
PR_2R'
$[Rh\{CH(NMe_2)\}Cl_3(PR_2R')_2]$
[70] R = R' = Et; [71] R = Me, R' = Ph
[74] R = R' = Et; [75] R = Me, R' = Ph
[P = PPh_3]

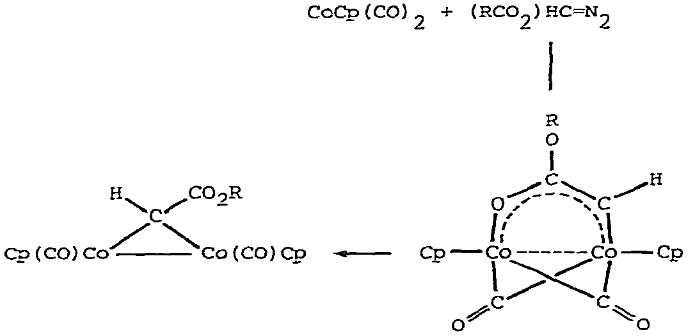
SCHEME 26



SCHEME 27



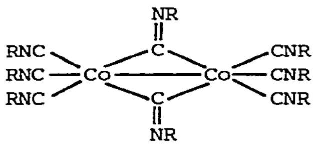
SCHEME 28



SCHEME 29

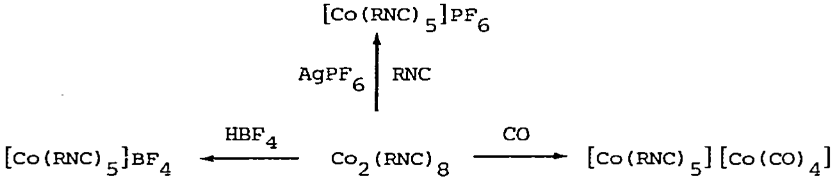
Metal isocyanide compounds

Reactions of $[Co_2(CO)_8]$ with RNC ($R = 2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$, $2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2$) at 80-90°C afford the dicobalt octaisocyanide compounds [79]. The ^1H n.m.r. spectra of these compounds indicate the presence of intra- and intermolecular ligand exchange



[79]

between bridging and terminal isocyanide ligands and between co-ordinated and free isocyanide ligands respectively. The compounds are not reduced by sodium amalgam but undergo oxidation with halogens to give $[Co(RNC)_4]X_2$ (X = Br, I). Some other reactions are outlined in Scheme 30 (ref. 57). The reactions of $C_5R'_5H$ (R′ = H, Me) with $[Co_2(RNC)_8]$ (R = 2,6-$Me_2C_6H_3$) afford [CoCp(RNC)$_2$] and [Co(η^5-C_5Me_5)(RNC)$_2$], which



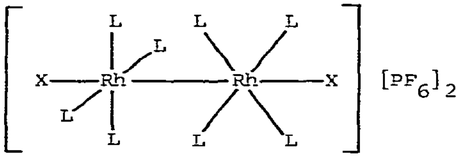
[R = 2,6-$Me_2C_6H_3$]

SCHEME 30

may also be obtained by heating the isocyanide with [CoCp(CO)$_2$]. At room temperature monosubstituted compounds e.g. [CoCp(CO)(RNC)] can be isolated. The reaction of [CoCp(RNC)$_2$] with iodine gives [CoICp(RNC)$_2$]I while with tetracyanoethylene the olefin complex [CoCp(RNC)(TCNE)] is formed (ref. 58). Some isocyanide complexes of rhodium(III) [RhCl$_2$(η^5-C_5Me_5)(CNR)], [RhCl(η^5-C_5Me_5)(CNR)$_2$Cl]PF$_6$ (R = Me, Et, ^{i}Pr, ^{t}Bu, C_6H_{11}, p-ClC_6H_4, or 1-naphthyl) as well as some related cyclopentadienyl complexes have been prepared by reactions of isocyanides with either [RhCl$_2$(η^5-C_5Me_5)]$_2$ or [RhCl$_2$Cp]$_2$. These rhodium(III) isocyanide complexes do not react with alcohols or amines to yield carbene complexes but the chloride ligands can be displaced from the rhodium(III) by a variety of nucleophiles including SC_6H_4Me-m$^-$, $S_2CNR_2^-$, $S_2PPh_2^-$, SCN^-, $SeCN^-$, $C_6Cl_5^-$. Treatment of [RhCl(η^5-C_5Me_5)(CNR)$_2$]PF$_6$ with $NaBH_4$ gives low yields of compounds tentatively formulated as [Rh(BH_4)(η^5-C_5Me_5)(CNR)$_2$]PF$_6$ (R = Me or Et) (ref. 59, 60).

The complexes [Rh(CNR)$_4$]PF$_6$ (R = Et, C_6H_{11}, p-$NH_2C_6H_4$ or 1-naphthyl), trans-[Rh(CNR)$_2$(PR′R″)$_2$]PF$_6$ (R′ = R″ = Ph, R = Et, C_6H_{11}, p-$NH_2C_6H_4$ or 1-naphthyl; R′ = Me, R″ = Ph or R′ = Ph, R″ = Me, R = 1-naphthyl and [Rh(CNR)$_3$(PPh$_3$)$_2$]PF$_6$ (R = Me, Et or C_6H_{11})

have been prepared by treatment of $[RhCl(CO)_2]_2$ or $[RhCl(CO)(PPh_3)_2]$ with RNC, or of $[Rh(CNC_{10}H_7)_4]PF_6$ with PMe_2Ph, $PMePh_2$ or PPh_3. The mixed isocyanide complex $[Rh(CNEt)_2(CNC_6Cl_4\text{-}p)(PPh_3)_2]PF_6$ is obtained by addition of stoichiometric amounts of $p\text{-}ClC_6H_4NC$ to the co-ordinatively unsaturated $[Rh(CNEt)_2(PPh_3)_2]PF_6$. Both of the species $[Rh(CNR)_4]^+$ and *trans*-$[(CNR)_2(PPh_3)_2]^+$ readily undergo oxidative-additions with halogens, MeI, MeCOCl, CF_3I and $HgCl_2$ giving *trans*-addition products. Addition of MeCOCl to $[Rh(CNEt)_4]^+$ gives *trans*-$[RhCl(COMe)(CNEt)_4]^+$ without decarbonylation, however, treatment of $[Rh(CNMe)_2(PPh_3)_2]^+$ with MeCOCl gives only $[RhCl_2(CNMe)_2\text{-}(PPh_3)_2]^+$. Addition of sulphur dioxide to $[Rh(CNMe)_4]^+$ and $[Rh(CNMe)_2(PPh_3)_2]^+$ give 1:1 adducts which have a square-pyramidal geometry (ref. 61). Further studies on oxidations of $[Rh(CNR)_4]PF_6$ ($R = p\text{-}MeC_6H_4$) with one half mole of iodine or bromine reveal that the rhodium(II) dimers [80] are formed. An X-ray study on the iodide complex establishes the existence of a direct Rh-Rh bond (2.785 Å). Aryl isocyanide



($L = p\text{-}MeC_6H_4NC$, X = Br, I)

[80]

complexes of this type have previously been formulated as polymers with -Rh-I-Rh-I- chains or as mixed valence Rh(I)-Rh(III) materials. Alkyl isocyanide complexes of Rh(II) are formed by the association of Rh(I) and Rh(III) complexes, e.g.

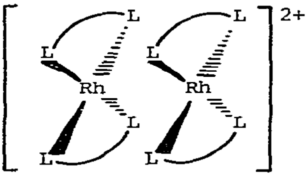
$$[Rh(CNR)_4]^+ + [RhX_2(CNR)_4]^+ \rightleftharpoons \underset{[81]}{[Rh_2X_2(CNR)_8]^{2+}}$$

SCHEME 30a

The rhodium(II) cations [80] are similar to their alkyl analogues [81]. Thus in solution the dimers [80] dissociate into $[Rh(CNR)_4]^+$ and $[RhX_2(CNR)_4]^+$ according to the reverse of the equation in Scheme 30a. This equilibrium is established rapidly in both directions but is strongly solvent dependent. Dissociation is essentially complete in solvents of low dielectric constant (chloroform, dichloromethane) but appreciable amounts of the dimer exist in acetone or acetonitrile solution (ref. 62).

Tetrakis(isocyanide)rhodium(I) and iridium(I) cations are known to exhibit oligomerisation in solution. Thus $[Rh(CNPh)_4]^+$ units oligomerise in acetonitrile solutions yielding species such as $[Rh_2(CNPh)_8]^{2+}$ and $[Rh_3(CNPh)_{12}]^{3+}$. The structures of these oligomers are considered to feature face-to-face contact of

$[Rh(CNPh)_4]^+$ units, with weak, direct Rh(I)-Rh(I) bonds. An X-ray study of purple crystalline samples of $[Rh(CNPh)_4]BPh_4$ has established that the compound contains $[Rh_2(CNPh)_8]^{2+}$ units with two $[Rh(CNPh)_4]^+$ units bonded face-to-face to give a staggered configuration of ligands. The Rh-Rh distance is 3.139 Å. The electronic spectra of $[Rh(CNR)_4]^+$ (R = Ph, ^{i}Pr, cyclohexyl, ^{t}Bu, vinyl) in solution show that these cations also oligomerise in solution to form dimers and trimers (ref. 63). Treatment of $[RhCl(1,5\text{-cod})]_2$ with a bidentate isocyanide affords cationic complexes of the type $[Rh(L\text{-}L)_2]^+$ [L-L = $CN(CH_2)_8NC$, $CN(CH_2)_7NC$] and $[Rh_2(L\text{-}L)_4]^{2+}$ [L-L = $CN(CH_2)_6NC$, $CN(CH_2)_4NC$] which have been isolated as their hexafluorophosphate salts. The electronic spectra of the complexes at various concentrations reveal that in dilute solutions the compounds of $CN(CH_2)_8NC$ and $CN(CH_2)_7NC$ exist as monomers with chelating isocyanides which form dimers of the type [81a] in concentrated solution.

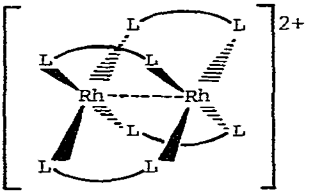


L = $CN(CH_2)_nNC$

(n = 7 or 8)

[81a]

Molecular models indicate that $CN(CH_2)_4NC$ would not be able to chelate to rhodium(I) and it is suggested that the complex $[Rh_2(L\text{-}L)_4]^{2+}$ formed by this isocyanide probably contains bridging isocyanide to form the dimer [82] with an intramolecular Rh-Rh interaction as the smallest unit in dilute solution. The complex derived from



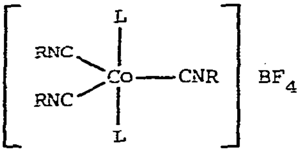
L = $CN(CH_2)_nNC$

(n = 4 or 6)

[82]

$CN(CH_2)_6NC$ probably has a similar structure. In concentrated solution the cations [82] form tetramers through intermolecular Rh-Rh interactions (ref. 64). Flash kinetic spectroscopic studies of the complexes $[Rh(tol)_4]PF_6$ (tol = p-methylphenyl isocyanide) and $[Rh_2(bridge)_4][BPh_4]_2$ (bridge = $CN(CH_2)_3NC$) in acetonitrile solutions have been investigated (ref. 65). The blue-black solid $[Ir(CNMe)_4]Cl$ which is conveniently obtained from MeNC and $[IrCl(1,5\text{-cod})]_2$ has also been shown to exist as an oligomeric species, $[Ir(CNMe)_4]_n^{n+}$. *Upon photolysis dissociation of the solution* oligomers occurs to generate monomeric $[Ir(CNMe)_4]^+$ which can subsequently add CNMe or CO to give five-co-ordinate adducts (ref. 66). Previous photochemical studies on this system had been interpreted in terms of a photoinduced association of solvent to monomeric $[Ir(CNMe)_4]^+$. In contrast to $[Ir(CNMe)_4]_n^{n+}$, the tertiarybutyl isocyanide cation $[Ir(CNBu^t)_4]^+$ exists as a monomer (ref. 66).

The crystal structure of the cobalt(I) isocyanide complex [83] has been reported



[L = P(OMe)$_3$; R = *p*-FC$_6$H$_4$]

[83]

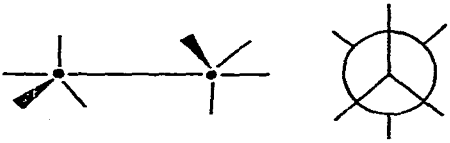
(ref. 67). Magnetic susceptibility studies on pentakis(aromatic isocyanide)cobalt(II) complexes indicate that complexes of phenyl- and *para*-substituted phenylisocyanides are low spin. However, complexes of *ortho*-substituted phenylisocyanides exhibit magnetic moments which are high for a low-spin ground state. It is suggested that all complexes are low spin and that increases in μ_{eff} result through distortion from idealised square pyramidal co-ordination for sterically hindered arylisocyanides (ref. 68).

Metal carbonyl and related compounds

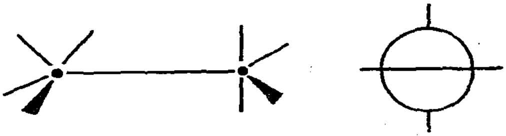
(a) Homonuclear carbonyl compounds

It is now established that three isomers of $[Co_2(CO)_8]$ exist in solution and in frozen matrices. The crystal structure of $[Co_2(CO)_8]$ indicates that the solid state isomer [84] has two bridging carbonyls and on the basis of vibrational data, a second isomer has been assigned a D_{3d} symmetry [85]. The third isomer has been assigned a D_{2d} symmetry structure [86]. A substantial portion of the $[Co_2(CO)_8]$ in solution or

[84]

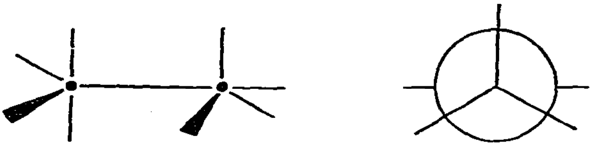


[85]



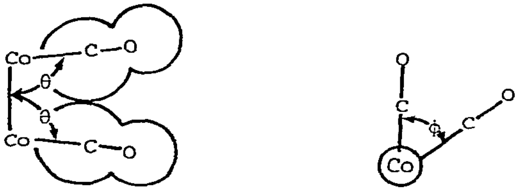
[86]

in the gas phase exists mainly as a mixture of isomers [85] and [86]. At room temperature about 30% of $[Co_2(CO)_8]$ possesses structure [86] and this form dominates at higher temperatures. It has now been shown that the relative stabilities of structures [85] and [86] and the instability of another possible isomer [87], in



[87]

which the $Co(CO)_4$ group on one cobalt is positioned in an axial site and on the other in an equatorial site, can be rationalised in terms of steric interactions between the CO groups bound to the metal centres and metal-metal bond energies. Thus a consideration of the van der Waals contact angle θ (the angle between the Co-CO and Co-Co vectors at which the van der Waals radii of the carbonyls are in contact), figure 1a, reveals that θ is dependent, figure 2, on the dihedral angle ϕ, between



a. b.

Figure 1

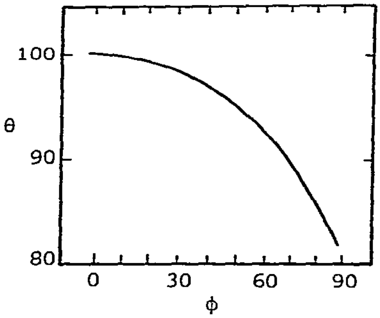


Figure 2

the two Co-CO vectors viewed down the cobalt-cobalt axis, figure 1b. Since the stability of a particular isomer will be influenced by non-bonded repulsions between the carbonyls if contact occurs at angles of θ much greater than 90°, it is apparent that isomers [85] and [86] are reasonable structures for dicobalt octacarbonyl. For isomer [85] angle θ equals 60° while for isomer [86] θ is 90°. Isomer [87] requires a dihedral angle φ of 30° or less and is clearly not favoured on steric grounds. Although isomer [85] would appear to be less favourable than [86] on the basis of steric factors alone, this steric effect must be cancelled by a corresponding electronic contribution to the stability of [86]. Molecular orbital calculations have shown that the Co-Co bond is stronger in [85] than in [86] because of more effective hybridisation of the axial orbital of the $Co(CO)_4$ group. Thus it appears that the greater Co-Co bond strength in [85] just compensates for the increased steric interactions in this isomer (ref. 69).

Variable-temperature ^{13}C n.m.r. spectra of the carbonyls $[Rh_2Cp_2(CO)_3]$, $[Rh_2Cp_2(CO)_2(PR_3)]$, $[Co_2(CO)_8]$, $[Rh_4(CO)_{12}]$, $[Rh_4(CO)_{11}(PPh_2R)]$ (R = Ph, Me), $[Co_4(CO)_{12}]$, $[Co_4(C_6H_5Me)(CO)_9]$, $[Co_4(RC_2R)(CO)_{10}]$ (R = CO_2Me or Ph), $[RhCo_3(CO)_{12}]$ and $[Rh_6(CO)_{15}I]^-$ have been studied and apart from $[Co_2(CO)_8]$, $[Co_4(RC_2R)(CO)_{10}]$, and $[Co_4(CO)_{12}]$ solution structures have been determined. The ^{13}C n.m.r. spectrum of $[Co_4(CO)_{12}]$ suggests that the structure in solution is of D_{2d} symmetry rather than of C_{3v} symmetry as in the crystal. However, since both i.r. and ^{59}Co n.m.r. measurements suggest that the solid state structure of $Co_4(CO)_{12}$ is retained in solution it is possible that an intensity distortion of the ^{13}C resonances occurs due to the presence of the cobalt nuclei which possess a high quadrupole moment (ref. 70). Variable temperature ^{13}C n.m.r. spectra of $[Co_4(CO)_{12}]$ in viscous solutions (which limits the broadening of the resonances of carbon nuclei bonded to a metal with $I > 1/2$ are consistent with maintainment of the solid state structure in solution (ref. 71). A review on the mechanistic features of metal cluster rearrangements has been published (ref. 72) and an important paper describing a new approach to fluxional behaviour has appeared (ref. 73). The crystal structure of $Ir_4(CO)_{12}$ has been reported. The complex disorder problem leads to difficulties in determining accurate atomic positions but the essential T_d symmetry of the $[Ir_4(CO)_{12}]$ molecule is confirmed (ref. 74).

A measure of the strength of the metal-metal interaction in the dinuclear carbonyls $[Co(CO)_3L]_2$ has been determined by obtaining the energies of the $\sigma \rightarrow \sigma^*$ transitions involving orbitals along the metal-metal bond axis. This excitation energy, $h\nu(\sigma \rightarrow \sigma^*)$, is an approximation of the energy required to move each of the two electrons from the bonding σ M.O. into the atomic orbitals, on the metals, from which the M.O. was constructed, and is thus a measure of the σ-interaction between the two metals. These studies reveal that the interaction energies increase as the axial substituents increase in σ basicity and π-acidity. Steric weakening of the interaction occurs but it is only substantial for particularly large ligands such as

$P(C_6H_{11})_3$ (ref. 75). A new method has been outlined for assigning energies to the metal-metal and metal-ligand bonds of metal clusters $M_x(CO)_y$ using the lengths (d) and strengths (E) of the bonds in the metals as a basis, and assuming that E(M-M) to be proportional $[d(M\text{-}M)]^{-k}$. This method has been applied to examples with M = Fe, Ru, Os, Co, Rh, or Ir, and it suggests that their metal-ligand bonds are generally stronger, and their metal-metal bonds generally weaker, than previous treatments have indicated. Further the strength of binding of the carbonyl ligands to a particular metal increases with x, the cluster nuclearity. It also appears that the metal-metal bonds in $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ are weaker than in the metal itself (ref. 76, 77). The valence force constants of the Co-Co bonds in $[Co_4(CO)_{12}]$ have been determined from Raman spectral data of $[Co_4(CO)_{12}]$ in heptane solutions and these force constants have been compared with those of Rh-Rh and Ir-Ir bonds in $[Rh_4(CO)_{12}]$ and $[Ir_4(CO)_{12}]$ (ref. 78). A review on force constant calculations and infrared spectra of transition metal carbonyls has appeared (ref. 79).

The synthesis of transition metal carbonyls from an appropriate metal oxide and carbon monoxide is thermodynamically possible for all of the transition metals at 25°C and one atmosphere pressure according to the equation:

$$MO_x + (x+y)CO \longrightarrow M(CO)_y + xCO_2$$

The reaction of cobalt(II) oxide with carbon monoxide at 80°C and 1900 atm. pressure occurs quantitatively to give $[Co_2(CO)_8]$ but no reaction takes place at 50°C and 2450 atm. No $[Co_4(CO)_{12}]$ is observed at temperatures up to 300°C (ref. 80), and the kinetics of the reaction of $[Co_4(CO)_{12}]$ in n-hexane with carbon monoxide to form $[Co_2(CO)_8]$ have been investigated over a wide range of temperature and pressure. The reaction is first order in $[Co_4(CO)_{12}]$; the order in [CO] is one at low pressures and high temperatures and two at high pressures and low temperatures. A mechanism involving initial reversible breaking of one Co-Co bond followed by irreversible breaking of a second Co-Co bond is proposed (ref. 81). The reaction

$$2Co_2(CO)_8 \longrightarrow Co_4(CO)_{12} + 4CO$$

occurs *via* the formation of co-ordinatively unsaturated complexes (ref. 82). A review on matrix isolation studies on transition metal carbonyls has appeared (ref. 83).

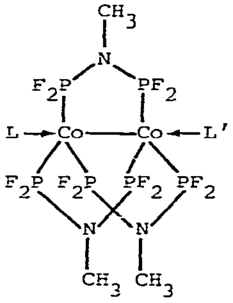
A kinetic study of the disproportionation reaction occurring in methanol in the

$$[Co(CO)_3L]_2 \xrightarrow{CO} [Co(CO)_3L_2][Co(CO)_4]$$

$$(L = P^nBu_3)$$

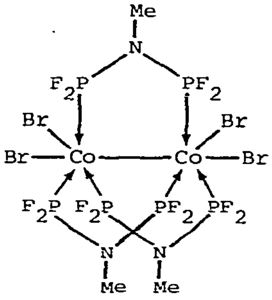
presence of carbon monoxide has been investigated. It is proposed that the reaction proceeds via a bridged carbonyl intermediate, $[Co_2(CO)_6L_2L']$, (L′ = CO, L, or MeOH) which breaks down by internal electron transfer to form the final ionic species (ref. 84).

The reaction of $MeN(PF_2)_2$ with $[Co_2(CO)_8]$ at or below room temperature gives a purple crystalline product (88; L = L′ = CO) the structure of which has been confirmed by a single crystal X-ray study. However, ultraviolet irradiation of $[Co_2(CO)_8]$ with $MeN(PF_2)_2$ gives the homoleptic complex $[88;\ L = L' = MeN(PF_2)_2]$ which contains two monodentate phosphorus co-ordinated $MeN(PF_2)_2$ ligands. Column chromatography of this product results in solvolysis of the monodentate ligands to give (88; L = L′ = PF_2NHMe) the structure of which has also been confirmed by a single crystal X-ray study. Ultraviolet irradiation of (88; L = L′ = CO) with the monodentate ligands L = Me_2NPF_2, $P(OEt)_3$, PPh_3 and ^tBuNC results in the stepwise replacement of the two carbonyl ligands to afford the derivatives $[Co_2(CO)L\{MeN(PF_2)_2\}]$ and $[Co_2L_2\{MeN(PF_2)_2\}]$. A monosubstituted product $[Co_2(CO)(PF_2NHMe)\{MeN(PF_2)_2\}]$ can also be isolated from the reaction of $[Co_2(CO)_8]$ with $MeN(PF_2)_2$ and the carbonyl ligand in this monosubstituted product can also be displaced by $P(OEt)_3$ and Me_2NPF_2. The reaction of (88; L = L′ = CO) with $Ph_2PCH_2CH_2PPh_2$ under ultraviolet irradiation gives (88; L = CO, L′ = $Ph_2PCH_2CH_2PPh_2$) which contains a monodentate di(tertiary phosphine). The ability of $MeN(PF_2)_2$ ligands to bridge metal-metal bonds thus forming five-membered rings has prompted a study of the reactions of $MeN(PF_2)_2$ with $[Co_4(CO)_{12}]$. These reactions afford black crystalline products of the type $[Co_4(CO)_{12-n}\{MeN(PF_2)_2\}_n]$, (n = 2, 3, 4, and 5) which appear to have structures in which two to five of the six edges in the Co_4 tetrahedron of $[Co_4(CO)_{12}]$ are bridged by $MeN(PF_2)_2$ ligands. The reaction of $MeN(PF_2)_2$ with $[Rh_4(CO)_{12}]$ proceeds rapidly to give a yellow insoluble product $[Rh_4\{MeN(PF_2)_2\}_6]_n$. The facile formation of this rhodium compound provides a further example of the weaker metal-carbon bonds formed by 4d transition metals relative to corresponding systems involving 3d and 5d transition metals (ref. 85). The co-condensation of Co vapours with a 1:4 (vol) mixture of the



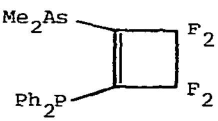
[88]

bidentate $MeN(PF_2)_2$ and monodentate Me_2NPF_2 affords the deep-violet air-stable compound (88; $L = L' = Me_2NPF_2$) which has been the subject of a single crystal X-ray study. This compound can also be obtained by ultraviolet irradiation of (88; $L = L' = CO$) with Me_2NPF_2 together with (88; $L = CO$, $L' = Me_2NPF_2$) (ref. 86). The reaction of (88; $L = L' = CO$) with bromine affords the red-brown compound [89] shown by a single crystal X-ray study to retain the $Co_2[MeN(PF_2)_2]_3$ unit the stability of which appears to be little affected by an increase in oxidation state of the cobalt atoms from 0 to +2 (ref. 87). Oxidation of $[Co_2(CO)_8]$ with FO_2SOOSO_2F gives $Co(SO_3F)_2$ (ref. 88).



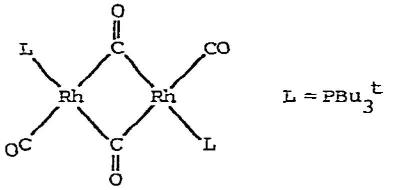
[89]

The reaction of the ligand $(MeO)_2PCH_2CH_2P(OMe)_2$ with $Co_2(CO)_8$ affords the cation $[Co(CO)\{(MeO)_2PCH_2CH_2P(OMe)_2\}_2]^+$ isolated as its PF_6^- salt. This reaction contrasts with the reactions of $[Co_2(CO)_8]$ with the more usual alkyl and aryl di(tertiary phosphines) which lead only to $[Co(CO)_3(diphos)]^+$ (ref. 89). The tricarbonylcobalt cationic complexes $[Co(CO)_3\{PBu_2(CH_2)_3Si(OEt)_{3-n}Me_n\}_2][Co(CO)_4]$, (n = 1, 2), have also been obtained and on heating these salts the neutral compounds $[Co(CO)_3\{PBu_2(CH_2)_3Si(OEt)_{3-n}Me_n\}]_2$ are obtained (ref. 90, 91). A single crystal X-ray study of the compound $[Co(CO)_3(P\text{-}As)]_2$, (P-As = 90) reveals that the molecule contains a cobalt-cobalt bond, each cobalt atom having an irregular trigonal bipyramidal arrangement with equatorial carbonyl groups (ref. 92).



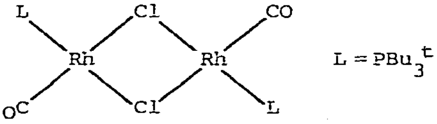
[90]

The reaction of sodium borohydride with trans-$[RhCl(CO)\{PBu_3^t\}_2]$ gives the bridged carbonyl compound [91] which can also be obtained by the reaction of tri-t-butylphosphine with either $[Rh_4(CO)_{12}]$ or $[Rh(OMe)(CO)_2]_2$. Hydrated rhodium(III)

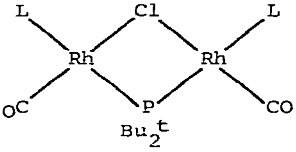


[91]

chloride reacts with tri-t-butylphosphine to give $[RhH_2Cl(PBu_3^t)_2]$ but in the presence of carbon monoxide the compounds [92] and [93] are formed. The bridged di-



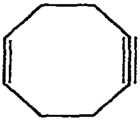
[92]



[93]

t-butylphosphine compound [93] can also be obtained by the action of $Me_3SiPBu_2^t$ on [92] (ref. 93).

The reaction of norbornadiene with $[Co_2(CO)_8]$ is known to give $[Co_2(CO)_4(C_7H_8)_2]$ and the crystal structure of this bridged carbonyl compound has now been determined (ref. 94). The reaction of $[Ir_4(CO)_{12}]$ with cyclo-octa-1,5-diene provides a complex mixture of products. The major product has been characterised as $[Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})]$ which contains the C_8H_{10} cyclo-octa-1-ene-5-yne ligand[94]. Single crystal



[94]

X-ray diffraction data have shown the complex to have a <u>closo</u>-Ir_4C_2 pseudo-octahedral framework analogous to $[Co_4(CO)_{10}(C_2Et_2)]$. The compounds $[Ir_4(CO)_{12-2x}(C_8H_{12})_x]$ may also be obtained by using $Me_3NO.2H_2O$ as an oxidative decarbonylation reagent. Thermal decomposition of both $[Ir_4(CO)_8(C_8H_{12})_2]$ and $[Ir_4(CO)_6(C_8H_{12})_3]$ affords $[Ir_4(CO)_7(C_8H_{12})(C_8H_{10})]$ which reacts further with cyclo-octa-1,5-diene to give $[Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})]$. The mechanism of formation of the C_8H_{10} ligand [94] is considered to involve oxidative-addition of vinylic C-H bonds of co-ordinated C_8H_{12} and C_8H_{11} groups but the fate of the hydrogen atoms removed is not known (ref. 95).

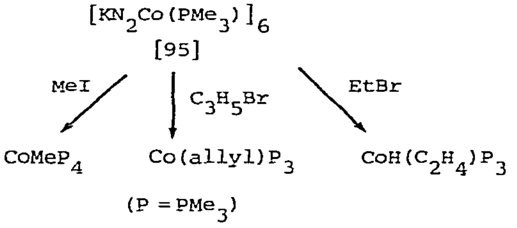
A minor product of the reaction of cyclo-octa-1,5-diene with $[Ir_4(CO)_{12}]$ is a heptanuclear cluster $[Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})]$ which exhibits three stages of cyclo-octadiene co-ordination and dehydrogenation. The crystal structure of the cluster reveals that the seven iridium atoms adopt a capped octahedral geometry as has been observed in the three other heptanuclear clusters, $[Rh_7(CO)_{16}]^{3-}$, $[Os_7(CO)_{21}]$, and $[Rh_7I(CO)_{16}]^-$ which have been previously characterised. The co-ordination of the C_8H_{11} "enyl" moiety to an edge and of the C_8H_{10} "yne" moiety to a face of the Ir_7 polyhedron is similar to the manner in which such groups are bound to an edge or to a face of a triangular cluster framework (ref. 96). The known substituted derivatives of $[Ir_4(CO)_{12}]$ mainly contain phosphorus donor ligands, however, treatment of $[Ir_4(CO)_{12}]$ with halide and pseudo-halide anions affords the new species $[Ir_4X(CO)_{11}]^-$, (X = Cl, Br, I, CN, SCN). The crystal structure of the bromide derivative has been determined and the structure is found to be similar to $[Co_4(CO)_{12}]$. One terminal CO group in the basal $M_3(CO)_9$ moiety is replaced by bromide and two of the resulting bridging CO groups become markedly asymmetric (ref. 97).

The reactions of the alkoxides RO^- in ROH (R = Me, Et) with $[Ir_4(CO)_{12}]$ and subsequent reactions of the carboalkoxy species $[Ir_4(COOR)(CO)_{11}]^-$ with alcoholic alkaline hydroxides produces the novel anionic cluster $[Ir_4H_2(CO)_{10}]^{2-}$. The structure of this anion is similar to that of $[M_4(CO)_{12}]$ (M = Co, Rh) but with two terminal CO groups in the basal plane replaced by the hydride ligands. In the tetrahedral metal cluster the Ir-Ir bonds <u>trans</u> to the hydride ligands are significantly longer than the others (ref. 98). The mild pyrolysis of $Na_2[Rh_{12}(CO)_{30}]$ or of mixtures of $[Rh_4(CO)_{12}]$ and NaOH gives a mixture of brown anionic species from which the anion $[Rh_{15}(\mu\text{-}CO)_{14}(CO)_{13}]^{3-}$ can be isolated. Treatment of this anion with bromide ion in acetonitrile results in fragmentation of the cluster to give $[RhBr_2(CO)_2]^-$ and $[Rh_{14}(\mu\text{-}CO)_{16}(CO)_9]^{4-}$. Addition of $[Rh(CO)_2(MeCN)_2]BF_4$ to $[Rh_{14}(CO)_{25}]^{4-}$ results in a quantitative conversion of the tetra-anion to $[Rh_{15}(CO)_{27}]^{3-}$. These metallic lattices in rhodium carbonyl cluster chemistry show a stepwise hexagonal close-packed-body centred cubic interconversion (ref. 99).

Although there have been several reports on the preparation of catalysts by combining metal cluster compounds with supports the structure of the attached cluster has not been fully determined. However, reduction of $[IrCl(CO)_2(\underline{p}\text{-toluidine})]$ with zinc in the presence of phosphinated polystyrene gives the polymer-bound tetranuclear iridium carbonyl catalyst $[Ir_4(CO)_{11}Ph_2P(\text{polymer})]$ where the polymer is poly(styrene-divinylbenzene). The solid is an active catalyst for ethylene hydrogenation at 30°C and 1 atm. (ref. 100). It has been shown that silicas bearing phosphine, mono- and diamine ligands bind the rhodium cluster, $[Rh_6(CO)_{16}]$, with retention of its structural integrity (ref. 101). The reactivity of $[Rh_6(CO)_{16}]$ supported on silica has also been studied (ref. 102).

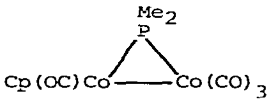
The carbonylate anions, $K[Co(CO)_4]$ and $K[Co(CO)_3PPh_3]$ can be obtained in near quantitative yield by reductive cleavage of $[Co_2(CO)_8]$ and $[Co_2(CO)_6(PPh_3)_2]$ respectively by potassium hydride in THF or HMPA/THF (ref. 103). A tetrahydrofuran solution of sodium N,N′-ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na, reacts reversibly with carbon monoxide to give a monocarbonyl species Co(salen)NaCO which reacts further to produce the deep red species $[Co(salen)_2NaCo(CO)_4THF]$. This species contains a Na^+ ion octahedrally surrounded by six oxygen atoms provided by two Co(salen) groups, acting as bidentate chelating ligands, THF, and $[Co(CO)_4]^-$ bonded to Na^+ by one of its carbonyl oxygen atoms (ref. 104). Ion sites for $Na[Co(CO)_4]$ in oxetane, 1,2-dimethoxyethane, and tetrahydrofuran from 300 to 150 K have been determined by infrared spectral studies (ref. 105).

Although the highly nucleophilic species $[FeCp(CO)_2]^-$ reacts with carbon dioxide to give $[FeCp(CO)_2]_2$ and carbonate the less nucleophilic anion $[Co(CO)_4]^-$ is unreactive towards carbon dioxide (ref. 106). The reaction of $[Mg(THF)_4][CoN_2(PMe_3)_3]_2$ with potassium affords the complex [95] which forms a double cube type of structure made up from six KN_2 units with six exo PMe_3 groups. Some reactions of the complex [95] are depicted in Scheme 31. The stability of the anions $[CoL(PMe_3)_3]^-$ increase in the order L = olefin $< N_2 < PMe_3$ (ref. 107a). The compounds $[Mg(THF)_2][CoN_2(PR_3)_3]$, ($PR_3 = PPh_3$, $PEtPh_2$) have also been described (ref. 107b).



SCHEME 31

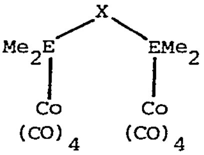
The cobalt-cobalt bonded compound [96] is formed from $[Co(\eta^3\text{-}C_3H_5)(CO)_3]$ and $[CoCp(CO)_2PMe_2H]$ (ref. 108). However, propene elimination from $[Co(\eta^3\text{-}C_3H_5)(CO)_3]$ and PMe_2H affords the trimer $[Co(\mu\text{-}PMe_2)(CO)_2]_3$ *via* the unstable intermediate $[Co(\eta^3\text{-}C_3H_5)(CO)_2PMe_2H]$ (ref. 109). A review on compounds containing metal-metal bonds has been published (ref. 110).



[96]

(b) Heteronuclear metal-metal bonded carbonyl compounds

Dicobalt octacarbonyl reacts with $(Me_2SiH)_2O$, $(Me_2GeH)_2O$, or $(Me_2SiH)_2CH_2$ to yield the complexes [97]. These complexes are thermolabile, decomposing slowly at

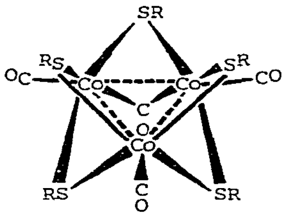


96a; E = Si, X = O
96b; E = Ge, X = O
96c; E = Si, X = CH_2

-78°C to give $[Co_4(CO)_{12}]$ and unidentified polysiloxanes or polygermoxanes (ref. 111). The reaction of Ge_2H_5Cl with $Na[Co(CO)_4]$ gives $[Co(Ge_2H_5)(CO)_4]$. An equilibrium mixture which mainly contains this compound is also formed upon mixing Ge_2H_5Cl and $[Co(GeH_3)(CO)_4]$. The Co-Ge bond in $[Co(Ge_2H_5)(CO)_4]$ is cleaved by $HgCl_2$ but no reaction occurs with CCl_4 or $GeCl_4$. The carbonylate anion $[Mn(CO)_5]^-$ displaces $[Co(CO)_4]^-$ from $[Co(Ge_2H_5)(CO)_4]$. All these reactions parallel those of $[Co(GeH_3)(CO)_4]$ (ref. 112). Thermolysis of $[Co(GeH_3)(CO)_4]$ under vacuum at 150°C gives the high temperature β-modification of cobalt metal and at 400°C CoGe and $CoGe_2$ are formed (ref. 113). Ionisation and appearance potential data for the compound $[Co(SnMe_3)(CO)_4]$ have been obtained (ref. 114).

Studies on the silver compound $[AgCo(CO)_4]$ reveal that it is isomorphous with the isoelectronic compound $[CdFe(CO)_4]_4$ and thus like $[CdFe(CO)_4]_4$ the silver compound probably contains metal atoms arranged in an approximately planar, centrosymmetric eight-membered ring. However, the complex $[2,2'\text{-bipyAgCo}(CO)_4]$ is at most only partly associated in non-co-ordinating solvents (ref. 115). The complex $[Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp]$ can mimic the reactions of acetylenes. Thus a study of the reaction of this molybdenum complex with $[Co_2(CO)_8]$ suggests that an unstable "acetylene" cobalt carbonyl complex is formed which breaks down to give a mixture containing $[MoCp(CO)_3]_2$, $[Co_4(CO)_{12}]$, and $[(CO)_3CpMoCo(CO)_4]$ (ref. 116). This latter complex and its tungsten analogue can be prepared by photolysis of mixtures of $[Co_2(CO)_8]$ with $[MCp(CO)_3]_2$, (M = Mo or W). These mixed metal-metal bonded compounds exhibit low-energy absorptions which are attributable to $d_{\pi-\sigma}*$ and $\sigma_b-\sigma^*$ transitions. Photoexcitation of the complexes results in homolytic cleavage of the M-M' metal-metal bond. Flash photolysis of the M-M' complexes in benzene results in >90% yields of the M-M and M'-M' complexes. Irradiation of the M-M' complexes in carbon tetrachloride gives stoichiometric amounts of $[MClCp(CO)_3]_2$ but the fate of the $Co(CO)_4$ fragment is not known. In some cases trace amounts of $[Co_3(CO)_9CCl]$ are observed. The ordering of metal radical reactivity toward halogen atom abstraction is $[WCp(CO)_3] > [MoCp(CO)_3] > [FeCp(CO)_2] > [Co(CO)_4]$ (ref. 117).

Reactions of $[Co_3(CO)_9CBr]$ with alcohols, phenols or amines are known to result in migration of a CO ligand from cobalt to the apical carbon atom to give products which can be regarded as formally resulting from reaction of the acylium ion $[Co_3(CO)_9CCO]^+$ with the nucleophilic reagent. Similar reactions of alkanethiols with $[Co_3(CO)_9CBr]$ in the presence of triethylamine and carbon monoxide have now been found to give analogous products $[Co_3(CO)_9CC(O)SR]$. However, in contrast benzenethiol reacts to give a mixture of $[Co_3(CO)_9CSPh]$, PhSSPh, and much tar. The compound $[Co_3(CO)_9CSPh]$, which may also be obtained from the reaction of $[Co_3(CO)_9CCl]$ and benzenethiol in the presence of triethylamine and carbon monoxide, is the first $Co_3(CO)_9C$ cluster with an organosulphur group attached to the apical carbon atom. In addition the $[Co_3(CO)_9CCl]/PhSH/Et_3N/CO$ reaction gives the complex [97] and the



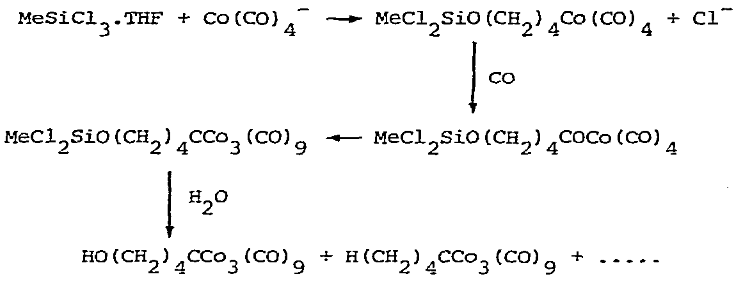
[97]

isolation of this complex represents the first example of the interception of an intermediate in the chemical destruction of a $[Co_3(CO)_9CR]$ cluster complex. Careful re-examination of the reactions of $[Co_3(CO)_9CBr]$ with alkanethiols reveal that in addition to the complexes $[Co_3(CO)_9CC(O)SR]$, small amounts of $[Co_3(CO)_9CSR]$ and $[Co_3(CO)_4(SR)_5]$ type complexes are also formed. Interestingly when $[Co_3(CO)_9CBr]$ is treated with LiSPh the initially sought product, $[Co_3(CO)_9CC(O)SPh]$ is obtained. However, when this reaction is repeated in the presence of Et_3N only $[Co_3(CO)_9(SPh)_5]$, [97] is isolated. The mechanism of the reaction which produces the $[Co_3(CO)_9CSR]$ complexes is not known. Direct nucleophilic attack at the sterically hindered apical carbon atom seems unlikely (ref. 118). The reaction of carbon disulphide with $[Co_2(CO)_8]$ is known to give a variety of products. Among the complexes formed, $[Co_3(CO)_9S]$, $[Co_3(CO)_9C]_2$, $[(CO)_9Co_3CSCS(CO)_7Co_3S]$ and $[(CO)_8Co_3(CS_2)(CO)_7Co_3S]$ have been identified previously but now two other complexes $[Co_6C(CO)_{12}S_2]$ and $[Co_3(CO)_9CS]_2$ have been characterised by X-ray studies. The complex $[Co_6C(CO)_{12}S_2]$ is composed of a trigonal prism of six cobalt atoms, and each triangular face of this prism is symmetrically capped by a sulphur atom. The carbide atom is in the centre of the prism. The geometry of the $(CO)_9Co_3C$ units in the complex $[(CO)_9Co_3CS{-}SCCo_3(CO)_9]$ is similar to that found for other $[Co_3(CO)_9CR]$ complexes. One unusual feature of the structure, however, is that the directions of the C-S bonds do not point along the local threefold axes of the Co_3C pyramids. The short S-S bond also suggests that there is considerable double bond character in this bond (ref. 119).

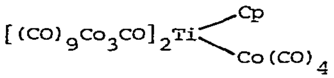
Although a stable set of salts of the carbonium ion metal cluster $[Co_3(CO)_9CCH_2]^+$ exist, no crystallographic data on these compounds are available. By analogy with the many known $[Co_3(CO)_9CR]$ structures an upright positioning of the CC bond above the centre of the tricobalt triangle might be expected. However, an extended Hückel calculation on the ion suggests a deformation away from the upright position. This preference may be traced to interaction between the $-CH_2$ $\underline{p}$ orbital and an $\underline{e}$ type occupied frontier orbital of the cluster (ref. 120).

The decomposition of organic derivatives of the clusters $[Co_3(CO)_9CR]$ could proceed in principle by release of the organic fragment as a carbyne. Studies on the thermolysis of $[Co_3(CO)_9CH]$ do indeed suggest the generation of a carbyne, $H\dot{C}:$ (ref. 121) and in a separate study it has been shown the organocarbyne complexes <u>trans</u>-$MCl(CR)(CO)_4$, ($M = Cr$, Mo, or W) and $[MnCp(CR)(CO)_2]BCl_4$ react with $[Co_2(CO)_8]$ under very mild conditions to give either alkyne complexes $[Co_2(CO)_6(C_2R_2)]$ or the clusters $[Co_3(CO)_9CR]$ (ref. 122). The ground state electronic structure of the clusters $[Co_3(CO)_9CR]$, ($R = H$, Me, Ph, PhCO, CF_3, $EtCO_2$, Cl, $MeCO_2$, MeO, and Et_3Si) have been examined by ^{59}Co n.q.r. spectroscopy. The ^{59}Co nuclear quadrupole coupling constants are found to correlate with the Hammett σ function and the σ_R^- resonance parameter for the R groups, and it appears that the apical carbon atom in the cluster transmits electronic character between the R group and the cobalt atoms by a π-resonance mechanism and not by a through-bond inductive mechanism. Thus in these complexes something like delocalised carbyne bonding between the carbon atom and the three cobalt atoms can be envisaged. Alternatively transmission of the π character of R to cobalt could involve an ethylidyne type structure. The ^{35}Cl resonance in $[Co_3(CO)_9CCl]$ indicates a significant amount of Cl-C multiple bond character (ref. 123). Treatment of $[Co_2(CO)_8]$ with Cl_2CHOR gives the clusters $[Co_3(CO)_9COR]$, ($R = Me$, Et, or ^iPr) (ref. 124). The crystal structures of the complexes $[Co_3(CO)_7(\text{norbornadiene})CEt]$ and bis(η-cyclopentadienyl)(methylmethinyl)-tetracarbonyltricobalt have been published (ref. 125, 126).

The reactions of $Na[Co(CO)_4]$ with Me_nSiCl_{4-n} ($n = 0$-3) in diethylether and tetrahydrofuran have been studied and three distinct reaction pathways have been recognised which depend on the acidity of the chlorosilane and basicity of the solvent. Attack at the silicon centre via the cobalt atom of the $[Co(CO)_4]^-$ anion leads to formation of a Si-Co bond. However, the strong affinity of silicon for oxygen favours reactions involving carbonyl ligands to give the clusters $[Co_3(CO)_9COSiR_3]$. The third pathway involves chlorosilane induced attack of $[Co(CO)_4]^-$ in the solvent to give products derived from THF molecules (Scheme 32) (ref. 127). The reaction of $Na[Co(CO)_4]$ with $[TiCl_3Cp]$ leads to the cobalt-titanium bonded complex [98] the structure of which has been determined by a single crystal X-ray study (ref. 128). Similar reactions occur when the bis(cyclopentadienyl)metal chlorides $[MCl_2Cp_2]$, ($M = Ti$, Zr, or Hf) react with $Li[Co_3(CO)_{10}]$ to form the cluster



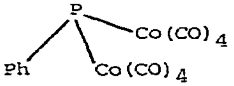
SCHEME 32



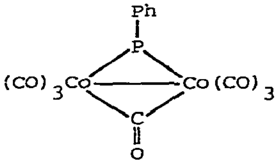
[98]

compounds $[MClCp_2\{OCCo_3(CO)_9\}]$ and $[MCp_2\{OCCo_3(CO)_9\}_2]$. The monochloro compounds react with sodium hydroxide to give the oxygen bridged complexes $[O\{MOCCo_3(CO)_9Cp_2\}_2]$ (ref. 129). An oxymethylidyne cluster $[(CO)_9Co_3COUCp_3]$ also results from the reaction of $Li[Co_3(CO)_{10}]$ with $[UClCp_3]$. This is the first uranium and cobalt containing organometallic compound. It has a μ_{eff} value of 3.0 B.M. (ref. 130). In contrast to these reactions $Na[Co(CO)_4]$ reacts with $[VCl_2Cp_2]$ to give the vanadylidyne cluster $[CpVCo_3(CO)_9]$ (ref. 131).

A variety of general methods is available for the synthesis of tetrahedral heteronuclear cobalt clusters of the type $[Co_3(CO)_9E(L)_n]$, (E = hetero element) and the topic has been reviewed (ref. 132). It is apparent that the size of E has a limiting effect on the existence of such compounds and no compounds have so far been prepared in which the covalent radius of E exceeds 1.30 Å. Elements such as Ir, Sn, Pb, Sb, or Bi do not fit into the tetrahedral Co_3E cluster unit and form open chain complexes $[E\{Co(CO)_4\}_n]$. The reaction of $Na[Co(CO)_4]$ with $PPhCl_2$ at -78°C gives the complex [99] in good yield. A solution of [99] evolves carbon monoxide gas at 60°C



[99]



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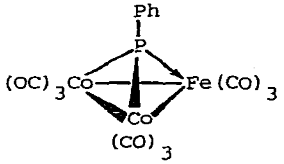
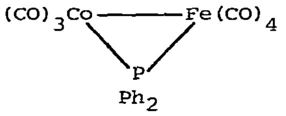
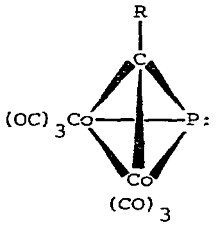


[101]

to give [100] which probably contains a cobalt-cobalt bond. The reaction of [99] with $[Fe_2(CO)_9]$ gives the new mixed metal cluster [101] (ref. 133). The reaction of PPh_2Cl with $Li[Co_3(CO)_{10}]$ or $Co_2(CO)_8$ gives the new complex $[Co_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$; the complex $[(CO)_9Co_3COPPh_2]$ is not formed. The known complex $[Co(CO)_3(\mu\text{-}PPh_2)]_2$ can also be isolated from this reaction. The intermediate species $[Co(CO)_4PPh_2]$ appears to be involved in these reactions and it may be trapped using $[Fe_2(CO)_9]$ as [102] (ref. 134). The reaction of $RCCl_2PCl_2$ (R = Me, Ph, $SiMe_3$) with $[Co_2(CO)_8]$ in tetrahydrofuran at -78°C gives the new complexes [103] as air sensitive red oils. These complexes may be viewed as the hexacarbonyl-dicobalt complexes of the respective phospha-acetylenes $RC\equiv P$. The complex (103; R = Me) reacts with $[M(CO)_5(THF)]$, (M = Cr, W) to give the phosphorus co-ordinated $M(CO)_5$ adducts and the complex (103; R = Ph) can be acetylated in the <u>para</u> position with $MeCOCl/AlCl_3$ (ref. 135). The arsenic analogues of [103], (R = Me, Ph) can similarly be prepared. These $[(RCAs)Co_2(CO)_6]$ complexes appear to be chemically quite robust. They are air stable and the phenyl derivative may be <u>para</u> acetylated. Attempted methylation of the arsenic atom in the phenyl derivative with methyl fluorosulphate and reactions with $[M(CO)_5(THF)]$, (M = Cr, W) were unsuccessful. Thermal decomposition of the $[(RCAs)Co_2(CO)_6]$ complexes does not appear to release the arsa-acetylenes $RC\equiv As$. Thus thermal decomposition of the $PhC\equiv As$ complex in the presence of tetraphenylcyclopentadienone did not give pentaphenylarsabenzene (ref. 136). The cobalt containing arsenic bridged polynuclear complexes [104] readily eliminate the sparingly soluble product $[CoAsMe_2(CO)_3]_x$ which effects introduction of the heterometal atom in place of the cobalt. The resulting green complexes [105] which are formed, are air-stable and a single crystal X-ray structure determination has been carried out on the complex



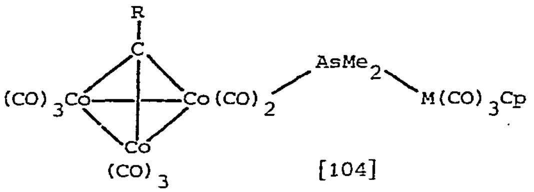
[102]



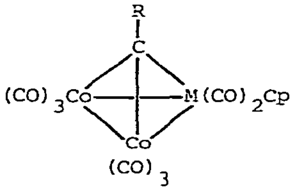
(R = Me, Ph, $SiMe_3$)

[103]

(105; M = Mo, R = Ph) (ref. 137).



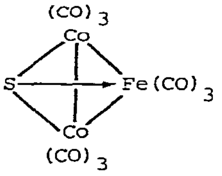
[104]



[M = Cr, Mo, W; R = H, Me, Ph]

[105]

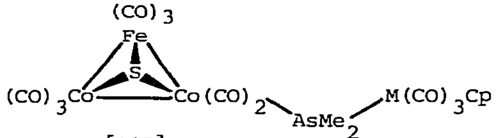
The organometallic Lewis base [106] is much less reactive than the isoelectronic compound $[PCo_3(CO)_9]$. However, the sulphur atom in [106] will displace THF from the complex $[Cr(CO)_5(THF)]$ to give an adduct which contains a sulphur atom linked to three different metal atoms (ref. 138). The kinetics of ^{14}CO exchange and CO replacement in [106] have been studied with a variety of ligands. The first [equation (1)] and the second [equation (2)] substitutions occur on the cobalt centres whereas substitution at iron only occurs at the third stage [equation (3)], (Scheme 33), (ref. 139). Elimination of $[CoAsMe_2(CO)_3]_x$ from the complexes [107] provides a route to the first μ_3-bridged trinuclear complexes [108] whose tetrahedral



[106]

$$[FeCo_2(CO)_9S] + L \longrightarrow [FeCo_2(CO)_8(L)S] + CO \qquad (1)$$
$$[FeCo_2(CO)_8(L)S] + L \longrightarrow [FeCo_2(CO)_7L_2S] + CO \qquad (2)$$
$$[FeCo_2(CO)_7L_2S] + L \longrightarrow [FeCo_2(CO)_6L_3S] + CO \qquad (3)$$

SCHEME 33



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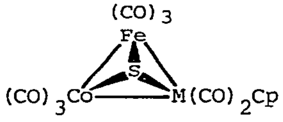
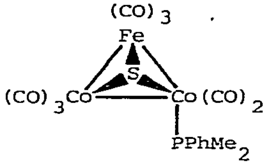


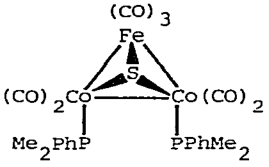
M = Cr, Mo, W

[108]

skeleton is made up of four different entities. The chirality of the clusters [108] can be demonstrated by the ^1H n.m.r. spectra of suitable phosphine derivatives with diastereotopic P-substituents. The starting complex [106] similarly becomes chiral on CO/PR_2R' exchange and the chiral dimethylphenylphosphine complexes [109]-[112] have been prepared (ref. 140).



[109]



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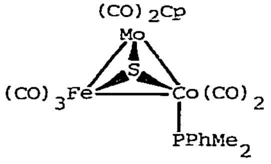
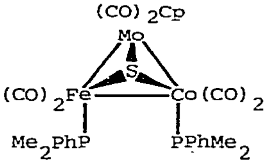


[111]



[112]

The tetrasubstituted carbonyltrifluorophosphine complex $[Co_2Rh_2(CO)_8(PF_3)_4]$ has been obtained by mixing hexane solutions of $[RhCl(PF_3)_2]_2$ and $[Co_2(CO)_8]$. This preparative route is similar to that described for $[Co_2Rh_2(CO)_{12}]$. Higher yields of $[Co_2Rh_2(CO)_8(PF_3)_4]$, however, can be obtained by treating $[RhCl(PF_3)_2]_2$ with $Tl[Co(CO)_4]$. The bis(trifluorophosphine) complex $[Co_2Rh_2(CO)_{10}(PF_3)_2]$ can be obtained by the reaction of $[RhCl(CO)(PF_3)]_2$ with $Tl[Co(CO)_4]$ and this bis compound can also be obtained by mixing pentane solutions of $[Co_2Rh_2(CO)_{12}]$ with $[Co_2Rh_2(CO)_8(PF_3)_4]$ at room temperature:

$$Co_2Rh_2(CO)_{12} + Co_2Rh_2(CO)_8(PF_3)_4 \longrightarrow 2Co_2Rh_2(CO)_{10}(PF_3)_2$$

The structures of these complexes are based on that of the parent complex $[Co_2Rh_2(CO)_{12}]$ in which some or all of the axial and equatorial carbonyls attached to the basal rhodium atoms have been replaced by PF_3 groups, the three bridging carbonyl groups in the basal plane being retained. Intermolecular ligand exchange is shown to occur between several tetranuclear cluster complexes. Although no evidence for $[Rh_4(PF_3)_{12}]$ was obtained, the action of $K[Rh(PF_3)_4]$ on $[RhCl(CO)_2]$ gives a product formulated as $[Rh_4(CO)_4(PF_3)_8]$. The iridium compound $[Co_2Ir_2(CO)_8(PF_3)_2]$ can be obtained from the reaction of $[IrCl(PF_3)_2]_2$ with $Tl[Co(CO)_4]$ (ref. 141). Variable temperature ^{13}C n.m.r. spectra of $[HFeCo_3(CO)_{12}]$ reveal that this molecule is stereochemically non-rigid only in the Co_3 unit. In derivatives in which one or more CO's are substituted with a group V ligand the cobalt bonded carbonyls are rigid (ref. 71). The ^{13}C n.m.r. spectrum of $[RhCo_3(CO)_{12}]$ at -85°C is consistent with a structure in which the rhodium atom occupies a basal position of the $[Co_4(CO)_{12}]$ structure (ref. 70). The series of complexes $[HFeCo_3(CO)_{12-x}\{P(OMe)_3\}_x]$, (x = 1, 2, 3, 4) have been prepared from $[HFeCo_3(CO)_{12}]$ and $P(OMe)_3$ under a variety of conditions. A single crystal X-ray study on the tris-substituted complex $[HFeCo_3(CO)_9\{P(OMe)_3\}_3]$ at -139°C shows that the four metal atoms are at the corners of a tetrahedron and that six of the nine carbonyl groups are terminally bound, three to iron and one to each cobalt. The other three carbonyl groups form symmetric Co-C-Co bridges. The hydrogen atom is located outside the metal cluster (ref. 142) and this structure has been confirmed by a neutron diffraction study, the hydrogen atom being located 0.978(3)Å from the Co_3 face (ref. 143, 144). The cluster $[H_3CoOs_3(CO)_{12}]$ has been prepared from the reaction of $[H_2Os_3(CO)_{10}]$ with $[Co_4(CO)_{12}]$. A single crystal X-ray study reveals a tetrahedral arrangement of the four metal atoms with twelve terminally bound CO ligands. It appears that the three hydrogen atoms edge-bridge the Os-Os bonds (ref. 145).

The reaction of a solution of $[Rh(acac)(CO)_2]$ and alkali carboxylates in a glyme solvent with H_2S or SO_2 under a 300 atm. pressure of hydrogen and carbon monoxide at 140-160°C generates the anionic species $[Rh_{17}(S)_2(CO)_{32}]^{3-}$. The structure consists of 16 rhodium atoms distributed at the corners of four stacked parallel squares and of a S-Rh-S group located inside the cluster. Sixteen carbonyl ligands are terminally bonded to an equal number of rhodium atoms, there are eight bridging carbonyls on the basal planes located along the edges, while the other bridging ligands are along the rhodium-rhodium bonds connecting the two internal planes. The anion exhibits Brønsted acid-base behaviour according to the equation:

$$[Rh_{17}(S)_2(CO)_{32}]^{3-} \quad \underset{2OH^-}{\overset{2H^+}{\rightleftharpoons}} \quad [Rh_{17}(S)_2(CO)_{32}H_2]^-$$

^{13}C n.m.r. spectral studies indicate that the solid state structure is retained in solution and the anion is able to activate hydrogen at ambient conditions (ref. 146).

Rhodium carbonyl species are known to react with $CHCl_3$ or CCl_4 according to the equation:

$$6[Rh(CO)_4] + CCl_4 \xrightarrow[25^{\circ}C]{Pr^{i}OH} [Rh_6C(CO)_{15}]^{2-} + 4Cl^{-} + 9CO$$

Oxidation of $[Rh_6C(CO)_{15}]^{2-}$ leads to other species such as $[Rh_8(CO)_{19}]^{2-}$ and $[Rh_{15}C_2(CO)_{28}]^{-}$. This last monoanion is unstable in solution and slowly gives a new carbide species $[Rh_{12}C_2(CO)_{25}]$. This complex is asymmetric and the rhodium atom cluster is an irregular closed polyhedron which can be described in terms of layer packing of atoms. The C_2 unit occupies an irregular cavity. There are fourteen terminal carbonyls, ten edge-bridging carbonyls and one face-bridging carbonyl (ref. 147). The condensation reaction

$$2[Co_6C(CO)_{15}]^{2-} + [Co_4(CO)_{12}] \xrightarrow[60^{\circ}C]{Pr_2^{i}O} 2[Co_8C(CO)_{18}]^{2-} + 6CO$$

leads to the anion $[Co_8C(CO)_{18}]^{2-}$ which has also been characterised by a crystallographic study. The anion contains a deformed tetragonal antiprism of cobalt atoms, the carbide carbon occupying the centre of the cluster. There are eight terminal carbonyl ligands, one per cobalt atom, and the other ten carbonyls range from partially bent to symmetrically edge bridging ligands (ref. 148). The dodecametal carbonyl dianions of platinum and rhodium react according to the equation:

$$[Pt_{12}(CO)_{24}]^{2-} + 5[Rh_{12}(CO)_{30}]^{2-} \xrightarrow[\text{THF, } 25^{\circ}C]{\text{CO, 1 atm.}} 12[Rh_5Pt(CO)_{15}]^{-}$$

The same rhodium-platinum species can be obtained on a larger scale by reducing a mixture of $Na_2PtCl_6.6H_2O$ and $RhCl_3.3H_2O$ according to the equation:

$$\begin{array}{c} 5RhCl_3 + [PtCl_6]^{2-} + 2OH^- + 25CO \\ \Big\downarrow \begin{array}{l} CO,\ 1\ atm. \\ MeOH,\ Na_2CO_3,\ 25^{\circ}C \end{array} \\ [Rh_5Pt(CO)_{15}]^- + 10CO_2 + 21Cl^- + H_2O \end{array}$$

The structure of $[Rh_5Pt(CO)_{11}(\mu_3\text{-}CO)_4]^-$ is structurally related to $[Rh_6(CO)_{12}(\mu_3\text{-}CO_4)]$, (one $Rh(CO)_2$ being replaced by a Pt(CO) group), both in solution and in the solid state. A further reduced mixed anion, $[Rh_2Pt(CO)_x]_n{}^-$ also exists (ref. 149).

(c) Metal oxidation state (I), (II), and (III) compounds

Although the co-ordinatively unsaturated species $[CoH(CO)_3]$ is proposed as an intermediate in the hydroformylation reaction there is no spectroscopic evidence for hydridotricarbonylcobalt or its olefin complex. However, the spectra of $[CoH(CO)_4]$ in a low temperature matrix show a weak band at 2018 cm^{-1} which grows upon irradiation and additional bands appear at 2025 and 485 cm^{-1}. These three bands are assigned to $[CoH(CO)_3]$. The reaction of the ligand $P(CF_3)_2(OCH_2CH_2Cl)$, L, with $[CoH(PF_3)_4]$ affords $[CoH(PF_3)_3L]$ as a mixture of isomers (ref. 151). The insertion of carbon dioxide into the cobalt-hydrogen bonds of $[CoH_3(PPh_3)_3]$ and $[CoH(N_2)(PPh_3)_3]$ has previously been reported. Further studies have now been described on the reactions of carbon dioxide with $[CoHL_2]$, ($L = Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH=CHPPh_2$) and the formation of CO_2 carbonate complexes has been postulated, (Scheme 34) (ref. 152).

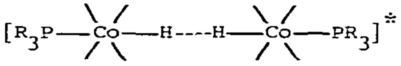
$$\begin{array}{l} CoHL_2 + CO_2 \rightleftharpoons CoH(CO_2)L_2 \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad H_2 + LO_2 + Co\text{-}species \\ 2CO_2 + 2e^- \longrightarrow CO + CO_3{}^{2-} \end{array}$$

SCHEME 34

A study of the reactions of diphenylphosphine with cobalt(II) salts of the type CoY_2 and CoXY ($Y = ClO_4{}^-$, $BF_4{}^-$, $X = Br^-$, I^-, NCS^-, CN^-) has led to the isolation of a new series of hydrido complexes of cobalt(III) of the type <u>trans</u>-$[CoHX(PHPh_2)_4]Y$ and the unusual cobalt(II) complexes $[Co(PPh_2)(PHPh_2)_3]Y$. A yellow diamagnetic complex, $[CoBr(PHPh_2)_4]_2Br_2$, formulated as a binuclear species, previously isolated as one of the products from the reaction of diphenylphosphine with methanolic solutions of cobalt(II) bromide, has been shown to be the hydrido derivative $[CoHBr(PHPh_2)_4]Br$. The $[Co(PPh_2)(PHPh_2)_3]Y$ complexes react with H_2 to give <u>cis</u>-$[CoH_2(PHPh_2)_4]Y$. The formation of these <u>cis</u>-dihydro complexes from the reactions of isopropanol solutions of $CoY_2.6H_2O$ and $PHPh_2$ in the presence of H_2 appears to proceed via oxidative addition of hydrogen to $[Co(phosphine)_4]^+$ intermediates (ref. 153). The forward rate of the reaction

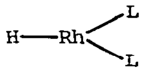
$$2[CoH(dmgH)_2PBu_3{}^n] \longrightarrow H_2 + 2[Co(dmgH)_2PBu_3{}^n]$$

has been determined in methanol-water solutions as a function of perchloric acid concentration, 0.003-0.10M. The reaction proceeds by two parallel pathways, with respective first-order and second-order dependencies upon the concentration of the hydridocobaloxime. Parallel heterolytic and homolytic cleavage of the cobalt-hydrogen bond appears to be involved. The rate-limiting step in the second-order path appears to involve an activated complex in which the bond between the two hydrogen atoms is being formed directly as in [113] (ref. 154).



[113]

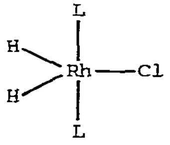
Hydridotris(triphenylphosphine)rhodium(I), $[RhH(PPh_3)_3]$ is an olefin isomerisation catalyst and is about forty times more active than $[RhCl(PPh_3)_3]$ as an ethylene hydrogenation catalyst. The structure of $[RhH(PPh_3)_3].Me_2NH.THF$ has been determined by single crystal X-ray methods. The dimethylamine and THF molecules are not co-ordinated to the rhodium and the co-ordination about the metal is nearly planar with the mutually trans phosphine ligands displaced toward the presumed position of the hydride ligand. There are no ortho hydrogen-rhodium distances shorter than 3.01 Å. The ^{31}P n.m.r. spectrum of $[RhH(PPh_3)_3]$ at -86°C indicates a C_s or C_{2v} structure at -86°C and shows that at -13°C there is a rapid intramolecular re-arrangement of the phosphine ligands which possibly occurs via a tetrahedral intermediate. $\Delta G^{\ddagger}$ for this re-arrangement of the hydride is smaller than that observed for $[RhMe(PPh_3)_3]$ and $[RhCl(PPh_3)_3]$. At the most there is only 0.4% of $[RhH(PPh_3)_2]$ present in solutions of $[RhH(PPh_3)_3]$ at 30°C. It seems likely that $[RhMe(PPh_3)_3]$ is a square planar complex rather than a tetrahedral one as previously suggested (ref. 155). The rhodium(I) hydrido dinitrogen complex trans-$[RhH(N_2)(PBu_3{}^t)_2]$ and trans-$[HL_2Rh\text{-}N{\equiv}N\text{-}RhL_2H]$, (L = tricyclohexylphosphine) dissociate dinitrogen to give novel three-co-ordinate complexes [114]. The dinitrogen complexes are readily prepared by reducing $RhCl_3.xH_2O$ with Na-Hg in the presence of the appropriate phosphine. However, by



$L = PBu_3{}^t$ or PCy_3

[114]

using less bulky phosphines PPr^i_3 and PEt_3 the four- and five-co-ordinate complexes $[RhHL_n]$ ($n = 3$, $L = PPr^i_3$; $n = 4$, $L = PEt_3$) are formed. The three-co-ordinate hydrido complexes as well as their dinitrogen precursors are efficient catalysts for the hydrogenation of unsaturated organic compounds and for H-O exchange of aromatic compounds with D_2O which occurs via water activation (ref. 156). Hydrogenolysis of triphenylphosphine co-ordinated to rhodium(I) occurs in reactions of $[RhCl(PPh_3)_3]$ and $[RhH(PPh_3)_4]$ with amines, alcohols, hydroaromatic compounds, and dioxane. Thus, for example, about 8 or 10 mols of benzene are formed from a mol of $[RhCl(PPh_3)_3]$ or $[RhH(PPh_3)_4]$ respectively when these complexes were heated at 100°C for six hours in pyrrolidine. In the reaction of $[RhCl(PPh_3)_3]$ with pyrrolidine, $PHPh_2$ and biphenyl were also detected together with a bright yellow complex tentatively identified as $[RhCl(PPh_3)_2(\text{pyrrolidine})]$. This complex also gave benzene on being heated in inert solvents (ref. 157). In an argon atmosphere a triphenylphosphine ligand in $[RhCl(PPh_3)_3]$ can be displaced by (+)-α-methylbenzylamine, (L). In the presence of hydrogen $[RhH_2Cl(PPh_3)_2L]$ is formed. These complexes can induce asymmetric hydrogenation of $PhCH=C(NHAc)CO_2R$, (R = H, Me) (ref. 158). The cationic rhodium complex, $[Rh(\text{norbornadiene})(PPh_3)(\text{dios})]^+$, [(-) dios is the 2R, 3R-bis(methylsulphinyl)butane analogue of (-) diop, (-) diop is 2R, 3R (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] is an active hydrogenation catalyst but no asymmetry is observed in the products (ref. 159). The species $[RhH_2Cl(PPh_3)_2]$ or $[RhH_2Cl(PPh_3)_2(\text{solvent})]$ is an important intermediate in catalytic hydrogenations involving $[RhCl(PPh_3)]$. Co-ordinatively unsaturated complexes of the type $[RhH_2Cl(PR_3)_2]$ stabilised with bulky phosphines are known and an X-ray analysis of one of these complexes [115] has now been reported. The nearly eclipsed conformation of the P-C bonds in the PBu^t_3 ligands appears to be due to steric interaction between the t-butyl groups and the Cl atom. The most remarkable feature of the structure is the very short Rh-H distance, [1.36(8) Å], which is the shortest metal-hydride distance found by X-ray studies. The short Rh-H distance is reflected in the high values of ν(Rh-H), (2220, 2205 cm^{-1}) as compared to the values of ν(Rh-H) found for $[RhH_2Cl(PCy_3)_2]$, (2165, 2120 cm^{-1}) and $[RhH_2Cl(PPh_3)_2]$, (2066, 2051 cm^{-1}). These ν(Rh-H) values parallel the increase in cone angle of the phosphines and not their electron donating properties as is usually observed for phosphine hydride complexes. This strong Rh-H bonding and steric crowding in [115] reduce the catalytic

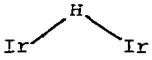


$L = PBu^t_3$

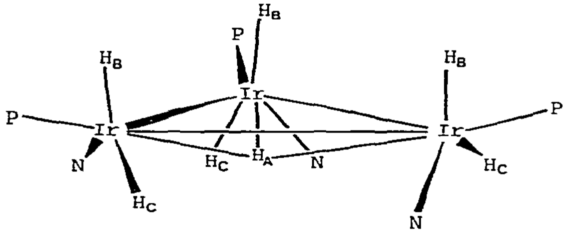
[115]

activity of [115] for hydrogenation (ref. 160). The iridium hydrides $[IrH_3(PPh_3)_3]$, $[IrH_2Cl(PPh_3)_3]$, and $[IrHCl_2(PPh_3)_3]$ reduce Me_3COH at 70°C under 100 atm. of hydrogen to give Me_3CH (ref. 161).

The dinuclear iridium(I) complexes $[Ir(\mu\text{-}SBu^t)(CO)(PR_3)_2]$, (R = Me, NMe_2, Ph, OMe) are known to activate hydrogen to give the symmetric dinuclear complexes of iridium (II), $[IrH(\mu\text{-}SBu^t)(CO)(PR_3)]_2$. The existence of iridium-iridium bonds in these complexes has prompted an investigation of the protonation of these complexes with perchloric acid. These reactions lead to complexes of the type $[\{IrH(\mu\text{-}SBu^t)(CO)(PR_3)\}_2H]ClO_4$ which contain a two-electron three-centre bent IrHIr bond [116] (ref. 162). A tri-co-ordinated hydrogen has been found in the complex $[\{IrH_2(PCy_3)py\}_3(\mu_3\text{-}H)][PF_6]_2$ [117]. This and related complexes can be isolated from solutions formed by the action of hydrogen on $[Ir(cod)(PR_3)(py)]PF_6$, ($PR_3 = PCy_3$, PPr^i_3). These trinuclear complexes do not exhibit fluxional behaviour (ref. 163). A series of cationic iridium hydride complexes of the type $[IrHL(P\text{-}P)_2][BF_4]_2$, (P-P = $Ph_2PCH_2CH_2PPh_2$; L = Me_2CO, py, MeCN, Et_3N, $PhMe_2N$, CO, PF_3, or Me_2NPF_2; P-P = $Ph_2P(CH_2)_3PPh_2$; L = py) have been prepared and their stereochemistry in solution determined by n.m.r. spectroscopy. The stereochemistry of the complexes $[IrHL(Ph_2PCH_2CH_2PPh_2)_2][BF_4]_2$ appears to be governed initially by electronic effects, ligands with a high <u>trans</u>-effect adopting a <u>trans</u>- H-L geometry. The observation that $[IrH(py)(Ph_2PCH_2CH_2CH_2PPh_2)][BF_4]_2$ has a static <u>cis</u>-structure while $[IrH(py)(Ph_2PCH_2CH_2PPh_2)][BF_4]_2$ is stereochemically non-rigid in solution is a further illustration of the fact that rearrangement barriers decrease with decreasing ring size (ref. 164).

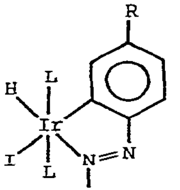


[116]



[117]

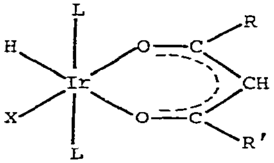
Investigations of the reactions of $[IrH_3(PPh_3)_3]$ and $[IrH(CO)(PPh_3)_3]$ with aryldiazonium salts have been reported. A single crystal X-ray study on one of the complexes isolated from these studies has been carried out and formulated as shown in [118] (ref. 165, 166). β-Diketones react with <u>mer</u>-$[IrH_3(PPh_3)_3]$ in the presence of



$L = PPh_3$; $R = OMe$

[118]

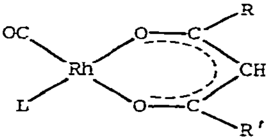
triethylamine in refluxing 2-methoxyethanol to give the <u>cis</u>-dihydro complexes [119]. $[IrCl_2H(PPh_3)_3]$ (<u>trans</u>-chlorides) reacts with equimolar quantities of acetylacetone



[119]

$L = PPh_3$
($X = H$; $R = R' = Me$, CF_3; $R = Me$, $R' = CF_3$)
($X = Cl$; $R = R' = Me$)

and base (triethylamine) in boiling 2-methoxyethanol to give (119; $X = Cl$, $R = R' = Me$). In the presence of a slight excess of base, small amounts of $[IrClH_2(PPh_3)_3]$ form, and if a large excess of base and acetylacetone is employed the major product is $[IrH_2(acac)(PPh_3)_2]$ (ref. 167). The crystal structures of the rhodium(I) β-diketonato complexes [120] have been determined (ref. 168-170). The triphenylphosphine

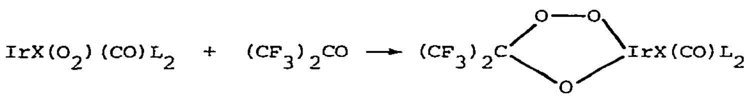


[120]

($L = PPh_3$; $R = CF_3$, $R' =$ thenoyl; $R = R' = Me$)
($L = CO$; $R = CF_3$, $R' = Ph$)

ligand exerts a stronger <u>trans</u>-influence than carbon monoxide in these compounds. Some new oximato complexes of rhodium(I), $[Rh(SOX)(CO)_2]$, $[Rh(BNX)(CO)_2]$, $[Rh(FOX)(CO)_2]$, $[Rh(CO)(PPh_3)(SOX)]$, $[Rh(CO)(PPh_3)(BNX)]$, (SOX = salicyldoximato, BNX = α-benzoinoximato, FOX = α-furildioximato) have been reported (ref. 171).

The electronic structures of the side-bonded dioxygen compounds $[MX(O_2)(CO)(PH_3)_2]$ ($M = Rh$, Ir; $X = Cl$, I) (<u>trans</u>-phosphines) have been investigated using a CNDO-type MO method. These calculations show that the metal ion has a formal charge of 3+ and that the dioxygen ligand donates about 0.1 electron from its $1\sigma_y$ orbital to the metal and about 0.2 electron from its π_u orbital and accepts 1.0-1.4 electrons from the metal $d\pi$ orbital into its π_y orbital. The dioxygen ligand can be considered to form a three-membered ring with the metal (ref. 172). Treatment of the complexes [121]



$L = PPh_3$; $X = Cl, Br, I$
$X = Cl$; $L = AsPh_3$, $PMePh_2$,
$P(C_6H_4Me\text{-}\underline{p})_3$, $P(C_6H_4OMe\text{-}\underline{p})_3$

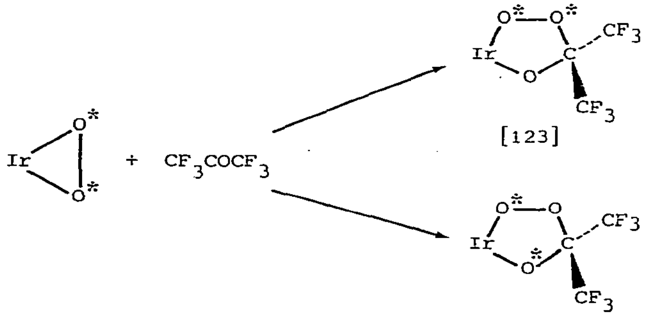
[121]

[122]

with hexafluoroacetone affords the iridium(III) ozonide complexes [122]. The reactions follow the rate law:

$$rate = k[IrX(O_2)(CO)L_2][CF_3COCF_3]$$

When $L = PPh_3$, the rate of reaction follows the sequence $Cl > Br > I$ and for the compounds with $X = Cl$, the relative rates for changing L are $AsPh_3 \sim PMePh_2 > PPh_3$. The mechanism of the reactions is considered to involve direct nucleophilic attack of the co-ordinated dioxygen on the hexafluoroacetone _via_ an ionic transition state. An $^{18}O_2$ labelling study suggests that [123] is the preferred structure for the labelled adduct (ref. 173). Treatment of the complexes _trans_-$[RhCl(CO)P_2]$ with dioxygen in



[123]

refluxing benzene, toluene, or dichloromethane affords the dark-brown diamagnetic products [124] according to the equation:

$$4RhCl(CO)P_2 + 5O_2 \longrightarrow Rh_4Cl_4(O_2)_2(CO)_4P_2 + 6P{=}O$$

[124]

$P = PPh_3$, PPh_2OBu^i,
$PPhEt_2$, PEt_3,
poly(methallyl)diphenylphosphinite

The proposed structures for the complexes [124] contain bridging chloride and peroxo (or superoxo) ligands. The oxidation of PPh_2OBu^i is shown to proceed mainly via a radical pathway (ref. 174). The stoichiometries of the reactions of the complexes [124] with both dihydrogen and carbon monoxide have confirmed the formulation of the tetranuclear complexes [124]. The stoichiometry of the reactions with dihydrogen is:

$$Rh_4Cl_4(O_2)_2(CO)_4P_2 + 6P + 2H_2 \longrightarrow 4RhCl(CO)P_2 + 2\text{"}H_2O_2\text{"}$$

$$2RhCl(CO)P_2 + 2\text{"}H_2O_2\text{"} \longrightarrow [RhClP_2]_2 + 2H_2O + 2CO_2$$

while the stoichiometry for reactions with carbon monoxide is:

$$\begin{array}{c} Rh_4Cl_4(O_2)_2(CO)_4P_2 \;+\; 7CO \\ \Big\downarrow \; CH_2Cl_2 \\ \textit{cis}\text{-}RhCl(CO)_2P + 4CO_2 + \tfrac{1}{2}[RhCl(CO)_2]_2 + Rh_2Cl_2(CO)_3P \end{array}$$

The complexes [124] are effective catalysts for the hydrogenation and hydroformylation of olefinic substrates (ref. 175).

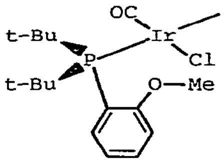
A study of the reaction of sulphur dioxide with $[RhCl_2(CO)_2]^-$ reveals an initial 1:1 stoichiometry:

$$[RhCl_2(CO)_2]^- \;+\; SO_2 \longrightarrow [RhCl_2(CO)_2(SO_2)]^-$$

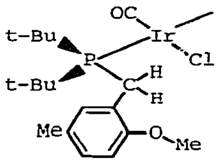
However, after 48 hours a 2:1 stoichiometry is observed (ref. 176).

$$[RhCl_2(CO)_2]^- \;+\; 2SO_2 \longrightarrow [RhCl_2(CO)_2(SO_2)_2]^-$$

The reactions of bulky phosphines with various rhodium and iridium complexes continue to attract attention. Thus reactions of $[Rh_2Cl_2(CO)_4]$ with the phosphines $L = PBu_2{}^tMMe_3$ (M = Si, Ge, or Sn) or $PBu_2{}^tGeClMe_2$ afford the complexes *trans*-$[RhCl(CO)L_2]$. However, the analogous complexes with $PBu^t(MMe_3)_2$ could only be detected at -10°C and the phosphines $P(MMe_3)_3$ react with $[Rh_2Cl_2(CO)_4]$ even at -78°C with cleavage of the phosphorus-M bond (ref. 177). Cleavage of a phosphorus-carbon bond of $PBu_3{}^t$ has also been shown to occur when $PBu_3{}^t$ is heated in dimethylformamide with either hydrated rhodium or iridium trichloride. These novel reactions lead to the secondary phosphine complexes *trans*-$[MCl(CO)(PHBu_2{}^t)_2]$ together with evolution of $CH_2=CMe_2$. ^1H n.m.r. indicate that the formation of these complexes occurs *via* intermediate hydrido rhodium(III) or iridium(III) complexes, e.g. $[RhHCl_2(PBu_3{}^t)_x(DMF)_y]$ (six-co-ordinate), $[RhHCl_2(PBu_3{}^t)_x(DMF)_y]$ (five-co-ordinate), $[IrH_2Cl(PBu_3{}^t)_2(DMF)]$ (ref. 178). In contrast with the behaviour of $P(C_6H_4OMe\text{-}2)Bu_2{}^t$ which demethylates on treatment with various chloro-rhodium and -iridium species, the new phosphine $P(CH_2C_6H_3\text{-5-Me-2-OMe})Bu_2^t$ L, does not undergo O-demethylation. This phosphine L gives the complexes trans-$[RhCl_2L_2]$, $[RhHClL_2]$, trans-$[RhCl(CO)L_2]$, trans-$[Rh_2Cl_2(CO)_2L_2]$, $[IrH_2ClL_2]$, $[IrH_2Cl(CO)L_2]$, $IrH_2Cl(CNMe)L_2$, and trans-$[IrCl(CO)L_2]$. The different reactivity of L from the 2-anisylphosphine can be explained in terms of steric effects. Thus whereas in the case of $P(C_6H_4OMe\text{-}2)Bu_2^t$ complexed to an OC-Ir-Cl species, restricted rotation around the Ir-P and aryl-P bonds will lead to a preferred conformation [125] in which the ether oxygen is held in close proximity to the metal-chlorine bond, the methylene group in L [126] allows the 2-methoxyphenol group to point away from the metal (ref. 179).

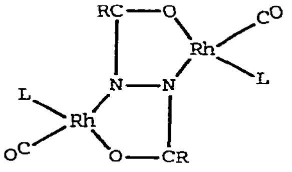


[125]



[126]

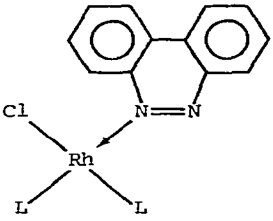
The reaction of 1,2-dibenzoylhydrazine with mer-$[RhCl_3L_3]$ ($L = PPh_3$, PMe_2Ph) yields a dimeric product which is considered to have the structure [127]. A crystal structure analysis of the related dicarbonyl complex (127; L = CO) has confirmed the novel tetradentate bridging configuration. The molecules exhibit one-dimensional stacking in the crystal, with Rh-Rh contacts of 3.347(5) Å between adjacent dimers



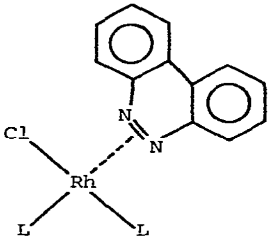
R = Ph

[127]

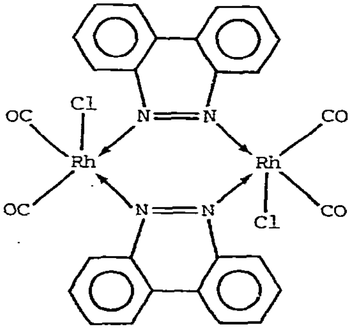
(ref. 180). Benzo[c]cinnoline reacts readily with $[Rh_2Cl_2(CO)_4]$ to give a yellow crystalline material which can be formulated as either (128a; L = CO) or (128b; L = CO) and an insoluble red powder which is considered to have the structure [129]. The reactions of benzo[c]cinnoline with $[Rh_2Cl_2(PF_3)_4]$ and $[RhCl(PPh_3)_3]$ afford the complexes $[RhClL_2$(benzo[c]cinnoline)] while reaction of benzo[c]cinnoline with hydrated rhodium trichloride gives the insoluble complex $[RhCl_3$(benzo[c]cinnoline)]. The reaction of $[RhCl(PF_3)(PPh_3)_2]$ with $Me_3SiN=NPh$ affords $[RhCl(PF_2N=NPh)(PPh_3)_2]$ (ref. 181). The cis-dicarbonyl compound cis-$[RhCl(CO)_2L]$, (L = 1-methyl-2(2,4-dinitrobenzyl)benzimidazole) has been prepared by addition of the ligand L in dimethylformamide to a carbonylated solution of rhodium(I) prepared from $RhCl_3$ xH_2O



[128a]



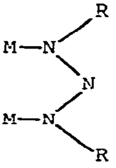
[128b]



[129]

and dimethylformamide. cis-[RhCl(CO)L′], [L′ = 2-(2,4-dinitrobenzyl)pyridine] has been similarly prepared (ref. 182).

The triazenido ligand can function as a bridging group between two metal centres [130], a bidentate, three-electron donor [131], or a monodentate, one-electron donor [132]. The conjugate base of benzotriazole [133] is an interesting triazenido ligand because of the conformational rigidity imposed by the fused benzene ring and the anticipated delocalisation energy associated with the cyclic anionic system. Reaction of the thallium salt of [133] with trans-[IrCl(CO)(PPh_3)$_2$], without prior removal of the chloro ligand, affords a violet complex [134] which can be formulated as either [134a] or [134b]. In methanol this complex rapidly forms a yellow solution



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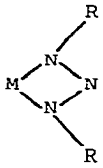
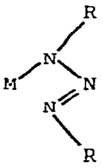
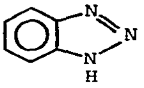


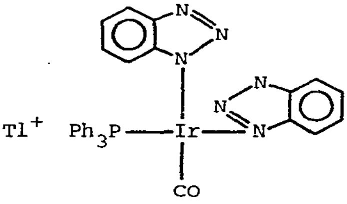
[131]



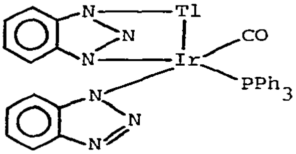
[132]



[133]



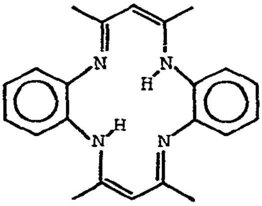
[134a]



[134b]

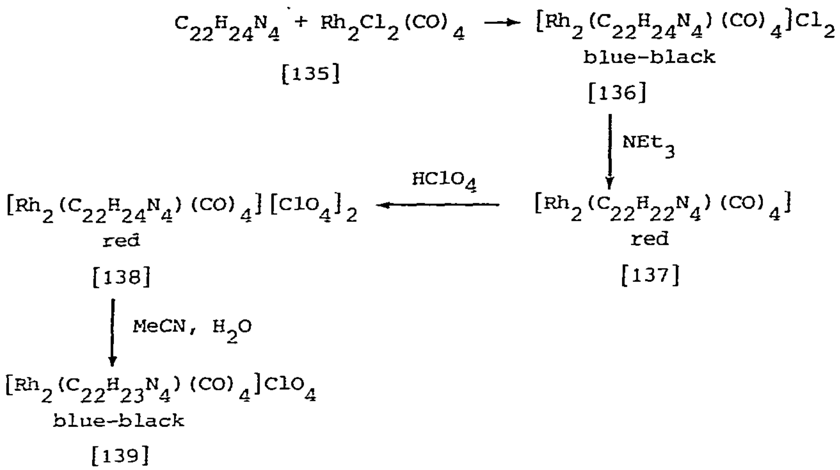
from which the complex trans-[Ir(BTA)(CO)$(PPh_3)_2$], (BTA = benzotriazenido) can be isolated. A single crystal X-ray structure determination of this complex reveals that the BTA ligand is co-ordinated to the iridium atom through one nitrogen atom since there appears to be insufficient room to enable the benzotriazenido ligand to interact with the iridium in a π-allylic fashion. Thallium benzotriazenide reacts with [Ir(CO)(acetone)$(PPh_3)_2$][PF_6] to yield the tetramer [Ir(BTA)(CO)$(PPh_3)_2]_4$ and a similar reaction with trans-[RhCl(CO)$(PPh_3)_2$] gives the hexamer [Rh(BTA)(CO)$(PPh_3)_2]_6$ (ref. 183).

The interest in polynuclear metal complexes and their potential role in catalysis continues to prompt the syntheses of complexes which contain two or more metal centres in close proximity to enable co-operative interactions of metal centres with substrates. The reaction of the macrocyclic ligand [135] with [$Rh_2Cl_2(CO)_4$] gives a

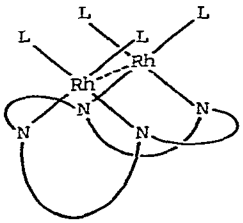


[135]

blue-black complex [136] which on treatment with base affords [137] (Scheme 35). An X-ray structure analysis of [137] reveals that the ligand has an extremely warped conformation and differs dramatically from the free ligand and its metal complexes which have been structurally characterised previously. The Rh-Rh separation of

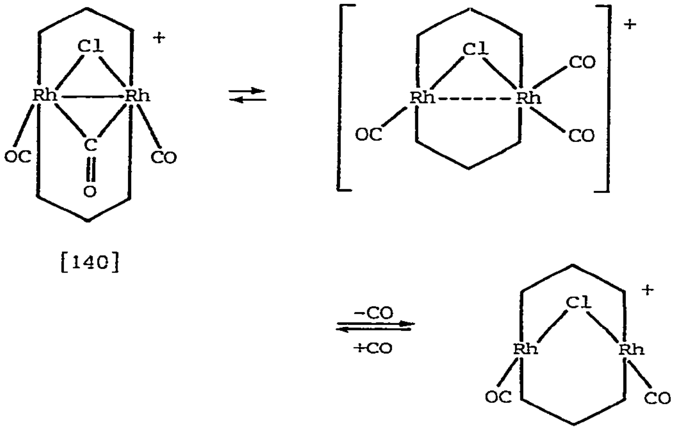


SCHEME 35



[137]

3.086 Å is indicative of a weak bonding interaction. Monorhodium macrocyclic ligand species are not isolated when a large excess of the ligand [135] is employed and the co-ordinated carbon monoxide is not displaced by triphenylphosphine. Reactions with alkyl halides leads to alkylation at the methine carbon of the 2,4-pentanediiminato rings rather than oxidative-addition at the rhodium(I) centres. Similarly, protonation occurs at the methine carbon atom and not at the rhodium as indicated by an X-ray structure analysis of [139] (ref. 184). Successive treatment of an ethanolic solution of $[RhCl_2(CO)_2]^-$ with equimolar quantities of $Ph_2PCH_2PPh_2$ (DPM) in chloroform and $NaBPh_4$ in ethanol under an atmosphere of carbon monoxide affords the "A-frame" type complex [140], isolated as its tetraphenylborate salt, and characterised by an X-ray study. Complex [140] is interesting in that it provides an example of a system which can reversibly bind carbon monoxide at a bridging position. Thus passage of argon or dinitrogen through a solution of [140] affords the orange complex [141] which on treatment with carbon monoxide regenerates [140]. Exchange experiments with ^{13}CO suggest that terminal carbonyl ligands in both [140] and [141] are also readily exchanged and it is apparent that the interconversion [140] ⇌ [141] occurs via a bridge-terminal exchange. The iridium complex $[Ir_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DPM)_2]$-



[140]

[141]

$[IrCl_2(CO)_2]$ has also been obtained (ref. 185). Treatment of [141] with sulphur dioxide gives the bridged SO_2 complex [142] which on prolonged treatment with sulphur

$$[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+ \underset{N_2}{\overset{SO_2}{\rightleftharpoons}} [Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}Cl)(DPM)_2]^+$$

[141] [142]

$$\downarrow$$

$$[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2] + [?]$$

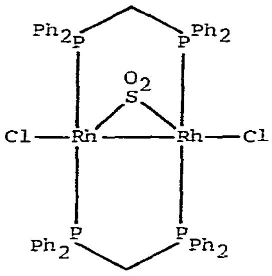
[143]

$$\downarrow CO$$

$$\underline{cis}\text{-}[Rh_2Cl_2(CO)_2(DPM)_2] \underset{-CO}{\overset{CO}{\rightleftharpoons}} \underline{cis}\text{-}[Rh_2Cl_2(CO)_2(\mu\text{-}CO)(DPM)_2]$$

[145] [144]

dioxide affords [143] which has been characterised by an X-ray study. Reaction of [143] with carbon monoxide forms the novel species [144] which reversibly loses carbon monoxide in solution to give [145]. The analogous trans-dicarbonyl species, trans-$[Rh_2Cl_2(CO)_2(DPM)_2]$ does not react with carbon monoxide under the same conditions as cis-$[Rh_2Cl_2(CO)_2(DPM)_2]$, [145] (ref. 186). An X-ray study of $[RhCl(CO)(P\text{-}P)]$ (P-P = $Ph_2PCH_2C_8H_{10}CH_2PPh_2$ = 2,11-bis(diphenylphosphinomethyl)benzo[c]-

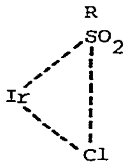


[143]

phenanthrene) reveals that the metal atom is four co-ordinate with a slightly distorted square-planar configuration and that the ligand P-P spans trans-positions (ref. 187).

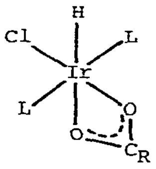
The ^{19}F n.m.r. chemical shifts of meta and para fluorophenyl phosphines co-ordinated to a range of group VIII transition metal complexes have been measured. It appears that the acceptor or donor properties of a metal ion containing species are determined more by the nature of the ligands present than by the formal oxidation state of the metal (ref. 188). Excitation polarisation of the luminescent complexes $[M(P=P)_2]Cl$ and $[M(P-P)_2]Cl$ (M = Rh(I), Ir(I); P = P is cis-$Ph_2PCH=CHPPh_2$, P-P is $Ph_2PCH_2CH_2PPh_2$) have been measured (ref. 189). Infrared studies indicate that phosphine complexes are formed upon treatment of $[Rh_2Cl_2(CO)_4]$ with β-diphenylphosphenolethylphenylphosphine and chloromethylated divinylbenzene-styrene copolymers (ref. 190).

The kinetics of the oxidative addition of sulphonyl chlorides RSO_2Cl to trans-$[IrX(CO)L_2]$ show that the rates of reaction increase with increasing basicity of the ligand L and X in the order $P(OPh)_3 < PPh_3 < P(p\text{-}MeC_6H_4)_3 < PMePh_2$, $Cl < Br < I$. The dependence of the rate on R in the sulphonyl chlorides is $p\text{-}ClC_6H_4 < Ph < p\text{-}MeC_6H_4 < Pr^n$. The activation parameters for the reaction of trans-$[IrCl(CO)(PPh_3)_2]$ with $PhSO_2Cl$ in benzene are $\Delta H^{\ddagger} = 16$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14$ cal deg^{-1} mol^{-1}. This reaction is not inhibited by the radical scavengers duroquinone or galvinoxyl and not promoted by benzoyl peroxide and it is thus not likely that the reaction of RSO_2Cl with trans-$[IrCl(CO)(PPh_3)_2]$ proceeds via a free-radical mechanism. The transition state [146] appears to be involved in these reactions (ref. 191). Simple carboxylic acids have been shown to oxidatively add to iridium(I) complexes of the type trans-$[IrX(CO)L_2]$ (L = PEt_3, PMe_2Ph, or PPh_3; X = Cl, Br, or I) to give iridium (III) complexes $[IrXH(O_2CR)(CO)L_2]$ (R = H, Me, CF_3, Ph, or 1-naphthyl) corresponding to formal cis and/or trans addition depending on the acid. In solution these complexes undergo anion exchange to give, at equilibrium, two additional species



[146]

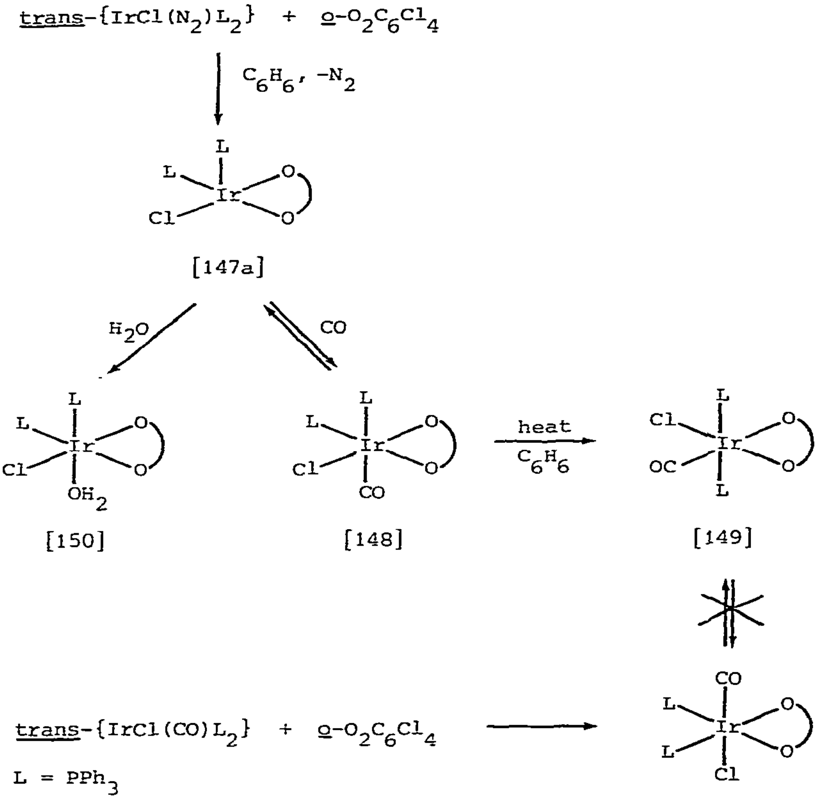
$[IrX_2H(CO)L_2]$ and $[IrH(O_2CR)_2(CO)L_2]$. In all these octahedral complexes, the hydride and carbonyls groups are mutually cis, the tertiary phosphines are trans, and the carboxylate is unidentate. The cis adducts containing chloride and having hydride and carbonyl mutually trans can be prepared by the action of carbon monoxide upon [147]. The adducts formed from trans-$[IrX(CO)L_2]$ and formic acid can be converted on



L = PPh_3

[147]

heating in solution into the dihydrido complexes $[IrXH_2(CO)L_2]$ with release of carbon dioxide. Trihydro complexes $[IrH_3(CO)L_2]$ (L = PPh_3, PEt_3) are also formed (ref. 192). The oxidative-addition reaction of tetrachloro-1,2-benzoquinone with trans-$[IrCl(N_2)(PPh_3)_2]$ gives the co-ordinatively unsaturated complex [147a] which reacts with carbon monoxide to afford [148] and with water to give [150] (Scheme 36). These reactions provide further support to the proposal that nucleophilic addition to co-ordinatively unsaturated iridium(III) is kinetically directed trans to the ligand of highest trans-influence. Other reactions of these complexes are illustrated in Scheme 36. An analysis of the infrared spectra of octahedral iridium(III) complexes containing two PPh_3 ligands show that when the phosphines are cis there is a strong band in the 530–550 cm^{-1} region (ref. 193). N_2O_4 reacts with trans-$[IrCl(CO)(PPh_3)_2]$ and $[IrCl(CO)(NO)(PPh_3)_2]BF_4$ to give the nitrato-nitro complex $[IrCl(NO_2)(NO_3)(CO)(PPh_3)_2]$. Nitrato-nitro complexes are also formed in reactions of N_2O_4 with $[IrCl(CO)(PMePh_2)_2]$ to give $[IrCl(NO_2)(NO_3)(PMePh_2)_2]$, $[IrH(CO)(PPh_3)_3]$ to give $[IrH(NO_2)(NO_3)(CO)(PPh_3)_2]$, $[Ir(CO)_3(PPh_3)_2]BPh_4$ to give $[Ir(NO_2)(NO_3)_2(CO)(PPh_3)_2]$ and $[Ir(CO)(NO)(PPh_3)_2]$ to give $[Ir(NO)(NO_2)(NO_3)(PPh_3)_2]$. However, $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ reacts with N_2O_4 to give the dinitro complex $[Ir(NO_2)_2(Ph_2PCH_2CH_2PPh_2)_2]Cl$. In the solid state, trans-$[RhCl(CO)(PPh_3)_2]$ reacts with N_2O_4 to give $[Rh_2Cl(NO_2)_2(NO_3)_3(PPh_3)_4]$ but in dichloromethane solution $[RhCl_2(NO_3)(PPh_3)_2]$ is formed. This nitrato complex is also formed in the reaction of N_2O_4 with $[RhCl_2(NO)(PPh_3)_2]$ and in the photochemical



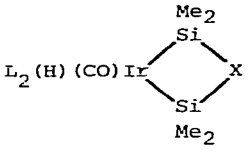
SCHEME 36

reaction of dioxygen with $[RhCl_2(NO)(PPh_3)_2]$. $NOBF_4$ reacts with trans-$[RhCl(CO)(PPh_3)_2]$ to give $[RhCl(NO)(CO)(PPh_3)_2]BF_4$ which with chloride ion gives $[RhCl_2(NO)(PPh_3)_2]$ (ref. 194). A review on platinum metal nitrato complexes has been published (ref. 195).

The reaction of trans-$[RhCl(CS)(PPh_3)_2]$ with $AgClO_4$ followed by filtration of AgCl and addition of a donor ligand L (L = py, 2-Etpy, 4-Etpy, o-$C_6H_4(CN)_2$, PPh_3) affords the cationic thiocarbonyl complexes $[Rh(CS)(PPh_3)_2L]ClO_4$. Similar reactions with bipyridyl or ortho-phenanothroline gives the five-co-ordinate compounds $[Rh(CS)(PPh_3)_2(N\text{-}N)]ClO_4$ but reaction with N,N,N′,N′-tetramethylethylene diamine (tmed) results in displacement of one triphenylphosphine ligand to give the four-co-ordinate complex $[Rh(CS)(PPh_3)(tmed)]ClO_4$. Some of these cationic thiocarbonyl complexes react with carbon monoxide and the complex $[Rh(CS)(PPh_3)_2(py)]ClO_4$ undergoes oxidative-addition reactions with halogens. However, only the iodine derivative

$[RhI_2(CS)(PPh_3)_2py]ClO_4$ could be isolated. The reaction of $[RhCl(CS)(PPh_3)_2]$ with $HgCl_2$ affords a metal-donor-metal acceptor adduct $[(PPh_3)_2(CS)(Cl)Rh \rightarrow HgCl_2]$. Both $[Rh(CS)(PPh_3)_3]ClO_4$ and $[Rh(CO)(PPh_3)_3]ClO_4$ act as catalysts for the hydrogenation of cyclic and terminal alkenes at room temperature and one atmosphere pressure of H_2, the thiocarbonyl complex being less active (ref. 196). The mercaptoalkylphosphine PhHPZSH ($Z = CH(Me)CH_2$) oxidatively adds to $[RhCl(PPh_3)_3]$ to give $[RhH(SZPHPh)Cl(PPh_3)_2]$ which reacts with ammonia to give the rhodium(I) complex $[Rh(SZPHPh)(NH_3)_2]$, (ref. 197). Bidentate, monodentate and bridging N,N-dialkylthiocarboxamide ($SCNR_2$) complexes of rhodium and iridium have been obtained via oxidative-addition reactions of $Me_2NC(S)Cl$ with various iridium(I) and rhodium(I) complexes. Thus reactions of $Me_2NC(S)Cl$ with "$[IrCl(PPh_3)_2]$", trans-$[IrCl(CO)(PPh_3)_2]$ and $[IrH(CO)(PPh_3)_3]$ give cis- and trans-$[IrCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2]$, trans-$[IrCl(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]Cl$, and trans-$[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]Cl$ respectively. Dehydrohalogenation of trans-$[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]Cl$ by triethylamine gives trans-$[Ir(\eta^1\text{-}SCNMe_2)(CO)(PPh_3)_2]$ and the dimeric complex $[Ir(\mu\text{-}SCNMe_2)(CO)(PPh_3)]_2$ and dehydrohalogenation of trans-$[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]Cl$ in the presence of $Me_2NC(S)Cl$ gives the bis(η^2-thiocarboxamido) complex $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]Cl$ which has been the subject of an X-ray study. The reaction of $Me_2NC(S)Cl$ with $[RhH(CO)(PPh_3)_2]$ results in displacement of carbon monoxide to give $[RhCl(\eta^2\text{-}SCNMe_2)(PPh_3)_2]$ which also results from the action of $Me_2NC(S)Cl$ upon $[RhH(PPh_3)_4]$ (ref. 198).

The new metallacycles [151] have been prepared by the reactions of $(HMe_2Si)_2X$

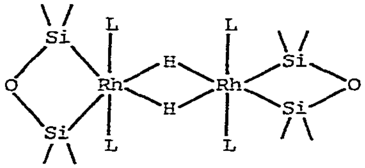


($L = PPh_3$; $X = O$ or CH_2)

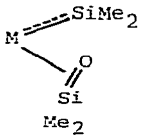
[151]

($X = O$ or CH_2) with trans-$[IrCl(CO)(PPh_3)_2]$. However, the metallacycle (151; $X = CH_2$) is rather unstable and rapidly decomposes to $[IrH(CO)(PPh_3)_2]$ and unidentified silanes. $(HMe_2Si)_2O$ does not react with trans-$[RhCl(CO)(PPh_3)_2]$ but with $[RhCl(PPh_3)_3]$ it gives an unstable metallacyclic complex which may have the structure [152]. This complex [152] rapidly reacts with carbon monoxide to give a carbonyl complex which may be $[RhH(CO)(Si_2Me_4O)(PPh_3)_2]$. Catalytic amounts of these complexes induce disproportionation of $(HMe_2Si)_2O$ into Me_2SiH_2 and higher polysiloxanes. This disproportionation involves the breaking and re-forming of Si-O bonds. The proposed mechanism of these reactions involves cleavage of the four-membered ring via an intermediate of the type [153] (ref. 199).

The crystal structure determination of $[Rh_2Cl_2(PPh_3)_4]$ reveals that the $RhCl_2Rh$ ring is planar in this complex (ref. 200). The crystal structure of the tri-iodo



[152]



[153]

bridged complex $[Ir_2(\mu\text{-}I)_3I_2(PMePh_2)_4]I_3$, formed by the oxidative-addition of iodine to $[Ir(PMePh_2)_4]^+$, has also been reported (ref. 201).

The rhodium(I) compounds $[Rh_2Cl_2(\text{cyclo-octene})_4]$, $[Rh_2Cl_2(1,5\text{-cod})_2]$, or $[Rh(acac)(\text{cyclo-octene})_2]$ in dimethylformamide or $(Me_2N)_3PO$ effect the complete decarbonylation of $[Cr(CO)_6]$, $[Mo(CO)_6]$, $[W(CO)_6]$, $[Fe(CO)_5]$, $[Ni(CO)_4]$, $[Co(CO)_4]^-$ at room temperature (ref. 202). A water soluble rhodium(I) complex, chlorotris-(sulphonated triphenylphosphine) rhodium(I) has been reported. This complex reacts with carbon monoxide and its ability to act as a hydrogenation catalyst has been reported (ref. 203).

The cobalt(II) complexes $[CoX_2(PPhF_2)_3]$ $(X = Br, I)$ are reduced by excess of $PPhF_2$ to give the cobalt(I) complex $[CoX(PPhF_2)_4]$. These cobalt(I) complexes are also formed if the complexes $[CoX_2(PBu_2{}^tF)_2]$ are treated with $PPhF_2$. Reduction of $[CoX_2(PPhF_2)_3]$ with zinc/mercury affords the cobalt-mercury bonded complex $Hg[Co(PPhF_2)_4]$ (ref. 204). The reduction of cobalt(II) compounds with $NaBH_4$ in the presence of triphenylphosphine in ethanol and benzene solutions leads to the cobalt(I) compounds $[Co(BH_4)(PPh_3)_n]$ $(n = 2, 3)$ and the conditions for the isolation of these complexes have been established (ref. 204a). Radiation induced one-electron reduction of some cobalt(II) and rhodium(I) chelating diphosphine complexes has also been reported. Thus in deaerated methanolic solution $[CoBr(Ph_2PCH_2CH_2PPh_2)_2]Br$ is reduced by $e^-_{solv.}$ to $[CoBr(Ph_2PCH_2CH_2PPh_2)_2]$ which rapidly loses Br^- $(k = 8.0 \pm 0.4 \times 10^{-5}\ s^{-1})$ to give $[Co(Ph_2PCH_2CH_2PPh_2)_2]$. There is also evidence for reactions of $[CoBr(Ph_2PCH_2CH_2PPh_2)_2]^+$ with the radicals $H^\bullet$, $^\bullet CH_2OH$, and $Me_2C^\bullet OH$ to give ultimately $[Co(Ph_2PCH_2CH_2PPh_2)_2]^+$. Results on some rhodium(I) compounds are outlined in Scheme 37. A reaction of $[Rh(\text{diphosphine})_2]$ with the solvent methanol also occurs to give $[Rh(\text{diphosphine})_2]^+$ together with other products (ref. 205). The e.s.r. and

$$[\mathrm{Rh(dpe)_2}]^+ + e^-_{\mathrm{solv.}} \longrightarrow [\mathrm{Rh(dpe)_2}]; \quad k = 3.0 \pm 0.3 \times 10^{10}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$$

$$[\mathrm{Rh(vpp)_2}]^+ + e^-_{\mathrm{solv.}} \longrightarrow [\mathrm{Rh(vpp)_2}]; \quad k = 2.8 \pm 0.2 \times 10^{10}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$$

dpe = $Ph_2PCH_2CH_2PPh_2$

vpp = cis-$Ph_2PCH=CHPPh_2$

SCHEME 37

reflectance spectra of $[Co(dpe)_2][ClO_4]_2$ have been measured (ref. 206) and the low frequency infrared spectra of the cobalt(II) complexes $[CoX_2(PEt_3)_2]$ (X = Cl, Br, I) and $[CoBr_2(PPhEt_2)_2]$ have been recorded (ref. 207).

Cobalt(II) salts are known to disproportionate in the presence of excess trialkyl phosphite and if a poorly co-ordinating anion is present the following reaction occurs with trimethylphosphite:

$$2Co(II) + 11P(OMe)_3 \longrightarrow [Co\{P(OMe)_3\}_5]^+ + [Co\{P(OMe)_3\}_6]^{3+}$$

[154]

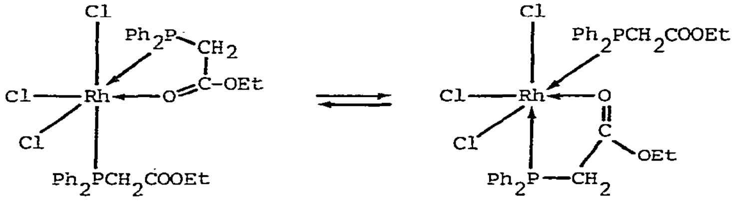
The cobalt(III) species [154] has been the subject of a ^1H and ^{59}Co n.m.r. study and in acetonitrile solution a pentakis(trimethylphosphite)cobalt(III) complex appears to be formed (ref. 208, 209). Some ^{103}Rh n.m.r. studies have also been carried out on some Me_2S and Me_2Te complexes of rhodium(III) (ref. 210). The reaction of $[RuCl_2(PPh_3)_3]$ with $[RhCl_3(PR_3)_3]$ affords the trichloro-bridged heterobimetallic complexes [155]. The reaction of $[RhCl_3(PF_3)(PPh_3)_2]$, prepared from trans-$[RhCl(PF_3)(PPh_3)_2]$ and chlorine with $[RuCl_2(PPh_3)_3]$ gives the complex (155; L = PPh_3) with displacement of PF_3 (ref. 211). The reaction of $[Co\{S_2P(OMe)_2\}_3]$ and $[Rh\{S_2P(OMe)_2\}_3]$ with either $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2AsPPh_2$ affords complexes containing the $S_2P(O)OMe^{2-}$ ligand e.g. $[M\{S_2P(O)(OMe)\}\{S_2P(OMe)_2\}(dpe)]$ (M = Co, Rh) and the kinetics of the reaction of the cobalt complex with dpe have been investigated (ref. 212, 213). The crystal structures of the complexes (ethylsulphito)[tris(2-diphenylphosphinoethyl)amine]cobalt(II) tetraphenylborate 0.5 dichloromethane, and $[Co(S_2PPh_2)_2.quinoline]$ have been reported (ref. 214, 215). Physical measurements on $[Co_2I_4(SPPh_3)_2]$ indicate that this complex has bridging S atoms and a weak Co-Co bond

$(Ph_3P)(L)ClRuCl_3RhClL_2$

L = PMe_2Ph, PEt_2Ph, $PBu^n{}_2Ph$, $PBu^n{}_3$, or PPh_3

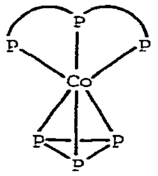
[155]

(ref. 216). Some rhodium(III) and iridium(III) complexes of the type fac-$[MX_3(Ph_2PCH_2COOEt)(Ph_2PCH_2COOEt)]$ (M = Rh, X = Cl, Br; M = Ir, X = Cl) and mer-$[RhCl_3(Ph_2PCH_2CN)_3]$ have been prepared. A variable temperature ^1H and ^{31}P n.m.r. study on the complex [156] suggests that an equilibrium between [156] and [157] exists in solution (ref. 217).

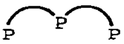


[156] [157]

The reaction of white phosphorus P_4 with hydrated cobalt(II) tetrafluoroborate in the presence of $MeC(CH_2PPh_2)_3$ (triphos) leads to a metal complex [158] containing cyclo-triphosphorus (δ-P_3) as a ligand. The complex [158] is diamagnetic and a non-electrolyte in dichloromethane solution (ref. 218). Yellow arsenic (As_4) also reacts smoothly with a cobalt(II) aquo ion in the presence of triphos to give $[(triphos)Co(As_3)Co(triphos)]^{2+}$ which contains a bridging cyclo-triarsenic entity. The complex is air stable and has a magnetic moment corresponding to one unpaired electron for each unit of the dinuclear structure. A mononuclear complex $[As_3Co(CO)_3]$ has been synthesized previously (ref. 219). An η^3-cyclo-triphosphorus complex $[Co(\eta^3-P_3)Co(np_3)]$ $\{np_3 = N(CH_2CH_2PPh_2)_3\}$ has also been obtained with the potentially tetradentate ligand np_3. A single crystal X-ray study on this diamagnetic complex indicates that the cobalt is co-ordinated by three phosphorus atoms of the np_3 ligand and by the three phosphorus atoms of the cyclic P_3 unit (ref. 219). A cobalt complex [159] which contains a bridging sulphur atom has been obtained according to the equation:



[158]



is $MeC(CH_2PPh_2)_3$

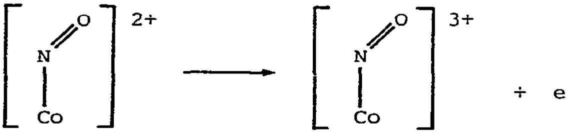
$$2[\mathrm{CoSH(np_3)}]\mathrm{BPh_4} + 4\mathrm{NaOEt} \downarrow [(\mathrm{np_3})\mathrm{CoSCo(np_3)}] + \mathrm{NaBPh_4} + \mathrm{Na_2S} + 2\mathrm{EtOH} + 2\mathrm{MeCHO} + \mathrm{H_2}$$

[159]

An X-ray structural investigation shows that the cobalt ions are tetrahedrally co-ordinated to the three phosphorus atoms of the ligand and to the bridging sulphur atom. This is the first example of a diamagnetic d^8 cobalt(I) complex in which the cobalt is tetrahedrally co-ordinated (ref. 221). A review on tertiary phosphane ligands in co-ordination and organometallic chemistry has been published (ref. 222).

Metal nitrosyl and aryldiazo compounds

Although a large number of cobalt nitrosyl complexes are known all the complexes so far characterised are diamagnetic. However, treatment of a deoxygenated solution of $[\mathrm{Co(NO)(diars)_2}][\mathrm{ClO_4}]$ {diars = o-phenylene-bis(dimethylarsine)} with chlorine produces a green precipitate of the paramagnetic complex trans-$[\mathrm{Co(NO)Cl(diars)_2}]$-$[\mathrm{ClO_4}]_2$ [160] which appears to contain a bent CoNO group. The X-ray photoelectron spectra of [160] and trans-$[\mathrm{Co(NO)Cl(diars)}][\mathrm{ClO_4}]$ [161] supports the view that oxidation [161] to [160] can be described as oxidation of co-ordinated $\mathrm{NO^-}$ to $\mathrm{NO^\bullet}$. The XPS spectrum of [161] is also consistent with the formulation of [161] as a derivative of cobalt(III) (ref. 223). The infrared spectra of diars and dimethyldithiocarbamate complexes of $[\mathrm{CoNO}]^n$ have been obtained from 33 to 4000 $\mathrm{cm^{-1}}$. The skeletal vibrations of the $[\mathrm{CoNO}]^n$ group have been identified and force constants have been derived. The results show that this three-body model will reproduce the frequencies of first-, second-, and third-row transition-metal mononitrosyls (ref. 224). The ESCA spectra of the monomeric square-pyramidal complexes $[\mathrm{Co(NO)(S\text{-}O)_2}]$ [S-O = thiodibenzoylmethanato or N-(morpholinothiocarbamoyl)benzamidate] indicate that the cobalt atom in these complexes has an oxidation state of three and that the nitrosyl ligand is negatively charged (ref. 225). It also appears that there is a comparatively high electron density on the co-ordinated NO ligand in the complexes $[\mathrm{Co(NO)L_2(H_2O)}]$, $[\mathrm{Co(NO)ClL'_2}]\mathrm{Cl}$, and $[\mathrm{Co(NO)L'_2(H_2O)}][\mathrm{SO_4}]$, (HL = N'-amidinoisourea, L' = O-alkyl-N'-amidinoisourea) (ref. 226). A single crystal X-ray study of the complex [Co(NO)(salen)], [salen = N,N'-ethylenebis(salicylideneiminato)] reveals the

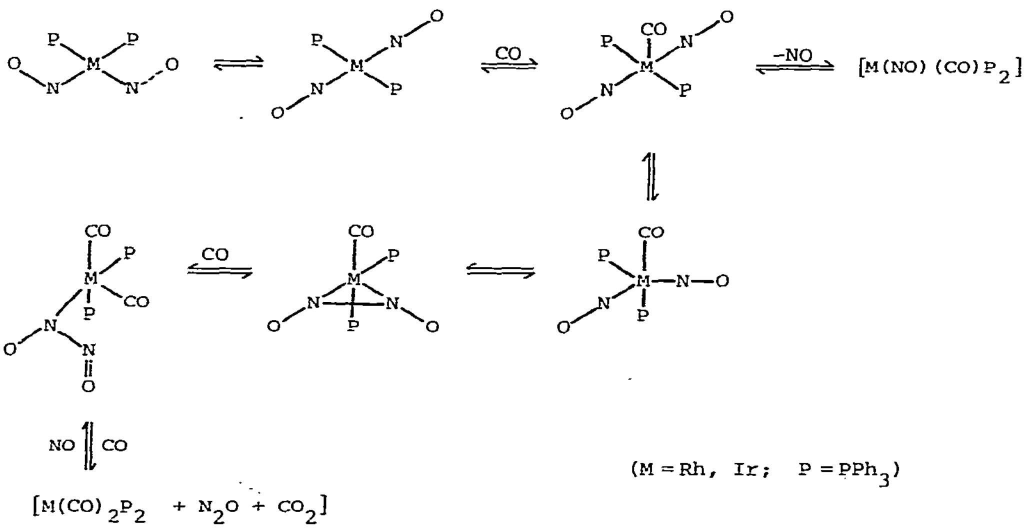


[161] [160]

presence of a five-co-ordinate tetragonal-pyramidal geometry about the cobalt, with the NO occupying the apical position in a bent geometry (Co-N-O = 127.0°) (ref. 227).

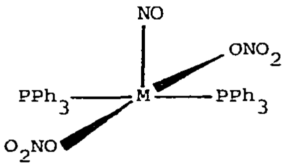
Treatment of $[Co(NO)(CO)_3]$ with the ligand $L = P(OCH_2CH_2Cl)(CF_3)_2$ affords the monosubstituted species $[Co(NO)(CO)_2L]$ and there is also evidence for the existence of trace amounts of $[Co(NO)(CO)L_2]$ (ref. 151). The ^{59}Co n.m.r. spectra of the related complexes $[Co(NO)(CO)_2\{P^tBu_{3-n}(MMe_3)_n\}]$ (n = 1, 2, 3; M = Si, Ge, Sn) have been obtained (ref. 228). Cobalt nitrosyl complexes have also been shown to result when Co^{2+} ions in zeolites A, X, and Y are treated with NO. A mononitrosyl complex is favoured in the A-type zeolite whereas a dinitrosyl complex is formed in the Y-type zeolite. However, both types of complexes result in the X-type zeolite (ref. 229).

The reaction of carbon monoxide with the cationic dinitrosyl $[M(NO)_2(PPh_3)_2]^+$ (M = Rh, Ir) under ambient conditions gives the tricarbonyl species $[M(CO)_3(PPh_3)_2]^+$ together with CO_2 and N_2O. However, the corresponding cobalt dinitrosyl complex does not undergo this reaction under similar conditions. The mechanism of the reaction is outlined in Scheme 38. The carbonyl species $[M(CO)_3(PPh_3)_2]^+$ are converted into the dinitrosyls on treatment with NO at about 80°C (ref. 230). The action of 16M nitric acid on benzene or chloroform solutions of the hydrides $[MH(CO)(PPh_3)_3]$ (M = Rh, Ir) affords the intractable air-stable yellow crystalline products $[M(NO_3)_3(PPh_3)_2]$ which may be formed *via* the nitrosyl intermediates $[M(NO_3)_2(NO)(PPh_3)_2]$. Treatment of $[Rh(NO_3)_3(PPh_3)_2]$ with carbon monoxide affords

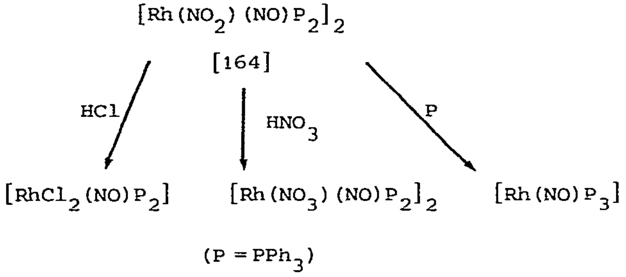


SCHEME 38

yellow crystals of a carbonyl-nitrate complex which could not be positively identified. Treatment of $[M(NO)(PPh_3)_3]$ with 2M ethanolic nitric acid gives the air-stable green products $[M(NO_3)_2(NO)(PPh_3)_2]$. Attempts to prepare the rhodium complex in degassed solvents under anaerobic conditions gave no reaction but introduction of a stoichiometric amount of dioxygen induced complete precipitation of the nitrosyl nitrate. The reactions of $[Rh(NO)(PPh_3)_3]$ with a number of other acids also require molar proportions of dioxygen for reaction to occur. The rhodium complex $[Rh(NO_3)_2(NO)(PPh_3)_2]$ can also be obtained by the action of neat (16M) nitric acid upon solid $[RhH(CO)(PPh_3)_3]$ and since it is identical with the complex "$[Rh(NO)_2(NO_3)(OPPh_3)_2]$", previously obtained from $[RhH(PPh_3)_4]$ and dilute nitric acid, this phosphine oxide complex should be reformulated as $[Rh(NO_3)_2(NO)(PPh_3)_2]$. These dinitrate complexes probably have the structure shown in [163] (ref. 231). The reaction of $[RhCl_2(NO)(PPh_3)_2]$ with $AgNO_3$ affords the complex $[Rh(NO_3)(NO)(PPh_3)_2]_2$ and some reactions of the related complex [164] are given in Scheme 39. The



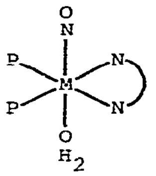
[163]



SCHEME 39

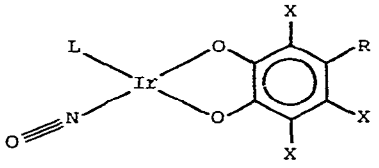
complex $[Rh(NO_2)(NO)_2(PPh_3)_2]$ also undergoes the same reactions as [164] (ref. 232). Treatment of the dicationic nitrosyl complexes $[M(NO)(MeCN)_2(PPh_3)_2]^{2+}$ with methyl-substituted 1,10-phenanthroline and 2,2'-bipyridyl afford the dicationic nitrosyl complexes [165] which appear to have octahedral structures with co-ordinated water (ref. 233).

The nitrosyl complexes [166] add a molecule of triphenylphosphine to give five-



(P = PPh_3; M = Rh, Ir)

[165]



X = R = Cl, Br, H

X = H; R = NO_2, CHO, $COOCH_3$, CH_2OH, CH_3

L = PPh_3

[166]

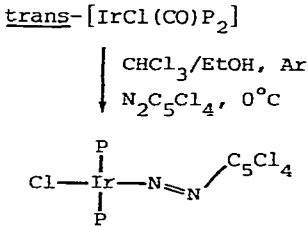
co-ordinate complexes and the equilibrium constants for the reaction

$$\underset{[166]}{\mathrm{Ir(cat)(NO)L}} + \mathrm{L} \rightleftharpoons \underset{(\mathrm{L} = \mathrm{PPh_3})}{\mathrm{Ir(cat)(NO)L_2}}$$

have been determined. It is apparent that the equilibrium constants parallel the electron-withdrawing power of the ring substituents (ref. 234). Further studies also show that the complex (166; X = R = Br) is a selective catalyst for the hydrogenation of cyclohexa-1,3-diene to cyclohexene and 1,3,5-cycloheptatriene to cycloheptadiene. However, the catalytic activity of the complex (166; X = R = H) is lower (ref. 235).

Treatment of $[Rh_2Cl_2(CO)_4]$ with NO and then with cyclopentadienyl-thallium affords $[Rh_2(NO)_2Cp_2]$ which is probably isostructural with the corresponding cobalt compound. The value of $^1J_{Rh-Rh}$ for this compound, $[Rh_2Cp_2(CO)_3]$ and $[Rh_2Cp_2(CH_2)(CO)_2]$ have been determined (ref. 236).

Although reactions of the aryldiazo ligand, RN_2^+, with metal complexes have been studied reactions of diazo molecules, RN_2 have not been widely investigated. It has now been found that tetrachlorodiazocyclopentadiene $N_2C_5Cl_4$ reacts with trans-[IrCl(CO)$(PPh_3)_2$] to give [167] which has been the subject of a single crystal X-ray

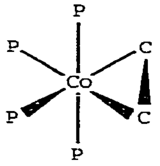


[167]

study. Compound [167] reacts with phosphines, phosphites, isocyanides, NO^+, PhN_2^+ to give five-co-ordinate species (ref. 237).

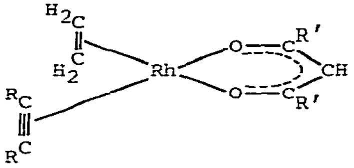
Metal alkene compounds

The use of cobalt atom-ethylene cryochemistry techniques has provided access to a novel series of mononuclear and binuclear binary cobalt-ethylene complexes $Co(C_2H_4)_x$ ($x = 1, 2$) and $Co_2(C_2H_4)_y$ ($y = 1, 2$) as well as a suspected tetranuclear species $Co_4(C_2H_4)_n$ (ref. 238). Protonation of $[CoMe\{P(OMe)_3\}_4]$ in the presence of an olefin gives the trigonal bipyramidal complexes $[Co(\eta^2\text{-}L)\{P(OMe)_3\}_4]^+$ with the unsaturated ligand co-ordinated at an equatorial site [168]. Complexes of the type $[CoL\{P(OMe)_3\}_4]^+$ undergo facile displacement reactions and based on the displacement reaction the ligand-cobalt interaction decreased in the series L = CO > $P(OMe)_3$ > H_2 > NH_3 ~ MeCN > ethylene ~ diphenylacetylene ≫ propene ~ hex-1-ene > methanol ~ acetone. The reaction of $[Co(\eta^3\text{-allyl})\{P(OMe)_3\}_3]$ with $[Et_2OH]PF_6$ in methanol at -50°C in the presence of conjugated dienes (butadiene, cyclohexa-1,3-diene) gives the insoluble salts $[Co(diene)\{P(OMe)_3\}_3]PF_6$. Cyclo-octa-1,3-diene and cyclo-octa-1,5-diene both give the same diene complex and the observation that no tractable complex could be isolated with the unconjugated diene bicyclo[2.2.1]hepta-2,5-diene is consistent with the fact that only conjugated dienes have appropriate symmetries to interact well with $d^8\text{-}ML_3$ species. The structures of these diene complexes could not be uniquely determined, the n.m.r. spectral data being consistent with η^4-diene complexes and with a hooked allyl formulation $\overline{Co\text{-}\eta^3\text{-}C_3H_4CH_2}$ (ref. 27). Some five-co-ordinate 1,3-dienecobalt(I) complexes $[Co(diene)(phosphine)_3]Y$ (diene = butadiene, isoprene; phosphine = PMe_3, PMe_2Ph, $PHPh_2$; Y = ClO_4, BF_4, or BPh_4) have also been obtained by reaction of the diene with a mixture of $CoY_2.6H_2O$ and the phosphine in isopropanol. These diene-cobalt phosphine complexes, like the corresponding phosphite complexes, are stereochemically non-rigid in solution. The low temperature n.m.r. spectra of the phosphine complexes have been interpreted in terms of a square-pyramidal structure in which the diene occupies two basal co-ordination sites (ref. 239).



[168]

The first mono-olefin acetylene complexes [169] have been synthesised by the action of hexafluorobut-2-yne upon the complexes $[Rh(O\text{-}O)(C_2H_4)_2]$ (O-O = MeCOCHCOMe, $Me_3CCOCHCOCMe_3$) at -78°C. The corresponding cyclo-octene complexes [Rh(O-O)(cyclo-octene)(C_4F_6)] can similarly be obtained from the reaction of hexafluorobut-2-yne with [Rh(O-O)(C_8H_{14})$_2$] at -78°C. The crystal structures of [169a] and the corresponding cyclo-octene complex have been determined and it is found that

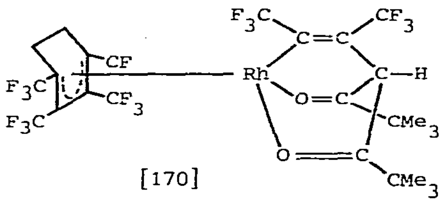


$R = CF_3$

169a; $R = Me$

169b; $R = CMe_3$

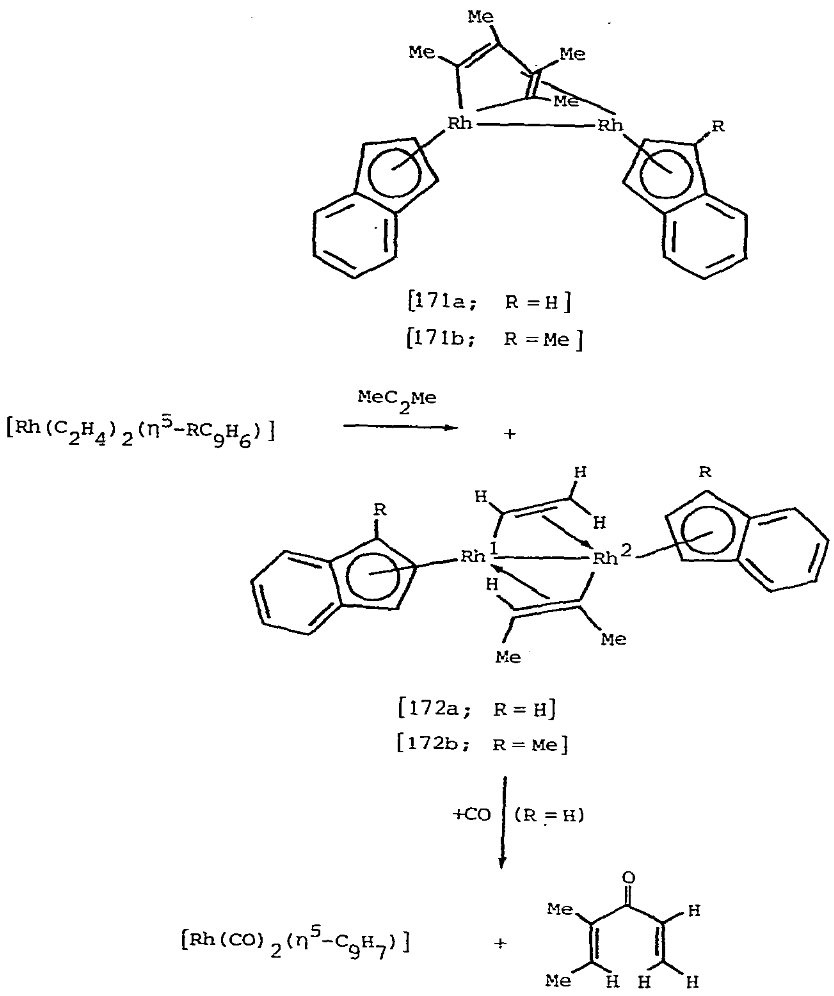
replacement of one olefin from the bis-olefin complexes by hexafluorobut-2-yne causes a considerable weakening in the bonding between rhodium and the remaining olefin. Treatment of [169b] with excess hexafluorobut-2-yne gives the cyclohexadiene complex [170] and this reaction provides good evidence for the involvement of



[170]

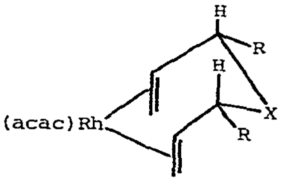
mono-olefin acetylene complexes in the formation of cyclohexadiene complexes from bis-olefin rhodium(I) complexes and hexafluorobut-2-yne. The reaction of triphenylphosphine, -arsine, and -stibine with [169b] leads to displacement of ethylene and formation of the complexes [Rh(O-O)(C_4F_6)L_2] (O-O = $Me_3CCOCHCOCMe_3$; $L_2 = PPh_3$, $AsPh_3$, $SbPh_3$) (ref. 240). The reaction of but-2-yne with the bis-ethylene complex [Rh(η^5-C_9H_7)(C_2H_4)$_2$] (C_9H_7 = indenyl) leads to catalytic formation of hexamethylbenzene and two dinuclear complexes [171a] and [172a] which have been characterised by X-ray diffraction studies on the related 1-methyl substituted indenyl analogues [171b] and [172b]. The formation of the bridged dinuclear vinyl complexes [172] must involve cleavage of an ethylenic carbon-hydrogen bond under very mild conditions. Since there seems to be no reason why a species such as [Rh(η^5-indenyl)-(C_2H_4)(MeC_2Me)] should be exceptionally reactive it is suggested that the oxidative attack on co-ordinated ethylene occurs within a polynuclear complex. The reactions of the complexes are outlined in Scheme 40 (ref. 241).

A range of stable diallyl ether complexes of rhodium(I) have been obtained by



SCHEME 40

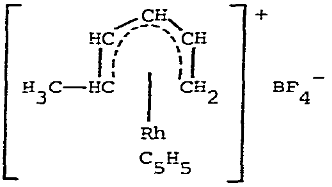
displacement of ethylene from [Rh(acac)$(C_2H_4)_2$]. Diallylamines, allyl acrylate, diallyl sulphone and 4,4'-diacetylhepta-1,6-diene also form related complexes. A



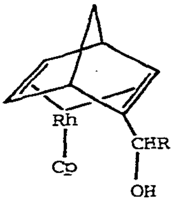
(X = O; R = Me)

[173]

single crystal X-ray structure determination of [173] reveals that the rhodium complex has an analogous structure to the related platinum complex $[PtCl_2\{(CH_2{=}CH{-}CHR)_2O\}]$ (ref. 242). The substituted butadienes RCH=CHCH=CHR′ [R = Me, R′ = CHO, COMe, CH_2OH or CHMe(OH); R = Ph, R′ = COPh] have also been shown to displace cyclo-octene from $[M_2Cl_2(\text{cyclo-octene})_2]$ (M = Rh, Ir) to give the diene complexes $[MCl(\text{diene})_2]$ except for R = Me, R′ = COMe, M = Rh where the complex $[Rh_2Cl_2(\text{diene})_2]$ is obtained. Treatment of the aldehyde and ketone complexes with TlCp give the cyclopentadienyl complexes [RhCp(diene)]. However, although attempts to attach the cyclopentadienyl group to the dienol complexes have not been successful, treatment of the crude product from the reaction of $[RhCl(\text{hexa-2,4-dien-1-ol})_2]$ with TlCp with fluoroboric acid in acetic anhydride at 0°C affords [174]. Apart from tricarbonyliron complexes, co-ordination of an acyclic η^5-pentadienyl ligand to transition metals is rare. Further although the η^5-syn-1-methylpentadienyl-tricarbonyliron cation readily reacts with water, the rhodium complex is much less reactive and can be handled in aqueous solution (ref. 243). Treatment of the carbinols [175] with concentrated sulphuric

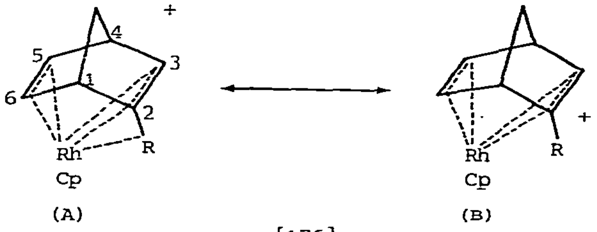


[174]



(R = H, Me)

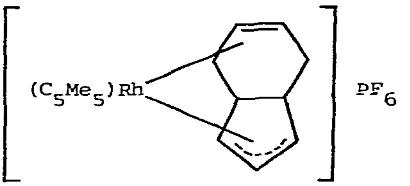
[175]



(A) (B)

[176]

acid gives the cationic species [176] in which there is an asymmetrical distribution of the positive charge along the π-allyl fragment. The cationic complexes may thus be considered as resonance hybrids (A)$\leftrightarrow$(B) with predominance of the π-allyl structure (ref. 244). Treatment of $[M(C_5Me_5)(MeCN)_3][PF_6]_2$ (M = Rh, Ir) with bicyclo[2.2.1]heptadiene (nbd) gives the dicationic diene complexes $[M(C_5Me_5)(nbd)(MeCN)][PF_6]_2$. However, with cyclo-octa-1,5-diene a deprotonation reaction occurs to give $[M(C_5Me_5)(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})][PF_6]$. Subsequent reaction of the iridium complex with BH_4^- gives $[Ir(C_5Me_5)(cod)]$. The olefins cyclopentadiene, dicyclopentadiene, and propene also undergo deprotonation reactions upon reaction with $[M(C_5Me_5)(Me_2CO)_3][PF_6]_2$ to give $[M(C_5Me_5)(C_5H_5)][PF_6]$, [177], and $[Ir(C_5Me_5)(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)][PF_6]$ respectively. However, cycloheptatriene undergoes nucleophilic attack by the solvent on reaction with $[M(C_5Me_5)(YH)_x][PF_6]_2$ (YH = Me_2CO, M = Rh, Ir; YH = MeOH, M = Rh) to give the 6-exo-acetonyl- or 6-exo-methoxy-1-5-η-cycloheptadienyl complex $[M(C_5Me_5)(C_7H_8Y)][PF_6]$ (ref. 245). The single crystal X-ray structure determination of the η^5-C_5Me_5 complex $[Rh(C_5Me_5)(C_2H_4)(PPh_3)]$ reveals some localisation of charge on one of the five C-C bonds of the C_5Me_5 ring and indicates that of the two localised forms [178] and [179] the largest contribution comes from [178]. The hydrogen atoms of the ethylene ligand have also been located and it is clear that the co-ordinated ethylene is non-planar there being a twist of 20° of the CH_2 groups about the C-C bond axis and a near tetrahedral geometry about the C atoms. This distortion together with the lengthened C-C bond indicate an important π-component in the rhodium-ethylene bond (ref. 246). The crystal and molecular structure of [RhCp{(+)-(4S-carvone)}] has also been determined and reveals that π-complexation of carvone occurs diastereospecifically (ref. 247).



(Rh also = Ir)

[177]

[178]

[179]

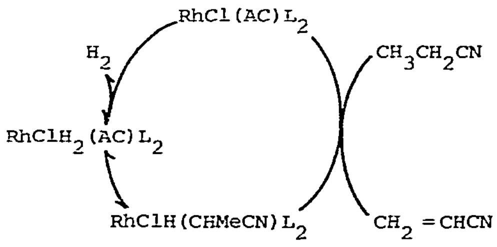
Kinetic studies on the reactions of ethylenediamine with $[Rh(cod)(N\text{-}N)]^+$ (N-N = 2,2'-bipyridyl, o-phenanthroline), [RhCl(cod)(piperidine)] with 2,2'-bipyridyl and $[Rh_2X_2(cod)_2]$ (X = Cl, Br, SCN, N_3) with 2,2'-bipyridyl and $[RhCl(cod)(PCy_3)]$ with

SCN, ethylenediamine and N,N′-dimethylethylenediamine have been published (refs. 248-251). However, the unusual dependence of the rate constant for the slow step on the initial concentration of $[Rh_2Cl_2(cod)_2]$ in the reaction of $[Rh_2Cl_2(cod)_2]$ with 2,2′-bipyridyl can be explained if the reactive intermediate is the ion pair $[Rh(cod)(bipy)][RhCl_2(cod)]$ (ref. 252). Some new cyclo-octa-1,5-diene complexes $[RhCl(cod)(2\text{-}\alpha\text{-thienylbenzimidazole})]$, $[IrX(cod)(2,2'\text{-biquinoline})]$ (X = Cl, Br) and the carbonyl complex $[Rh(CO)(2\text{-}\alpha\text{-thienylbenzimidazole})(PPh_3)_2][ClO_4]$ have also been reported (ref. 253). Studies on the reactions of $[M_2Cl_2(diene)_2]$ (M = Rh, diene = cod, nbd; M = Ir; diene = nbd) with phosphorus donor ligands and $[Rh(diene)_2][ClO_4]$ with Group V donor ligands (L) have confirmed the greater stability of the Rh-nbd bond compared to the Rh-cod bond. Using the ligands L compounds of the type $[Rh(diene)(L)(S)]^+$, $[Rh(diene)L_2]^+$, and $[Rh(diene)_2L]^+$ (S = solvent) have been obtained (ref. 254, 255).

The reactions of the salts $[Ir(cod)L_2]PF_6$ [$L = PPh_2(OMe)$; $PMePh_2$, $PEtPh_2$] with HX (X = Cl, Br, I) give the complexes $[IrHX(cod)L_2]PF_6$ [X = Cl, Br, I; $L = PPh_2(OMe)$, $PMePh_2$; X = Cl, Br, $L = PEtPh_2$] and $[IrHX_2(cod)L]$ (X = Br, I, $L = PMePh_2$, $PEtPh_2$). As a result of steric crowding the equilibrium

$$\underset{[180]}{[Ir(cod)L_2]^+} + Cl^- \rightleftharpoons \underset{[181]}{[IrCl(cod)L]} + L$$

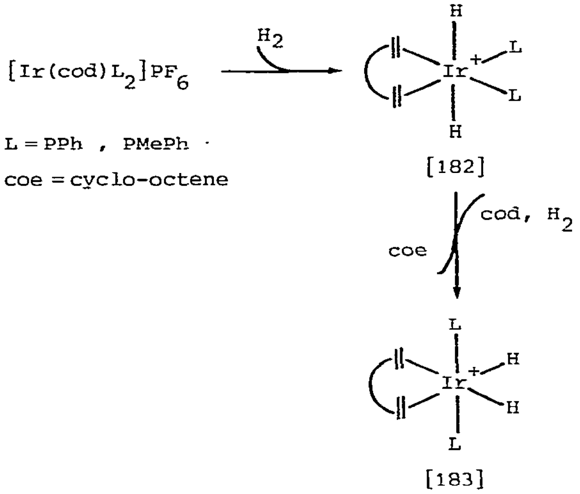
exists and this explains the formation of the two types of products $[IrHX(cod)L_2]PF_6$ and $[IrHX_2(cod)L]$. Kinetic studies on the oxidative-addition reactions of [180] and [181] with HCl show that nucleophilic attack of Cl^- precedes the protonation of the complexes (ref. 256). A study on the oxidative-addition of hydrogen to $[RhCl(CH_2{=}CHCN)(PPh_3)_2]$ in the presence of acrylonitrile reveals that the initial fast reaction is the oxidative-addition of hydrogen to $[RhCl(CH_2{=}CHCN)(PPh_3)_2]$ which is followed by a slower process in which the hydrogen is consumed in the course of the hydrogenation of acrylonitrile and $[RhCl(CH_2{=}CHCN)(PPh_3)_2]$ is reproduced. The mechanism is outlined in Scheme 41 (ref. 257).



($L = PPh_3$; AC = acrylonitrile)

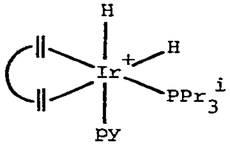
SCHEME 41

Some novel dihydride iridium complexes have been isolated during the hydrogenation of cod by $[Ir(cod)L_2][PF_6]$. The hydrogenation of cod proceeds in two stages. Initially two mol of H_2 per mol of iridium are absorbed and cyclo-octene is formed. In the second stage cyclo-octene is formed much more slowly. The proposed mechanism is outlined in Scheme 42.



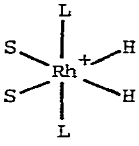
SCHEME 42

The intermediates [182] and [183] can be isolated and it is suggested that the rate determining step in the hydrogenation of cyclo-octa-1,5-diene is the insertion of co-ordinate olefin into the M-H bonds since only dihydrido-diolefin complexes are observed. It also appears that this insertion requires a co-planar M(C=C)H system since the complexes [182] which have this stereochemistry undergo the insertion reaction about 40 times faster than the complexes [183]. The dihydrido-diolefin complexes may also be obtained by addition of cyclo-octa-1,5-diene to $[IrH_2(Me_2CO)L_2]$-PF_6. Addition of H_2 to an olefin complex as well as olefin addition to a hydrido complex have both been considered as pathways for the formation of these complexes in homogeneous hydrogenation. The complex [184] is also an excellent selective catalyst for the hydrogenation of cyclo-octa-1,5-diene to cyclo-octene (ref. 258). The complex



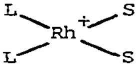
[184]

[IrCl(cod)(PCy$_3$)] is also an efficient hydrogenation catalyst (ref. 259). The reaction of hydrogen with [Rh(nbd)(PPh$_3$)$_2$][BF$_4$] in methanol is known to result in the formation of norbornane and the dihydride complex [185]. However, the complex,



S = MeOH L = PPh$_3$

[185]



L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$

[186]

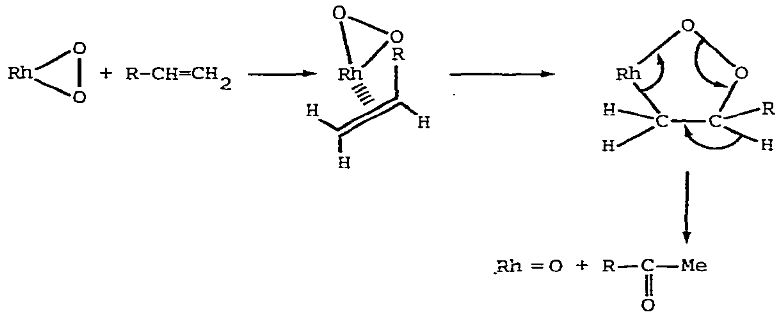
[Rh(nbd)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]ClO$_4$ reacts with hydrogen to form norbornane and the methanol complex [186]. The chelating phosphine cannot form a <u>trans</u>-bisphosphine complex and it has been suggested that this factor causes the change in reaction path. Further studies on these types of complexes have now revealed that the equilibrium between [185] and [186] and their relative ease of formation is very dependent on the nature of the phosphine. Thus while the complex [Rh(nbd)(PPh$_3$)$_2$]$^+$ reacts with hydrogen to form [185], the corresponding complex [Rh(nbd)(PMePh$_2$)$_2$]$^+$ takes up hydrogen much more slowly, the dihydride is initially observed but the complex (186; L = PMePh$_2$) is much more readily formed. Treatment of the complex derived from rac-o-methoxyphenyl methylphenylphosphine, which exists as an approximately equal mixture of (R*R*) and (RS)-diastereoisomers in solution, with hydrogen, also gives only one methanol complex (186; L = o-MeOC$_6$H$_4$PPhMe), the (R*R*)-diastereoisomer. The stability of this methanol complex towards hydrogenation and the stereoselectivity observed in its formation is considered to be due to weak bonding of the methoxy oxygen atoms of the ligand to the rhodium. Further, the (RR)-diastereoisomer which is constrained by methoxy-metal bonding has a methyl-methyl non-bonded interaction whereas the (RS)-diastereoisomer would possess a much more unfavourable methyl-phenyl interaction. It is clear from these studies that the major intermediate present under hydrogenation conditions is very dependent on the structure of the phosphine (ref. 260). Intermediates identified in the hydrogenation of (E)- and (Z)-α-benzamidocinnamic acids and their methyl esters by asymmetric rhodium(I) complexes also show that the stereochemical course in these reactions is defined by an olefin-binding step and that subsequent addition of hydrogen has only a minor influence on the optical yield (ref. 261). The reaction of the chiral ligand, (R)-1,2-bis(diphenylphosphino)propane, (R)-prophos, with $[Rh(nbd)_2]ClO_4$ gives $[Rh(nbd)\{(R)\text{-prophos}\}]ClO_4$ which acts as an efficient asymmetric hydrogenation catalyst for the formation of amino acids. This catalyst is also capable of breeding its own chirality (ref. 262). The reaction of $[Rh_2Cl_2(C_2H_4)_4]$ with (+)-Diop in benzene affords the highly air-sensitive compound $[RhCl(Diop)(C_6H_6)]_2$ which can be oxidised and reactivated in the presence of hydrogen (ref. 263). The system $[RhCl(PPh_3)_3]$ + $AlEt_3$ has been shown to produce the hydride, $[RhH(PPh_3)_3]$ which is 39 times more active than $[RhCl(PPh_3)_3]$ as an ethylene hydrogenation catalyst. The major catalytic path is given in Scheme 43 (ref. 264).

$$\begin{tikzcd}
RhHP_3 + C_2H_4 \arrow[r] & RhH(C_2H_4)P_3 \arrow[d, "\text{rapid}"] \\
C_2H_6 + RhHP_3 & Rh(C_2H_5)P_3 \arrow[l, "H_2"']
\end{tikzcd}$$

$(P = PPh_3)$

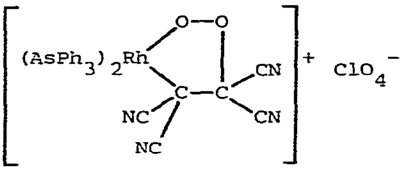
SCHEME 43

Alcoholic solutions of rhodium trichloride containing copper(II) perchlorate or nitrate have been shown to catalyse the oxidation of terminal olefins to methyl ketones. The proposed mechanism for this process is outlined in Scheme 44 (ref. 265).



SCHEME 44

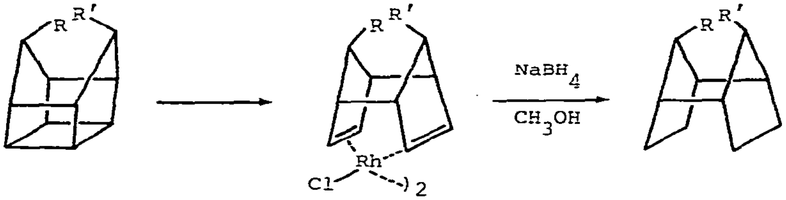
Evidence for this mechanism has been obtained by examining the reactivity of $[Rh(O_2)(AsPh_3)_4]^+A^-$ ($A = ClO_4$, PF_6) under deoxygenated argon and anhydrous conditions towards terminal olefins. These reactions result in direct oxygen transfer from the rhodium dioxygen complex to the terminal olefin to give methyl ketones with high selectivity and the observation that tetracyanoethylene reacts with $[Rh(O_2)(AsPh_3)_4]$-ClO_4 to give [187] provides evidence for the cyclic peroxo intermediate in Scheme 44



[187]

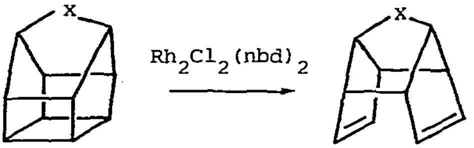
(ref. 266). Cyclo-octa-1,5-diene has been shown to be resistant to autoxidation at a rhodium(I) centre. Thus at 74°C, where co-ordinated cyclo-octene is oxidised, $[Rh_2Cl_2(cod)_2]$ is unchanged by treatment with oxygen. This observation is in agreement with the strong chelating ability of the diene and with the idea that metal-centred autoxidation requires co-ordination of O_2 at a square-planar intermediate (ref. 267).

The strained molecule, secopentaprismane, [188], has been shown to react with an equivalent of $[Rh_2Cl_2(nbd)_2]$ to give bicyclo[2.2.1]heptadiene (nbd) and the diene



[188], R = R′ = H	[189], R = R′ = H	[192], R = R′ = H
[190], R = H; R′ = Me	[191], R = H; R′ = Me	[196], R = R′ = OAc
[193], R = R′ = Me	[195], R = R′ = OAc	
[194], R = R′ = OAc		

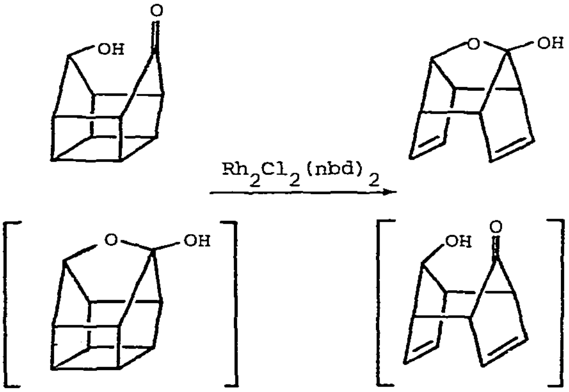
complex [189]. A similar reaction of [190] gives [191]. However, these studies reveal that methano bridge substituents have a profound effect on the reactivity of the secopentaprismanes and related complexes. Thus a comparison of the rates of reaction of [188] and [190] with [Rh(acac)(nbd)] reveal that introduction of a methyl group results in a tenfold decrease in the second-order rate constant for the reactions while introduction of a second <u>endo</u>-methyl group, compound [193], stop the reaction completely. It appears that the effect of the <u>endo</u>-methyl groups is a consequence of steric interferences in the intranuclear movements which accompany opening of the cage. Indeed the stability of [189] and [191] towards CO and phosphines probably results from the increase in steric compression which would result if the diene were to become free of the metal. The <u>endo</u> diacetate [194] also gives a diene complex [195]. However, treatment of [195] with excess nbd reverses the cyclobutane-diolefin cleavage reaction and regenerates [194]. Presumably the energy changes associated with strain release and rebonding which occur with cage cleavage are similar to, but opposite in sign to those changes in non-bonding interactions that accompany the process. Thus if the non-bonded interactions destabilising the free ligands of [189], [191] and [195] are removed by bonding the groups together as in [197] and [198] then these bridged secopentaprismanes are



[197], X = O
[198], X = CH_2

[199], X = O
[200], X = CH_2

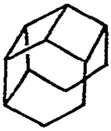
cleaved catalytically by [$Rh_2Cl_2(nbd)_2$] to the free dienes [199] and [200]. In these catalytic cycles ligand exchange with nbd occurs, the diene is liberated, and [$Rh_2Cl_2(nbd)_2$] is reformed and this complex can cleave the secopentaprismane again. The transformations depicted in Scheme 45 can similarly be achieved (ref. 268).



SCHEME 45

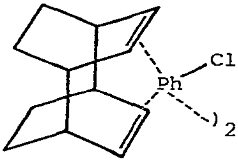
The reaction of [201] with [$Rh_2Cl_2(nbd)_2$] gives the diene complex [202] (ref. 269).

Several rhodium(I) complexes of the tertiary phosphine-olefin ligand $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH{=}CH_2$ (ppol) including [RhCl(ppol)], [Rh(ppol)PPh_3][AsF_6], [Rh(CO)(ppol)(PPh_3)][AsF_6] and [Rh$(CO)_2$(ppol)][AsF_6] have been prepared. The crystal structure determination of [RhCl(ppol)] [203] reveals an essentially square planar arrangement about the rhodium with the olefinic portion of ligand perpendicular to the basal plane. There is a large weakening of the metal-olefin bond due to the <u>trans</u> influence of the phosphine group (ref. 270). The reactions of tricyclohexylphosphine, PCy_3, with the cyclo-octene complexes [$M_2Cl_2(C_8H_{14})_4$] (M = Rh, Ir) in

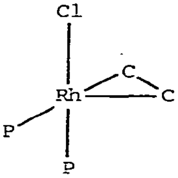


[201]

$\Big\downarrow$ $Rh_2Cl_2(nbd)_2$



[202]



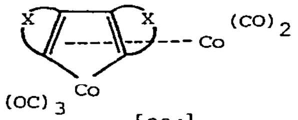
[203]

refluxing toluene have been shown to give $[MClH_2(PCy_3)_2]$ and the four-co-ordinate complexes $[\overline{MP(C_6H_9})Cy_2(Cl)(PCy_3)]$ in which one cyclohexyl group has been dehydrogenated to a cyclohexene group, the double bond of which occupies a co-ordination site. The four-co-ordinate iridium compounds undergo an oxidative addition reaction with hydrogen and both the rhodium and iridium compounds react with carbon monoxide to give trans-$[MCl(CO)(PCy_3)\{PCy_2(C_6H_9)\}]$. Tri-isopropylphosphine reacts with $[M_2Cl_2(C_8H_{14})_4]$ to give $[MClH_2(PPr_3^i)_2]$. The complexes $[MClH_2(PR_3)_2]$ are catalysts for the hydrogenation of olefins at 100°C and one atmosphere pressure (ref. 271). The full paper on the crystal structures of $[RhCl(CO)\{Bu_2^tP(CH_2)_4C \equiv C(CH_2)_4PBu_2^t\}]$ (triple bond not co-ordinated) and $[RhCl\{Bu_2^tP(CH_2)_2CH{=}CH(CH_2)_2PBu_2^t\}]$ (double bond co-ordinated) has been published (ref. 272).

Metal alkyne compounds

Dicobalt octacarbonyl, $[Co_2(CO)_8]$, is known to react with acetylenes to give a variety of organic and organometallic products. The reaction of cyclo-octyne with $[Co_2(CO)_8]$ has now been studied and has been shown to give the air-stable complex

$[Co_2(CO)_5(C_8H_{12})_2]$ [204] as the major product, the μ-cyclo-octyne complex, $[Co_2(CO)_6(C_8H_{12})]$ and tris(hexamethylene)benzene. The crystal structure of [204] has been determined. This type of metallacyclopentadiene complex has not been isolated

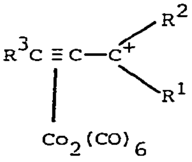


[204]

$(X = (CH_2)_6)$

hitherto from cobalt carbonyl-acetylene reactions but its structure is similar to the complexes $[Rh_2(PF_3)_5(ac)_2]$ isolated from the reactions of $[Rh_2(PF_3)_8]$ with dimethylacetylene dicarboxylate or methyl propiolate. Since [204] is isoelectronic with the well-known ferracyclopentadienes the stability of [204] is not unexpected but it is not clear why the formation of a metallacyclopentadiene should be restricted to cyclo-octyne. These results provide further evidence for the intermediacy of $[Co_2(CO)_5(ac)_2]$ complexes in $Co_2(CO)_8$-acetylene reactions and it has been found that [204] reacts with methyl propiolate to give a pair of isomeric "fly-over" complexes $[Co_2(CO)_4\{(C_8H_{12})_2HC_2CO_2Me\}]$ (ref. 273). The acetylene, MeSC≡CSMe, reacts with $[Co_2(CO)_8]$ to give a μ-acetylene complex $[Co_2(CO)_6(MeSC{\equiv}CSMe)]$, (ref. 274). The crystal structure of $[Co_2(CO)_4(PMe_3)_2(C_2H_2)]$ has been reported (ref. 275).

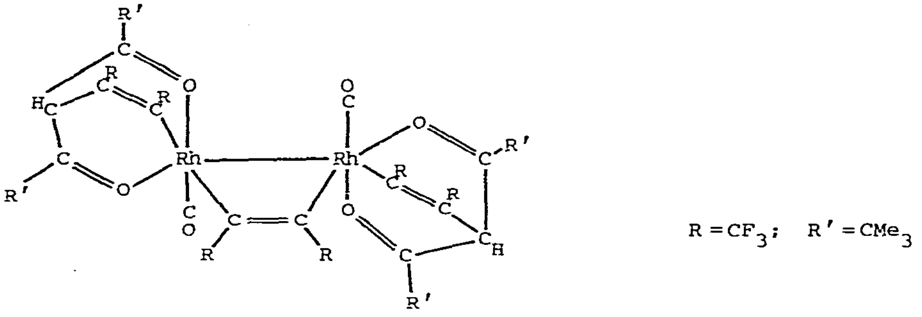
Carbenium ions are known to be stabilised when flanked by organometallic moieties. The carbenium ions [205] are known to be stabilised by the $Co_2(CO)_6$ unit and they have been shown to react with anisole at 0°C to give complexes in which the (propargyl)$Co_2(CO)_6$ unit has been introduced into the aromatic ring (ref. 277).



[205]

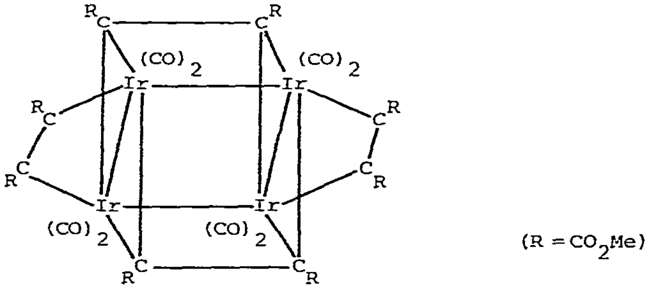
Protonation of $[CoMe\{P(OMe)_3\}_4]^+$ in the presence of diphenylacetylene gives the trigonal bipyramidal complex $[Co(PhC{\equiv}CPh)\{P(OMe)_3\}_4]^+$, (ref. 277) and cobalt atoms have been reported to form a complex with hexafluorobut-2-yne (ref. 277).

The first mono-olefin-acetylene complexes $[Rh(olefin)(CF_3C{\equiv}CCF_3)(O\text{-}O)]$, (olefin = ethylene, cyclo-octene; O-O = MeCOCHCOMe, $Me_3CCOCHCOCMe_3$) have been described (ref. 240) and the properties and structures of these complexes have been discussed in the previous section on metal alkene compounds. The reaction of hexafluorobut-2-yne with $[Rh(dpm)(CO)_2]$ (dpm = $Me_3CCOCHCOCMe_3$) gives the complex [206]



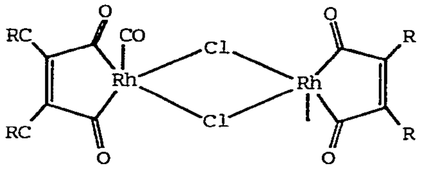
[206]

which is shown by an X-ray study to contain an acetylene co-ordinated parallel to a metal-metal bond. The η^4-hexakis(trifluoromethyl)benzene complex [Rh(dpm C_4F_6){η^4-$C_6(CF_3)_6$}], which contains a hexafluorobut-2-yne molecule added 1,4 to the rhodium β-ketoenolate ring, is formed both from the reaction of hexafluorobut-2-yne with [Rh(dpm)$(CO)_2$] at 110°C or hexafluorobut-2-yne and [206] at 110°C (ref. 278). A complex also containing an acetylene co-ordinated parallel to a metal-metal bond [207] results from the irradiation of [$Ir_4(CO)_{12}$] with excess $MeCO_2C{\equiv}CCO_2Me$. The observed C-C distances indicate that the edge-bridging acetylenes donate two electrons each to the complex and the face capping acetylenes four (ref. 279). The

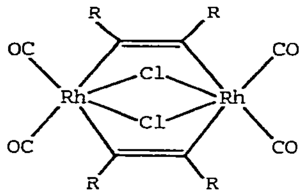


[207]

reaction of hexafluorobut-2-yne with [$Rh_2Cl_2(CO)_4$] gives a fluorocarbon-rhodium complex of approximate formula [$RhCl(CO)_{2\text{ or }3}(C_4F_6)_n$, xH_2O, yC_6H_6] [208] of unknown structure. It is an intermediate in the formation of tetrakis(trifluoromethyl)-cyclopentadiene from $CF_3C{\equiv}CCF_3$ and CO in the presence of [$Rh_2Cl_2(CO)_4$] and reacts with CO and TlCp to give respectively <u>trans</u>-[RhCl(CO)$(PPh_3)_2$] and [$Rh_2Cp_2(CO)_2(C_4F_6)$]. It is not clear whether this complex [208] contains the structural unit [208a] or [208b] (ref. 280). A comparison of the reactions of $MeC{\equiv}CMe$ and $CF_3C{\equiv}CCF_3$ with the



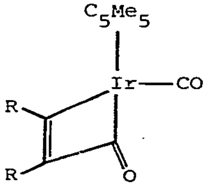
[208a]



[208b]

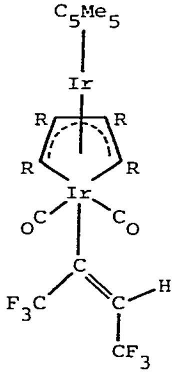
$R = CF_3$

complexes $[M(C_5Me_5)(CO)_2]$ (M = Co, Rh, Ir) has been made. The reactions of Me_2C_2 and C_4F_6 with $[M(C_5Me_5)(CO)_2]$ (M = Rh, Ir) give the cyclopentadienone complexes $[M(C_5Me_5)(C_4Me_4CO)]$ and $[M(C_5Me_5)\{C_4(CF_3)_4CO\}]$ as the major products. The Me_2C_2-cobalt system also gives some hexamethylbenzene and the rhodium systems give the dirhodium complexes $[Rh_2(C_5Me_5)_2(MeC_2Me)_2CO]$ and small amounts of $[Rh_2(C_5Me_5)_2(CF_3C_2CF_3)_2(CO)_n]$ (n = 1 or 2). No products could be isolated from the reaction of C_2Me_2 with $[Ir(C_5Me_5)(CO)_2]$, but the reaction with C_4F_6 gave the iridium compounds [209] and [210]. The complex [210] has been characterised by an X-ray study and it is interesting to find that one η^5-C_5Me_5-Ir link has been broken during the reaction (ref. 281). Treatment of the dinuclear iridium complexes [211] with hexafluorobut-2-yne affords the acetylene complex [212]. The complex (212; R = OMe) slowly loses hydrogen in solution to give the symmetrical dinuclear iridium-iridium bonded complex [213] (ref. 282).



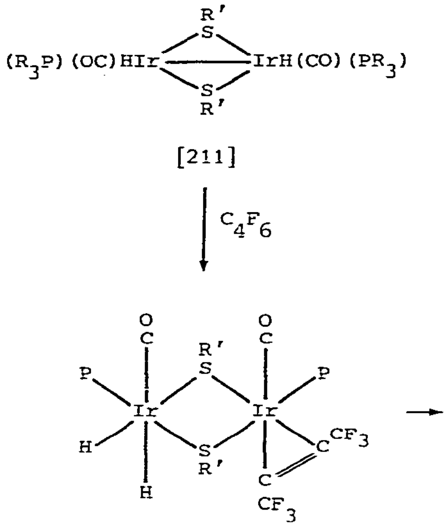
[209]

$(R = CF_3)$



[210]

The reaction of diphenylacetylene with $[CoCpMe_2(PPh_3)]$ is known to lead to the metallacyclopentadiene complex $[CoCp(C_4Ph_4)(PPh_3)]$ and $[CoCp(\eta^4$-$C_4Ph_4)]$. Further studies on this reaction reveal that an organic product [214] is formed in high yield and a mechanism for this reaction has been proposed which is briefly outlined in



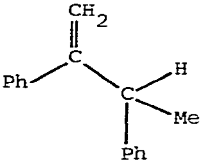
(R' = Bu^t; R = Me, OMe)

[211]

[212]

$\rightarrow [Ir(\mu\text{-}SBu^t)Co\{P(OMe)_3\}]_2C_4F_6$

[213]



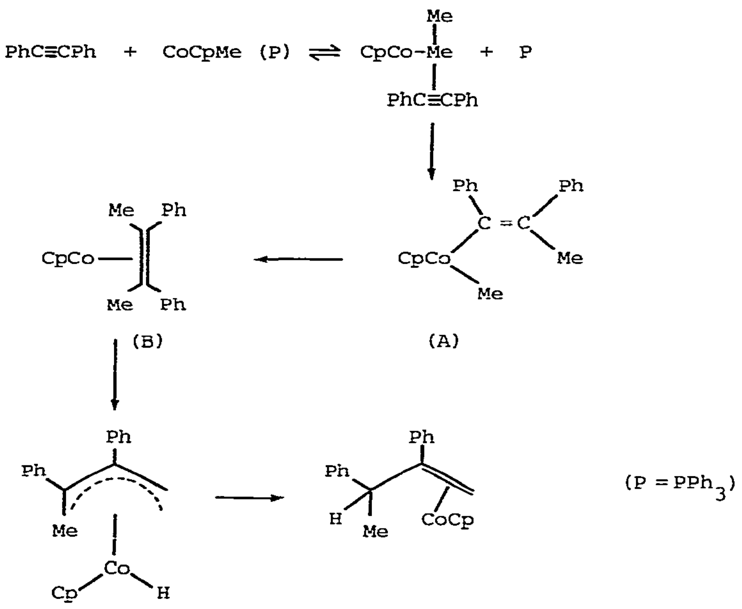
[214]

Scheme 46. An interesting feature of this mechanism is the reductive elimination step (A → B) which occurs rapidly at 56°C whereas the complex $[CoCpMe_2(PPh_3)]$ does not give ethane even at 140°C. It is suggested that co-ordination of the π-electrons of the alkenyl ligand in (A) to the metal in the reductive elimination transition state provides a low-energy route for this process which is not available in the reductive elimination reaction of $[CoCpMe_2(PPh_3)]$ (ref. 283).

Crystal structure determinations on the complexes $[RhCl(CO)\{Bu^t_2P(CH_2)_4C\equiv C(CH_2)_4\text{-}PBu^t_2\}]$ and $[IrClCO\{Bu^t_2PC\equiv C(CH_2)_5C\equiv CPBu^t_2\}]$ show that the diphosphine ligands span _trans_-co-ordination sites but that the triple bonds are not co-ordinated to the metal atoms (ref. 272, 284).

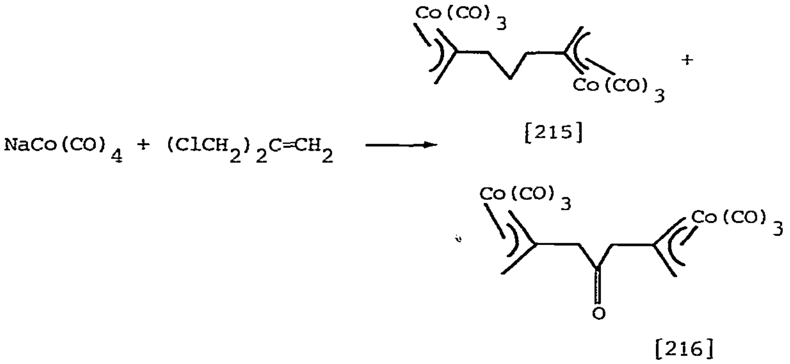
Metal allyl compounds

Attempts to obtain a precursor of a cobalt-trimethylenemethane complex by reaction of $NaCo(CO)_4$ with (chloromethyl)allyl chloride have given the unexpected π-allyl



SCHEME 46

complexes [215] and [216]. A mechanism which accounts for the formation of these complexes has been suggested and the crystal structures of the complexes [215] and [216] have been determined (ref. 285). Some π-allyl complexes of the type



$[CoL(CO)_2(PPh_3)]$ ($L = \pi$-allyl group substituted in the 1- and 2- position with a *m*- or *p*- FC_6H_4 group) have been prepared by the action of $NaCo(CO)_4/PPh_3$ upon $[PCl_2Cl_2(allyl)_2]$ and the electronic effects of the substituents on the allyl group have been assessed (ref. 286, 287). Nucleophilic substitution upon the complex

$[\mathrm{Co}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{CO})_3]$ has been correlated with frontier orbital indices (ref. 288). The complex $[\mathrm{Co}(\eta^3\text{-}\mathrm{C_3H_5})\{\mathrm{P(OMe)_3}\}_3]$ is a catalyst precursor for the homogeneous hydrogenation of arenes at room temperature and low pressure. There is a pronounced stereoselectivity for the *cis* addition of H_2 and the formation of *cis* ring junctions. Thus benzene + D_2 gives $\geqslant$ 95% of all *cis*-$C_6H_6D_6$, naphthalene + H_2 gives all *cis* decalin and anthracene + H_2 gives > 95% of *cis*-*syn*-*cis*-perhydroanthracene. The catalytic hydrogenation of benzenes containing the substituents -R, -OR, $-CO_2R$, -COR, -CH=CHR, -C≡CR, and $-NR_2$ can also be achieved but electron-withdrawing substituents and nucleophilic substituents, e.g. halogen, $-NO_2$, -CN inhibit the reaction. The reaction is also inhibited by substituents on the arene ring which exhibit steric effects (ref. 289). Allyl species of the form $[\mathrm{CoH(allyl)}\{\mathrm{P(OR)_3}\}_3]^+$ have been shown to be key intermediates in the olefin isomerisation catalysed by $[\mathrm{Co}\{\mathrm{P(OMe)_3}\}_4]^+$ (ref. 27).

Allylcobaloximes have been shown to exhibit temperature-dependent ^1H n.m.r. spectra which can be interpreted in terms of a dynamic process in which interchange between the two possible σ-allylcobaloximes occurs. Two processes are considered to take place: allylaquabis(dioximato)cobalt(III) complexes undergo a unimolecular reaction which involves loss of the aqua ligand and formation of a transient η-allylcobaloxime; allylbis(dioximato)pyridinecobalt(III) complexes undergo a bimolecular reaction which involves S_H2' attack of a cobaloxime(II) impurity at the δ-carbon of the allyl group and displacement of cobaloxime(II) from the α-carbon. The propadienyl complex (217; L = H_2O) exhibits no dynamic behaviour and shows no tendency to transform to the isomeric compound [218]. However, the complex previously formulated as bis(dimethylglyoximato)prop-2-ynyl(pyridine)cobalt(III) does not have the structure type [218] but is probably the bimetallic complex [219]. The σ-allyl complexes [220] react with tetracyanoethylene to give the cyclopentyl complexes [221], the reaction with the *trans*-cinnamyl complex involving a σ-π-σ antarafacial migration of the cobalt from the α- to the β- carbon of the allyl group. The propadienyl complex [222] also undergoes cycloaddition reactions with tetracyanoethylene and hexafluoroacetone to give [223] and [224] respectively. The mechanism postulated for these reactions suggests the formulation of [224] as 4,5-dihydrofurylmetal complexes although corresponding products from propadienyliron complexes have been formulated as 2,3-dihydrofuryliron complexes (ref. 290). Allyl-, propadienyl-, and benzyl-cobaloximes are known to react with polyhalogenomethanes to give halogenocobaloxime and poly-

$[\mathrm{Co(CH{=}C{=}CH_2)(Hdmg)_2L}]$

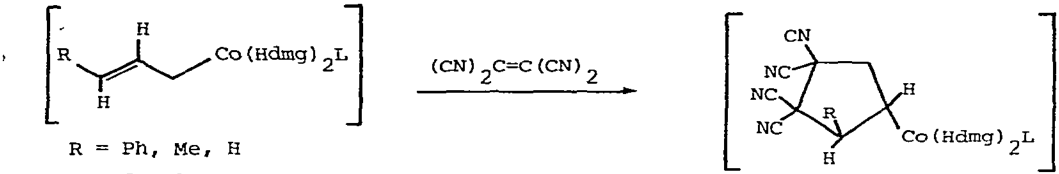
[217]

$[\mathrm{Co(CH_2C{\equiv}CH)(Hdmg)_2L}]$

[218]

$[\mathrm{(py)(Hdmg)_2Co(C{\equiv}CCH_2)Co(Hdmg)_2(py)}]$

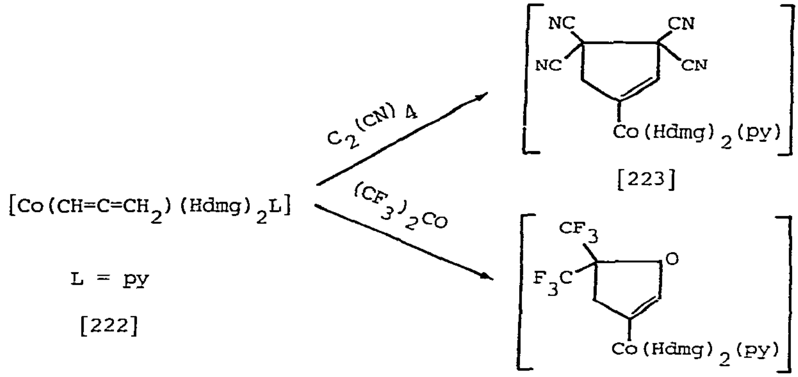
[219]



R = Ph, Me, H

[220]

[221]



[223]

L = py

[222]

[224]

halogeno-organic products *via* the mechanism outlined in Scheme 48. Several allylcarbonyldihalogeno bis(phosphine)-rhodium(III) and iridium(III) complexes have now

$$M^{\bullet} + CBrCl_3 \longrightarrow MBr + CCl_3^{\bullet}$$

$$CCl_3 + MR \longrightarrow RCCl_3 + M^{\bullet}$$

$$M = Co(Hdmg)_2L$$

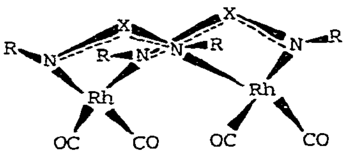
SCHEME 48

been shown to react with $CBrCl_3$ to give the carbonyltrihalogenobis(phosphine)metal (III) complex and 4,4,4-trichlorobut-1-ene. More highly substituted allyl complexes give mixtures of the corresponding trichlorobutene and allyl halide. The related propadienyl complexes give $CCl_3CH_2C{\equiv}CH$ as the only organic product mixed with the corresponding organic halides. By analogy with the cobaloxime reactions, it is suggested that the organic products are formed by a chain reaction involving displacement of a five-co-ordinate rhodium(II) or iridium(II) complex by regiospecific attack of $CCl_3^{\bullet}$ on the γ-carbon of the allyl or propadienyl group and formation of $CCl_3^{\bullet}$ by reaction of the rhodium(II) or iridium(II) complex with $CBrCl_3$ (ref. 291).

An attempt to prepare an iridium metallacyclobutane complex by reaction of phenylcyclopropane with trans-[IrCl(N$_2$)(PPh$_3$)$_2$] has given the allyl metal hydride,

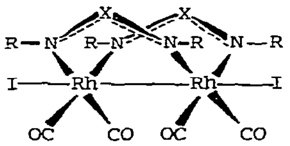
$[IrClH(\eta^3-C_3H_4Ph)(PPh_3)_2]$, which has been characterised by an X-ray study. This compound represents the first example of a stable, fully characterised η^3-allyl metal hydride complex. This complex also results from the reaction of allylbenzene with trans-$[IrCl(N_2)(PPh_3)_2]$ a reaction which presumably involves initial olefin co-ordination followed by insertion into the olefinic C-H bond. This process is often suggested as the initiation step for catalytic olefin transformations in which allyl metal hydride complexes are implicated (ref. 292). The vibrational spectra of the complexes, $[Rh(allyl)_3]$, $[Rh_2X_2(allyl)_4]$, (X = Cl, Br) have been studied (ref. 293).

Some rhodium(I) compounds of the pseudo allyl ligands, triazenido-, $[RNNNR]^-$ and 1-iminoethylamido, $[RNC(Me)NR]^-$ have been prepared and reactions of the complexes have been studied. $[Rh_2Cl_2(CO)_4]$ reacts with $Na[RNNNR]$ ($R = C_6H_4Me$-p) or $Li[RNC(Me)NR]$ (R = Ph or C_6H_4Me-p) to give the dimeric complexes [225]. These complexes undergo substitution reactions with triphenylphosphine to give the complexes $[Rh(RNNNR)(CO)(PPh_3)]_2$ ($R = C_6H_4Me$-p) and $[Rh_2\{RNC(Me)NR\}_2(CO)_3(PPh_3)]$ (R = Ph). Treatment of the complexes [225] with iodine gives the rhodium-rhodium bonded complexes [226].



X = N; X = CMe

[225]

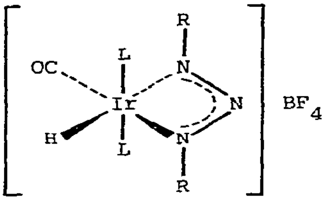


X = N; X = CMe

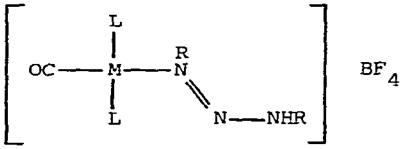
[226]

With cyclo-octa-1,5-diene or norbornadiene the complexes $[Rh_2(RNNNR)_2(CO)_2(cod)]$ and $[Rh(RNNNR)(diene)]_n$ have been isolated while reaction of (225; X = N) with cycloheptatriene (cht) gives a complex $[Rh_2(RNNNR)_2(CO)(\mu-CO)(\mu-cht)]$ (ref. 294). The complexes (225; R = Ph, C_6H_4Me-p, X = N) have also been obtained by the reactions of $[Rh_2Cl_2(CO)_4]$ with Me_3SnN_3R (ref. 295). Protonation of the rhodium and iridium complexes $[M(CO)L_2(RNNNR)]$ with HBF_4 affords either (227; $L = PPh_3$, R = p-MeC_6H_4 or p-FC_6H_4; $L = PMePh_2$, R = p-FC_6H_4) or (228; M = Rh, $L = PPh_3$, R = Ph, p-MeC_6H_4, or

p-FC$_6$H$_4$). The complex [Rh(CO)(PPh$_3$)$_2$(RNNNHR)]BF$_4$ undergoes triazene displacement with chloride ion or with iodine to give [RhCl(CO)(PPh$_3$)$_2$] and [RhI$_3$(CO)(PPh$_3$)$_2$] respectively and quantitative deprotonation with NEt$_3$. However, attempts to alkylate the co-ordinated triazenido-ligand were not successful. On standing in the solid state the complex (227; L = PPh$_3$, R = Ph) partially isomerises to (228; M = Ir). The complexes (228; M = Ir, Rh) and [M(CO)L$_2${MeC(=NR)NHR}][BF$_4$] (M = Rh, Ir, L = PPh$_3$, R = Ph or p-MeC$_6$H$_4$) may be prepared directly from the appropriate diaryltriazene or diarylacetamidine and [M(CO)L$_2$(acetone)][BF$_4$] (ref. 296).



[227]



[228]

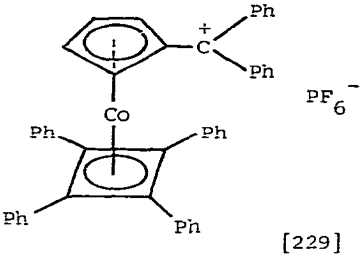
Metal carbocyclic and carbaborane compounds

The electrochemical generation of the dication [(CpCo)$_2$(cot)]$^{2+}$ (cot = cyclooctatetraene), a triple-decker sandwich molecule, has been reported. This 34 valence electron species is isoelectronic with [Cp$_3$Ni$_2$]$^+$, the only charged triple decker to be previously reported, and the chemistry of these two cations is very similar. The complex [(CpCo)$_2$(cot)]$^{2+}$ undergoes a set of electron-transfer reactions as indicated below (ref. 297):

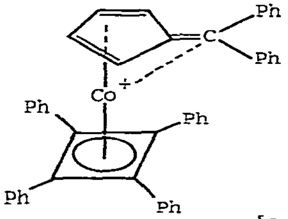
$$\begin{tikzcd}
{[(CpCo)_2(cot)]^{2+}} \arrow[r, "2e^-", leftrightharpoons] & {[(CpCo)_2(cot)]} \arrow[d, "e^-", leftrightharpoons] \\
{[(CpCo)_2(cot)]^{2-}} & {[(CpCo)_2(cot)]^-} \arrow[l, "e^-"', leftrightharpoons]
\end{tikzcd}$$

Mercuration of [CoCp(C$_4$Ph$_4$)] followed by transmetalation with LiBu^n and reaction of the lithium derivative with benzophenone gives the alcohol [Co(C$_5$H$_4$CPh$_2$OH)(C$_4$Ph$_4$)].

Treatment of this alcohol with $Et_2OH^+PF_6^-$ gives the deep-blue metal stabilised carbonium ion [229]. This cationic species acts as a carbon electrophile with MeOH, $MeNH_2$ and N-methylpyrrole. However, with N,N-dimethylaniline and anisole the cation acts as a cobalt electrophile and the $C_5H_4CPh_2$ ligand is displaced to give the η^6-arene-η^4-tetraphenylcyclobutadiene complexes $[Co(\eta^6-C_6H_5Z)(\eta^4-C_4Ph_4)]^+$ (Z = NMe_2, OMe). Similar reactions occur with benzene, toluene, and mesitylene if aluminium trichloride is present. The ^{13}C n.m.r. spectrum of [229] suggests that there is electron transfer from cobalt to the electron-deficient carbon centre and in the extreme, the structure can be drawn as [230] and the complex can be regarded as containing the 6,6′-diphenylfulvene ligand. The rôle of aluminium trichloride in the displacement reactions with benzene, toluene, and mesitylene is considered to be two-fold since two molar equivalents of aluminium trichloride are necessary for the reaction to occur. One of these serves to generate the cation [229] and the second mole of $AlCl_3$ interacts with the exo C=C bond, disrupting its interaction with the cobalt. The cobalt atom then becomes more susceptible to nucleophilic attack by an arene (ref. 298).



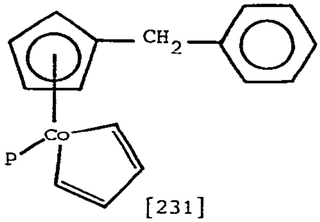
[229]



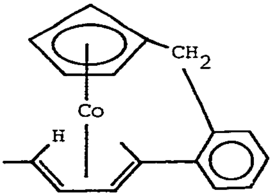
[230]

Molecular orbital calculations have been carried out for the compound $[CoCp(C_4H_4)]$. The dominant bonding interaction is between the metal d_{xz}, d_{yz} (e) orbitals and the ligand e π-C_4H_4 level, the π-Cp orbitals being less strongly involved (ref. 299). It is known that thermolysis of $[\overline{CoCPh=CPhCPh=C}Ph(Cp)(PPh_3)]$ gives the tetraphenylcyclobutadiene complex $[CoCp(C_4Ph_4)]$. Further studies have now shown that a variety of substituted cyclobutadiene complexes can be obtained by thermolysis of (η^5-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene complexes. Similar treatment of benzyl-substituted cyclopentadienyl complexes [231] gives diene complexes of the type

(P = PPh$_3$)

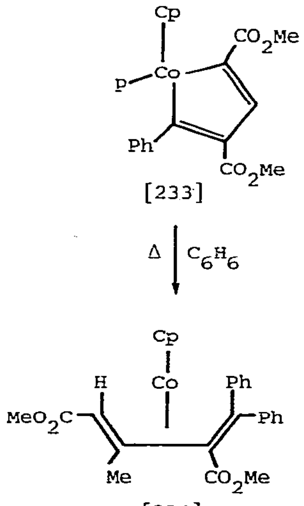


[231]



[232]

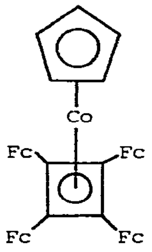
[232] which are formed by addition of the ortho hydrogen of the benzyl group to the cobaltacyclopentadiene ring. Further, if an unsubstituted cyclopentadienyl derivative is heated in benzene, e.g. [233] then the diene complex [234] can be



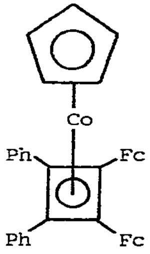
P = PPh$_3$

[234]

obtained as a minor product. Dissociation of triphenylphosphine is considered to be the first step in these reactions (ref. 300). The reaction of [CoCp(CO)$_2$] with diferrocenylacetylene produces the tetraferrocenylcyclobutadiene complex [235]. A similar reaction between [CoCp(CO)$_2$] and ferrocenylphenylacetylene also results in dimerisation of the acetylene to give the isomers [236] and [237], the structure of the latter being established by an X-ray structure determination (ref. 301). The interaction of the diacetylene [238] with [MCp(CO)$_2$] (M = Co, Rh) results in an intramolecular cyclodimerisation to form the respective η^4-1,2-diphenylcyclobuta[ℓ]-phenanthrene complexes [239] (ref. 302). A study of the reactions of the alkadiynes [240] with [CoCp(PPh$_3$)$_2$] has shown that these reactions lead initially to a complex in which one of the triple bonds is co-ordinated to the cobalt, the complex subsequently undergoing conversion to a metallacycle. Thus the reaction of (240; n = 4) with [CoCp(PPh$_3$)$_2$] proceeds *via* a mono-acetylene complex to give (241; n = 4). A similar reaction of 2,7-nonadiyne with [CoCp(PPh$_3$)$_2$] also gives a metallacycle (241; n = 3) but an intermediate acetylene complex could not be detected and a shorter chain length apparently results in faster cyclisation. In reactions where the acetylene functions are joined by larger or smaller bridges the reactions are more complex and both inter- and intramolecular metallacycles are formed. The reaction of [242] with [CoCp(PPh$_3$)$_2$] gives an isolable stable acetylene complex [243] which in benzene solution undergoes conversion to [244] (ref. 303). Vacuum sublimation of the cyclobutadiene complex [245] through a hot quartz tube initiates the clean rearrangement to isomer [246]. This reaction possibly proceeds *via* a novel



[235]



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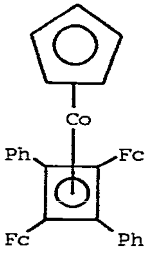

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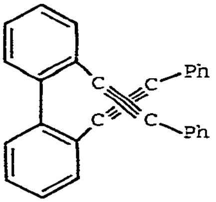
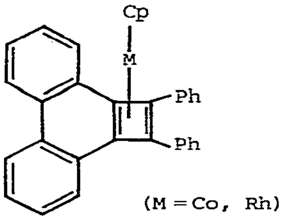
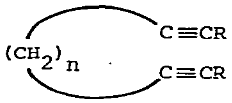


[238]

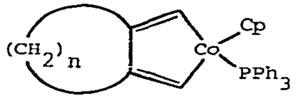


[239]

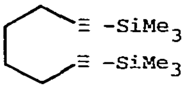


[240]

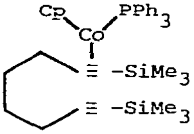
(R = Me)·



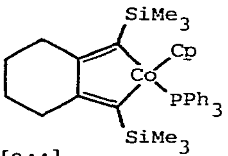
[241]



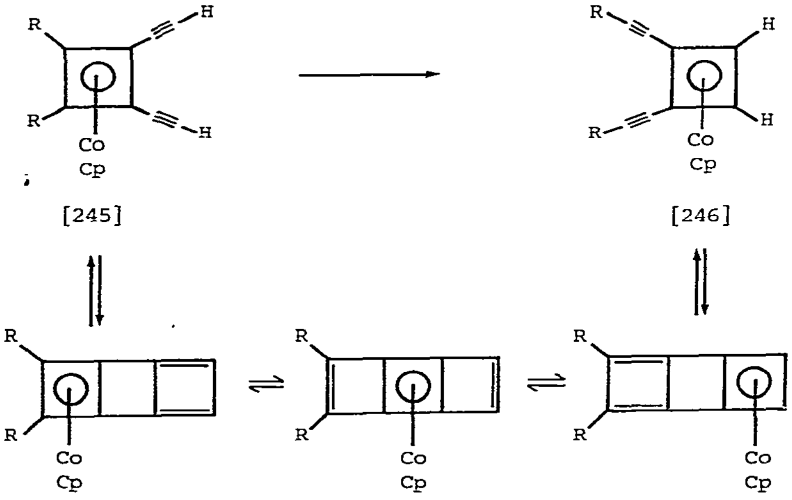
[242]



[243]



[244]



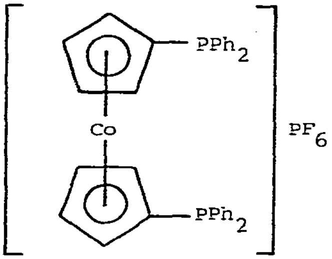
SCHEME 49

bicyclobutadienylene ligand (Scheme 49) (ref. 304).

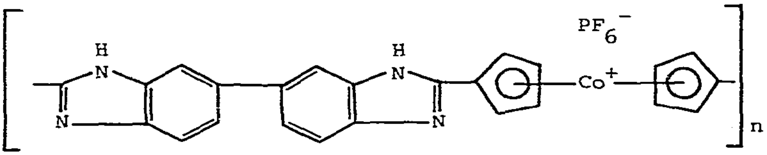
The complexes $[Co(CR^1=CR^2-CR^3=CR^4)Cp(PPh_3)]$ have been shown to react with nitriles to give highly substituted pyridines and when $R^4=CO_2Me$, the nitriles react regioselectively such that the nitrogen atom in the pyridine formed occupies a position away from the carbon to which the CO_2Me group is linked (ref. 305). The cyclotrimerisation of acetylenes with isocyanates in the presence of [247] or $[CoCp_2]$

to give 2-oxo-1,2-dihydropyridines has been achieved and if diphenylcarbodiimide and acetylenes are used then 2-imino-1,2-dihydropyridines are formed (ref. 306). A review on the cobalt catalysed pyridine synthesis from alkynes and nitriles has been published (ref. 307).

A comparative study of 1,1'-bis(diphenylphosphino)cobaltocenium hexafluorophosphate [247] and 1,1'-bis(diphenylphosphino)ferrocene as bidentate ligands has been made. The ferrocene ligand behaves much like aromatic phosphines such as $Ph_2PCH_2CH_2$-PPh_2 but in contrast, the cationic cobaltocenium ligand [247] causes a shift of the carbonyl stretching frequencies to higher wave numbers in its complexes with group VI metal carbonyls. In addition, it requires changes in synthetic procedure such as the need for additional chloride ion to prepare the nickel(II) chloride complex $[Ni(cdpp)Cl_3]$ (cdpp = 247). It is also noteworthy that the reaction of $[cdpp]PF_6$ with copper(I) yields a dark purple complex $[Cu(cdpp)Cl_2]$ which displays a field-dependent paramagnetism indicative of an electron-transfer process between the ligand and the copper ion (ref. 308). Some metallocene polymers have been obtained by the polycondensation of 1,1'-dicarboxycobaltocenium chloride with 1,4-phenylenediamine, 4,4'-biphenylenediamine or 4,4'-methylenedianiline in molten $SbCl_3$ (ref. 309). Polycondensation of 1,1'-dicarboxycobaltocenium with 3,3'-diaminobenzidine or 3,3'-dimercaptobenzidine in ethylated polyphosphoric acid at 100-240°C gives linear, soluble polymeric intermediates containing alternating cobaltocenium-1,1'-diyl and bibenzimidazoline-2,2'-diyl or bibenzothiazoline-2,2'-diyl units which when heated at 300°C are aromatized to give [248] (ref. 310).



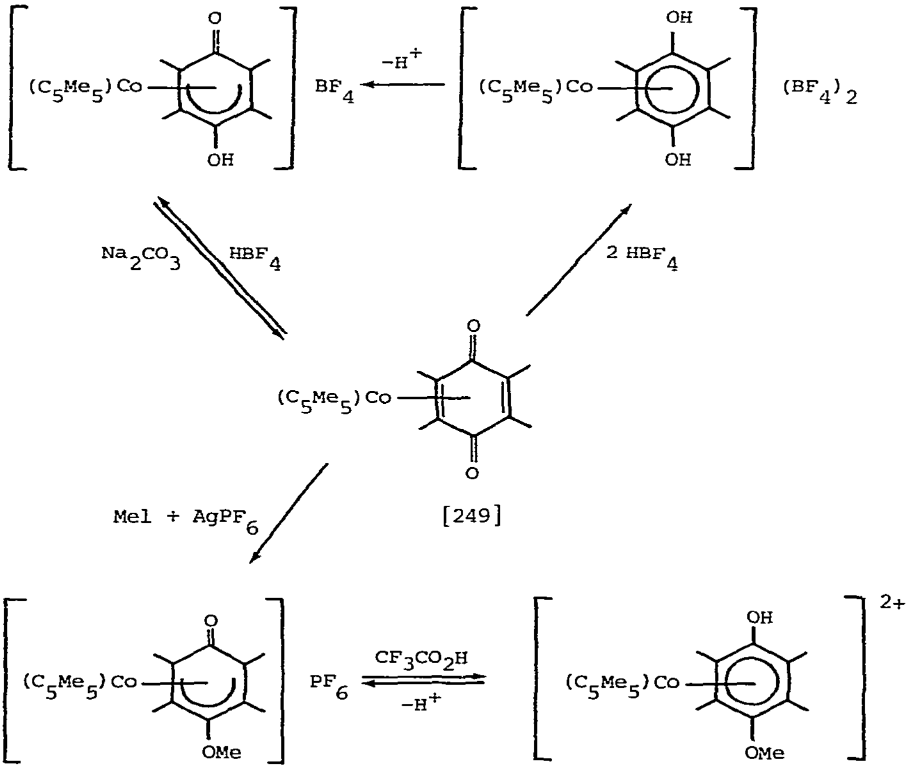
[247]



[248]

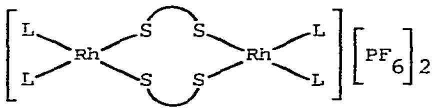
A crystal structure determination on the salt $[CpCo(C_5H_4CO_2H)]PF_6$ reveals that hydrogen bonded dimers of $[CpCo(C_5H_4CO_2H)]^+$ and discrete PF_6^- anions are present. The mean Co-C(Cp) distance found appears to be shorter than in cobaltocene (ref. 311). INDO SCF calculations have been carried out on $[CoCp_2]^+$ and $[CoCp(C_4H_4)]$ (ref. 312, 313). The temperature dependent paramagnetic ^{13}C and ^1H n.m.r. spectra of $[Co(C_5H_4R)_2]$ ($R = H$, Me, Et, Pr^i, Bu^n, Bu^t) have been investigated (ref. 314) as has the ^{13}C n.m.r. spectrum of $[Co(C_5D_5)_2]$ (ref. 315). The magnetic susceptibility of cobaltocene between 0.90 and 300 K (ref. 316) and heat capacity of cobaltocene (ref. 317) have been determined. Solid coatings of cobalt on a palladium-activated surface of copper have been prepared by the reaction of $[CoCp_2]$ with hydrogen at 150–350°C (ref. 318).

Pentamethylcyclopentadienyl complexes of the cobalt, rhodium, iridium triad continue to attract attention and a review on (pentamethylcyclopentadienyl)rhodium and -iridium complexes and their applications to homogeneous catalysis has been published (ref. 319). The preparation of the η^4-2,3,5,6-tetramethyl-1,4-benzoquinone complex [249] has been reported and some reactions of this complex are illustrated in Scheme 50 (ref. 320). A number of pentamethylcyclopentadienyl-rhodium and -iridium



SCHEME 50

complexes catalyse the hydrogenation of alkenes under mild conditions. Thus $[MX_2(C_5Me_5)]_2$ (M = Rh, Ir, X = Cl, Br, I; M = Rh, X = NO_3), $[\{M(C_5Me_5)\}_2HX_3]$ (M = Rh, X = Cl, Br; M = Ir, X = Cl, Br, I) and $[IrHX(C_5Me_5)]_2$ (X = Cl, Br) in the presence of Et_3N are efficient catalysts in propan-2-ol. In the presence of base the complexes $[MCl_2(C_5Me_5)]_2$ (M = Rh or Ir) are more active than the μ-hydrido-complexes $[\{M(C_5Me_5)\}_2H_xCl_{4-x}]$ (M = Rh, x = 1; M = Ir, x = 1 or 2). The tri-μ-hydrido complex $[\{Ir(C_5Me_5)\}_2H_3]Cl$ is inactive. Dienes, acetylenes, and olefins bearing functional groups are readily reduced by $[\{M(C_5Me_5)\}_2HCl_3]$ (M = Rh, Ir) at 100 atm. and 20°C but the functional groups are not reduced (ref. 321). The structures of $[RhBr(\mu\text{-}Br)(C_5Me_5)]_2$ and of the partially halide-exchanged species $[RhX(\mu\text{-}X)(C_5Me_5)]_2$ obtained by recrystallisation of the bromo complex from 1,2-dichloroethane have been determined by single-crystal X-ray studies (ref. 322). The activity of these pentamethylcyclopentadienyl-rhodium and -iridium hydrogenation catalysts is inhibited by other ligands, in particular those containing sulphur as a donor atom. These observations have led to an investigation of the reactions of the complexes with sulphur donor ligands and a variety of complexes have been prepared and studied. These include $[\{Rh(C_5Me_5)\}_2Cl_4(SMe_2)]$, $[Rh(C_5Me_5)(SMe_2)_3][PF_6]_2$, $[Rh(C_5Me_5)(MeCN)(dithan)][PF_6]_2$, $[\{Rh(C_5Me_5)\}_2(SS)Cl_4]$ (SS = 1,4-dithan, 2,5-dithiahexane), $[Rh(C_5Me_5)(2,5\text{-dithiahexane})_2][PF_6]_2$, $[Rh(C_5Me_5)Cl(SR)]_n$ (R = Me, Ph, $PhCH_2$), $[Rh(C_5Me_5)Cl(S_2CNEt_2)]$, $[Rh(C_5Me_5)(S_2CNMe_2)_2]$, $[Rh(C_5Me_5)(S_2CMe)_2]$, $[Rh(C_5Me_5)\{S_2C_2(CN)_2\}]$, $[Rh(C_5Me_5)(3,4\text{-}S_2C_6H_3Me)_2]$, $[Ir(C_5Me_5)(S_2CNMe_2)_2]$, and $[Ir(C_5Me_5)\{S_2C_2(CN)_2\}]$. The complexes $[Rh(C_5Me_5)(S_2CNMe_2)_2]$, $[Rh(C_5Me_5)(S_2CMe)_2]$, and $[Ir(C_5Me_5)(S_2CNMe_2)_2]$ have one uni- and one bidentate dithio-ligand. In conjunction with this study some 1,4-dithian complexes of rhodium(I) have also been prepared. Thus addition of dithian (dt) to $[Rh_2Cl_2(\text{cyclo-octene})_4]$ gives the insoluble complex $[Rh(dt)Cl]_n$. However, more tractable cationic complexes can be obtained by the addition of dithian to $[Rh_2Cl_2(\text{diene})_2]$ (diene = cyclo-octa-1,5-diene, norbornadiene) in the presence of $AgPF_6$. These cationic complexes are of the type $[Rh(\text{diene})(dt)]^+$, however, on reaction of the cod complexes with PPh_3 or $P(OPh)_3$ the dinuclear complexes [250] are formed. A study of these rhodium complexes as potential hydrogenation catalysts under conditions where $[Rh(C_5Me_5)Cl_2]_2$ is active has been made and it is found that while sulphur-containing ligands are very effective poisons toward catalytic hydrogenation some complexes containing sulphur ligands can act as catalysts under more vigorous conditions. Possibly the sulphur ligands are first displaced under these conditions.



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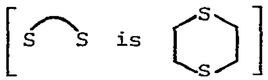
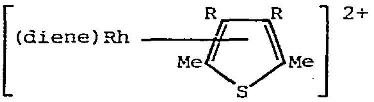


Another reason for the low catalytic activity of these types of complexes may be caused by the low tendency of sulphur-containing complexes to form hydrides. Few transition-metal hydrides containing sulphur ligands are known and attempts to obtain such complexes from $[Rh(C_5Me_5)(S_2CMe)_2]$ have not been successful (ref. 323). Thiophen also poisons the olefin hydrogenation catalyst $[Rh(C_5Me_5)Cl_2]_2$, but since thiophen does not appear to form a complex with $[Rh(C_5Me_5)Cl_2]_2$ it seems that thiophen must act as a poison towards the actual catalytic species formed in the hydrogenations. However, 2,5-dimethylthiophen (dmt) and 2,3,4,5-tetramethylthiophen (tmt) react with $[M(C_5Me_5)(solvent)_3]^{2+}$ to give the π-complexes $[M(C_5Me_5)(tmt)][PF_6]_2$ ($M = Rh$, Ir) and $[Ir(C_5Me_5)(dmt)][PF_6]_2$ in which the thiophen ligands are acting as tridentate, η^5-bonded, ligands. The cationic complexes [251] of rhodium(I) can also be obtained by the reaction of $[Rh_2Cl_2(diene)_2]$ (diene = cod, nbd) with dmt or tmt in the presence of $AgPF_6$. The cyclo-octa-1,5-diene complex $[Rh(C_5Me_5)(C_4Me_4S)][PF_6]$

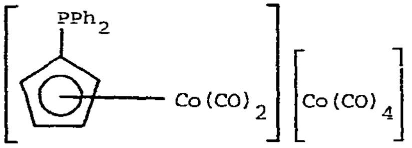


diene = cod, R = Me
diene = nbd, R = Me
diene = cod, R = H

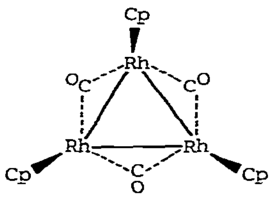
[251]

is about 15% dissociated in acetone solution and the corresponding cod-dmt complex is about 85 ± 5% dissociated in acetone solution and it is clear that the more methylated the thiophen the more stable is the complex. The complex $[Rh(C_5Me_5)$-$(tmt)][PF_6]_2$ is not such an effective hydrogenation catalyst as $[Rh(C_5Me_5)Cl_2]_2$ but some of the thiophen complexes do show substantial catalytic activity for cyclohexene hydrogenation (ref. 324). Reaction of the complexes $[M(C_5Me_5)Cl_2]_2$ with excess of various dithioacid anions gives the monomeric complexes $[M(C_5Me_5)(S\text{-}S)_2]$ ($M = Rh$, $S\text{-}S = S_2PR_2^-$, $S_2CNR_2^-$, S_2COR^-; $M = Ir$; $S\text{-}S = S_2CNMe_2^-$, $S_2PMe_2^-$). These complexes contain both uni- and bi-dentate dithioacid groups both in the solid state and in solution but in solution at higher temperatures there is exchange between the uni- and bi-dentate ligands probably <u>via</u> a dissociatively controlled intramolecular mechanism. The reaction of $[Rh(C_5Me_5)Cl_2]$ with $S\text{-}S^-$ in a 1:1 mol ratio gives $[Rh(C_5Me_5)Cl(S\text{-}S)]$, ($S\text{-}S = S_2CNMe_2^-$, $S_2PMe_2^-$, $S_2PPh_2^-$). This complex can be used to obtain a range of complexes such as $[Rh(C_5Me_5)X(S_2CNMe_2)]$ ($X = Br^-$, I^-, SCN^-, $S_2PMe_2^-$, $S_2PPh_2^-$, S_2COMe^-). In methanol it gives the solvated cation $[Rh(C_5Me_5)(MeOH)(S_2CNMe_2)]^+$ which reacts with donor ligands L to give $[Rh(C_5Me_5)(L)(S_2CNMe_2)]^+$ ($L = PPh_3$, $PMePh_2$, CO, $AsPh_3$, C_5H_5N). With chelating phosphines the dimeric cations $[Rh(C_5Me_5)(S_2CNMe_2)]_2(P\text{-}P)$, ($P\text{-}P = Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2PPh_2$) are formed and the reaction of $[Rh(C_5Me_5)Cl(S_2CNMe_2)]$ with $C_2(CN)_4$ and $NaBPh_4$ gives the cyanotriphenylborate complex $[Rh(C_5Me_5)(NCBPh_3)(S_2CNMe_2)]$ (ref. 325). Since pentamethylcyclopentadienyl metal complexes are generally more crystalline and soluble than their cyclopentadienyl analogues the ethyltetramethylcyclopentadienyl complexes $[Co(C_5Me_4Et)(CO)_2]$, $[M(C_5Me_4Et)Cl_2]$ (M = Rh, Ir) have been prepared. These complexes also exhibit high solubility and the availability of $C_5Me_4Et(H)$ provides a convenient route to these complexes (ref. 326). The crystal structures of the complexes $[Co(C_5Me_4Et)Cl_2(PPh_3)]$ and $[Co_2(\mu\text{-}Cl)_3(C_5Me_4Et)_2]$ have been reported (ref. 327).

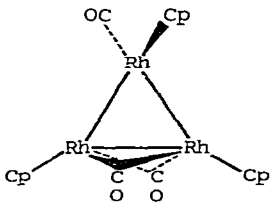
The reaction of $[Co\{C_5H_4SiMe_2OEt\}(CO)_2]$ and $[Co\{C_5H_4Si(OEt)_3\}(CO)_2]$ with a silica gel support provides the corresponding covalently linked silica gel supported compounds. In contrast to their unsupported analogues no binuclear or polynuclear species are formed even at 200°C. The cobalt derivative is a hydroformylation catalyst (ref. 328). The reaction of the ylide $C_5H_4PPh_3$ with $[Co_2(CO)_8]$ affords [252] which on reaction with oct-4-yne and diphenylacetylene gives hexa-n-propylbenzene and hexaphenylbenzene respectively (ref. 329). Extended photolysis of $[RhCp(CO)_2]$ gives the isomers [253] and [254]. Further studies have now shown that direct uv photolysis of a deoxygenated benzene solution of [253] provides [254] in high yield and the carbonyl ligand mobility in this isomer has been studied (ref. 330). Reduction of $[RhCp(CO)_2]$ with sodium amalgam gives $Na[Rh(CO)_4]$ and the complex [255] which has been characterised by an X-ray study. This complex can be envisaged as the product of either the coupling of the paramagnetic fragments $[RhCp(CO)]_2^-$ and $[Rh(CO)_2]$ or of co-ordination of the highly unsaturated $[Rh(CO)_2]^-$ to the Rh = Rh unit in $[RhCp(CO)]_2$. Co-ordination of the $[Rh(CO)_2]^-$ fragment induces the two bridging



[252]

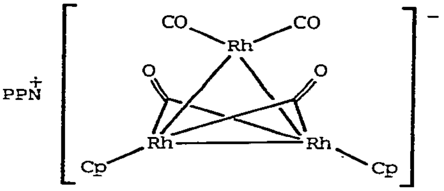


[253]



[254]

carbonyls to lean toward the unique rhodium atom and thus become "semi-triple-bridging" carbonyls (ref. 331). A negative ion mass spectrometric study of

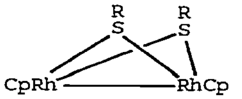


[255]

$\overset{+}{PPN} = \overset{+}{N}(PPh_3)_2$

$[CoCp(CO)_2]$ has been reported (ref. 332). Application of extended X-ray absorption fine structure (EXAFS) spectroscopy to the one-electron cobalt-cobalt bonded dimer $[CoCp(\mu\text{-}PPh_2)]_2^+$ provides evidence that the cobalt-cobalt bond weakens significantly upon oxidation of the neutral to the cationic species. However, the cobalt-cobalt distance increases by only 0.08 Å on going from the neutral compound (2.57 Å) to its monocation (2.65 Å). The metal-ligand and, if present, metal-metal distances of $[CoCp_2]$ and $[CoCp(\mu\text{-}PPh_2)]_2(OH)_m^n$ ($m = 0$, $n = 0$, $+1$ $m = 1$, $n = +1$) have also been determined by this technique (ref. 333).

The reaction of $[RhCp(CO)_2]$ with RSSR gives $[RhCp(\mu\text{-}SR)]_2$ [256] which exists as

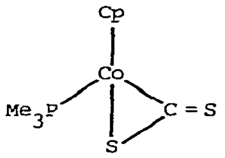


[256]

($R = Ph$, $C_6H_4Me\text{-}p$)

mixture of *syn* and *anti* isomers. Each isomer is not fluxional but *syn*-*anti* isomerisation occurs *via* a bridge-opening mechanism at room temperature. Both isomers undergo irreversible one-electron oxidation and the complex *syn*-$[RhCp(\mu\text{-}SR)]_2$ ($R = C_6H_4Me\text{-}\underline{p}$) reacts with RSSR in the presence of $NOPF_6$ to give $[Rh_2(SR)_3Cp_2][PF_6]$ and with $[N(C_6H_4Br\text{-}\underline{p})_3][SbCl_6]$ to give $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR)_2Cp_2][SbCl_6]$ *via* one-electron oxidation followed by insertion into the metal-metal bond of the radical cation $[Rh(\mu\text{-}SR)Cp]_2^+$ (ref. 334).

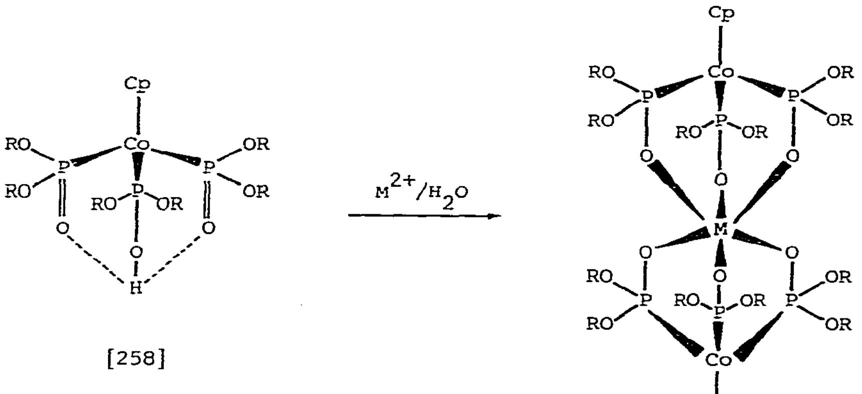
Treatment of $[CoCp(PMe_3)_2]$ with carbon disulphide gives a quantitative yield of the complex [257] which contains a π-bonded carbon disulphide ligand. This complex has been characterised by a single crystal X-ray study and it can also be prepared by the reaction of carbon disulphide with the heterobinuclear compound $[Cp(PMe_3)Co(\mu\text{-}CO)_2Mn(C_5H_4Me)]$. The sulphur atom which is not co-ordinated to the cobalt in the complex [257] also has ligand properties and it can displace tetrahydrofuran from the complexes $[Cr(CO)_5(THF)]$ and $[MnCp(CO)_2(THF)]$ (ref. 335). Treatment of



[257]

$[CoCp(CO)_2]$ with carbon disulphide in the presence of PPh_3 affords the thiocarbonyl complexes $[CoCp(CO)(CS)]$ and $[CoCp(CS)_2]$ and treatment of $[CoCp(CO)(CS)]$ with $MeNH_2$ gives $[CoCp(CO)(MeCN)]$ (ref. 336).

Solvolysis of the cyclopentadienyl complex $[CoCp\{P(OR)_2O\}_3BF]BF_4$ gives the half-sandwich complex [258] which reacts with the divalent metal ions M^{2+} to give the trinuclear compounds [259]. The i.r. spectrum of (259; M = Cu) reveals that the Jahn-Teller distorted octahedral co-ordination of the copper(II) is converted to a regular one under high pressure (35 kbar) (ref. 337).



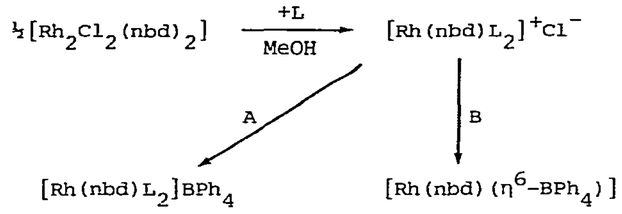
[258]

(M = Mg, Ca, Sr, Ba, Pb, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg)

[259]

The reaction of cobalt atoms with benzene, benzene-$\underline{d}_6$ and fluorobenzene have been shown to lead to π-complexes and a comparison of similar reactions with other metal atoms shows that the relative strengths of the metal arene bonds are Cr > Fe > Co > Ni (ref. 338). A study has been made on the ability of a phenyl ring of the BPh_4^- anion to π-bond to rhodium in the presence of various nitrogen donor ligands. The results are summarised in Scheme 51 (ref. 339).

The bis(borinato)cobalt complexes $[Co(C_5H_5BR)_2]$ (R = Me, Ph) can be reduced by sodium amalgam to give the 20-electron complexes $Na[Co(C_5H_5BR)_2]$. Metathesis with



Process A: L_2 = 1,10-phenanthroline, 2,2′-bipyridine; L = pyridine, 4-ethylpyridine, 3-methylpyridine, 4-methylpyridine, isoquinoline.

Process A + B: L = 2-methylpyridine, 2,4-dimethylpyridine.

Process B: L_2 = succinonitrile, malononitrile; L = acetonitrile, phenylacetonitrile, benzonitrile, aniline, 2-benzylpyridine, 2-ethylpyridine, 2,5-dimethylpyridine, 2,6-dimethylpyridine, quinoline.

SCHEME 51

$Ph_4P^+Br^-$ gives the stable crystalline salt $[Ph_4P][Co(C_5H_5BPh)_2]$ which has a μ_{eff} of 2.85 ± 0.05 BM. Thermal decomposition of the anions in the presence of donor ligands L gives complexes of the type $[Co(C_5H_5BR)L_2]$, e.g. $[Co(C_5H_5BPh)(cod)]$ and $[Co(C_5H_5BPh)(nbd)]$ (ref. 340). Borabenzene cobalt complexes have also been shown to undergo reversible one-electron oxidation to the respective cations and reversible one-electron reduction to the anions, the measured redox potentials being shifted anodically as compared to cobaltocene (ref. 341).

Halopentaboranes have been shown to oxidatively add to trans-$[IrCl(CO)(PMe_3)_2]$. The kinetic product derived by treatment of 1- or 2- halopentaboranes with trans-$[IrCl(CO)(PMe_3)_2]$ is that formed by insertion of iridium(I) into a basal B-H bond, the site which is predicted to be most susceptible to nucleophilic substitution. The qualitative order of reactivity is $2\text{-}BrB_5H_8 \approx 2\text{-}ClB_5H_8 > 1\text{-}BrB_5H_8 > 1\text{-}ClB_5H_8 \approx B_5H_9 \gg 1\text{-}MeB_5H_8$. The initially formed iridium hydride isomerises, formally exchanging hydrogen bound to iridium for halogen bound to boron with the exception of 2-Cl-4-$[IrHCl(CO)(PMe_3)_2]B_5H_7$ which on warming to 25°C gives $[IrHCl_2(CO)(PMe_3)_2]$. Apically metalated intermediates were not observed (ref. 342). The reaction of pentaborane-(9), cyclopentadiene, and but-2-yne with cobalt atoms has been shown to give the three metallacarborane complexes, $[2,3\text{-}Me_2\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_4]$, $[2,3\text{-}Me_2\text{-}1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_3]$ and $[2,5\text{-}Me_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5]$. This synthesis of metallocarborane clusters without the prior synthesis of the carborane system has also been extended to include an organometallic reagent. Thus the reaction of but-2-yne and pentaborane(9) with $[CoCp(CO)_2]$ gives $[5,6\text{-}Me_2\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5]$, and $[1,7\text{-}Me_2\text{-}3,5,1,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_4H_4]$ (ref. 343). Pentaborane(9) is structurally analogous to $[2\text{-}(\eta\text{-}C_5H_5)CoB_4H_8]$ and the chemical properties of these two compounds have been compared. Thus like B_5H_9, $[2\text{-}(\eta\text{-}C_5H_5)CoB_4H_8]$ undergoes deprotonation with NaH at a bridging position forming the $[(C_5H_5)CoB_4H_7]^-$ anion, the proton removed being adjacent to cobalt. Reaction of the anion with NaC_5H_5 and $CoCl_2$ gives the known cluster $[1,2\text{-}(\eta\text{-}C_5H_5)Co_2B_4H_6]$ together with smaller amounts of tri- and tetracobalt metalloboron species. Acetylene and $[2\text{-}(\eta\text{-}C_5H_5)CoB_4H_8]$ gives the known metallocarborane $[1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_3H_7]$, a process analogous to the insertion of C_2H_2 into B_5H_9 to give $C_2B_4H_8$. The reaction of $[2\text{-}(\eta\text{-}C_5H_5)CoB_4H_8]$ with higher alkynes gives the corresponding metallocarboranes $[(C_5H_5)CoRR'C_2B_3H_5]$ together with an adduct $[(C_5H_5)CoB_4H_8.C_2RR']$ which is an intermediate in the formation of the metallocarboranes. A novel mixed-metal metallocarborane cluster, $[1,2,3\text{-}(\eta\text{-}C_5H_5)Co_2\text{-}(CO)_4FeB_3H_3]$, whose proposed structure consists of an octahedral Co_2FeB_3 cage with all metal atoms on the same triangular face, has been obtained from the reaction of $[2\text{-}(\eta\text{-}C_5H_5)CoB_4H_8]$ with $Fe(CO)_5$ (ref. 344). The reaction of $[2,3\text{-}Me_2C_2B_3H_5\ CoH\ 2,3\text{-}Me_2C_2B_4H_4]$ with $[CoCp(CO)_2]$ in tetrahydrofuran gives the tetrahydrofuran derivative $\sigma\text{-}(CH_2)_4O\text{-}[2,3\text{-}Me_2C_2B_4H_3]Co[2,3\text{-}Me_2C_2B_3H_5]$ and the cobaltocenium derivative $5\text{-}[(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4)][2,3\text{-}Me_2C_2B_4H_3]Co[2,3\text{-}Me_2C_2B_3H_5]$. A single crystal X-ray structure determination of the cobaltocenium derivative shows that the molecule is a zwitterion composed of a $[Me_2C_2B_4H_3]Co^{III}[Me_2C_2B_3H_5]^-$ unit and a $(C_5H_5)Co^{III}(C_5H_4)$ group which is attached to the closo portion of the metallocarborane system at B(5) (ref. 345). Treatment of the dicarbon metallocarboranes *closo*-$[1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6]$ (A), *nido*-$[1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_3H_7]$ (B), or their C,C'-dimethyl derivatives with a 10% KOH-ethanol solution in the presence of atmospheric oxygen results in oxidative fusion of the dicarbon species to give tetracarbon 12-vertex cage systems containing a $Co_2C_4B_6$ or a CoC_4B_7 framework. These reactions give the first parent tetracarbon metallocarboranes, $[(\eta\text{-}C_5H_5)CoC_4B_7H_{11}]$ and three isomers of $[(\eta\text{-}C_5H_5)_2\text{-}Co_2C_4B_6H_{10}]$. An X-ray diffraction study of one of these isomers reveals an open 12-vertex cage system with the cobalt atoms in five- and six-co-ordinate vertices and all four cage carbons on the open face (ref. 346). The crystal structures of $[(\eta\text{-}C_5H_5)CoMe_4C_4B_7H_6(OEt)]$, (ref. 347), $[\mu(2,3)\text{-}1,3\text{-}C_3H_4\text{-}1,7,2,3\text{-}(\eta\text{-}C_5H_5)Co_2C_2B_3H_3]$, a complex containing a bicyclic planar carborane ligand related to pentalene, (ref. 348), $[2,3\text{-}(\eta\text{-}C_5H_5)_2\text{-}(2,3)\text{-}NiCo\text{-}10\text{-}CB_7H_8]$, (ref. 349), $[1,8\text{-}(\eta\text{-}C_5H_5)_2\text{-}1\text{-}Fe\text{-}8\text{-}Co\text{-}2,3\text{-}C_2B_7H_9]$, (ref. 350) and $Me_4N[(\eta\text{-}C_5H_5)_2Co_2CB_9H_{10}]$, (ref. 351) have been reported. The reaction of metallocarboranes with sulphur and $AlCl_3$ produces mixtures of HS-derivatives, e.g. 8- and $[9\text{-}HS\text{-}3(\eta\text{-}C_5H_5)\text{-}3,1,2\text{-}Co_2C_2B_9H_{10}]$ and $[8,8'\text{-}HS\text{-}3\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$. The reaction of $[3\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ with $AlCl_3$ in benzene gives an o-phenylene bridged derivative $[8,8'\text{-}(1,2\text{-}C_6H_4)\text{-}3\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (ref. 352). 1,2-Dicarbadodecaborane (12) has been attached to polystyrene and the polymer-bound rhodium catalyst $(Ph_3P)_2RhH(C_2B_9H_{11})$, which has the polymer attached through a π-type interaction to the rhodium, has been prepared. It does not hydrogenate alkenes as rapidly as its homogeneous analogue (ref. 353).

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