# COBALT, RHODIUM, AND IRIDIUM*
# ANNUAL SURVEY COVERING THE YEAR 1977

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CONTENTS

## Metal carbon σ-bonded compounds

During the year 1977 reviews have been published which contain material of relevance to this section. These include reviews on cyclometalation reactions (ref. 1), di-organocobalt complexes of macrocyclic ligands and mono- and bidentate π-acceptor ligands (ref. 2), synthetic and mechanistic aspects of inorganic insertion reactions (ref. 3), and decarbonylation reactions using transition metal compounds (ref. 4).

Treatment of the tris(trimethyl)tris(trimethylphosphine)cobalt(III) complex [1] with $[Me_3PH]Cl$ and $NaPF_6$ gives the complex cation [2]. However, treatment of [1] with $NH_4PF_6$ results in displacement of trimethylphosphine by ammonia to give [3], (ref. 5). Stable cationic complexes of cobalt(III) also result upon reaction of the cyclopentadienyl complexes [4] with $HBF_4$, $HPF_6$ or MeI (Scheme 1). The ethyl and acyl complexes [5]-[7] can similarly be obtained. The hydride [8] reacts at higher temperatures with excess $HBF_4$ in propionic anhydride to give [9] and an intermediate compound [10] can be isolated from the reaction of [8] with propionic anhydride (ref.6)

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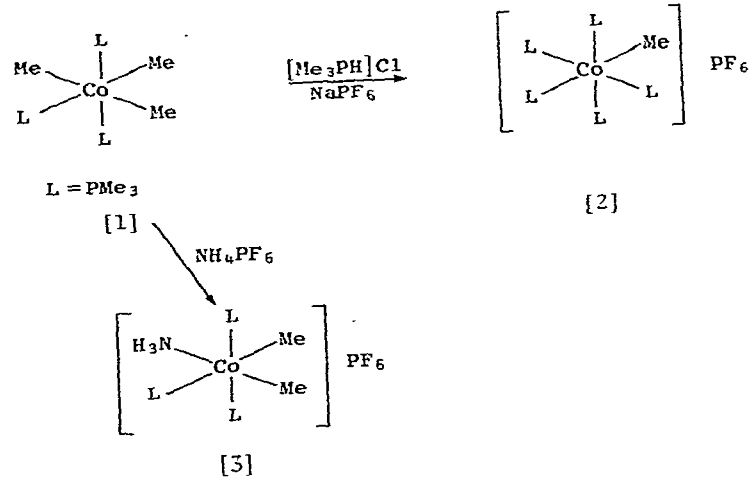
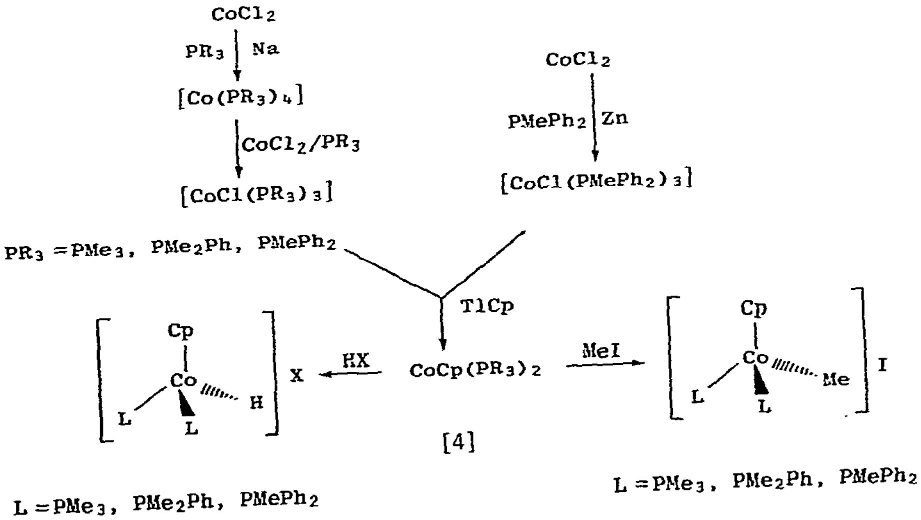
* Cobalt, rhodium and iridium, Annual Survey covering the year 1976 see J. Organometal. Chem., Vol. 167(1979) 135-264.

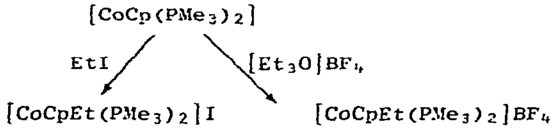




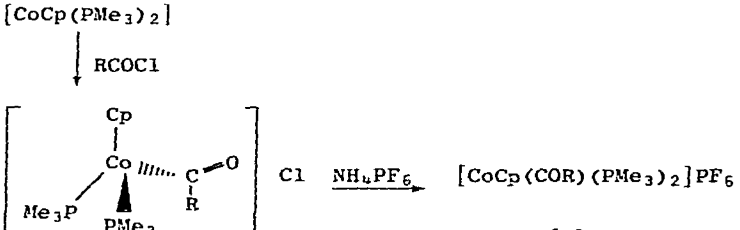
L = PMe$_3$, PMe$_2$Ph, PMePh$_2$

X = BF$_4^-$ or PF$_6^-$

Scheme 1



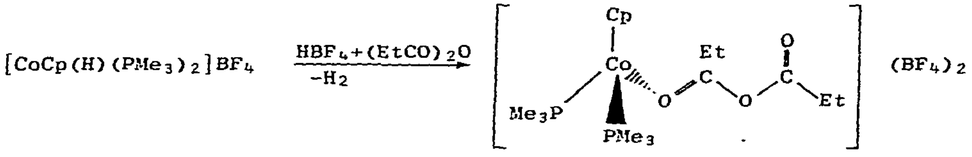
[5] [6]



[7] R = Me, Ph

$$[CoCp(H)(PMe_3)_2]BF_4 \xrightarrow[\Delta\ (EtCO)_2O]{HBF_4} [CoCp(PMe_3)_3][BF_4]_2$$

[8] [9]



[10]

Cobalt complexes of the type $[CoCp(R_f)(I)L]$, (L = optically active phosphine ligand) form pairs of diastereoisomers which differ only in the configuration at the cobalt atom. *The less soluble diastereoisomers can be prepared optically pure by* crystallization. On equilibration the diastereoisomer ratio is a measure of the optical induction of the asymmetric centre in the ligand L on formation of the two possible cobalt configurations. Variation of the $R_f$ group ($R_f$ = $CF_3$, $C_2F_5$, n-$C_3F_7$) has no influence on the diastereoisomer ratio of 30:70.. However, a change of the substituents R = H, Me, Et in the aminophosphines (S) - $Ph_2PNRCHMePh$ gives the following diastereoisomer ratios: 52:48, 30:70, 14:86 (ref. 7).

A study of the reaction of trimethylaluminium with $Co(acac)_3$ or $Co(acac)_2$ in the presence of 2,2′-dipyridyl reveals that both reactions give identical products. The slowest step in the reaction of $Co(acac)_3$ with $Me_3Al$ in the presence of dipy is considered to be reduction of cobalt(III) to cobalt(II). Complexes of formula [$\mathrm{CoMe_n(dipy)_2}$], (n = 1 or 2) are formed in these reactions (ref. 8). The reaction of $\mathrm{Co(acac)_3}$ with $\mathrm{Al(CH_2Ph)_3}$ and triphenylphosphine in diethyl ether as solvent gives the complexes $\mathrm{Co(CH_2Ph)(acac)_2.2PPh_3}$ and $\mathrm{Co(CH_2Ph).2PPh_3.2Et_2O}$ (ref. 9).

Six-co-ordinate anionic and neutral low-spin cobalt(II) complexes of the type $\mathrm{M'M''[Co(C{\equiv}CR')_4(PR_3)_2]}$ and $\mathrm{[Co(C{\equiv}CR')_2(Ph_2PCH_2CH_2PPh_2)_2]}$, (M = Na; M′= $\mathrm{Ph_4P}$; R = Et, Ph; R′= H, Ph, have been prepared according to the equations: (ref. 10)

$$\mathrm{[CoCl_2(PR_3)_2] + 4R'C{\equiv}C^- \xrightarrow[NH_3]{liquid} [Co(C{\equiv}CR')_4(PR_3)_2]^{2-} + 2Cl^-}$$

R′= Et, Ph; R′= H, Ph.

$$\mathrm{[CoBr(Ph_2PCH_2CH_2PPh_2)_2]Br + 2R'C{\equiv}C^- \xrightarrow[NH_3]{liquid} [Co(C{\equiv}CR')_2(Ph_2PCH_2CH_2PPh_2)_2] + 2Br^-}$$

R′= H, Ph.

However, simple acetylide complexes do not result from reactions between AgC≡CR, (R = Ph or $\mathrm{C_6F_5}$) and $\mathrm{[RhCl(PPh_3)_3]}$ or trans-$\mathrm{[IrCl(CO)(PPh_3)_2]}$. The reaction between AgC≡CPh and $\mathrm{[RhCl(PPh_3)_3]}$ in refluxing tetrahydrofuran gives a good yield of the cluster complex [11] together with 1,4-diphenylbuta-1,3-diyne, triphenylphosphine oxide, $\mathrm{[AgCl(PPh_3)]_4}$ and traces of trans-$\mathrm{[RhCl(CO)(PPh_3)_2]}$. The reaction between $\mathrm{[RhCl(PPh_3)_3]}$ and $\mathrm{AgC{\equiv}CC_6F_5}$ is more complex and the complexes [12] and [13] are obtained as well as small amounts of $\mathrm{C_6F_5C_2C_2C_6F_5}$. In refluxing 1,2-dimethoxyethane a third complex [14] can be isolated from this reaction. The reaction between AgC≡CPh and trans-$\mathrm{[IrCl(CO)(PPh_3)_2]}$ is more complex than the similar reaction using CuC≡CPh which has been reported previously. Products isolated from the reaction with

$$\mathrm{RhClP_3 + AgC_2Ar \longrightarrow Rh(C_2Ar)P_3 + AgCl}$$

$$\mathrm{Rh(C_2Ar)P_3 + AgC_2Ar \longrightarrow RhAg(C_2Ar)_2P_3}$$

$$\mathrm{RhAg(C_2Ar)_2P_3 + AgC_2Ar \longrightarrow RhAg_2(C_2Ar)_3P + P_2}$$

$$\mathrm{2RhAg_2(C_2Ar)_3P + 2AgC_2Ar \longrightarrow Rh_2Ag_4(C_2Ar)_8P_2 + 2Ag}$$

$\mathrm{(P = PPh_3)}$; (Ar = Ph) [11]

## Reaction Pathways

(i) replacement of halide by aryl acetylide

$$\mathrm{RhClP_3 + AgC_2Ar \longrightarrow Rh(C_2Ar)P_3 + AgCl}$$

(ii) oxidative-addition of arylacetylide moieties

$$\mathrm{Rh(C_2Ar)P_3 + AgC_2Ar \longrightarrow RhAg(C_2Ar)_2P_3}$$

$$\mathrm{RhAg(C_2Ar)_2P_3 + AgC_2Ar \longrightarrow Rh(C_2Ar)_3P_3 + 2Ag}$$

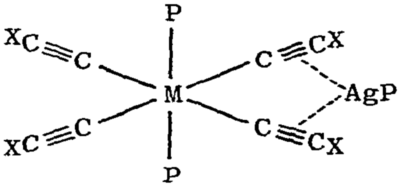
(iii) substitution of P (=$\mathrm{PPh_3}$) by arylacetylide

$$\mathrm{Rh(C_2Ar)_3P_3 + AgC_2Ar \longrightarrow [AgP][Rh(C_2Ar)_4P_2]}$$

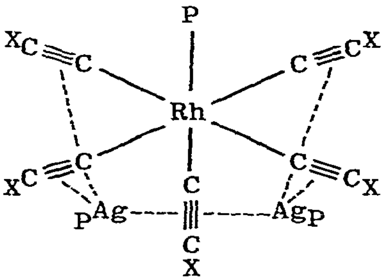
$$\mathrm{[13] + AgC_2Ar \longrightarrow [AgP_2][Rh(C_2Ar)_5P]}$$

$\mathrm{[M_2Ag_4(C_2Ar)_8P_2]}$

| | M | Ar |
|---|---|---|
| [11]; | Rh | Ph |
| [12]; | Rh | $C_6F_5$ |
| [15]; | Ir | Ph |
| [16]; | Ir | $C_6F_5$ |



[13]; M = Rh (X = $C_6F_5$)
[17]; M = Ir (P = $PPh_3$)



[14]

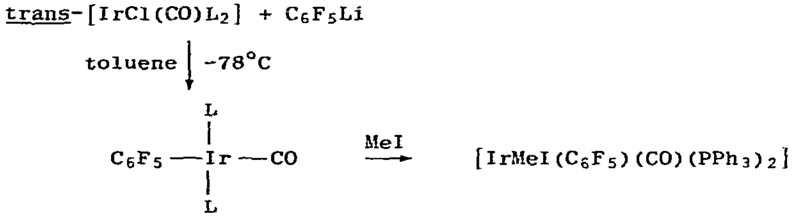
$AgC{\equiv}CPh$ include [15] and $[AgCl(PPh_3)]_4$. The reaction using $AgC{\equiv}CC_6F_5$ in refluxing toluene gives the complexes [16] and [17] (ref. 11).

A mesitylcobalt(II) complex, $LiCoR_3$, ($R = 2,4,6\text{-}Me_3C_6H_2$) has been prepared from the reactions of cobalt(II) halides with mesityllithium (ref. 12), and some tetra-perhalogenoaryl metallates of cobalt(II) have been obtained via the reaction:

$$[Bu_4{}^nN]_2\,[CoCl_4] + 4C_6X_5Li \xrightarrow{Et_2O} 4LiCl + [Bu_4{}^nN]_2[Co(C_6X_5)_4]$$

$X = F$ or $Cl$

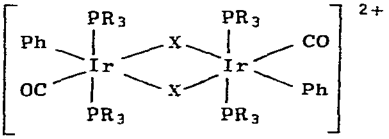
These homoleptic tetra-aryl derivatives of cobalt(II) are unstable in acetone solution and in the solid state and decompose in daylight and in atmospheric moisture (ref. 13). Further reactions of the σ-pentafluorophenyl iridium(I) complexes [18] have been described. These pentafluorophenyl complexes are obtained as bright yellow air-stable crystals which upon exposure to light gradually turn dark green over a period of a few months. The complexes [18] as a whole are much more soluble in organic solvents than their halide counterparts. They are also less reactive than the corresponding chloro complex from which they are derived. They will undergo oxidative-addition reactions with halogens and hydrohalic acids and in contrast to a previous report the complex (18; $L = PPh_3$) will undergo reaction with methyl iodide and acetyl chloride. Kinetic studies on the addition of methyl iodide to [18] show that rates of methyl iodide addition are comparable to rates of methyl iodide addition to <u>trans</u>-$[IrCl(CO)L_2]$ where L is a substituted triphenylphosphine containing electron withdrawing groups (ref. 14). Diphenyliodonium salts, $Ph_2I^+Cl^-$ and $Ph_2I^+BF_4^-$ readily react with <u>trans</u>-$[IrX(CO)(PR_3)_2]$, ($X = Cl, Br$; $PR_3 = PPh_3$ or $PMePh_2$) to yield iridium(III) σ-phenyl complexes of general composition $[IrXY(Ph)(CO)(PR_3)_2]$, ($Y = Cl, BF_4$). It is likely that the tetrafluoroborate salts do not contain discrete monomeric penta-co-ordinate cations and a halogen bridged structure [19] is proposed for these complexes. The formation of σ-phenyl complexes as a source of impurity in the reactions of benzenediazonium salts with trans-



$$\textit{trans}\text{-}[IrCl(CO)L_2] + C_6F_5Li \xrightarrow[-78^\circ C]{toluene} C_6F_5\text{—}\overset{L}{\underset{L}{Ir}}\text{—}CO \xrightarrow{MeI} [IrMeI(C_6F_5)(CO)(PPh_3)_2]$$

$L = Ph_3P,\ Ph_2PMe,\ (\underline{p}\text{-}MeC_6H_4)_3P$

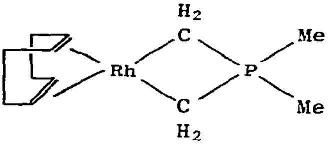
[18]



[19]

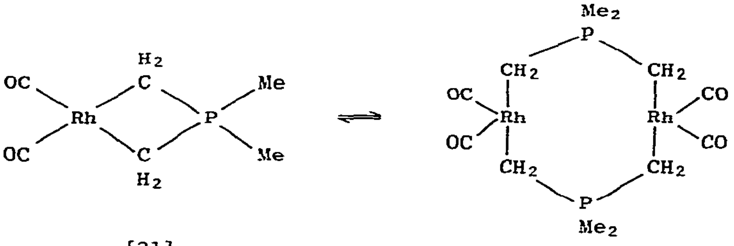
$[IrCl(CO)(PPh_3)_2]$ has been confirmed by deliberately conducting these reactions under reflux conditions so as to promote dinitrogen extrusion from the initially formed phenyldiazenato complexes. Thus $PhN_2^+BF_4^-$ and trans-$[IrCl(CO)(PPh_3)_2]$ react to give an initial orange solution of $[IrCl(N_2Ph)(CO)(PPh_3)_2][BF_4]$ which gradually loses its colour and the white σ-phenyl complex precipitates (ref. 15).

The reaction of an excess of trimethylphosphonium methylide, $Me_3PCH_2$, with $[RhCl(1,5\text{-cod})]_2$ yields the slightly air-sensitive complex [20]. Treatment of a



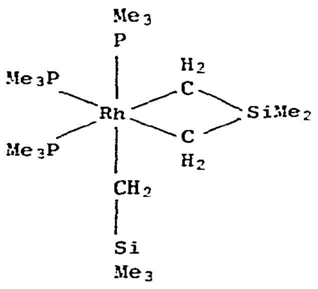
[20]

solution of [20] with carbon monoxide generates a red solution containing the complexes [21] and [22] which could not be separated. Variable temperature n.m.r.

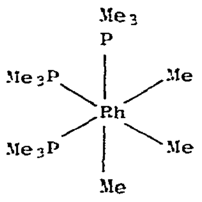


[21] [22]

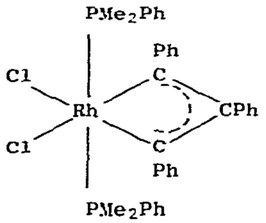
studies indicate that [21] and [22] are in equilibrium in solution. Benzene-methanol solutions of [21] and [22] catalyse the conversion of methyl iodide to methyl acetate and benzene solutions of [20] catalyse the hydrogenation of alkenes (ref. 16). A metallocyclic complex of rhodium(III), [23] has been obtained by the reaction of $Rh_2(O_2CMe)_4$ with $Mg(CH_2SiMe_3)_2$ in the presence of trimethylphosphine at 0°C. However, an analogous reaction using $MgMe_2$ gives the rhodium(III) methyl complex [24] (ref. 17). A four-membered metallacyclic ring complex [25] can also be obtained by the reaction $[C_3Ph_3]^+Cl^-$ with trans-$[RhCl(CO)(PMe_2Ph)_2]$. The complex [25] has been characterised by a single crystal X-ray study. These results reveal that



[23]

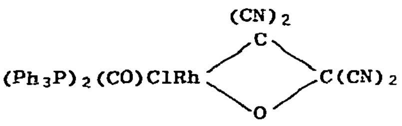


[24]

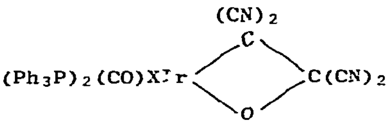


[25]

$[C_3Ph_3]^+Cl^-$ has oxidatively added to the rhodium(I) complex in a similar fashion to that observed for *trans*-$[IrCl(CO)(PMe_3)_2]$ with the exception that the carbonyl ligand has been displaced from the rhodium by chloride (ref. 18). The observation that carbon monoxide is not lost from the resulting iridium(III) complex may be a consequence of stronger iridium-carbonyl bonding. The low-valent complexes *trans*-$[IrX(CO)(PPh_3)_2]$ and *trans*-$[RhCl(CO)(PPh_3)_2]$ in boiling benzene cleave a carbon-oxygen bond in tetracyanoethylene oxide to give the cyclic complexes [26] and [27]. Treatment of *trans*-$[IrCl(CO)(PPh_3)_2]$ with the silver salt of tricyanoethenol gives [28] (ref. 19).

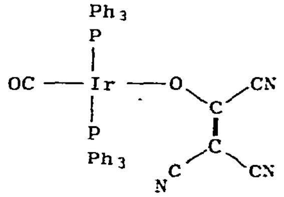


[26]



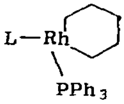
X = Cl or Br

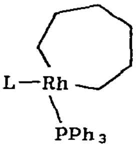
[27]

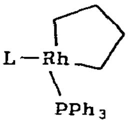


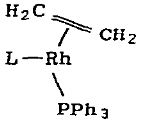
[28]

Metallacycloalkane derivatives have been postulated to be involved in a number of transition-metal-catalysed reactions, such as isomerisation of strained carbocyclic rings, [2 + 2] cycloaddition of alkenes and oligomerisation of 1,3- and 1,2-dienes. Some of these reactions are catalysed by rhodium compounds and some five-, six-, and seven-membered rhodacycloalkanes [29], [30], and [31] have been obtained by reactions of $[RhI_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ with the di-Grignard reagents $Br\text{-}Mg\text{-}[CH_2]_n\text{-}MgBr$ ($n$ = 4, 5, or 6). However, in the reaction involving $Br\text{-}Mg\text{-}[CH_2]_4\text{-}MgBr$ the ethylene complex [32] was the major product and ethylene was detected in the reaction mixture. The same results were obtained employing [33] as the alkylating reagent. It seems likely that the metallacyclopentane complex [31] is an intermediate in the formation of [32] (ref. 20). In contrast to these results, however, analogous reactions of [33] or $BrMg\text{-}[CH_2]_4\text{-}MgBr$ with $[CoI_2(\eta^5\text{-}C_5H_5)(PPh_3)]$ and $[IrCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ lead to the metallacyclopentane complexes [34] and [35] in a pure form. Free ethylene or ethylene metal complexes have not been detected as by-products (ref. 21).



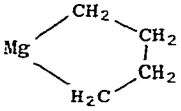




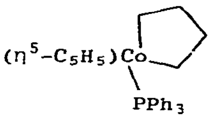


$L = \eta^5\text{-}C_5Me_5$

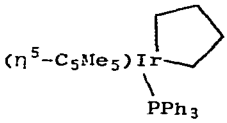
[30] [31] [29] [32]



[33]

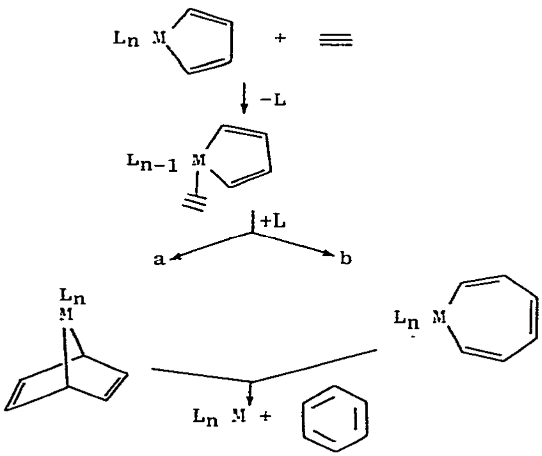


[34]



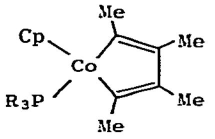
[35]

Metallacyclopentadienes have been implicated in the metal catalysed cyclotrimerisation of alkynes to arenes. Two types of reaction of alkynes with the metallacyclopentadiene intermediate have been suggested (Scheme 2):



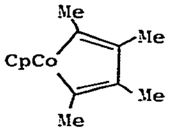
Scheme 2

(a) Diels-Alder addition of a co-ordinated alkyne to the metallacyclopentadiene and (b) insertion of a co-ordinated alkyne into a metal-carbon σ-bond. In this proposed scheme it is assumed that co-ordination of the alkyne precedes either path (a) or path (b). However, studies on alkyne cyclotrimerisation catalysed by the complexes [36] reveal that the mechanism is dependent upon the nature of the alkyne. Thus the complex (36; R = Ph) catalyses the cyclotrimerisation of but-2-yne to hexamethylbenzene and the rate law found for this reaction is consistent with the mechanism outlined in Scheme 2, involving substitution of triphenylphosphine by the alkyne via the co-ordinatively unsaturated intermediate [37]. However, the high affinity of triethylphosphine and trimethylphosphine for the cobalt(III) centre of [37] prevents ready dissociation of these ligands from [36] and these complexes do not catalyse the cyclotrimerisation reaction. In contrast dimethyl acetylenedicarboxylate reacts with (36; R = Me) rapidly at room temperature affording stoichiometrically the expected arene. Kinetic data for this reaction reveal that reaction proceeds without prior dissociation of a phosphine ligand. A mechanism consistent with the data



R = Ph, Et, Me

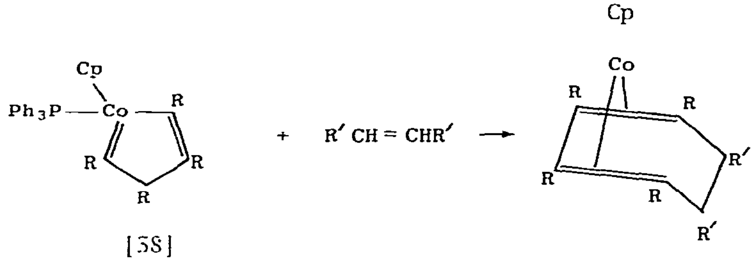
[36]



[37]

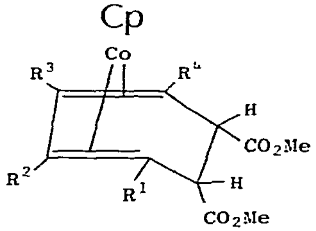
involves direct Diels-Alder addition of the powerful dienophile, dimethyl acetylenedicarboxylate, with the electron-rich diene present in [36] (ref. 22).

The reactions of alkenes with the metallacyclopentadiene complex (36: R = Ph) leads to cyclohexadiene complexes and a study on the reactions of various metallacyclopentadiene complexes [38] with ethylene, propene, styrene, methyl acrylate, and dimethyl maleate has been reported. These reactions proceed via initial displacement

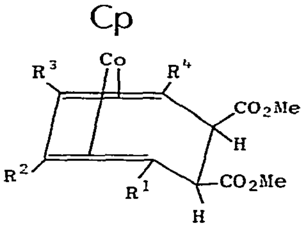


[38] [39]

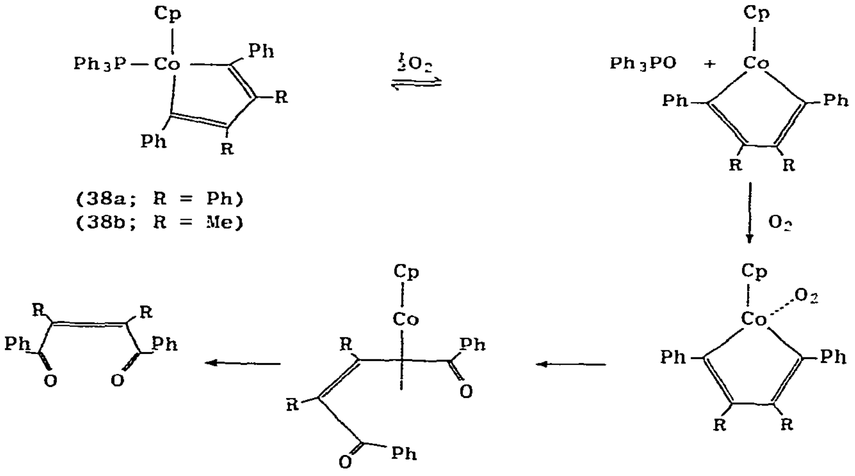
of triphenylphosphine from the cobalt and the second step is considered to be a Diels-Alder reaction which takes place within the co-ordination sphere of the cobalt. The reactions of [38] with dimethyl maleate lead in general to isomeric cyclohexadiene complexes [39] namely the endo [40] and exo [41] isomers. The endo rule is obeyed when $R^1$,$R^4$ = Ph, but not in certain other cases (ref. 23). It is known that endo-peroxides are produced in the reactions of conjugated dienes with singlet dioxygen and it has now been shown that both [38a] and [38b] react with ground state dioxygen at 70°C and at room temperature with singlet dioxygen to give but-2-ene-1,4-diones. An intermediate cobalt complex of the diene [42] can be isolated and the proposed mechanism of the reaction is illustrated in Scheme 3 (ref. 24). The cobaltacyclopentadienes [43] also react with isocyanates at 130°C to provide a synthetic route to 2-oxo-1,2-dihydropyridines [44]. In the reaction of (43; $R^1 = R^2 = R^3 = R^4 = Ph$)



[40]

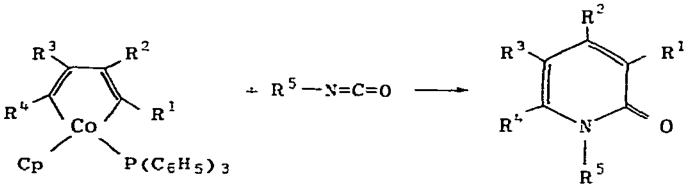


[41]



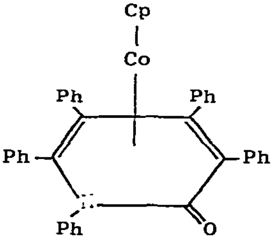
(38a; R = Ph)
(38b; R = Me)

[42]



[43] [44]

with phenyl isocyanate at 80°C a cobalt complex [45] can be isolated and such complexes may be intermediates in the formation of pyridones (ref. 25). Cobaltacyclopentadienes containing a variety of substituents can be prepared by the stepwise reactions of acetylenes with [CoCp(PPh$_3$)$_2$], (ref. 26).



[45]

Activated hydrocarbons such as acetonitrile, acrylonitrile and phenylacetylene oxidatively add to the complexes $[ML_4]^+$, M = Rh, Ir; L = trialkylphosphine or -arsine and in the presence of carbon dioxide carboxylation of the carbon hydrogen bond can be achieved. Thus addition of hydrogen chloride then $BF_3$/MeOH to the colourless solution of [46] and carbon dioxide in acetonitrile affords methyl cyanoacetate. Rhodium complexes are less reactive than the corresponding iridium

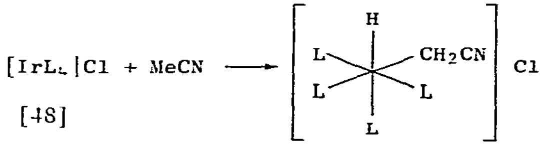
$$\underset{[46]}{[Ir(depe)_2]Cl} + CH_3CN \overset{K_1'}{\rightleftharpoons} [Ir(H)(CH_2CN)(depe)_2]Cl$$

$$\underset{[46]}{[Ir(depe)_2]Cl} + CH_3CN + CO_2 \overset{K_2'}{\rightleftharpoons} \underset{[47]}{[Ir(H)(O_2CCH_2CN)(depe)_2]Cl}$$

$$K_2' \gg K_1'$$

$$\text{depe} = Et_2PCH_2CH_2PEt_2$$

species and bulky ligands inhibit reactivity. The observed correlation of extent of reaction with metal basicity (Ir > Rh) and C-H bond acidity is indicative of a process involving electrophilic attack at the metal. The n.m.r. of spectra of [47] are consistent with both a _trans_ or _cis_-fluxional geometry. The complex [48] which is much more reactive than [46] reacts rapidly with acetonitrile to give [49] (ref. 27). Methyl iodide undergoes _trans_-addition to _trans_-$[IrCl(CO)L_2]$. However, while there

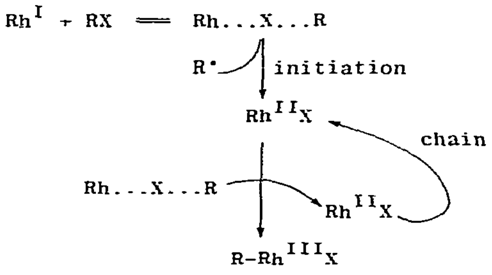


[48]

L = $PMe_3$

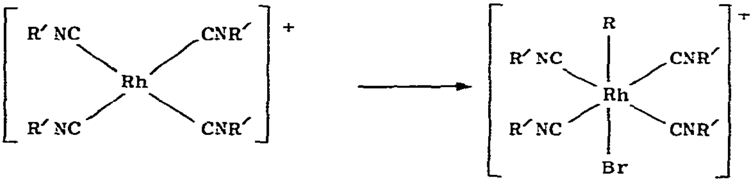
[49]

have been several studies on the effect of the ligand L on the rate of _cis_-oxidative addition, no corresponding studies have hitherto been reported on the effects of phosphine ligand on the rate of _trans_-addition. For the complexes _trans_-$[IrCl(CO)\{P(C_6H_4X\text{-}p)_3\}_2]$, (X = F, Br, Me, MeO, H) a linear relationship is observed between log $k_2$ vs. $\Sigma\sigma^{ph}$, the $\sigma^{ph}$ substituent constants being derived by use of the Hammett equation from measurements of the ionisation constants of organophosphorous acids in water and 50% aqueous ethanol. A study of the complexes _trans_-$[IrCl(CO)L_2]$, [L = $(p\text{-}ClC_6H_4)_nPh_{3-n}P$] where _n_ is varied from 3-0 verified that the substituents were additive for this system. Increasing the number of unsubstituted phenyl groups resulted in the expected corresponding increase in reaction rate. The change in steric effects upon moving a methyl substituent from the _para_ to the _meta_ position appears to be negligible. However, trans-$[IrCl(CO)\{P(C_6H_4Me\text{-}o)_3\}_2]$ has no measure-able reaction with methyl iodide as a consequence of steric factors. For a series of alkyl substituted phosphines the order of ligand dependence was found to be MePh$_2$P > EtPh$_2$P > Et$_2$PhP and it appears from these and other studies that a methyl group and a phenyl group are comparable in their steric requirements whereas ethyl and presumably higher alkyl groups exhibit increasing steric interference (ref. 28). Studies on the oxidative-addition of α-bromo esters to tetrakis(isocyanide)rhodium(I) complexes are consistent with a chain mechanism for this reaction (Scheme 5). The isocyanide



Scheme 5

complexes [50] oxidatively add the chiral alkyl halides, (*S*)-(-)-ethyl α-bromopropionate and (*S*)-(+)-ethyl α-phenylbromoacetate to give the *trans*-adducts [51] which are optically inactive. The relative rate of addition of *p*-$XC_6H_4CHBrCO_2Et$ to



R′ = Bu$^t$, *p*-MeC$_6$H$_4$

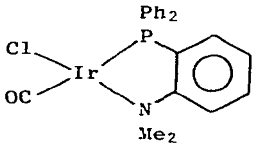
[50]

R′ = MeCHCO$_2$Et, PhCHCO$_2$Et

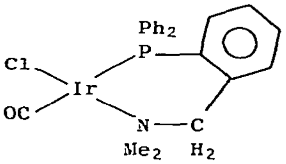
[51]

(50; R = Bu$^t$) decreases in the order X = Cl > H > Me (ref. 29). The reactions of a mixture of methyl iodide and iodide or HCl with the *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline, PN, [52] and o-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine, PCN, [53] complexes have also been reported. These complexes are prepared by treating Li[IrCl$_2$(CO)$_2$] with one equivalent of the appropriate ligand. The use of excess ligand leads to the formation of the four co-ordinate complexes [IrCl(CO)(PN)$_2$] and [IrCl(CO)(PCN)$_2$]. Although *o*-(diphenylphosphino)anisole, PO, [54] acts as a bidentate ligand to ruthenium(II) attempts to obtain a similar complex of iridium were not successful. The four co-ordinate complex [IrCl(CO)(PO)$_2$] is instead formed

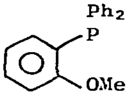
With HCl or a mixture of methyl iodide and iodide the complexes [52] and [53] give



[52]



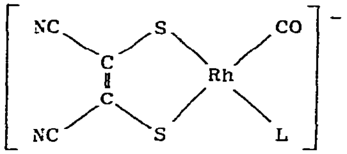
[53]



[54]

$[IrHCl_2(CO)(PN)]$, $[IrHCl_2(CO)(PCN)]$, $[IrMeI_2(CO)(PN)]$, and $[IrMeI_2(CO)(PCN)]$. The relative order of effectiveness for the catalytic hydrogenation of hex-1-ene is [53] > [52] > trans-$[IrCl(CO)(PPh_3)_2]$. Equilibrium measurements of [Ir(III)]/[Ir(I)] for the addition of benzoic acid to these iridium complexes reveal that there is little difference in the basicities of the three metal centres and it appears unlikely that either basicity or steric effects are important in promoting the oxidative addition step in the catalytic cycle. The compound [53] is conformationally mobile because of inversion of the six-membered chelate ring (ref. 30).

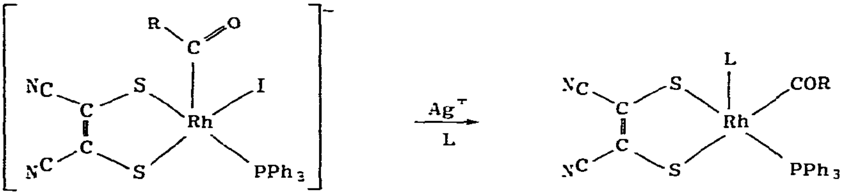
The addition of methyl iodide to the complexes [52] and [53] is quite different from what has been observed for the analogous rhodium complexes. For iridium(III) carbonyls the alkyl is stable whereas with the corresponding rhodium(III) complexes the alkylcarbonyl is unstable to migratory insertion and the acyl complex is isolated. Rhodium(III) acyl complexes have also been shown to result from the reaction of methyl iodide with the anionic complexes [55]. The product,



L = CO, $PPh_3$

[55]

$[RhI(COMe)L(mnt)]^-$, (L = CO) is unstable in solution and slowly decomposes on standing and with primary alkyl iodides only the triphenylphosphine complex reacts completely to give well characterised complexes [56]. The crystal structure of the complex (56; R = Et) has been determined. The co-ordination about the rhodium is square pyramidal. Reaction of the acyl anions [56] with $Ag^+$ results in the formation of neutral rhodium(III) acyl complexes [57] thought to have the structure illustrated. The α-methylene protons of the complexes [56] are found to be magnetically non-equivalent and the diastereotopic nature of these protons indicates that the acyl group is bonded to a chiral metal centre. In the neutral complexes

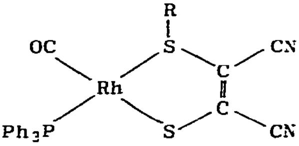


[56] [57]

R = Me, Et, Pr , Bu , $C_{10}H_{21}$ , $CH_2Ph$

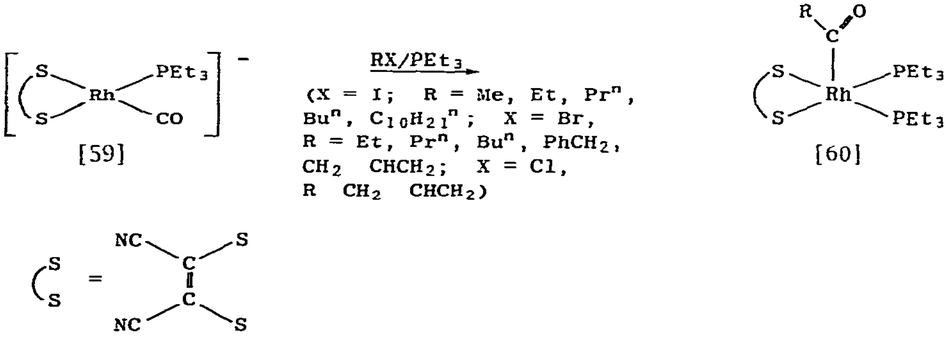
L = MeCN, pyridine

these hydrogens become magnetically equivalent as a result of rapid solvent exchang On heating methylene chloride or tetrahydrofuran solutions of the neutral acyl complexes [57; R = Me, Et, $CH_2Ph$) alkyl group migration from carbon to sulphur occurs to give the rhodium(I) complexes [58] (ref. 31). Some reactions of the related



[58]

triethylphosphine complex [59] have also been described, and are depicted in Scheme 4. The reactivity of [59] is significantly greater than the triphenylphosphine



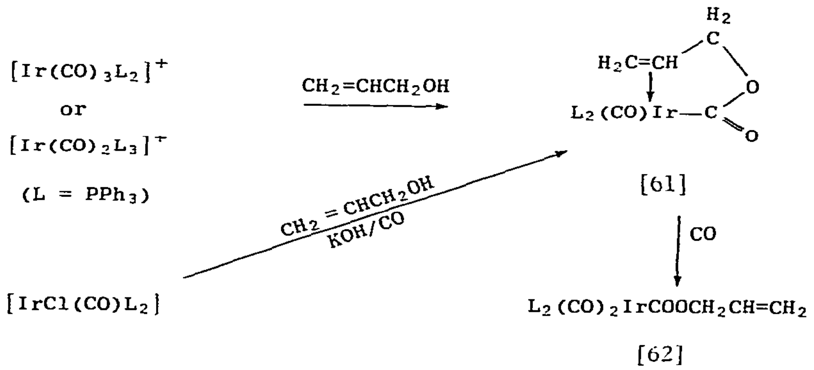
[59] [60]

$RX/PEt_3$ (X = I; R = Me, Et, $Pr^n$, $Bu^n$, $C_{10}H_{21}{}^n$; X = Br, R = Et, $Pr^n$, $Bu^n$, $PhCH_2$, $CH_2$ $CHCH_2$; X = Cl, R $CH_2$ $CHCH_2$)

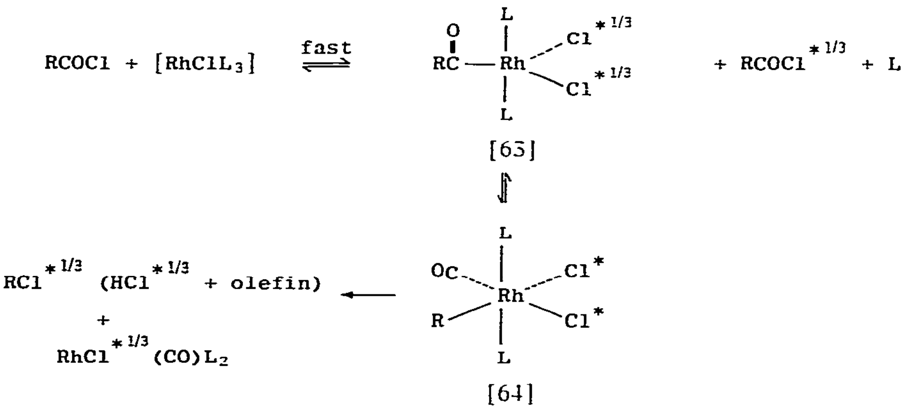
Scheme 4

analog [55] which reacts only with alkyl iodides and activated alkyl bromides. The single crystal X-ray structure of (60; R = $Pr^n$) has been determined. Addition of perchloric acid to [59] in the presence of triethylphosphine gives the hydride $[RhH(CO)(PEt_3)_2(mnt)]$. Addition of acid to [59] in the presence of ethylene leads to the acyl complex (60; R = Et). Alkyl group migration from carbon to sulphur is also observed in monophosphine systems. This migration appears to proceed via a sequence of 1,2-shifts from carbon to rhodium to sulphur, and is completely suppressed in co-ordinating solvents and in the presence of free phosphine (ref. 32)

Studies on the reactions of allyl alcohol with iridium carbonyl cations of the type $[Ir(CO)_3L_2]^+$ and $[Ir(CO)_2L_3]^+$ reveal a different behaviour to that observed in reactions with saturated alcohols. Thus while saturated alcohols give complexes of the type $[Ir(COOR)(CO)_2L_2]$ allyl alcohol gives a monocarbonyl complex [61]. Treatment of [61] with carbon monoxide gives [62] which slowly reforms [61] even in the solid state. Complex [61] cannot be transesterified even by prolonged boiling with saturated alcohols. However, if the reaction is carried out in an atmosphere of carbon monoxide [61] is transesterified presumably via initial formation of [62] (ref. 33).

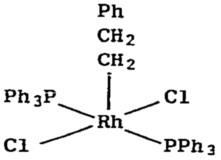


The stoichiometric decarbonylation of acid chlorides with $[RhCl(PPh_3)_3]$ takes place under mild conditions, acid chlorides containing β hydrogens producing olefins upon decarbonylation, while alkyl chlorides are formed from acid chlorides with no β-hydrogens. Further studies on the decarbonylation of acid chlorides containing no β hydrogens reveal that the reaction proceeds with low net retention of configuration on carbon. Further since the acyl ⇄ alkyl rearrangement is believed to take place with retention of configuration on carbon, the reductive elimination step must occur with the same stereochemistry and by microscopic reversibility, the oxidative addition of alkyl halides to $[RhCl(CO)(PPh_3)_2]$ should also proceed with retention of configuration on carbon. The decarbonylation of acyl chlorides containing β-deuterium atoms is non-stereoselective, the deuterium label being scrambled by inter and intramolecular hydride transfer. However, the decarbonylation of *erythro*- and *threo*-2,3-diphenylbutanoyl chloride is highly stereospecific, *trans*- and *cis*-methylstilbenes being formed respectively. These results imply that the addition of rhodium hydride species across the double bond and the reverse reaction are non-regioselective concerted processes with *cis*-stereochemistry. A study on the oxidative addition of acyl chlorides to $^{36}$Cl isotopically labelled [RhCl(PPh$_3$)$_3$] gives an even distribution of the $^{36}$Cl isotope among the unreacted starting material the product alkyl chloride (or olefin + HCl), and [RhCl(CO)(PPh$_3$)$_2$]. This result suggests a rapid equilibrium in the formation of the rhodium(III)-acyl complex and an equivalence of the chlorine atoms in the acyl complex [63], (Scheme 5). $^{31}$P n.m.r. studies indicate a stereochemically rigid structure in the range 218-313 K.



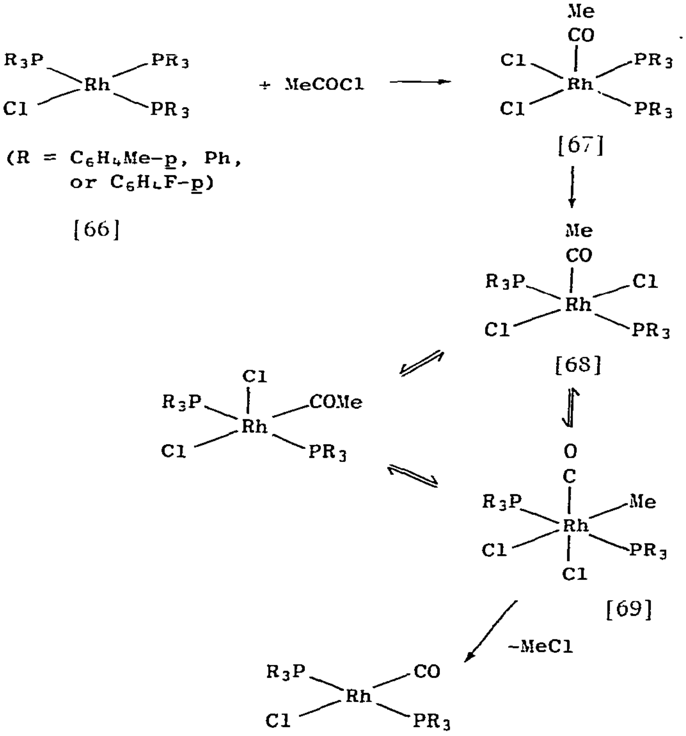
Scheme 5

A single crystal X-ray structure determination on the complex (63; R = PhCH$_2$) has been reported and the geometry around the rhodium has been described as trigonal bipyramidal (ref. 34). Interestingly the structure of the closely related complex [65] has been described as square pyramidal on the basis of an X-ray study (ref. 35). However, both these complexes, [65] and [63], are distorted and there are not great



[65]

differences between the two geometries found for each complex. Oxidative addition of acetyl chloride to the compounds [66] give the monomeric, five co-ordinate



Scheme 6

acetylrhodium(III) compounds [67]. The compounds [67] rearrange in solution to give the isomers [68], and isomerize further to six-co-ordinate compounds [69] and i.r. and n.m.r. data can be rationalized as outlined in Scheme 6 for this system. Equilibrium data at 298 K for acyl-alkyl isomerizations are illustrated in Scheme 7.

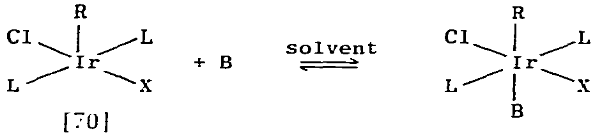
$$[RhCl_2(COR)(PR_3)_2] \rightleftharpoons [RhRCl_2(CO)(PR_3)_2]$$

| R | $PPh_3$ | $P(C_6H_4F\text{-}\underline{p})_3$ | $P(C_6H_4Me\text{-}\underline{p})_3$ |
|---|---|---|---|
| Me | 0.29±0.02 | 0.35±0.01 | 0.38±0.02 |
| Ph | >20 | | |
| R $CH_2CH_2$ | <0.1 | | |
| $\underline{p}$-$ClC_6H_4CH_2$ | 13.7 | | |
| $CH_2Cl$ | >20 | | |

Scheme 7

It is apparent that the acyl species are preferred for all three methyl systems but there appears to be no correlation between the position of equilibrium and the nature of the para substituent. There is at present little data on octahedral compounds such as [69]. However, n.m.r. studies on a solution of $[RhCl_2(COCH_2CH_2Ph)(PPh_3)_2]$ reveal the formation of the octahedral compound $[RhCl_2(CH_2CH_2Ph)(CO)(PPh_3)_2]$ (ref. 35).

A series of five-co-ordinate iridium(III) complexes having the general formula [70] have been prepared. These iridium(III) complexes, which are clearly related to the rhodium(III) complexes [63] and [65], are considered to have square-pyramidal structures with the organo ligand R, in the apical position. Such structures are in accord with predictions based on theoretical calculations for five-co-ordinate $d^5$ complexes. The complexes [70] add a variety of Lewis bases and in all systems studied the base adds, stereospecifically, trans to the R group to give the complexes [71]. The reaction of the trifluoroacetyliridium complex (70; X = Cl) with a series of bases in methylene chloride gives the following order of $-\Delta H$ values: $P(OCH_2)_3CEt > P(OMe)_3 > 4\text{-}MeC_5H_4N > Me_2SO > Me_2NCHO > MeCN >$ piperidine $> Et_2NH \gg PPh_3$ or $2\text{-}MeC_5H_4N$. Enthalpy changes for the addition of pyridine, $P(OCH_2)_3CEt$, and $P(OMe)_3$ to (70; X = Cl) have given a measure of the trans influence of the group R on the iridium-B bond. The trans influence series based on this data is $COCFH_2 > S(O)_2CF_3 > S(O)_2Et > S(O)_2Me > COCF_2H > CH_3 > COCF_3$. The position of the trifluoromethanesulphinato group in the series is not certain since there is evidence that in solutions of the five-co-ordinate complex there may be an equilibrium between S-bonded and O,O′-bidentate forms (ref. 36). Treatment of N-phthaloylamino-methyl chloride or -acetyl chloride with $Na[Co(CO)_4]$ in the presence of triphenylphosphine gives the five-co-ordinate cobalt acyl compound [72] (ref. 37).

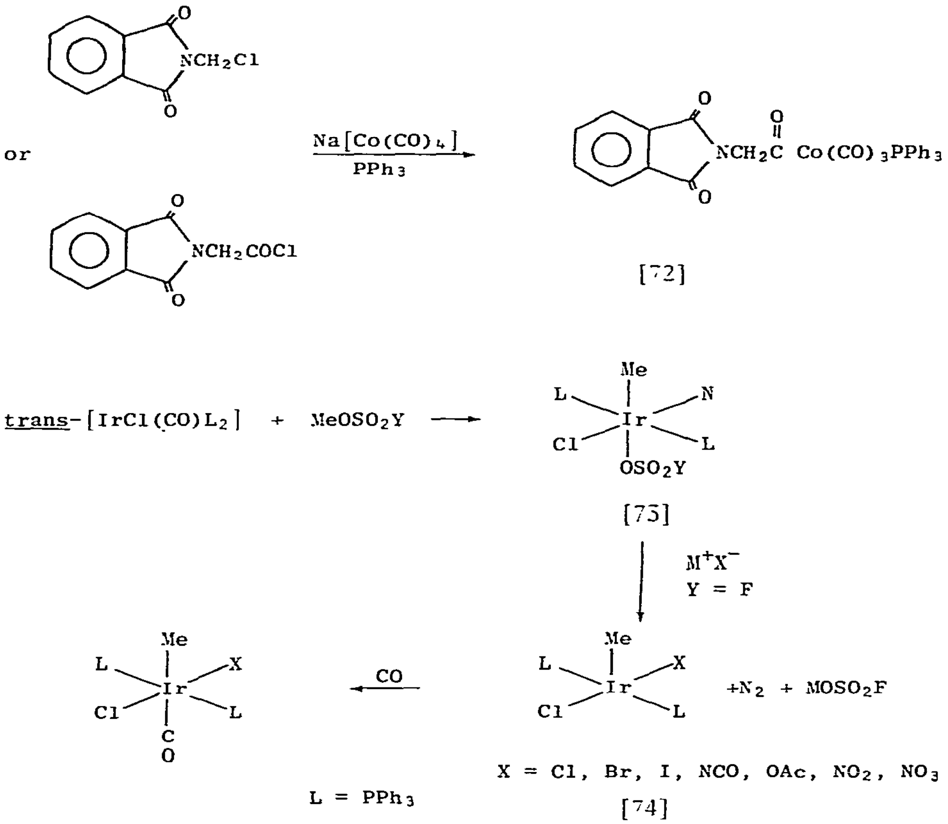


[70]

[71]

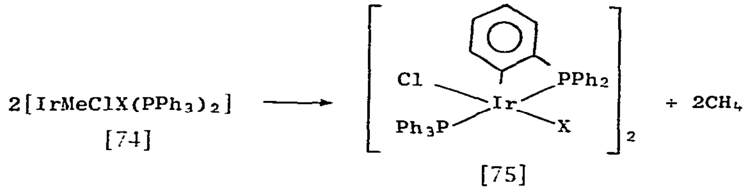
L = $PPh_3$
X = anion
R = H, COR, $S(O)_2R'$, $CH_3$

Six-co-ordinate methyliridium(III) complexes [73] containing two readily replaceable ligands are obtained by addition of the methyl sulphonates $MeOSO_2F$ and $MeOSO_2CF_3$ to trans-$[IrCl(N_2)(PPh_3)_2]$. Some reactions of the complex (73; Y = F) are illustrated in Scheme 8. The co-ordinatively unsaturated methyl complexes (74; X = Cl, Br, or NCO) undergo an ortho metallation of co-ordinated triphenylphosphine



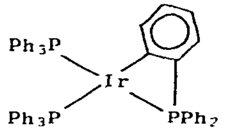
Scheme 8

and eliminate methane when they are heated to 170-180°C. In homogeneous 1,2-dichloroethane solution the dichloro and chlorobromo complexes (74; X = Cl or Br) cleanly give the ortho-metallated compounds (75; X = Cl or Br). The presence of a

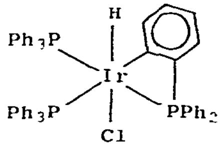


(X = Cl, Br or NCO)

vacant co-ordination site in [74] appears to enhance the orthometallation reactions. Thus octahedral $d^6$ complexes of phosphorus donor ligands undergo orthometallation only under forcing conditions whereas the complexes [74] do so at a significant rate at room temperature in solution. Furthermore the addition of triphenylphosphine to reactions involving the complexes [74] produces a significant decrease in the rate of orthometallation (ref. 58). The iridium(I) complex $[IrCl(PPh_3)_3]$ also undergoes an orthometallation reaction under mild conditions when treated with 1-Li-2-R-1,2-$B_{10}C_2H_{10}$, (R = Me or Ph), the internally metallated complex [76] being formed.



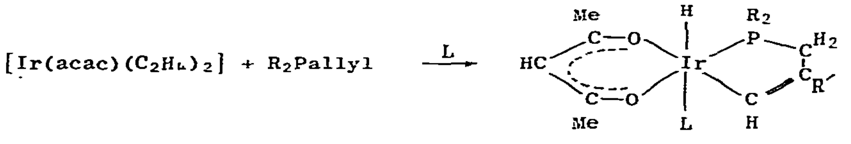
[76]



[77]

Further studies reveal that formation of the complex [76] only occurs when $[IrCl(PPh_3)_3]$ is treated with lithium or chloromagnesium derivatives of the C(2)-methyl or -phenyl substituted 1,2-carborane. However, the cyclometallated chlorohydrido-iridium(III), complex [77], is always formed when $[IrCl(PPh_3)_3]$ is treated with the organometallic derivatives of either the unsubstituted 1,2- and 1,7-carborane or the C(7)-methyl and -phenyl substituted 1,7-carborane (ref. 59).

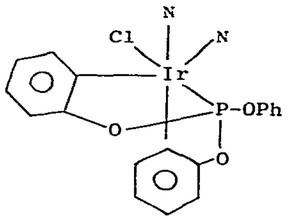
The olefinic phosphines $R_2$Pallyl (R = $Bu^t$ or Cy) react with $[Ir(acac)(C_2H_4)_2]$ in the presence of γ-picoline and acetonitrile to yield the six-co-ordinated metallated iridium(III) complexes [78]. Treatment of [78] with carbon monoxide, cyclohexylisocyanide or trimethylphosphite results in displacement of the ligand L, and several isomers of each complex can be obtained. The reactions of the olefinic phosphines with $[Ir(acac)(C_2H_4)_2]$ differ from those previously observed with $[IrCl(C_8H_{14})_2]_2$ in that when the bidentate acetylacetonate ligand is present, one bulky phosphine is



R = $Bu^t$ ; R′ = H, Me
R = Cy; R′ = Me
L = γ-picoline
R = $Bu^t$ ; R′ = H; L = MeCN

[78]

sufficient to cause metallation (ref. 40). Cyclometallation reactions involving aliphatic C-H bond breaking readily occur by reaction of the phosphines $PPr^{n}Bu_2{}^{t}$, $PBu^{n}Bu_2{}^{t}$, $PBu_3{}^{t}$, or $PPr_3{}^{i}$ with $[IrCl(C_8H_{14})_2]_2$ in the presence of γ-picoline or acetonitrile. The aliphatic parts of the $^{1}H$ n.m.r. spectra of the resulting complexes are complex and further since some of the complexes exist as mixtures of isomers the complexes were allowed to react with triphenylphosphite in order to displace the non-metallated phosphines and thus simplify the resulting n.m.r. spectra. From these studies it is apparent that a primary carbon atom is more easily metallated than a secondary carbon atom and that the reactivity towards metallation is $PPr_3{}^{i} \approx PPr^{n}Bu_2{}^{t} > PBu_2{}^{t}Bu^{n} > PBu_3{}^{t}$. Tri-n-butylphosphine yields no metallated products. It appears that the reactivity of the phosphine is determined by the cone angle of the phosphine. When this angle is small no metallation occurs and when the angle is very large the yields of metallated products are small. Only when the bulkiness of the phosphine is moderate are good yields of metallated products obtained. These reactions lead to both four- and five-membered rings (ref. 41). The interaction of three molar equivalents of tri-o-tolylphosphite with $[IrCl(1,5\text{-}C_8H_{12})]_2$ produces a yellow powder, $[Ir_2Cl_2\{P(O\text{-}\underline{o}\text{-tolyl})_3\}_3]$ which contains a single tri-o-tolylphosphite ligand co-ordinated as a tridentate dimetallated group. This complex undergoes bridge cleavage reactions with donor ligands and the crystal and molecular structure of the γ-picoline complex [79] has been determined (ref. 42).

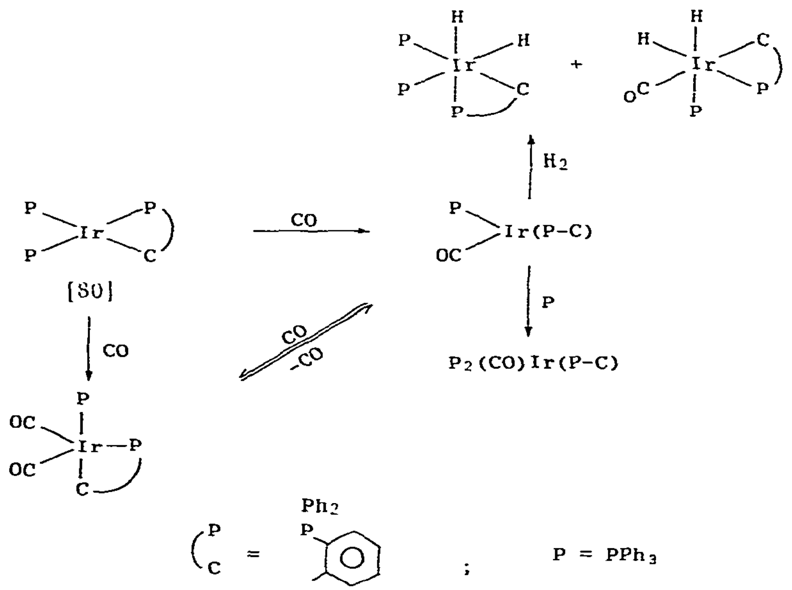


N = γ-picoline

[79]

The internally metallated complex [80] reacts instantaneously with carbon monoxide in solution at room temperature to give new carbonyl complexes of iridium (Scheme 9). Carbon monoxide insertion into the iridium-carbon bond is not observed in these reactions in contrast to the behaviour found for the reactions involving the corresponding rhodium complex. Complex [80] also reacts rapidly with dihydrogen, the iridium-carbon bond being cleaved stereospecifically to give pure <u>fac</u>-$[IrH_3(PPh_3)_3]$, [81]. Treatment of [80] with methanol gives the dihydride [82] which on further treatment with methanol gives [81] (ref. 43).

2,2′-Bis(diphenylphosphino)bibenzyl, (bdpbz) and its arsenic analogue, (bdabz) form monomeric complexes of rhodium(I) and iridium(I) [83], in which the Group V ligands span <u>trans</u>-co-ordination sites. The rhodium(I) complexes [83a] and [83c]



Scheme 9

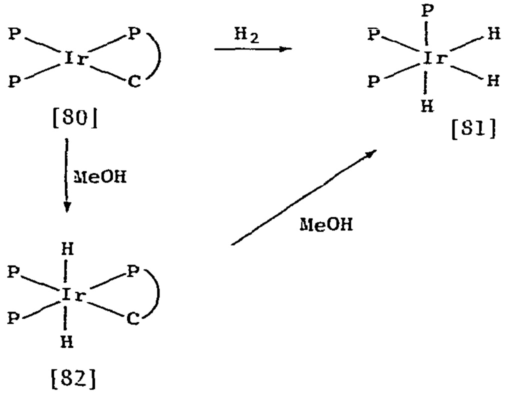
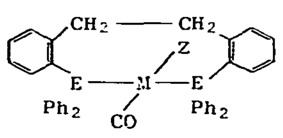
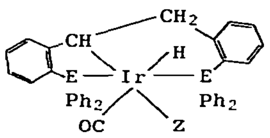


exhibit temperature-dependent $^1$H n.m.r. spectra which are considered to be due to inversion of the nine-membered chelate ring. Co-ordination of bdpbz and bdabz to the rhodium or iridium as trans-bidentate ligands brings the methylene groups in close proximity to the metal atoms and the iridium complexes have been shown to undergo metallation reactions. Thus reaction of bdpbz with [IrCl(cod)]$_2$ in methylene chloride in the presence of carbon monoxide gives the metallated species [84a]. The precursor to this complex [84a] is [83d] which can be isolated in an impure form by



(a) M = Rh, E = P, Z = Cl
(b) M = Rh, E = As, Z = Cl
(c) M = Rh, E = P, Z = CO
(d) M = Ir, E = P, Z = Cl
(e) M = Ir, E = As, Z = Cl

[83]

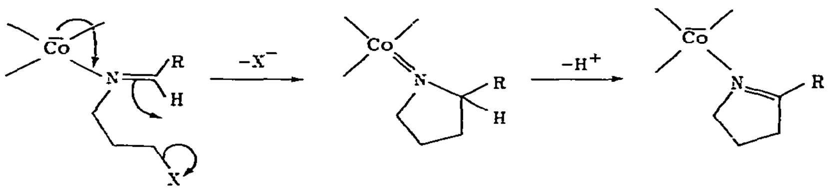


(a) E = P, Z = Cl
(b) E = As, Z = Cl
(c) E = As, Z = CO$^+$
(d) E = P, Z = CO$^+$

[84]

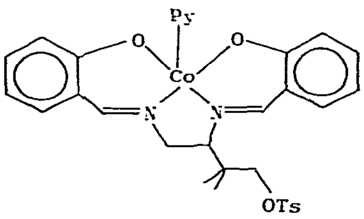
carrying out the reaction of [IrCl(cod)]$_2$ with bdpbz and carbon monoxide in toluene at -10°C. On refluxing in chloroform the arsine complex [83e] also undergoes metallation to give [84b]. Treatment of [83d] and [83e] with silver tetrafluoroborate under carbon monoxide gives the cationic metallated complexes [84c] and [84d] (ref. 44). A metallated pyrazolylphenyl complex of cobalt(II), $ML_2$, can be obtained by the reaction of LMgBr, (L = pyrazolylphenyl) with cobalt(II) halides (ref. 45).

Cobalt(I) compounds are powerful nucleophiles and react with alkyl halides and certain esters to give alkylcobalt compounds. The possibility of effecting intramolecular alkylation (Scheme 10) prompted an investigation of the reaction of [85]

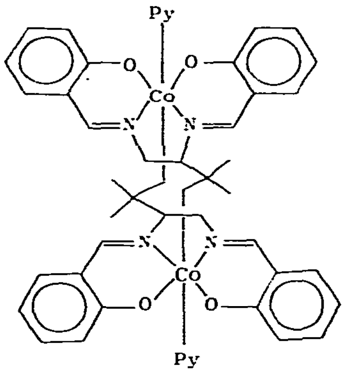


Scheme 10

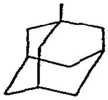
with lithium naphthalide. However, reduction of [85] with lithium naphthalide results in the formation of the novel alkylcobalt dimer, [86], (ref. 46). The reactions of the polycyclic bromides of adamantane and norbornane, [87]-[91] with cobaloxime(I) yield stable alkyl(pyridine)cobaloximes [92]. Displacement of bromide from [87], [88], and [89] proceeds with retention of configuration and since nucleophilic displacement is not likely with these bromides these reactions probably proceed either via a bridged intermediate [93] or via a radical process (Scheme 11). However, the displacement of bromide from the less sterically hindered bromides [90] and [91] by cobaloxime(I) gives the same alkyl(pyridine)cobaloxime compound, the configuration of which has not been determined (ref. 47). The reaction of $CoBr_2$(dpnH), [94] with pentafluorophenylmagnesium bromide gives the complex $[CoBr(C_6F_5)(dpnH)]$. Only one pentafluorophenyl group can be introduced into the



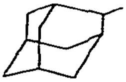
[85]



[86]

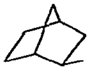


[87]



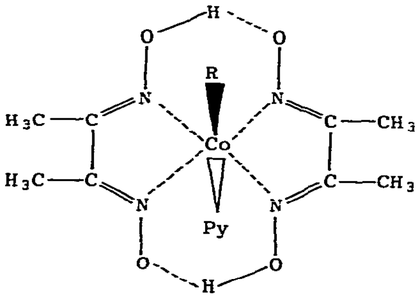
[88]

[89]

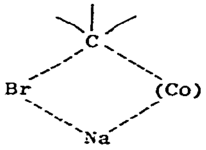


[90]

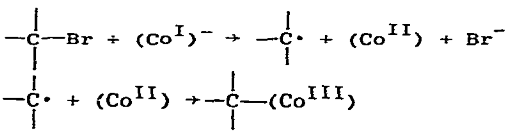
[91]



[92]



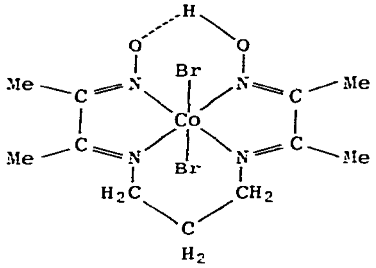
[93]



$$-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{Br} + (\mathrm{Co}^{\mathrm{I}})^{-} \rightarrow -\overset{|}{\underset{|}{\mathrm{C}}}\cdot + (\mathrm{Co}^{\mathrm{II}}) + \mathrm{Br}^{-}$$

$$-\overset{|}{\underset{|}{\mathrm{C}}}\cdot + (\mathrm{Co}^{\mathrm{II}}) \rightarrow -\overset{|}{\underset{|}{\mathrm{C}}}-(\mathrm{Co}^{\mathrm{III}})$$

Scheme 11

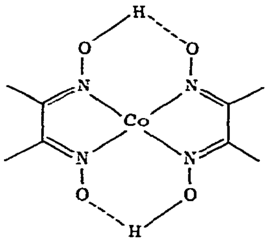


[94]

complex [94]. However, the remaining bromide ligand can be readily replaced by other ligands to give neutral complexes, $[CoX(C_6F_5)(dpnH)]$, ($X = CN^-$, $SCN^-$, $I^-$, $NO_2^-$), mononuclear cationic complexes, $[Co(C_6F_5)(L)(dpnH)]Y$, ($L = H_2O$, $NH_3$, py; $Y = ClO_4^-$, $BPh_4^-$) and binuclear complexes $[\{Co(C_6F_5)(dpnH)\}_2X]BPh_4$ (ref. 48). A general method used for the formation of cobalt-carbon bonds in macrocyclic chelate complexes such as vitamin $B_{12}$ involves the coupling reaction of an appropriately generated carbon-centred radical R• with a cobalt(II) chelate:

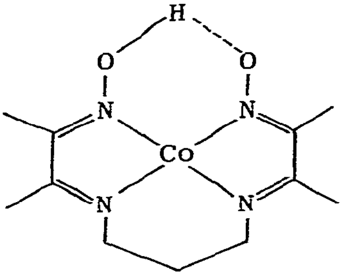
$$R\bullet + Co(II) \rightarrow R\text{-}Co(III).$$

It has now been found that organic hydroperoxides can be used as sources of organic radicals for the preparation of organocobalt complexes. This method has been used previously for the formation of organochromium complexes of the type $[CrR(H_2O)_5]^{2+}$. The reactions of the cobalt(II) macrocyclic complexes [95]-[99] with some tert-alkyl



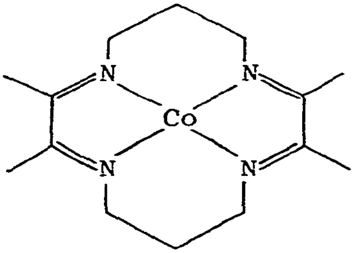
Co(dmgH)$_2$

[95]



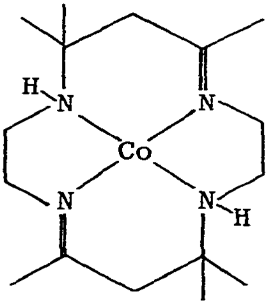
$Co(dpnH)^{+}$

[96]



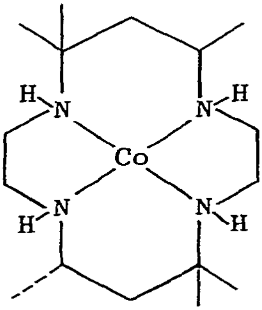
$Co(tim)^{2+}$

[97]



$Co(Me_6[14]diene(4,11)N_4)^{2+}$

[98]



$Co(meso\text{-}Me_6[14]aneN_4)^{2}$

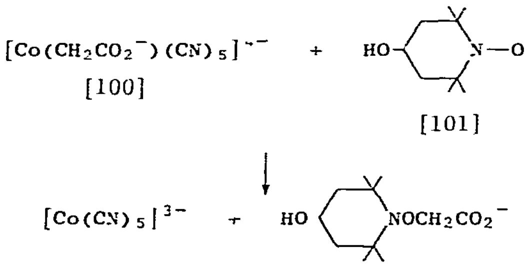
[99]

hydroperoxides occur with a 2:1 (cobalt:peroxide) stoichiometry and lead to the formation of alkyl-cobalt products. The reactivity order found for the complexes is $[Co(dmgH)_2] > [Co(dpnH)]^+ > B_{12r} \approx [Co(tim)]^{2+} > [98] > [99]$. An idealised stoichiometry for the reactions can be represented by the reactions in the following equations:

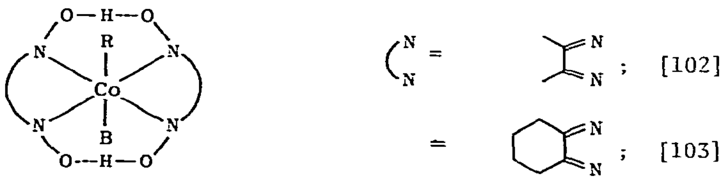
$$RCMe_2OOH + Co(II) \rightarrow RCMe_2O\cdot + Co(III)OH$$
$$RCMe_2O\cdot \rightarrow Me_2CO + R\cdot$$
$$R\cdot + Co(II) \rightarrow R\text{-}Co(III)$$

The reactions of $[Co(tim)]^{2+}$ with a variety of peroxides are not greatly effected by varying the alkyl group of the hydroperoxide. However, the reactions were substantially inhibited by substituting OR groups for the hydroxyl group of the hydroperoxides (ref. 49).

The photoinduced homolysis of the cobalt-carbon σ-bond in vitamin $B_{12}$ and the related synthetic macrocycles is a well known process. It has been suggested that the alkyl radicals thus obtained should react with nitroxides and hence provide a useful technique in spin-label studies, but the restricted solubilities of these cobalt compounds limit their use in aqueous systems. However, the highly water soluble complex [100] reacts rapidly with nitroxides, e.g. [101] when irradiated in the absence of dioxygen with light of 300-400 nm (ref. 50). Two main types of reaction have been observed to take place when the alkylcobaloximes [102] and [103] react with the cobaloxime(II) complexes $[Co(dmgH)_2py]$ and $[Co(chgH)_2py]$ in methanol or methylene chloride. First, homolytic displacement of cobaloxime(II) from the



[100]
[101]



[102]
[103]

alkylcobaloxime takes place by the attack of the cobaloxime(II) reagent on the alkyl group:

$$py(dmgH)_2Co^{II} + RCo^{III}(chgH)_2py \rightleftharpoons py(dmgH)_2Co^{III}R + Co^{II}(chgH)_2py$$

The reaction is first order in each reagent and occurs with inversion of configuration at the α-carbon of the alkyl group. The second-order rate coefficients for this displacement reaction decrease in the sequence $Me \gg Et \gg Pr \sim Bu \sim Oct > Pr^i > Bu^i > Bu^s$. Secondly after the onset of alkyl exchange, exchange of equatorial ligands between reagent cobaloxime(II) and displaced cobaloxime(II) complexes takes place rapidly. Displacement of cobaloxime(I) from the alkylcobaloxime complexes by cobaloxime(I) reagents, e.g. $[Co(xgH)_2py]^-$ in methanolic solution has also been shown to involve a bimolecular reaction of the cobaloxime(I) reagent with inversion of configuration at the α-carbon of the alkyl group, (ref. 51). In the displacement of cobaloxime(II) from alkylcobaloxime(III) complexes by other cobaloxime(II) reagents, the attacking cobalt(II) radical bears only partial resemblence to conventional organic radicals. However, it has now been found that benzylcobaloximes react with bromotrichloromethane thermally and photochemically to give good yields of trichloroethylbenzenes via a chain sequence in which one of the propagating steps involves homolytic displacement of cobaloxime(II) by attack of trichloromethyl radicals at the α-carbon. The reactions occurring are outlined in Scheme 12.

**Initiation:**

$$ArCH_2Co(dmgH)_2B \rightleftharpoons ArCH_2^{\bullet} + {}^{\bullet}Co^{II}(dmgH)_2B$$

**Propagation:**

$${}^{\bullet}Co^{II}(dmgH)_2B + BrCCl_3 \rightarrow BrCo^{III}(dmgH)_2B + {}^{\bullet}CCl_3$$

$${}^{\bullet}CCl_3 + ArCH_2Co^{III}(dmgH)_2B \rightarrow Cl_3CCH_2Ar + {}^{\bullet}Co^{II}(dmgH)_2B$$

**Termination:**

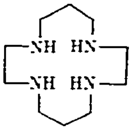
$$2Cl_3C^{\bullet} \rightarrow Cl_3CCCl_3$$

$$Cl_3C^{\bullet} + {}^{\bullet}Co^{II}(dmgH)_2B \rightleftharpoons Cl_3CCo^{III}(dmgH)_2B$$

(B = pyridine, imidazole, $PPh_3$)

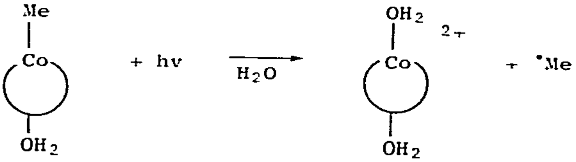
Scheme 12

These reactions provide the first examples of homolytic substitution at a saturated carbon atom and provide a useful synthetic route not only to trichloroethylbenzenes but also to a variety of other βββ-trisubstituted ethylbenzenes using other polyhalogenomethanes. An increase in the yield of trichloroethylbenzene is observed in the presence of imidazole as the base B (ref. 52). A photochemical investigation of the complex, $[Co([14]aneN_4)(OH_2)Me]^{2+}$, ($[14]aneN_4$ = 104) reveals that cobalt-methyl homolysis (Scheme 13) occurs following relatively low energy irradiations. The



[14]aneN₄

[104]



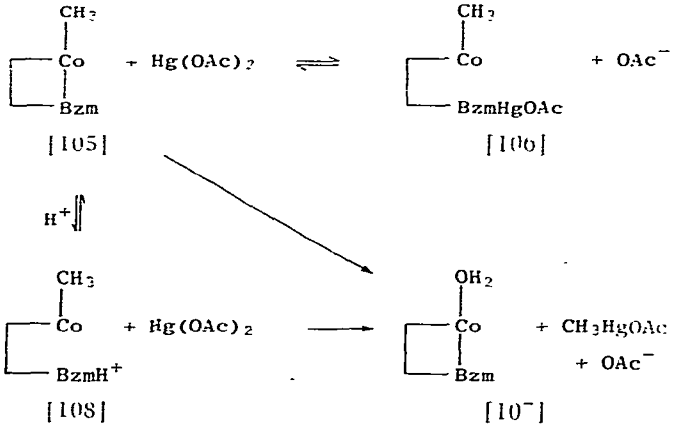
Scheme 15

quantum yield for this homolytic process is essentially independent of exciton wavelength. The differences between the photochemical behaviour of acidopentaamminecobalt(III) complexes and this organo-cobalt complex are striking. Thus homolysis of the cobalt-methyl bond is induced by irradiations of absorption bands much lower in energy than the charge transfer absorptions; homolytic cleavage of the Co-Me bond requires less energy than homolytic cleavage of most $Co^{III}-X^-$ bonds; most acidopentaammine complexes exhibit strongly wavelength dependent photochemistry; there is no distinct absorption feature which can be attributed to a $Me^- - Co(III)$ transition (ref. 53). Flash photolysis studies also confirm that cobalt-methyl bonds tend to undergo efficient homolysis at relatively low energy and in the sense of homolytic dissociation it is apparent that cobalt-carbon σ-bonds must be regarded as significantly weaker than the usual cobalt(III)-ligand bonds (ref. 54). The quantum yield for photodestruction for several alkylcobalamins in aerated solution is known to show an acid dependence (ref. 55). It has now been found that for anaerobic aqueous solution, alkylaquocobaloximes are very photosensitive at moderate acidities (pH 1-5); photoreaction is much less efficient at pH 7 than at lower pH; and the fate of the released axial alkyl group depends strongly on pH (ref. 56). Kinetic studies on the thermal and photochemical insertion reactions of dioxygen into the cobalt-carbon σ-bond of alkylcobaloximes suggest that the insertion

$$RCo(dmgH)_2L + O_2 \rightarrow ROOCo(dmgH)_2L$$

is not a chain reaction. The bimolecular reaction occurs in the non-dissociated $RCo(dmgH)_2L$ complex (ref. 57).

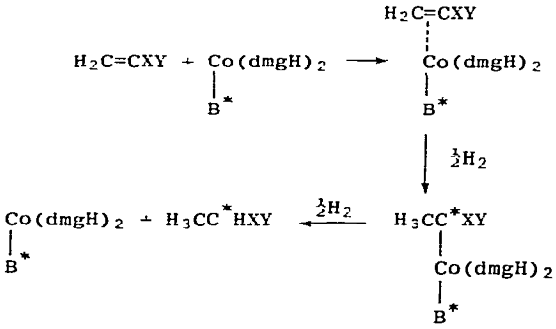
Micellar effects on methyl transfer involving vitamin $B_{12}$ have been investigated by studying the reaction between methylcobalamin and mercury(II) ion. The interaction of methylcobalamin [105] with $Hg(OAc)_2$ in water involves two consecutive steps: the initial rapid reversible formation of the "base-off" methylcobalamin mercury(II) acetate complex [106] which is followed by the slower formation of the aquocobalamin complex [107] (Scheme 14).



Scheme 14

Addition of excess chloride or bromide ion simplifies the overall reaction by eliminating the observable formation of [106]. Rate constants for methyl transfer from methylcobalamin to mercury(II) in water depend strongly on the nature of the anion. The reactivities are acetate > chloride > bromide. This order is the opposite to that observed for the stabilities of the corresponding mercury(II) complexes and supports a mechanism in which the cationic mercury(II) species acts as the electrophile. The addition of sodium dodecyl sulphate to the reaction involving mercury(II) chloride causes a marked decrease in the rate constant for attack of mercury(II) chloride on [105] in water. This inhibition is due to an alteration of the $pK_a$ for the dissociation constant of [105] to form the "base-off" complex [108]. Aqueous micellar hexadecyltrimethylammonium bromide completely stops the methyl transfer (ref. 58). Kinetic studies on the cleavage of the cobalt-carbon bond in organocobaloximes $[CoR(dmgH)_2(H_2O)]$ by iodine reveal the involvement of an $CoR(dmgH)_2(H_2O).I_2$ intermediate which undergoes intramolecular transalkylation and acts as an electrophile towards a second organocobaloxime molecule. The second-order rate constants found for these reactions vary in the order $PhCH_2 > Me > Pr^i > Et > CH_2Cl > Pr^n$. This order differs from that obtained for cleavage reactions with mercury(II) and thallium(III) where the order is $Me > Et > Pr^n > Pr^i > CH_2Cl$. It seems that electrophilic substitutions with halogens are less sterically dependent than the corresponding reactions with metal ions (ref. 59).

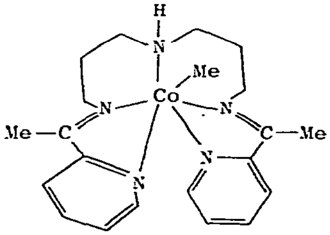
Complexes of $[Co(dmgH)_2]$ and optically active amine are known to catalyse asymmetric hydrogenation of alkenes (Scheme 15). In order to clarify the mechanism of induced asymmetry, the crystal structure of (R)-1-(methoxycarbonyl)ethyl(R)(+)-α-



Scheme 15

methylbenzylaminebis(dimethylglyoximato)cobalt(III) has been determined by X-ray analysis. The $Co(dmgH)_2$ moiety is twisted around its long axis, owing to the steric repulsion from the (R)-1-(methoxycarbonyl) ethyl group and the optically active amine. This twist is considered to be one of the factors inducing the asymmetry in the hydrogenation. The cobalt-carbon cleavage reaction in Scheme 15 proceeds through inversion of configuration (ref. 60). Cobaloximes undergo oxidative alkylation by vinyl ethers, 4-penten-1-ol or 4-pentenoic acid and the transalkylation of alkyl(pyridine)cobaloximes by these alkenes has also been reported (refs. 61, 62).

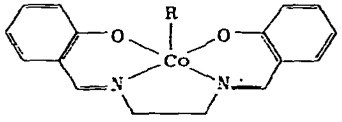
The $^{13}C$ n.m.r. spectra of a variety of cobaloximes of the type $[CoR(dmgH)_2L]$ including complexes in which R = $CHBr_2$, $C_6H_4Br$, $CH_2SiMe_3$, $CH_2C_6H_4CN$, Et, and $CH_2Ph$ have been recorded, (ref. 63), and the crystal structure of the di-iodide salt of the alkylcobalt(III) complex [109] has been determined (ref. 64).



[109]

Thermodynamic data have been obtained for the addition of bases to the complexes [110], [111], and $[CoMe(dmgH)_2]$. The strength of the ligand-cobalt bond formed is determined primarily by the inductive properties of the trans alkyl or aryl ligands, adduct stabilities being in the order $CF_3 > CH_2Cl > Ph > Me$. The nature of the cis ligands is also important in determining the acceptor strength of the cobalt centre. Thus the dmgH ligand renders the cobalt considerably more electron deficient than either the bae or salen systems (refs. 65, 66).

The reaction of polypyrrole macrocycles with $[Rh_2Cl_2(CO)_4]$ gives out-of-plane



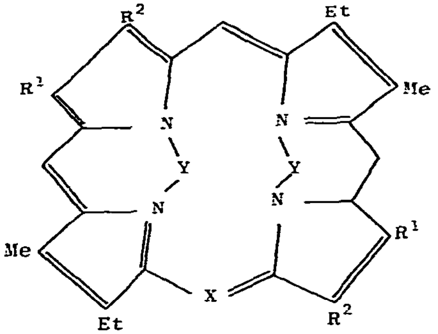
R = CF$_3$, p-MeOC$_6$H$_4$,
Ph, p-FC$_6$H$_4$, CH$_2$Cl, Me

[110]

R = Me, Et, Pr$^n$, Bu$^n$

[111]

mono- (with corroles and thiaphlorins) or bis-dicarbonylrhodium (with porphyrins and azaporphyrins) complexes, depending on the number of imino- and amino-groups present in the central macrocycle. The complexes of etioporphyrin [112a] and the monoazaporphyrin [112b] not only undergo oxidative reactions with alkyl halides, aryl halides, and carboxylic anhydrides but also insert into the C(1)-H bond of formate esters and aldehydes to give the complexes [113], [114], and [115]. The C-H bond of

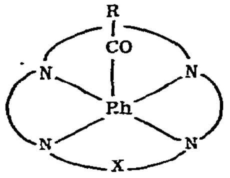


Y = Rh(CO)$_2$

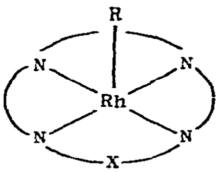
[112]

a; X = CH, R$^1$ = Et, R$^2$ = Me
b; X = N, R$^1$ = Me, R$^2$ = Et

RCHO (R = Ph or Bu$^n$)

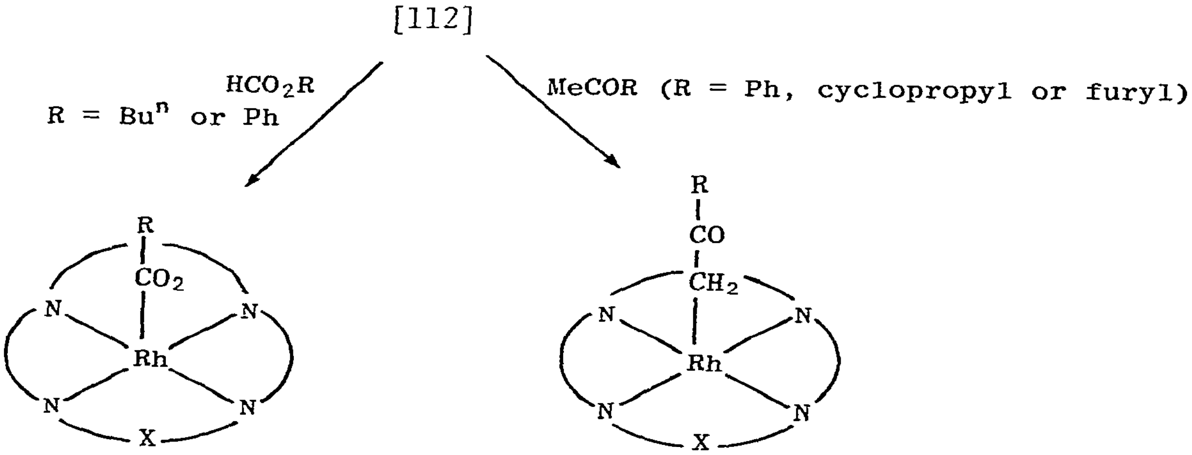


[113]



[114]

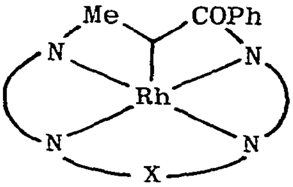
a; X = CH, R$^1$ = Et, R$^2$ = Me
b; X = N, R$^1$ = Me, R$^2$ = Et



[115]

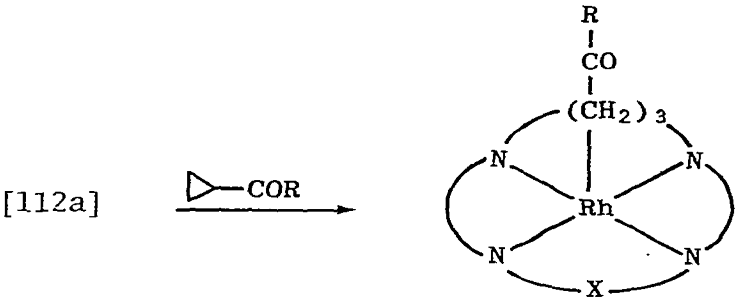
[116]

a; X = CH, $R^1$ = Et, $R^2$ = Me
b; X = N, $R^1$ = Me, $R^2$ = Et



X = CH; $R^1$ = Et, $R^2$ = Me

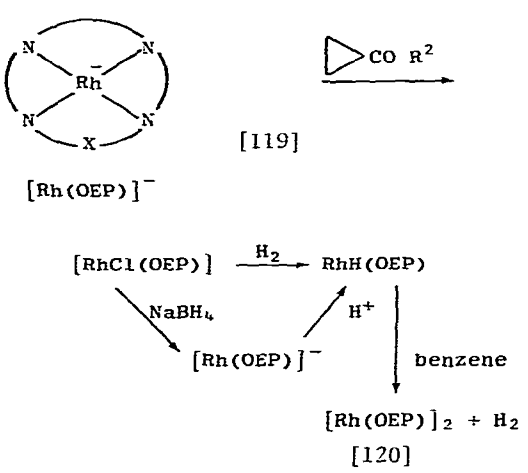
[117]



(X = CH, R = p-fluorophenyl ketone; $R^1$ = Et, $R^2$ = Me)

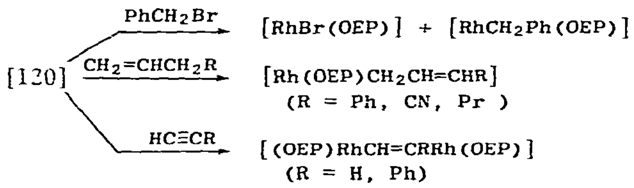
[118]

methyl ketones also oxidatively adds to the complexes [112a and b]. Thus [112a] reacts with MeCOR, (R = Ph, cyclopropyl, or furyl) at 110°-120°C to give the rhodium(III) porphyrin derivatives [116a]. A range of products are obtained from the reaction of [112b] with cyclopropyl methyl ketone. The major product is [116b] but smaller amounts of [115b] and [114b] are also formed. The reaction is not restricted to methyl ketones since [112a] and ethyl phenyl ketone react to give [117]. When the complex [112a] is heated in cyclopropyl p-fluorophenyl ketone, the cyclopropyl group undergoes fission to give (118: X = CH, R = p-$FC_6H_4$). Fission of the cyclopropyl ring also occurs on treating cyclopropyl methyl ketone with the anionic rhodium(I) porphyrin [119] the complex (118; X = CH, $R^2$ = Me) being formed (refs. 67, 68). The introduction of dihydrogen gas into a methanol solution of the rhodium(III) octaethylporphyrin complex [RhCl(OEP)] precipitates the hydrorhodium(III) porphyrin complex, [RhH(OEP)] and the same complex can be obtained by acidification of the anion $[Rh(OEP)]^-$, (Scheme 16). In benzene solution the hydride forms



Scheme 16

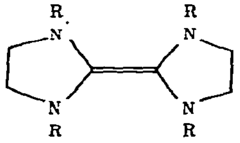
the metal-metal bonded dimer [120]. Some reactions of this dimer are summarised in Scheme 17 (ref. 69).



Scheme 17

Metal-carbene compounds

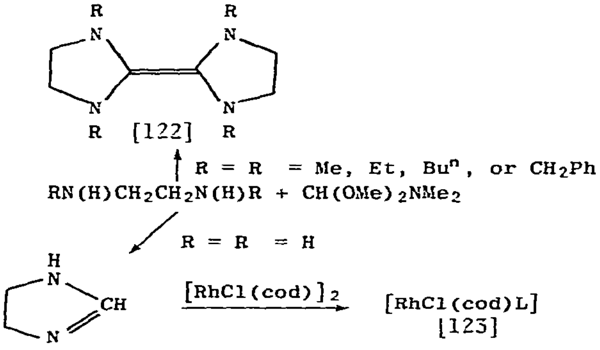
The electron-rich alkene [121] provides a source of stable metal-carbene complexes.



[121]

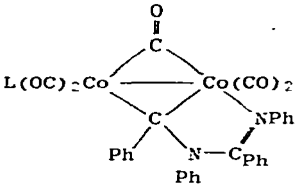
$L^R—L^R$ = [121]
$L^R$ ; R = Me and Et

Thus on heating a solution of $[Co(CO)_3(NO)]$ with [121] under varying conditions the carbene complexes $[Co(CO)_2(L^{Me})NO]$, $[Co(CO)(L^{Me})_2(NO)]$ and $[Co(CO)(L^{Et})_2(NO)]$ can be isolated. These cobaltate(-1) complexes are unaffected by heating to 100°C and the mono(carbene) derivatives readily lose CO on reaction with tertiary phosphines affording species such as $[Co(CO)L^R(NO)(PPh_3)]$ (ref. 70). Attempts to synthesise [122] via the reaction outlined in Scheme 18 affords 2-imidazoline which reacts with $[RhCl(cod)]_2$ to give a complex of 2-imidazoline [123]



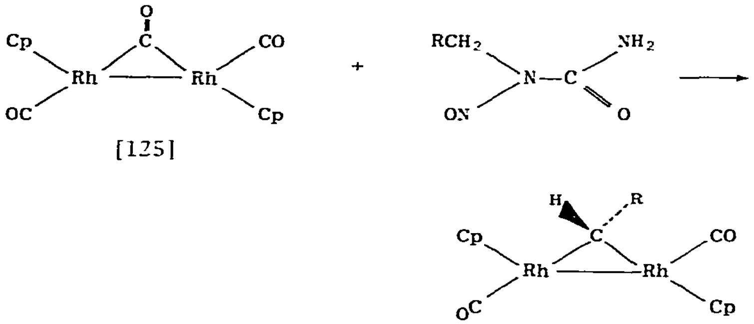
Scheme 18

(ref. 71). The reaction of $[Co(CO)_4]^-$ with Ph(Cl)C=NPh produces the compound $[Co_2(CO)_6(PhCNPh)_2]$. Treatment of this complex with $PMe_2Ph$ gives [124] the structure of which has been established by a single crystal X-ray study. The compound [124]



[124]

contains a bridging carbenoid carbon and a mechanism for the formation of [124] has been proposed (ref. 72). A bridged carbene complex of rhodium [126b] has been obtained by the reaction of [125] with *N*-methyl-*N*-nitrosourea. The structure of

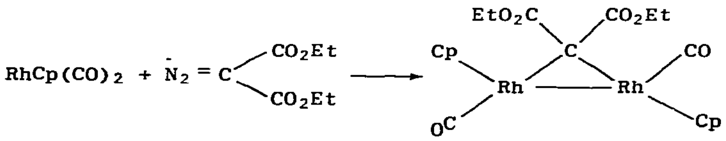


[125]

a = H
b = Me

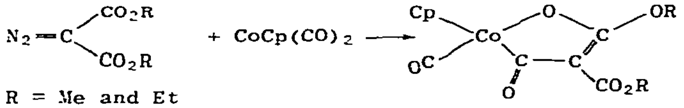
[126]

[126a] has been confirmed by a single crystal X-ray study and in view of the ready accessibility of numerous alkyl-substituted nitrosoureas these reactions provide a convenient source of the bridged carbene compounds [126] without using diazoalkanes. Deuterium labelling experiments show that the origin of the metal-stabilised methylene is the alkyl group of the organic precursor. The reaction of diazodiethyl malonate with [RhCp(CO)$_2$] gives the bis(ethoxycarbonyl)methylene complex [127]



[127]

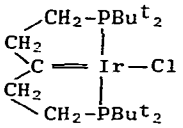
(refs. 73, 74). However, reactions of the diazo compounds [128] with CoCp(CO)$_2$ lead to the metallocycle [129], characterised by a single crystal X-ray study. The



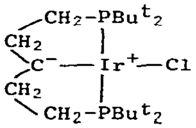
[128] [129]

formation of [129] proceeds via the unusual 1,3-addition of :C($CO_2R$) to [CoCp$(CO)_2$] (ref. 75).

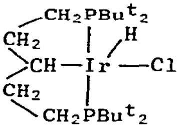
An unusual iridium ylide or carbene complex [130] results on heating the complex [131] at 170°C in vacuo. The X-ray structure of [130] reveals that the structure of this compound is somewhere between the extremes of an iridium(I) carbene [130a] and an iridium(III) ylide [130b]. The hydride [131] together with [132] is formed on treating hydrated $IrCl_3$ with $Bu^t_2P[CH_2]_5PBu^t_2$ (ref. 76).



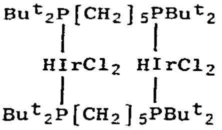
[130a]



[130b]

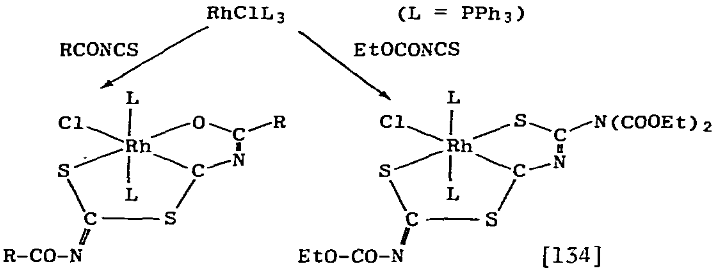


[131]



[132]

The reactions of [RhCl$(PPh_3)_3$] with benzoyl isothiocyanate or ethoxycarbonyl isothiocyanate yield the carbene complexes [133a] and [134] which are shown by single crystal X-ray structure determinations to contain planar tridentate carbene ligands.

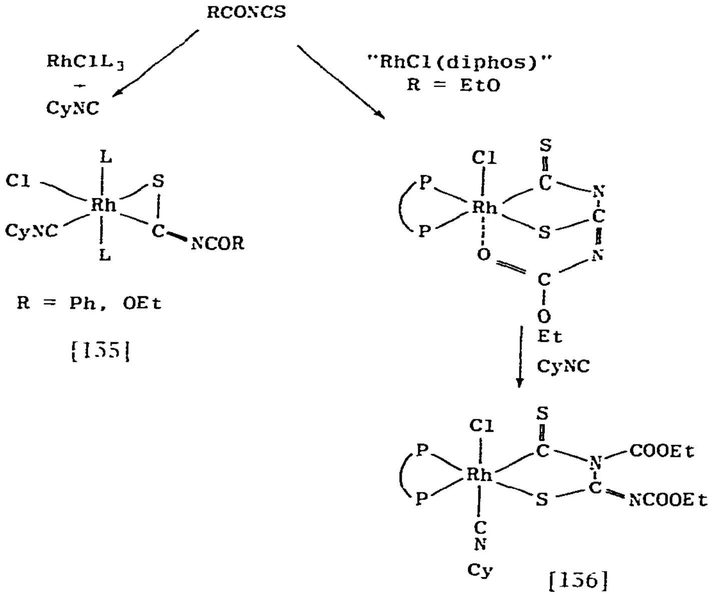


[134]

a; R = Ph
b; R = p-Me-$C_6H_4$
c; R = $Me_2N$

[133]

The presence of cyclohexyl isocyanide in these reactions inhibits the formation of the tridentate carbene complexes and $\eta^2$-isothiocyanate complexes are formed, (Scheme 19). The formation of the carbene complexes probably proceeds via $\eta^2$-isothiocyanate complexes [135] followed by σ-co-ordination of a second isothiocyanate molecule to the sixth co-ordination site which is occupied by cyclohexyl isocyanide, in [135]. The complex [134] is considered to be formed via a five-membered rhodiacyclic intermediate and this structure type, [136], has been isolated by the reaction of ethoxylcarbonyl isothiocyanate with "[RhCl(diphos)]" (ref. 77). Various rhodium carbene complexes have been found to active catalysts for the hydrosilylation of a wide variety of alkenes, alkynes and dienes (ref. 78).



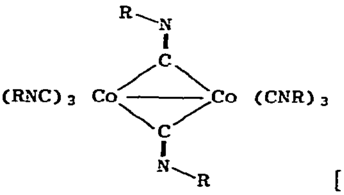
[135]

[136]

Scheme 19

## Metal-isocyanide compounds

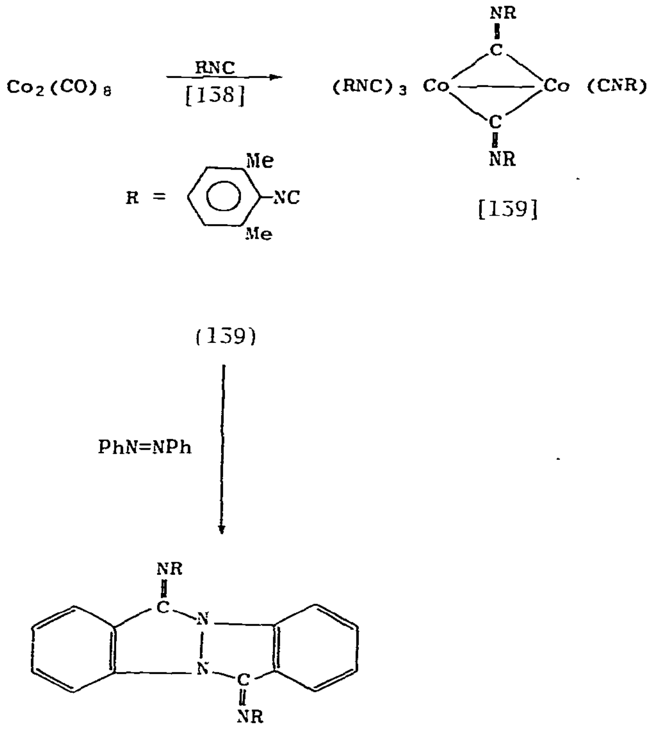
Reduction of $[Co(Bu^tNC)_5]PF_6$ with K-Hg in tetrahydrofuran affords the complex [137]. A single crystal X-ray structure determination shows that the $Co_2C_8$ skeleton



R = $Bu^t$

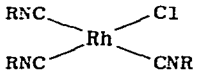
[137]

closely resembles that of [$Co_2(CO)_8$]. In solution [$Co_2(CO)_8$] exists in three isomeric forms and initial studies suggest a related situation with [137] (ref. 79). The reaction of [$Co_2(CO)_8$] with [138] also gives a zerovalent isocyanide complex [139] and some reactions of this complex are depicted in Scheme $20^{a,b}$. The complexe

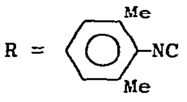


Scheme 20(a)

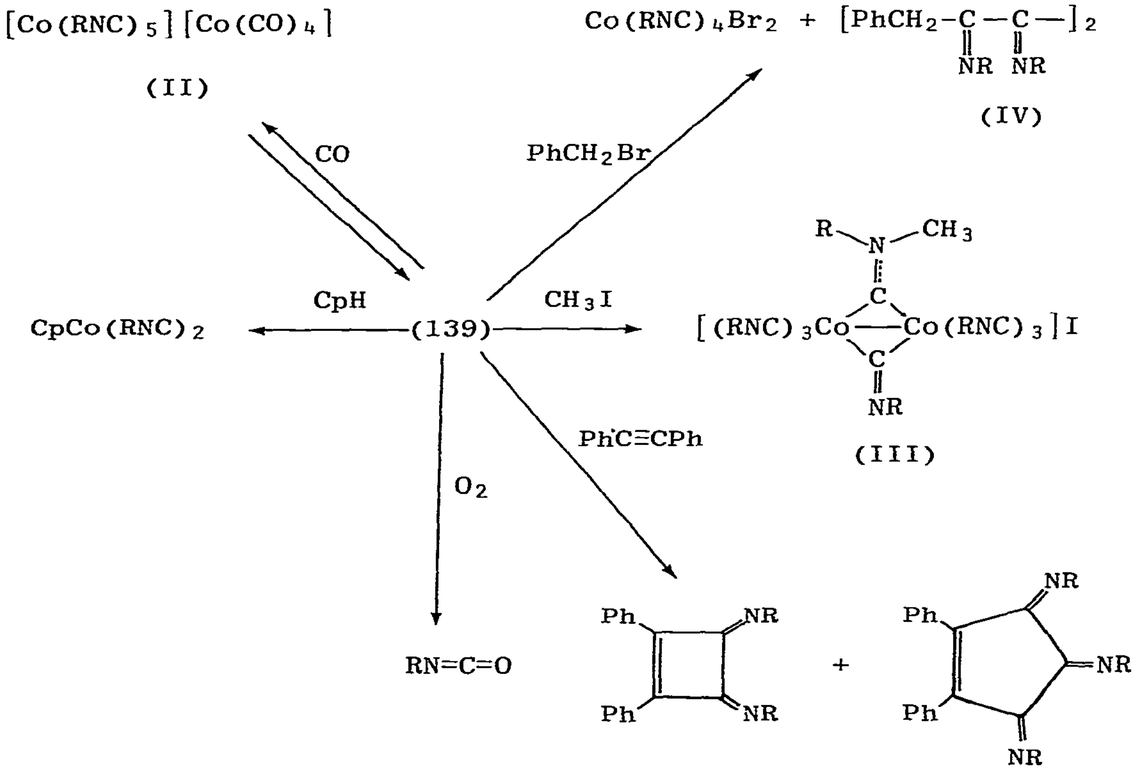
[137] and [139] are the first zerovalent cobalt complexes containing isocyanides as the sole ligand (ref. 80). The reaction of [$RhCl(cod)]_2$ with [138] gives a neutral complex [140] in contrast to a cationic complex [$Rh(RNC)_4$]Cl which is usually formed



[140]



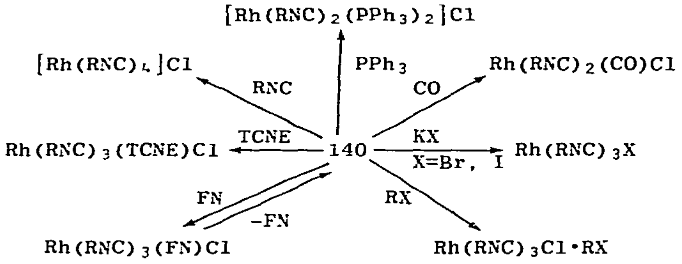
in this type of reaction. The reactions of [140] with bases, alkenes and alkyl



[Co(RNC)5][Co(CO)4]
(II)
CO
PhCH2Br
Co(RNC)4Br2 + [PhCH2-C-C-]2
NR NR
(IV)
CpH
CpCo(RNC)2
(139)
CH3I
R N CH3
C
[(RNC)3Co—Co(RNC)3]I
C
NR
(III)
PhC≡CPh
O2
RN=C=O
Ph
NR
Ph
NR
+
Ph
NR
NR
Ph
NR

Scheme 20(b)

halides have been described (Scheme 21). However, [140] does not decarbonylate aldehydes and is not an active hydrogenation catalyst (ref. 81).



FN = fumaronitrile

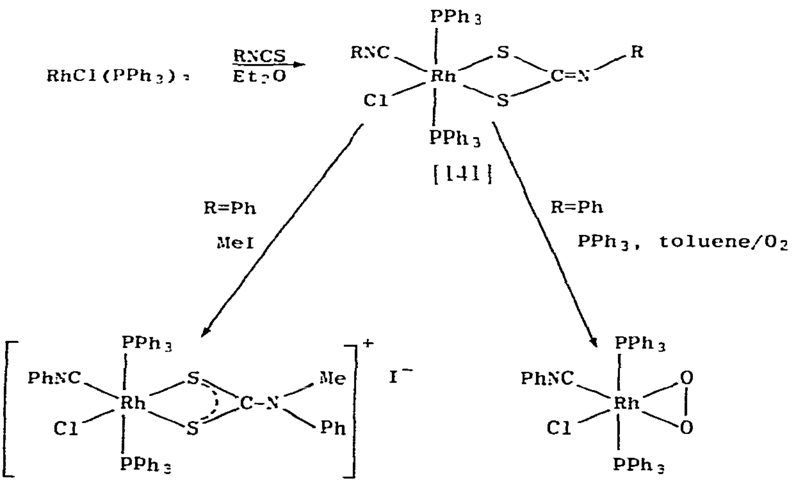
R=$CH_3$, $CH_2$=$CHCH_2$,
PhCO
X=Cl, I

Scheme 21

Triphenylphosphite and tris(p-chlorophenyl)phosphite replace aromatic isocyanide in the cationic complexes $[Co(RNC)_5]X$, (X = $BF_4$, $ClO_4$; R = $C_6H_4Y$-p, Y = H, F, Cl, Br, I; R = -$C_6H_4Me$-o, -$C_6H_3Me_2$-2,6) to give the complexes $[Co(RNC)_4P(OR')_3]X$ which have trigonal bipyramidal structures and exhibit stereochemical non-rigidity (ref. 82). The paramagnetic complexes $Co(RNC)_4I_2$ dimerize in organic solvents to give binuclear diamagnetic cations with linear iodide bridges. Treatment of these compounds with salts of the anions $ClO_4^-$ and $BPh_4^-$ gives diamagnetic complexes $[I\text{-}Co(CNR)_4\text{-}I\text{-}Co(CNR)_4I]X$, X = $ClO_4$ or $BPh_4$. The corresponding isocyanide complexes of rhodium(I) also associate in solution to yield linear stacks in the solid state. The rhodium(I) species interact with the corresponding tetrakis(arylisocyanide)-rhodium(III) complexes to give mixed valence complexes (ref. 83) and electrical conduction properties of some complexes of the type $[Rh(RNC)_4]PF_6$, (R = Pr$^i$, Bu$^t$, and -$C_6H_4Cl$-p), have been reported (ref. 84).

Some isocyanide-dithiocarbonimidato complexes [141] result from the reaction of the isothiocyanates RNCS, (R = Ph, $PhCH_2$, Cy, Bu$^t$, Bu$^n$, and Et) with $[RhCl(PPh_3)_3]$. The complex (141; R = Ph) has previously been formulated as $[RhCl(\sigma\text{-}PhNCS)(\pi\text{-}PhNCS)(PPh_3)_2]$, however, although $\pi$-bonded PhNCS complexes are probably involved in the formation of [141] no $\pi$-PhNCS complexes were isolated in this work. Some reactions of the complexes [141] are illustrated in Scheme 22. Reactions with triphenylphosphine provide a useful route to the complexes trans-$[RhCl(CNR)(PPh_3)_2]_8$ (ref. 85).

The reactions of cyclohexylisocyanide with the complexes $[CoXL_2L']$, (X = Cl, Br, I, $NO_2$; L = MeC(:NOH)C(:NO)Me; L$'$ = p-$H_2NC_6H_4SO_6H_4SO_2NHR$, R = H, Ac, $CONH_2$, Ph, 2-thiazolyl, $C_6H_4SO_2NH_2$) in methanol give $[CoXL_2(CNCy)]$, (ref. 86).



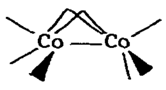
Scheme 22

## Metal carbonyls and related compounds

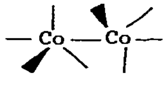
### a) Homonuclear carbonyl compounds

Reviews on thiocarbonyl compounds, (ref. 87), hydride compounds, (ref. 88), and thermochemical studies of organo-transition metal carbonyls and related compounds, (ref. 89), contain information on cobalt, rhodium and iridium compounds.

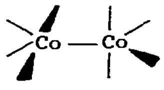
Matrix isolation infrared spectra of dicobalt octacarbonyl in various matrices show the presence of three distinct isomeric forms, with structures [142], [143], and [144]. Conversion of [144] to [142] occurs very readily (ref. 90). Dissociative loss of CO is invoked to account for the kinetics of several reactions of $[Co_2(CO)_8]$. The infrared spectrum of the product of photochemical decomposition of $[Co_2(CO)_8]$ in argon matrices reveals that the major product is $[Co_2(CO)_7]$ which contains no bridging carbonyls. There is no appearance of $[Co(CO)_4]$ radicals upon irradiation at 350 nm of matrix-isolated $[Co_2(CO)_8]$ in argon. However, irradiation of $[Co_2(CO)_8]$ in CO matrices at 254 nm causes formation of $[Co(CO)_4]$ in addition to $[Co_2(CO)_7]$. Passage of $[Co_2(CO)_8]$ over an active cobalt metal surface before matrix isolation causes complete decomposition, however, on less active cobalt species $[Co(CO)_4]$ is seen in the matrices as well as a second species, possibly $[Co_2(CO)_6]$ (ref. 91).



[142]



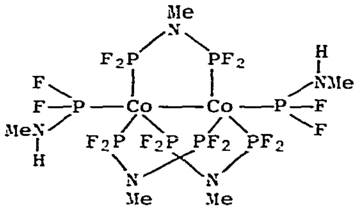
[143]



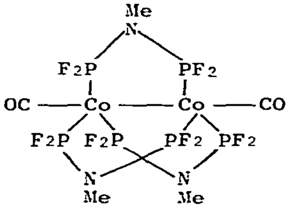
[144]

The uv spectrum of [Co$_2$(CO)$_8$] in *n*-heptane has been reinvestigated and the photochemical formation of [Co$_4$(CO)$_{12}$] at room temperature and its delayed formation unde γ-rays has been described (ref. 92). The electronic spectra of [Co$_2$(CO)$_6$L$_2$], (L = P(OMe)$_3$, PPh$_3$) have been interpreted, the intense absorptions at 393 nm in [Co$_2$(CO)$_6$(PPh$_3$)$_2$] and 360 nm in [Co$_2$(CO)$_6${P(OMe)$_3$}$_2$] being assigned to $\sigma\rightarrow\sigma^*$ transitions. Electronic spectral measurements on [Co$_2$(CO)$_8$] show features which can only be attributed to two isomers. The band at 350 nm is assigned to the $\sigma\rightarrow\sigma^*$ transition of the non-bridged species while the band at 280 nm is assigned to $\sigma\rightarrow\sigma^*$ in the bridged dimer. This higher energy transition is consistent with a shorter Co-Co band in the bridged form, consistent with Co-Co stretching frequencies (ref. 93). The reactivity of photogenerated metal carbonyl radicals toward 1-iodopentane and CCl$_4$ is [Re(CO)$_5$] > [Mn(CO)$_5$] > [WCp(CO)$_3$] > [MoCp(CO)$_3$] > [FeCp(CO)$_2$] > [Co(CO)$_4$]. The ordering of the reactivity correlates with the lability of the M-M bonds. Thus [Co(CO)$_4$] is the least reactive and [Co$_2$(CO)$_8$] has a labile Co-Co bond (ref. 94). Irradiation of a solution of [Co$_2$(CO)$_6${P(OEt)$_3$}$_2$] and nitrosodurene affords the spin trapped species, [Co(CO)$_3${N(O)R}{P(OEt)$_3$}] (ref. 95).

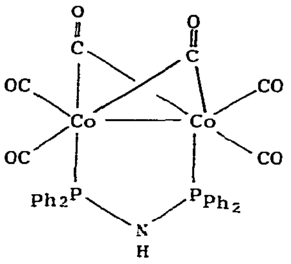
U.v. irradiation of a mixture of [Co$_2$(CO)$_8$] and MeN(PF$_2$)$_2$ gives [145] but in the absence of u.v. irradiation the compound [146] is formed, the apical carbonyl groups being retained. Both complexes have been characterised by X-ray studies. The PF$_2$NHMe ligands are considered to arise via facile hydrolysis of monodentate MeN(PF$_2$)$_2$ ligands (ref. 96). The bidentate MeN(PF$_2$)$_2$ ligand also bridges Co-Co bonds in the compounds [Co$_4$(CO)$_{12-2n}${MeN(PF$_2$)$_2$}$_n$], (n = 1-5) (ref. 97). Treatment of [Co$_2$(CO)$_8$] with Ph$_2$PCH$_2$CH$_2$NEt$_2$, (L) gives either [Co(CO)$_3$L$_2$][Co(CO)$_4$] or [Co$_2$(CO)$_6$L$_2$] depending on the reaction conditions. The norbornadiene compound [Co$_2$(CO)$_4$(C$_7$H$_8$)$_2$] reacts with L to give [Co$_2$(CO)$_6$L$_2$], (ref. 98). In all these compounds the ligand L is monodentate and P-bonded. Dicobalt octacarbonyl reacts with (Ph$_2$P)$_2$NH to give [147] which has been the subject of an X-ray study. This complex is also isolated as a by-product from the reaction of [Co$_2$(CO)$_8$] with Ph$_2$PCH$_2$CH$_2$PPh$_2$ since the literature preparation of the diphosphine can lead to a product which contains some (Ph$_2$P)$_2$NH, (ref. 99). Reactions of [Ir$_2$(CO)$_6$(PPh$_3$)$_2$], [148], with triphenyl-phosphite, triphenylphosphine, and sulphur dioxide have been investigated



[145]

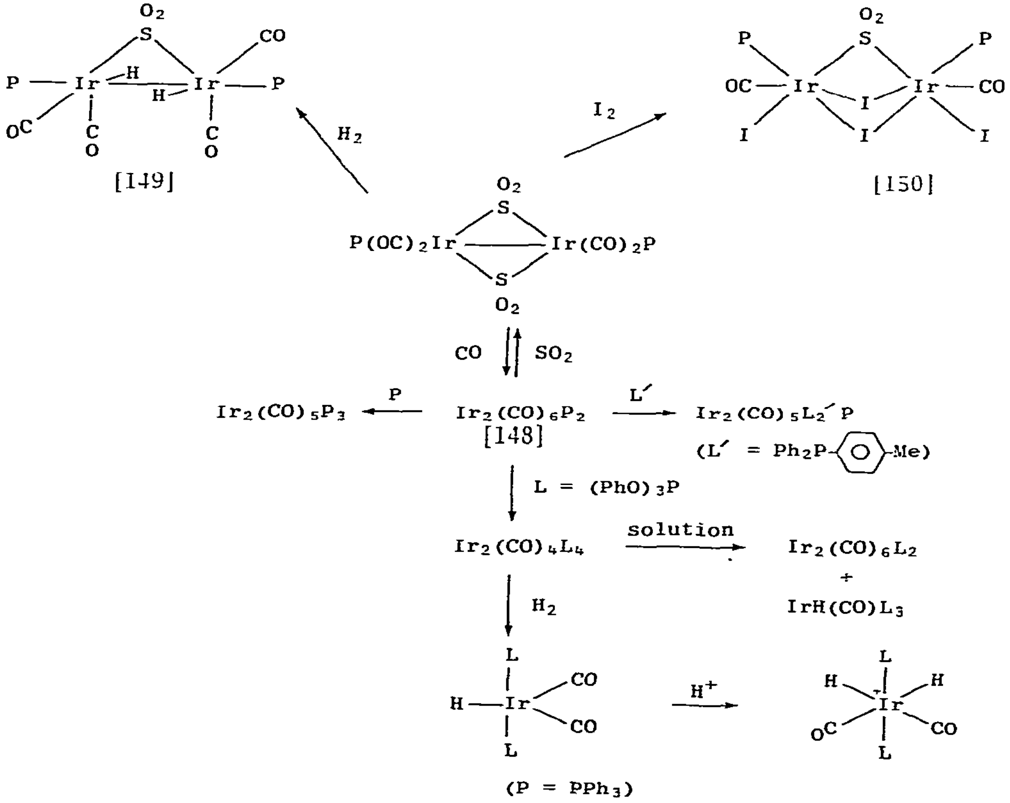


[146]



[147]

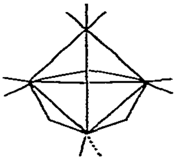
and the results are summarised in Scheme 23. The structures of [149] and [150] have



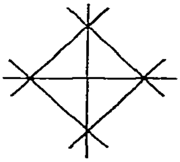
Scheme 23

been confirmed by single crystal X-ray structure determinations (ref. 100). Treatment of $[Co_2(CO)_8]$ with Lewis bases can lead to substitution and/or disproportionation reactions. With hard bases such as oxygen or nitrogen donor ligands disproportionation is favoured and the kinetics and mechanism of disproportionation of $[Co_2(CO)_8]$ induced by nitrogen bases has been reported (refs. 101, 102).

A review on tetranuclear carbonyl clusters has been published (ref. 103) and infrared spectroscopy has been used to study the decarbonylation of $[Ir_4(CO)_{12}]$ on $SiO_2$ and $Al_2O_3$ supports (ref. 104). The clusters $[M_4(CO)_{12}]$, (M = Co, Rh, Ir) maintain the same structures in solution as in the solid state; [151] for $[Co_4(CO)_{12}]$ and $[Rh_4(CO)_{12}]$, [152] for $[Ir_4(CO)_{12}]$.



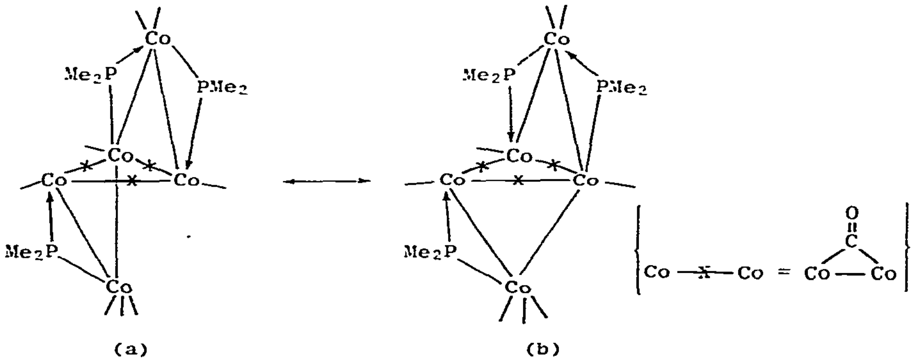
[151]



[152]

N.m.r. studies on the derivatives $[Ir_4(CO)_{12-x}(PPh_3)_x]$, (x = 1-3) and $[Ir_4(CO)_{12-y}(PMePh_2)_y]$ (y = 1-4) reveal that these compounds also adopt the solid state structure in solution each structure being based upon the bridged form [151]. The low energy exchange processes observed for $[Ir_4(CO)_{11}(PMePh_2)]$ can be interpreted in terms of formation of a non-bridged intermediate of the type [152]. Each of the other derivatives show evidence for carbonyl site exchange but at higher temperatures than required for $[Ir_4(CO)_{11}(PMePh_2)]$ and the data are not compatible with the intervention of [152] (ref. 105). The structures of $[Rh_4(CO)_8L_4]$ and $[Rh_6(CO)_{12}L_4]$, (L = $(PhO)_3P$) have been determined by single crystal X-ray studies and have been shown to be derived from those of $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ by replacement of terminal carbonyl groups, (ref. 106). N.m.r. studies show that the hydrogens in $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ (n = 2 and 3) migrate rapidly around the inside of the hexagonal close-packed cluster. At room temperature all the edge-bridging carbonyl groups, except for the three carbonyl groups which bridge the rhodium atoms in the hexagonal plane, undergo exchange with the twelve terminal carbonyl groups on the outside of the cluster (ref. 107).

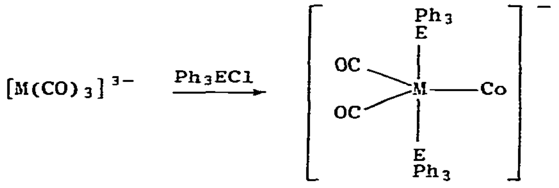
The reactions of complexes of secondary phosphines with π-allyl complexes have led to phosphorus-bridged dinuclear and trinuclear complexes containing metal-metal bonds. However, in an attempt to obtain a compound containing a cobalt-nickel bond by reacting $[Co(\eta^3\text{-}C_3H_5)(CO)_3]$ with $[Ni(CO)_3(PMe_2H)]$, the pentanuclear compound [153], which has been characterised by an X-ray study, is formed in low yield. The valence bond notation with the two resonance formulas [153a] and [153b] provides the cobalt atoms with a krypton electronic configuration and gives the long unbridged Co-Co bonds a bond order of one-half (ref. 108). The compound $[Rh_6(CO)_{16}]$ is an effective catalyst for the oxidation of CO to $CO_2$ and acetone to acetic acid. Both



[153]

$[Rh_6(CO)_{16}]$ and trans-$[IrCl(CO)(PPh_3)_2]$ catalyse the oxidation of butan-2-one, cyclohexanone, and pentan-3-one to acetic acid, adipic acid, and a mixture of acetic and propionic acids respectively. The mechanism is a free-radical autoxidation. Oxidation of cyclohexane in the presence of methanol or ethanol yields dimethyl and diethyl adipate, respectively (ref. 109).

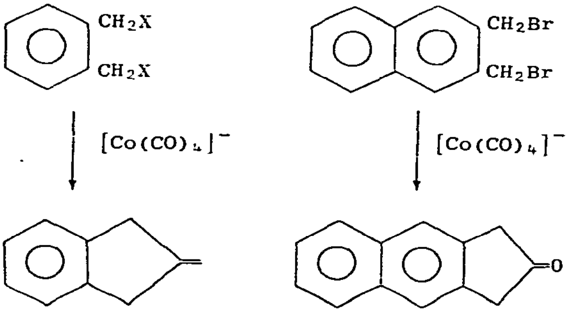
Reduction of $[Co(CO)_4]^-$ or $[M_4(CO)_{12}]$, (M = Rh and Ir) with sodium in liquid ammonia, naphthalene-tetrahydrofuran or hexamethylphosphoramide give the highly reduced $d^{10}s^2$ species $[M(CO)_3]^{3-}$. Treatment of these anions with $Ph_3ECl$, (E = Ge, Sn, or Pb) gives the air- and moisture stable anions [154] (ref. 110). Commercially available $LiBHEt_3$ rapidly and quantitatively cleaves $[Co_2(CO)_8]$ in tetrahydrofuran at room temperature to give $Li[Co(CO)_4]$. This reaction, which probably proceeds via a formyl intermediate, provides an attractive route to carbonylate anions since the by-products, dihydrogen and $BEt_3$, are volatile (ref. 111). Both $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ are known to disproportionate slowly in dry ethers to give $[Co(CO)_4]^-$ and solvated cobalt(II). Halide ions (free or complexed) have now been found to



(M = Co; E = Ge, Sn, Pb)
(M = Rh, Ir; E = Sn, Pb)

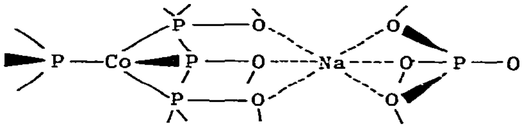
[154]

catalyse the reaction to provide another convenient route to $[Co(CO)_4]^-$. Some reactions of $[Co(CO)_4]^-$, generated via this procedure, with organic halides are illustrated in Scheme 24. Solutions of $[Co(CO)_4]^-$ can also be obtained in benzene or toluene by the action of $[K(crown)]_2[CoX_4]$ or K(crown)OH, (crown = dicyclohexyl-18-crown-6) on $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$ at room temperature. Such solutions are useful in subsequent reactions in which polar solvents would interfere. Thus sebacoyl chloride reacts with $[Co(CO)_4]^-$ in benzene to give $[(CO)_4CoCO(CH_2)_8COCo(CO)_4$ (ref. 112). Ion-pair dissociation constants of bis(triphenylphosphine) iminium salts of the metal carbonylates which vary in the order $\mu\text{-}H[Cr(CO)_5]_2^- > [HFe(CO)_4]^- > [V(CO)_6]^- > [Co(CO)_4]^-$ indicate extensive association of the salts in tetrahydrofuran solution (ref. 113).



Scheme 24

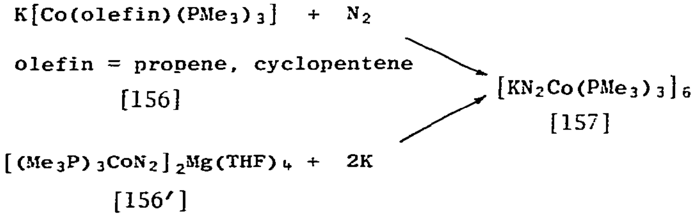
Reduction of cobalt(II) chloride with sodium amalgam in the presence of excess triisopropyl phosphite gives a complex of composition $NaCo\{P(OPr^i)_3\}_5$. This complex has a very high solubility in pentane in contrast to the complexes $M^+[Co\{P(OR)_3\}_4]^-$ and this observation together with n.m.r. evidence suggest the structure [155] for the triisopropyl phosphite complex. Treatment of [155] with allyl iodide gives the unusual paramagnetic salt $NaCo(C_3H_5)\{P(OPr^i)_3\}_3I$. A neutral cobalt(0) compound



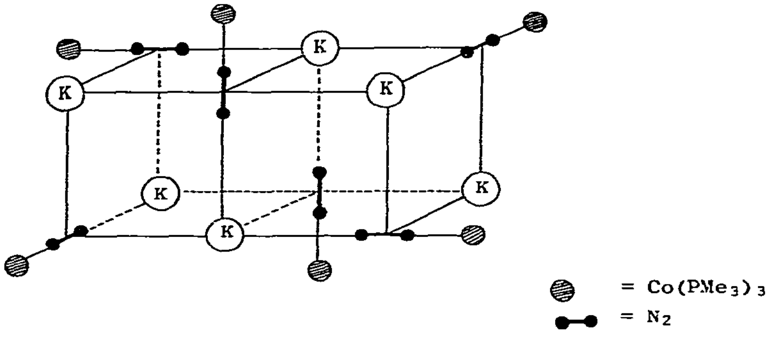
[155]

$[Co\{P(OPr^i)_3\}_4]$ can be obtained by reduction of $CoCl_2$ by two equivalents of sodium amalgam in the presence of excess phosphite. The compound is paramagnetic and shows no tendency to dimerise (ref. 114). Reduction of $[Co(PMe_3)_4]$ by alkali metals gives salts of the anion $[Co(PMe_3)_4]^-$. This anion is a powerful base and undergoes a variety of oxidative-addition reactions with both organic and inorganic halides. It readily exchanges three of its phosphine ligands for carbon monoxide (ref. 115). Some derivatives of dicobalt octacarbonyl can be obtained by treating cobalt metal with the appropriate ligand under a high pressure of carbon monoxide. Complexes isolated include $[Co(dipy)_3][Co(CO)_4]_2$, $[Co(phen)_3][Co(CO)_4]_2$, $[Co_2(diphos)_3(CO)_4]$-$[Co(CO)_4]$, $[Co_2(CO)_6(PPh_3)_2]$, $[Co_2(CO)_6(Ph_2PCH_2CH_2NEt_2)_2]$, and $[Co(CO)_3(Ph_2PCH_2CH_2NEt_2)]_2$ (ref. 116).

Dark brown solutions of the olefincobaltates [156] react readily with dinitrogen to give the hexameric compound $[KN_2Co(PMe_3)_3]_6$, [157] which may also be obtained fror



the magnesium compound [156′]. The structure of [157] has been determined by X-ray crystallography (ref. 117). The dinitrogen compound $[Co(N_2)(PPh_3)_3]$ reacts with



[157]

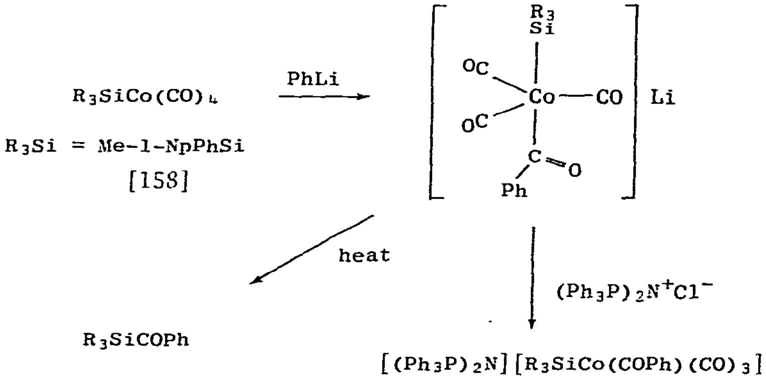
carbon dioxide to give $[Co(CO_2)(PPh_3)_2]_n$. With dioxygen at -50°C $[Co(N_2)(PPh_3)_3]$ gives $[(Ph_3P)_3CoO_2Co(PPh_3)_3]$ (ref. 118).

b) Heteronuclear metal-metal bonded compounds

Optically active compounds [Me-1-NpPhMCo(CO)$_4$], (Np = naphthyl, M = Si, Ge), can be obtained by reaction of the hydride Me-1-NpPhMH with [Co$_2$(CO)$_8$]:

$$\text{Me-1-NpPhMH} + \text{Co}_2(\text{CO})_8 \rightarrow \underset{[158]}{\text{Me-1-NpPhMCo(CO)}_4} + \text{HCo(CO)}_4$$

It is usually assumed that the M-H bond is cleaved with retention of configuration at the asymmetric centre and this has been confirmed by the determination of the crystal structure of the germanium derivative (ref. 119). Electrophiles have been shown to cleave the Si-Co bond of [158] with retention of configuration at silicon while the reagents (LiAlH$_4$, H$_2$O, MeOH, KOAc, Hg(OAc)$_2$) cleave the bond with inversion. Organolithium and Grignard reagents attack at carbonyl ligands to displace silicon as an anion, giving R$_3$SiLi and R$_3$SiMgX respectively (ref. 120). Reactions with phenyl-lithium, however, yield benzoylsilanes Me-1-NpPhSiCOPh with retention of configuration at silicon. An intermediate adduct, Li[R$_3$SiCo(COPh)(CO)$_3$], is probably formed, Scheme 25. Phenyl-lithium is known to attack the carbonyl ligand trans to the Ph$_3$M group in the compounds [Ph$_3$MCo(CO)$_4$], (M = Sn or Pb) and a similar behaviour is observed in the compounds [158] (ref. 121).



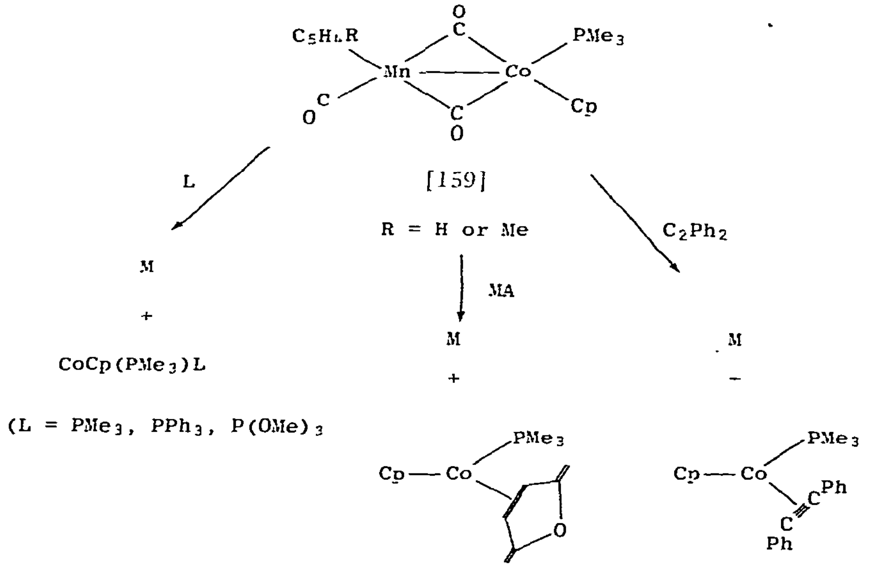
Scheme 25

Appearance potential measurements for the ions MMe$_3^+$ have provided M-Co bond dissociation energies for the compounds [Co(MMe$_3$)(CO)$_4$]. The bond dissociation energies found are >2.4 eV, (M = Si); 3.2 eV, (M = Ge); 2.8 eV, (M = Sn) (ref. 122). Pyrolysis of [Co(SiH$_3$)(CO)$_4$] gives CoSi (ref. 123).

Metallic tin and lead react with [Co$_2$(CO)$_8$] in diethyl ether to give [Sn{Co(CO)$_4$}$_4$] and [Pb{Co(CO)$_4$}$_4$] respectively. Treatment of the lead compound with triphenylphosphine gives $[Pb\{Co(CO)_3L\}_3Co(CO)_4]$ and $[Pb\{Co(CO)_3L\}_4]$. Lithium and sodium cleave the lead-cobalt bonds in $[Pb\{Co(CO)_4\}_4]$ to give $Li[Co(CO)_4]$ and $Na[Co(CO)_4]$ respectively. In the compounds $[M\{Co(CO)_4\}_4]$ the lead atom but not the tin can co-ordinate to polar solvents such as acetone or diethyl ether (ref. 124). Treatment of $[Co(SnCl_3)(CO)_4]$ with $PBu_3^n$, $PPh_3$, or $AsPh_3$ results in the formation of the ionic compounds, $[Co(CO)_3L_2][SnCl_3]$. A free radical chain mechanism is proposed to account for the chemical products and kinetics of the reactions. The mechanism involves homolytic cleavage of the Sn-Co bond to give $[Co(CO)_4]$ which readily undergoes carbonyl substitution. This mechanism is applicable to the disproportionation of $[Co_2(CO)_8]$ in basic solvents (ref. 125). Temperature-dependent $^{13}C$ n.m.r. spectra indicate that the compounds $[Co(MX_3)(CO)_4]$, (M = C, Si, Ge, Sn, or Pb; X = F, Cl, Me, Bu, $PhCH_2$, or Ph) undergo intramolecular axial-radial carbonyl exchange. The free energy barriers to intramolecular rearrangement are in the range 4.5-11.8 k cal $mol^{-1}$ and are determined mainly by the steric requirements of the $MX_3$ groups (ref. 126). Tin-cobalt and carbonyl stretching force constants for a series of tin-cobalt carbonyl compounds of the type $[X_{4-n}Sn\{Co(CO)_3L\}_n]$, (n = 1, 2, or 3) have been determined (refs. 127-129). $^{59}Co$ n.q.r. data on a series of compounds in which the $Co(CO)_4$ group is bound to the elements Bi, Si, Ge, Sn, Pb, Ga, In, Tl, Zn, Cd, Hg, Au, Mn, and Co indicate that the covalency of the element-cobalt bond increases on going down the periodic table in the groups 2B, 3A, and 4A and on going across the table from left to right. There is no strong evidence for metal-metal $\pi$-bonding in the majority of the compounds. However, an interaction of the $\pi^*$ level of the equatorial carbonyl groups in $-Co(CO)_4$ with the metal-cobalt bond or the heterometal appears to exist (ref. 130).

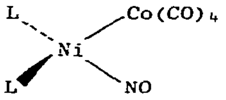
A variety of indium-, tin-, cadmium-, and mercury-cobalt bonded compounds can be obtained by treating cobalt metal with the metal halide and a donor ligand under a pressure of carbon monoxide. Complexes isolated by this technique include $[Cl_2Sn\{Co(CO)_4\}_2]$, $[ClIn\{Co(CO)_4\}_2]_2$, $[X_2Sn\{Co(CO)_3(PPh_3)\}_2]$, (X = Cl, Br, I), and $[M\{Co(CO)_3(PN)\}_2]$, (M = Cd, Hg; PN = $Ph_2PCH_2CH_2NEt_2$) (ref. 116). Group IIB metals and $SnCl_2$ also insert into the cobalt-cobalt bond of $[Co_2(CO)_6(PN)_2]$ (ref. 98).

The compound $[CoCp(PMe_3)_2]$ is a very strong nucleophile and forms 1:1 adducts with a variety of Lewis acids. However, reaction of $[CoCp(PMe_3)_2]$ with $[MnCp(CO)_2(THF)]$ gives the dinuclear compound (159; R = H). The compound (159; R = Me) can similarly be obtained via $[Mn(C_5H_4Me)(CO)_2(THF)]$. The compound (159; R = Me) undergoes unsymmetrical cleavage of the Mn-Co bridge fragment on treatment with a variety of Lewis bases, Scheme 26 (ref. 131). Nucleophilic substitution of the halide ligands in the compounds $[NiX_2(PPh_3)_2]$ by $[Co(CO)_4]^-$ leads to $[Ni(CO)_2(PPh_3)_2]$ via a metal-metal bonded intermediate. However, $[Co(CO)_4]^-$ and $[NiX(NO)(PPh_3)_2]$ give the nickel-cobalt bonded compound [160] (ref. 132). Treatment of the palladium compound [161] with $Na[Co(CO)_4]$ is known to give the palladium-



$M = Mn(C_5H_4Me)(CO)_3$; MA = maleic anhydride

Scheme 26

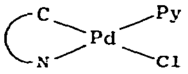


[160]

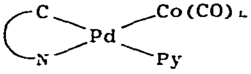
L = $PPh_3$

cobalt bonded compound [162]. The structure of [162] has now been determined by a single crystal X-ray study (ref. 133).

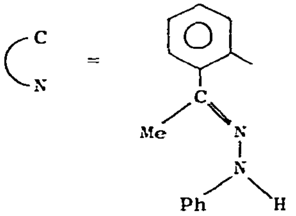
The phosphorus bridged iron-cobalt bonded compound [163] can be prepared by the reaction of $[(CO)_4Fe\text{-}PMe_2H]$ with $[Co(\eta^3\text{-}C_3H_5)(CO)_3]$ and the crystal structure of [163] has now been determined (ref. 134). The metal-metal bond in the related dimethylarsine bridged [164] is reactive and is readily opened by phosphines to give dinuclear complexes of the type $[(CO)_4FeAsMe_2Co(CO)_3PR_3]$ (ref. 135). Compounds such as [164] may therefore be regarded as complexes possessing latent free co-ordination sites capable of being exploited for catalytic reactions. An example of such a reaction has been demonstrated by the catalytic dimerisation of norbornadiene by

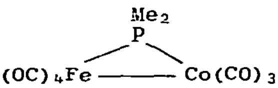


[161]



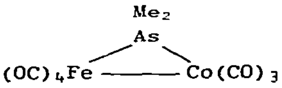
[162]





$\mathrm{(OC)_4Fe}-\overset{\mathrm{Me_2}}{\mathrm{P}}-\mathrm{Co(CO)_3}$

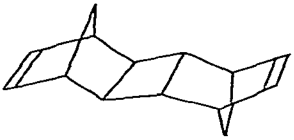
[163]



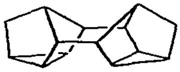
$\mathrm{(OC)_4Fe}-\overset{\mathrm{Me_2}}{\mathrm{As}}-\mathrm{Co(CO)_3}$

[164]

[164] at 60°C to the *exo*-*trans*-*oxo* dimer [165] and the dimer [166]. Reaction of

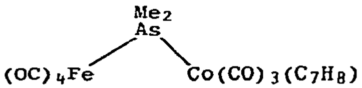


[165]



[166]

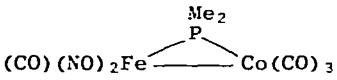
norbornadiene with [164] at 55°C gives the complex [167] which has been the subject of an X-ray study and [167] catalyses the same reaction as [164]. It is considered



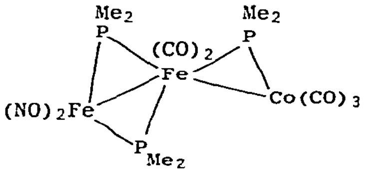
$\mathrm{(OC)_4Fe}\ \overset{\mathrm{Me_2}}{\mathrm{As}}\ \mathrm{Co(CO)_3(C_7H_8)}$

[167]

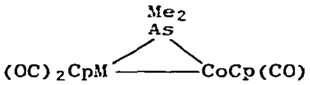
that only one of the metal atoms in [164] is the catalytic active centre in view of the unaltered presence of the $(CO)_4FeAsMe_2$ group in [167] (ref. 136). An attempt t obtain the dinuclear complex [168] by reaction of $[(CO)(NO)_2FePMe_2H]$ with $[Co(\eta^3\text{-}C_3H_5)(CO)_3]$ instead gives the trinuclear complex [169] together with several other complexes (ref. 137). However, the dinuclear complexes [170] are formed upon



[168]



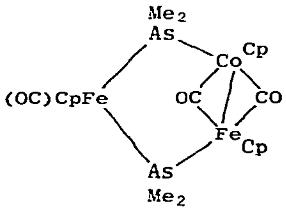
[169]



(M = Mo or W)

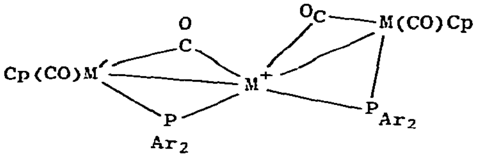
[170]

reaction of the arsines $[(CO)_3CpMAsMe_2]$, (M = Mo or W) with $[CoCp(CO)_2]$ (ref. 138). Interestingly the five-membered ring complex [171] is formed upon reaction of $[(CO)_2CpFeAsMe_2]$ with $[CoCp(CO)_2]$, (ref. 139), but the organometalloarsines



[171]

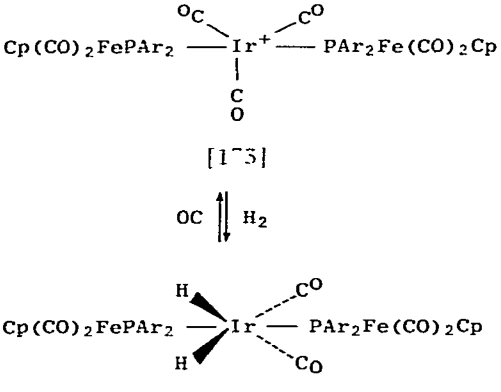
$M\text{-}AsMe_2$ (M = $MoCp(CO)_3$, $WCp(CO)_3$, $FeCp(CO)_2$), react with $[Co(NO)(CO)_3]$ to give dinuclear complexes $[MAsMe_2Co(NO)(CO)_2]$, (ref. 138). Treatment of cis-$[M(CO)_4(AsMe_2Cl)_2]$, (M = Cr, Mo, W) with $Na[Co(CO)_4]$ give the arsenic bridged complexes $[(CO)_4CoAsMe_2M(CO)_4AsMe_2Cl]$ (ref. 140).



| | M | M′ | Ar |
|---|---|---|---|
| a; | Rh | Fe | p-tolyl |
| b; | Ir | Fe | Ph |
| c; | Ir | Fe | p-tolyl |
| d; | Ir | Ru | Ph |
| e; | Ir | Ru | p-tolyl |

[172]

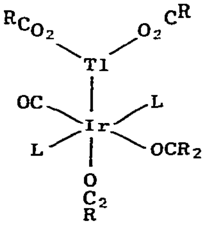
The framework of the chiral polynuclear cation [172a] racemizes with simultaneous bridge-terminal carbonyl exchange, $\Delta G^{\ddagger}$ being about 13 kcal mol$^{-1}$ for both processes. The related complexes [172] have also been prepared and the barriers to racemization in $C_2D_4Cl_2$ of [172c] and [172e] are 17.5 and 17.8 kcal mol$^{-1}$ respectively. Both clusters add $H_2$ reversibly at 1 atmosphere and room temperature and [172c] forms an adduct [173] with CO which reacts with $H_2$ to give [174] (refs. 141, 142).



[173]

[174]

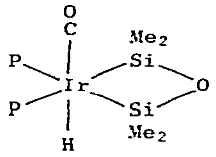
The reactions of trans-$[IrX(CO)L_2]$, (L = $Ph_3P$, $PhMe_2P$, $Ph_3As$; X = $O_2CR$) with $Tl(O_2CR)$ , (R = Me, Et, $CHMe_2$, $CF_3$) give the iridium-thallium bonded compounds [175]. When X = Cl a mixture of isomers is obtained. The iridium-thallium bond is remarkably stable and reactions of [175] with $H_2O$ and HCl give $[L_2(CO)(OH)(O_2CR)IrTl(O_2CR)_2]$ and $[L_2(CO)Cl_2IrTlCl_2]$ respectively. The reaction of $[Rh(O_2CR)(CO)L_2]$ with $Tl(O_2CR)_3$ results in reduction of thallium(III) to thallium(I) and complexes analogous to [175] cannot be isolated (ref. 143). The reaction of Vaska's complex with 1,1,3,3-tetramethyldisiloxane [176] gives the cyclic iridium-silicon bonded compound [177] and the molecular structure of this compound has been determined by an X-ray study. The rhodium compound $[RhCl(PPh_3)_3]$ also reacts with



[175]

$HMe_2SiOSiMe_2H$

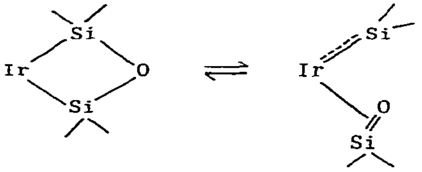
[176]



$P = PPh_3$

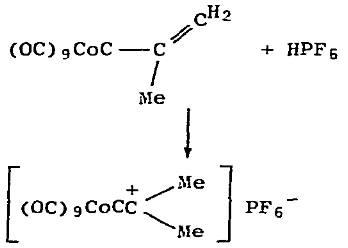
[177]

[176] to give an uncharacterised yellow powder and both this rhodium compound and [177] catalyse the disproportionation of [176] into $Me_2SiH_2$ and higher siloxane oligomers under mild conditions. These catalytic reactions are considered to proceed via cleavage of a cyclometalladisiloxane ring [178] to give an intermediate [179] containing co-ordinated $Me_2Si$ and a co-ordinated Si=O double bond (ref. 144).



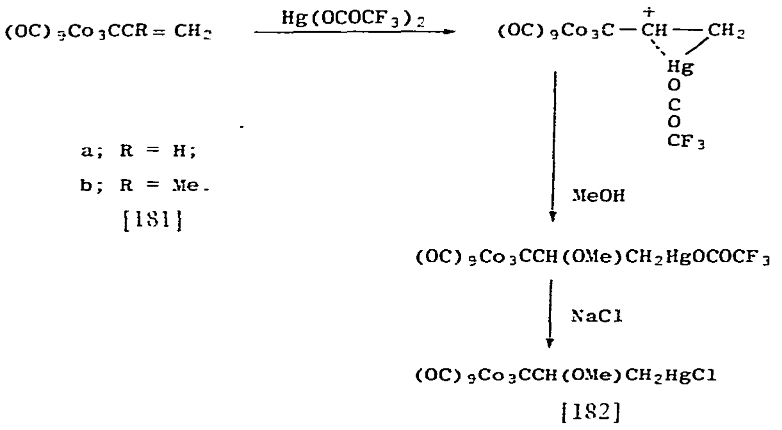
[178] [179]

Alkylidynetricobalt nonacarbonyl cluster complexes continue to attract attention and a review on these complexes has appeared (ref. 145). The reaction of $RCCl_3$ with $[Co_2(CO)_8]$ has been used to prepare α,β-unsaturated methylidynetricobalt nonacarbonyl complexes $[CH_2{=}CHCCo_3(CO)_9]$, $[CH_2{=}CMeCCo_3(CO)_9]$, $[Me_3SiCH{=}CHCCo_3(CO)_9]$ and $[MeCOCH{=}CHCCo_3(CO)_9]$. In order to obtain these vinyl derivatives rigorously dried tetrahydrofuran, water-free $[Co_2(CO)_8]$, and a non-hydrolytic, aprotic work-up are necessary. Protonation of these allylidynetricobalt nonacarbonyl complexes provides a route to cluster-substituted carbonium ions including the hitherto unavailable tertiary species [180].



[180]

Protonation of $[Me_3SiCH{=}CHCCo_3(CO)_9]$ results in desilylation. The MeCOCl/$AlCl_3$ reagent acetylates the complexes [181] in the 2-position and methoxymercuration of [181a] gives [182] (ref. 146). Treatment of $Li[Co_3(CO)_{10}]$ with MeCOBr gives



a; R = H;
b; R = Me.
[181]

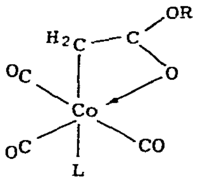
[182]

$(OC)_9Co_3C\text{-}OCOMe$ which has been characterised by a single crystal X-ray study. This is the first methylidyne-nonacarbonyltricobalt derivative with a $\mu_3$-C-O-C bond (ref. 147). The reaction of [183] with $(EtCO)_2O/HPF_6$ has previously been shown to give acylium salt [184]. It has now been found that the action of aluminium tri-

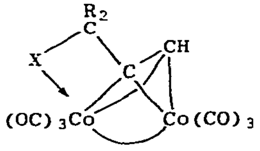
$$(OC)_9Co_3CCO_2R \xrightarrow[HPF_6]{(EtCO)_2O} (OC)_9Co_3CCO^+PF_6^-$$

[183] [184]

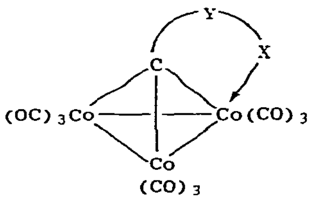
halides, $AlX_3$, (X = Cl, Br, I) on the complexes $(OC)_9Co_3CX$, (X = Cl, Br) results in formation of the acylium haloaluminate salt $[(OC)_9Co_3CCO][AlX_4.AlX_3]$, even when the reaction is carried out under dinitrogen. Co-ordination of a molecule of $AlX_3$ at a carbon monoxide ligand is presumed to provide the activation for migration of CO from cobalt to the electron-deficient apical carbon atom. Addition of a range of nucleophiles (alcohols, phenols, amines, thiols, $R_4Sn$ compounds, reactive aromatics, silicon hydrides) to the acylium ion produces cluster complexes of type $(CO)_9Co_3CCOY$, (Y = RO, ArO, RR'N, RS, R, Ar, H) (ref. 148). Clemmensen reduction has been shown to be an effective means of converting acyl- and vinylic methylidyne-tricobalt nonacarbonyl complexes to the corresponding saturated alkylidynetricobalt nonacarbonyl. Diborane in tetrahydrofuran reacts with acyl clusters to give a mixture of the corresponding alcohol and alkyl complexes (ref. 149). A variety of experimental evidence has shown the presence of a donor-acceptor interaction between the ester carbonyl group and one of the cobalt atoms in $[(CO)_9Co_3CCH{=}CRCO_2R']$. Similar interactions between the polar groups in an organic ligand and a metal atom have been detected in mono- [185], di- [186] and trinuclear [187] cobalt compounds (ref. 150).



[185]



[186]

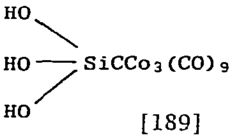


[187]

The general method for the preparation of alkylidynetricobalt nonacarbonyl complexes involves the reaction of an organic trihalide with $[Co_2(CO)_8]$. This reaction has been used to obtain silyl-substituted methylidynetricobalt nonacarbonyls $[R_3SiCCo_3(CO)_9]$, but has drawbacks in that it requires the preparation of the appropriate $R_3SiCCl_3$ derivative. A new and convenient route to the silicon functional compounds [188] has now been discovered using silicon hydrides and $[HCCo_3(CO)_9]$.

$$R_3SiH + HCCo_3(CO)_9 \xrightarrow[\text{reflux}\atop \text{30 min}]{\text{toluene}} \underset{[188]}{R_3SiCCo_3(CO)_9} + H_2$$

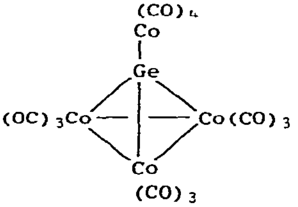
Hydrolysis of $[Cl_3SiCCo_3(CO)_9]$ gives the crystalline silane triol [189]. Very few



[189]

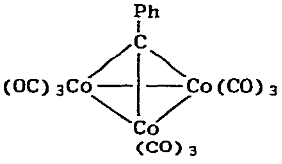
silanetriols are known but those which have been reported are very sensitive to condensation to siloxanes. The stability of [189] is probably due to the large $CCo_3(CO)_9$ group which inhibits the bimolecular condensation reaction. Treatment of $Ph_3GeH$ with $[HCCo_3(CO)_9]$ gives $[Ph_3GeCCo_3(CO)_9]$ (ref. 151).

The reaction of $GeBr_4$ with $Na[Co(CO)_4]$ gives the germylidyne-tricobalt cluster [190] which corresponds structurally to $[(CO)_9Co_3Si-Co(CO)_4]$. However, attempts to obtain the carbon homologue $[(CO)_9Co_3C-Co(CO)_4]$ have failed (ref. 152). Treatment of $[(CO)_9Co_3CMe]$ with tricyclohexylphosphine results in displacement of one axial carbonyl ligand and rearrangement of three equatorial ligands to give three bridging carbonyls, one across each of the sides of $Co_3$ triangle (ref. 153). A variety of methinyltricobalt enneacarbonyls, $[YCCo_3(CO)_9]$ undergo facile alkali metal and electrochemical one-electron reduction to produce stable radical anions. The cluster is retained on reduction and e.s.r. studies reveal hyperfine coupling to the three cobalt nuclei. $A^{Co}$ does not vary significantly with the nature of the apical substituent (ref. 154).

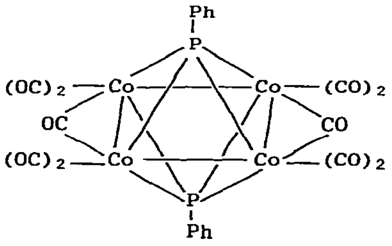


[190]

Few organometallic clusters have been reported as homogeneous catalysts. However, results have now been presented which reveal that the hydroformylation of pent-1-ene and pent-2-ene can be catalysed by [191] and [192] under mild conditions to give aldehydes in high yields with a fairly normal-to-branched selectivity. Hydrogenation of pent-1-yne and pent-2-yne to pent-1-ene and pent-2-ene respectively can also be



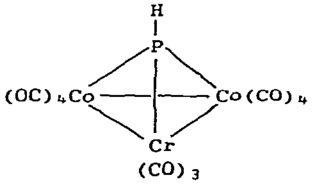
[191]



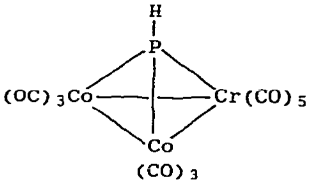
[192]

achieved (ref. 155). Photolysis of $[HCCo_3(CO)_9]$ in the presence of hydrogen and hex-1-ene has also been shown to lead to a catalytic reaction. In this example conversion of hex-1-ene to *cis*- and *trans*-hex-2-ene is observed. Irradiation of $[HCCo_3(CO)_9]$ under a hydrogen atmosphere with visible or u.v. light leads to quantitative formation of $[Co_4(CO)_{12}]$ and production of methane, photolysis in the presence of $D_2$ revealing that the methane derives from the apical CH group and not from CO. The photochemical properties of $[MeCCo_3(CO)_9]$ parallel those of $[HCCo_3(CO)_9]$. Irradiation of $[HFeCo_3(CO)_9]$ and $[HFeCo_3(CO)_{10}(PPh_3)_2]$ in degassed solutions also leads to declusterification with formation of $[Co_4(CO)_{12}]$ and $[Co_2(CO)_6(PPh_3)_2]$ respectively (ref. 156). Neutron diffraction studies on the cluster hydride, $[HFeCo_3(CO)_9\{P(OMe)_3\}_3]$ reveal that the hydrogen atom triply bridges the cobalt atoms on the side opposite to the iron atom (ref. 157).

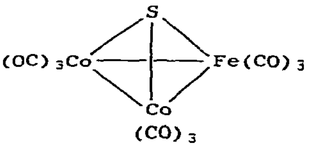
The reaction of $[Cr(PH_3)(CO)_5]$ with a deficiency of $[Co_2(CO)_8]$ gives the phosphorus-centred heterometallic cluster [193] although an alternative structure [194] has been proposed (ref. 158). Further substitution of the P-H bond in this cluster has not been achieved. Thus reactions with $[Co_2(CO)_8]$ or $[MnH(CO)_5]$ did not effect further metalation of the phosphorus (ref. 158). The reactions of $[MClCp(CO)_3]$, (M = Mo, W) with $Li[Co_3(CO)_{10}]$ gives a mixture of $[Cp(CO)_3MCo(CO)_4]$ and $[(CO)_9Co_3M(CO)_2Cp]$ (ref. 159). $^{13}C$ n.m.r. studies have revealed that the replacement of CO by a phosphorus donor ligand in [195] is at one cobalt atom in the monosubstituted derivative, at two cobalt atoms in the disubstituted derivative and at two cobalt atoms and one iron atom in the trisubstituted derivative. In each case substitution is at an equatorial position (ref. 160).



[193]



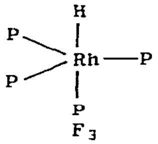
[194]



[195]

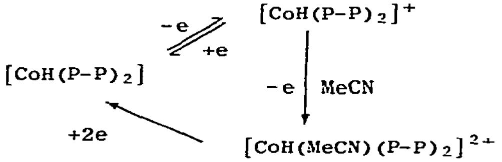
### c) Metal oxidation state (I), (II), and (III) compounds

The molecular structure of $[HCo(CO)_4]$ has been investigated by gas-phase electron diffraction. The hydride has $C_{3v}$ symmetry, with the hydrogen directly bonded to the cobalt at a distance of 1.556(18) Å. This is close to the distance of 1.593 Å reported for the diatomic hydride [CoH] (ref. 161). The structure of a benzene solvate of the related hydride, [196], has been determined by a single crystal X-ray study (ref. 162). The electrochemical oxidation of a series of $d^8$-hydrido complexes of cobalt, rhodium, and iridium has been shown to proceed in two one-electron steps and to involve rare $d^7$ paramagnetic hydrido complexes in the II state. Results on the electrochemical oxidation of $[CoH(Ph_2PCH_2CH_2PPh_2)_2]$ are summarised in Scheme 27 while Scheme 28 depicts the results observed with $[IrH(Ph_2PCH_2CH_2PPh_2)_2]$. The electrochemical pattern of $[RhH(Ph_2PCH_2CH_2PPh_2)_2]$ in an acetonitrile-toluene mixture



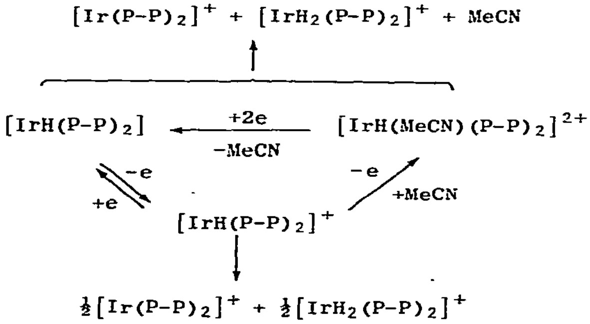
P = $PPh_3$

[196]



($P{-}P = Ph_2PCH_2CH_2PPh_2$)

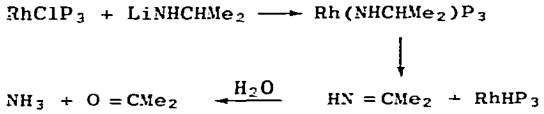
Scheme 27



Scheme 28

is virtually identical to that observed for the related iridium complex. The electrochemical behaviour of [MH(CO)(PPh$_3$)$_3$], (M= Rh, Ir) has also been investigated (ref. 163).

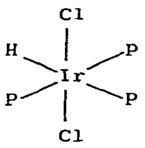
The β-elimination reaction from co-ordinated alkyls and alkoxides leads to metal hydrides. A similar reaction has been postulated for metal amide complexes and this mode of decomposition of a metal amide has now been established. Thus treatment of [RhCl(PPh$_3$)$_3$] with LiNMe$_2$ gives [RhH(PPh$_3$)$_3$] while in the presence of added phosphine [RhH(PPh$_3$)$_4$] is formed. Treatment of [RhCl(PPh$_3$)$_3$] with LiNHCHMe$_2$ proceeds as outlined in Scheme 29. Studies with LiNMeCD$_3$ reveals a large deuterium isotope effect indicative of the importance of C-H bond breaking in the transition state (ref. 164). The hydride [RhH(PPh$_3$)$_4$] also results from the action of dihydrogen upon [Rh(OAc)(PPh$_3$)$_3$] in the presence of excess phosphine. In the absence of phosphine [RhH$_2$(OAc)(PPh$_3$)$_2$] is formed (ref. 165). The crystal structure of cis-[IrH$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]PF$_6$ has been reported (ref. 166).



(P = PPh$_3$)

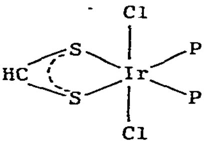
Scheme 29

The reaction of [197] with carbon disulphide gives the dithioformate complex [198]. With mer-[IrH$_3$(PPh$_3$)$_3$], carbon disulphide gives [199] (ref. 167). Alkyl

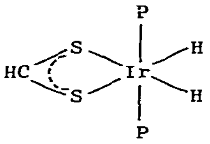


(P = PPh$_3$)

[197]



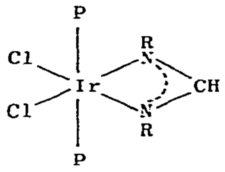
[198]



(P = PPh$_3$)

[199]

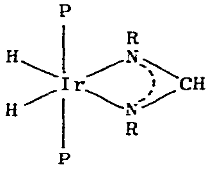
and aryl isothiocyanates (RNCS, R = Me, Et, Ph, $MeC_6H_4$) also undergo "insertion" reactions with metal hydrides. Thus products of stoichiometry $[IrX_2(RN{=}CH{=}S)(PPh_3)_2]$ are obtained by treating the hydrides $[IrHX_2(PPh_3)_3]$ with RNCS (ref. 168). Similar "insertion" reactions again occur upon treatment of [197] and *mer*-$[IrH_3(PPh_3)_3]$ with N,N'-di-*p*-tolylcarbodiimide to give [200] and [201] respectively (ref. 169). The hydrides $[IrH_3L_2]$, (L = $PPh_3$, $AsPh_3$) react with *para*-



[200]

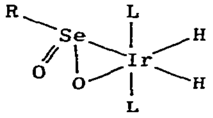
P = $PPh_3$

R = *p*-$MeC_6H_4$



[201]

and *meta*-substituted benzeneseleninic acids to give the complexes [202] formulated with iridium-selenium bonds (refs. 170, 171). The butyldiphenylarsine (L) complexes



(L = $PPh_3$; R = H, *p*-Cl, *m*-Cl, *m*-Br, *m*-$NO_2$; L = $AsPh_3$; R = *m*-Cl)

[202]

*mer*-$[MX_3L_3]$, (M = Rh, Ir; X = Cl, Br), $[IrHX_2L_3]$, (X = Cl, Br), $[IrHX_2(CO)L_2]$, (X = Cl, Br, I), and $[IrX_3(CO)L_2]$, (X = Cl, Br) have been reported (ref. 172).

SCF-Xα-SW calculations have been carried out on $[Rh_2Cl_2(CO)_4]$ in both the experimental bent conformation and the hypothetical planar one. It appears that the molecule bends because the resultant lowering of symmetry converts a very weak Rh-Rh π-interaction into a stronger interaction which is mainly σ in character (ref. 173). A detailed vibrational analysis of the carbonyl stretching frequencies in $[Rh_2Cl_2(CO)_{4-n}(^{13}CO)_n]$ has been reported and infrared, Raman and n.m.r. studies on the complexes *cis*-$[RhX_2(CO)_2]^-$, (X = Cl, Br), *cis*-$[IrCl_2(CO)_2]^-$, *trans*-$[RhX(CO)(PMe_3)_2]$ and $[RhX_3(CO)(PMe_3)_2]$, (X = Cl, Br) have been reported (refs. 174, 175). The complexes $[MX_2(CO)_2]^-$, *trans*-$[MCl(CO)(PPh_3)_2]$, $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[M(Ph_2PCH{=}CHPPh_2)_2]^+$, (M = Rh, Ir; X = Cl, Br), and $[Ir(CN)_2(CO)_2]^-$ exhibit intense absorptions in the visible and ultraviolet region which have been assigned as metal to ligand charge-transfer transitions (ref. 176).

The ability of $[RhCl_2(CO)_2]^-$ to catalyse the carbon monoxide reduction of iron (III) and the ability of rhodium(III) halide complexes to activate dihydrogen suggest that such systems might be potential catalyst systems for Fischer-Tropsch type reactions (the $H_2$ reduction of CO to hydrocarbons). In view of the importance of this latter reaction the kinetics have been studied for the decomposition of $[RhBr_5(CO)]^{2-}$ to cis-$[RhBr_2(CO)_2]^-$ in aqueous HBr solutions at 60°C under a CO atmosphere. A hydrolysis step leads to the formation of rhodium(I) which forms the dicarbonyl. Reaction of the dicarbonyl with $[RhBr_5(CO)]^{2-}$ then occurs in an autocatalytic process to give more $[RhBr_2(CO)_2]^-$ via a bridged intermediate [203]. The

$$Rh^{I}\text{----}Br\text{----}Rh^{III}$$

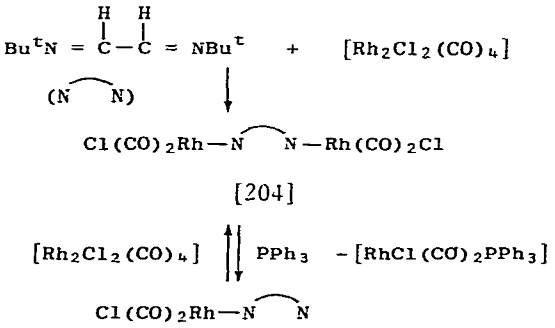
[203]

bromorhodate (III or I) complexes catalyse the reduction of iron(III) according to the equation: (ref. 177)

$$2Fe^{III} + CO + H_2O \rightarrow 2Fe^{II} + CO_2 + 2H^+$$

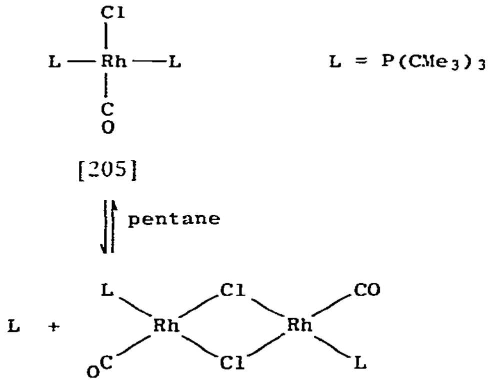
Recent controversy has arisen concerning the carbonyl halide originally characterised as $[IrCl(CO)_3]$ but later considered to be non-stoichiometric, $[IrCl_{1.1}(CO)_3]$ or $[IrCl_{1.07}(CO)_{2.93}]$. However, a single crystal X-ray study reveals that $[IrCl(CO)_3]$ is a stoichiometric material which contains short iridium-iridium interactions of length 2.844(1) Å. This compound is a one-dimensional highly conducting material (ref. 178).

The use of rhodium complexes in the catalysed hydrogenation of diimines has prompted a study of the reaction of di(t-butyl)diimine with $[Rh_2Cl_2(CO)_4]$. This reaction leads to [204] and reactions of the complex are illustrated in Scheme 30



Scheme 30

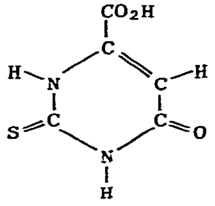
(ref. 179). Treatment of $[Rh_2Cl_2(CO)_4]$ with $P(CMe_3)_3$ gives the monomer [205] which in pentane solution exists in equilibrium with the dimer [206]. The crystal structure of [205] has also been reported (ref. 180). Some rhodium(I) complexes,



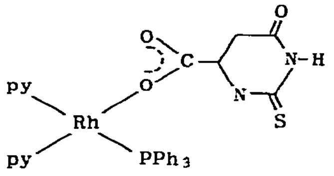
[205]

[206]

$[RhCl(CO)_2L]$, (L = R substituted benzo-2,1,3-thiadiazole, R = H, 4-Me, 5-Me, 4-$NH_2$, 5-$NH_2$, 4-MeO, 5-MeO, 5-EtO) have also been obtained. Treatment of these complexes with ammonia gas give the complexes $[RhCl(CO)_2(NH_3)_2L]$ (ref. 181). The complex $Rh(C_5H_3N_2O_3S)(PPh_3)(py)_2(H_2O)_2$, prepared by the reaction of [207] with $[RhCl(PPh_3)_3]$ followed by addition of pyridine, is considered to contain the square planar unit [208] (ref. 182).

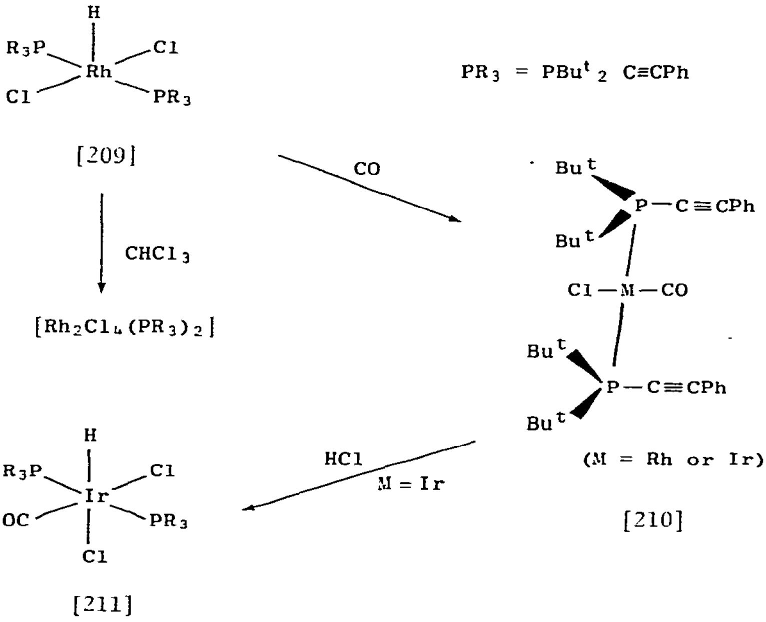


[207]

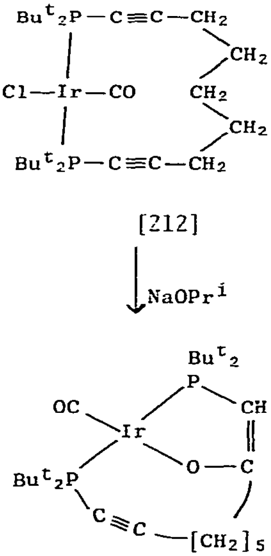


[208]

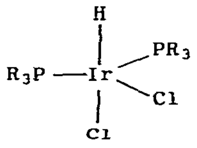
Since transition metal complexes with tertiary di-t-butylphosphines, $PBu^t_2R$ (R = alkyl or aryl), frequently show unusual chemistry and n.m.r. phenomena, (ref. 183), complexes of the ligand $PBu^t_2(C{\equiv}CPh)$, (L), have been investigated. Treatment of hydrated rhodium(III) chloride with 4 mol equivalents of L at 20°C gives the five-co-ordinate hydride [209]. Some reactions of [209] are illustrated in Scheme 31. The preferred conformation of both the rhodium and iridium complexes [210] is considered to be the one illustrated since an X-ray structure of [212] shows that



Scheme 51

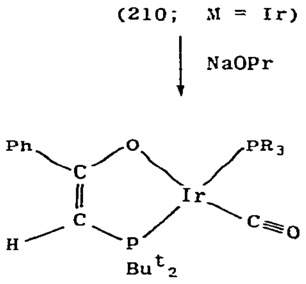


only the conformer with C≡O and C≡C adjacent is present in the solid state. Treatment of $H_2IrCl_6$ with 4 mol equivalents of $PBu^t_2(C{\equiv}CPh)$ gives the trigonal bipyramidal hydride [213] (refs. 184, 185). New tertiary phosphine esters



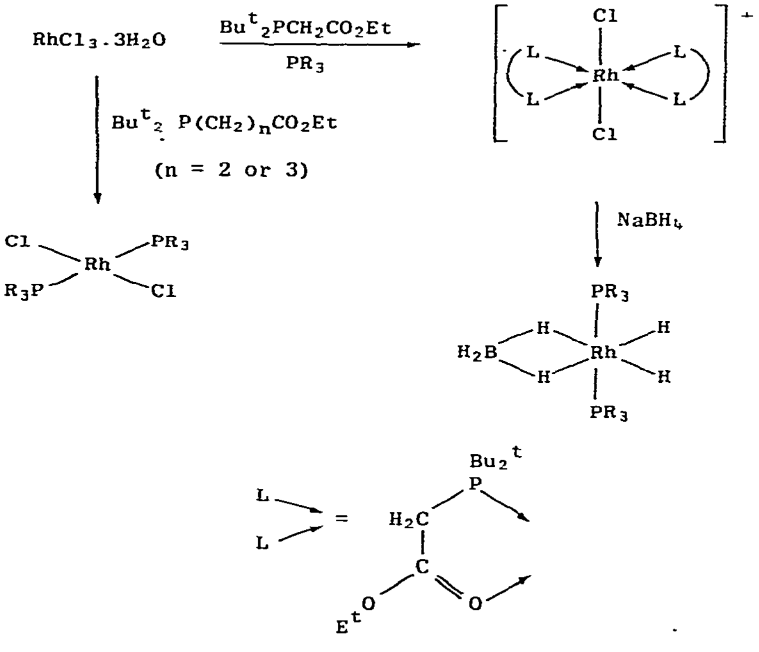
[213]

$\{PR_3 = PBu^t_2(C{\equiv}CPh)\}$



[214]

$Bu^t_2P(CH_2)_nCO_2Et$ (n = 1, 2, or 3) have been described and some reactions of these phosphines are illustrated in Scheme 32.(ref. 186).

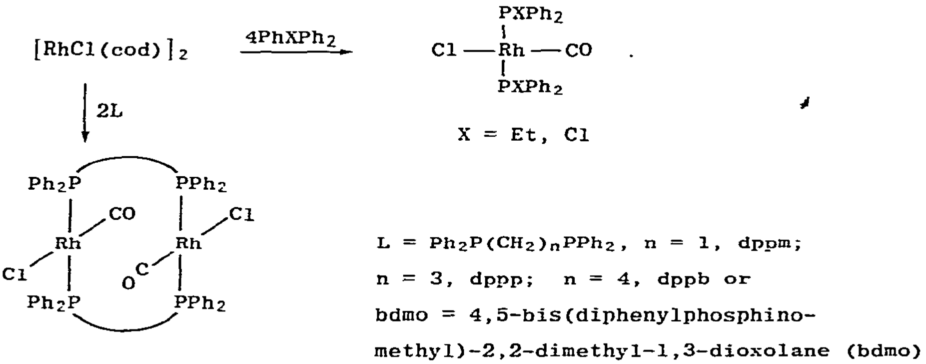


Scheme 32

Various complexes of rhodium(I) with phosphites, $[RhX(CO)\{P(OR)_3\}_2]$, (X = Cl, Br, I;

R = Me, Et, Pr, Pr$^i$, Bu, Bu$^i$), [RhCl(CO)(PEtCl$_2$)$_2$], [Rh$_2$Cl$_2${P(OR)$_3$}$_4$], [Rh$_2$Cl$_2${P(OR$'$)$_2$OH}$_4$], (R$'$ = Me, Et) have also been reported (ref. 187).

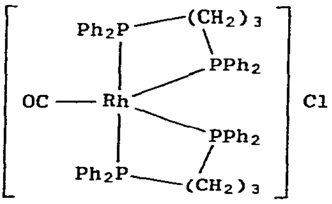
Treatment of [RhCl(1,5-cod)]$_2$ with stoichiometric amounts of monophosphines or diphosphines under an atmosphere of carbon monoxide or carbon monoxide and dihydrogen give complexes containing one carbonyl ligand per rhodium (Scheme 33).



L = Ph$_2$P(CH$_2$)$_n$PPh$_2$, n = 1, dppm;
n = 3, dppp; n = 4, dppb or
bdmo = 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (bdmo)

Scheme 33

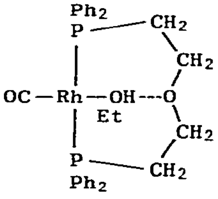
With dppen, (Ph$_2$PCH=CHPPh$_2$) and CO, [Rh(dppen)$_2$][RhCl$_2$(CO)$_2$] is formed while with dppe, (Ph$_2$PCH$_2$CH$_2$PPh$_2$), [RhCl(CO)(dppe)] and [Rh$_2$Cl$_2$(CO)(cod)(dppe)] can be isolated. An excess of dppe gives [Rh(dppe)$_2$]Cl while an excess of dppp or dppb gives an equilibrium mixture of [RhCl(CO)L]$_2$ and [Rh(CO)L$_2$]Cl, [215]. Reactions of these complexes with chlorine, hydrogen chloride, or methyl iodide have also been described (ref. 188). The diphosphines Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1-4) form trans-carbonyl complexes of iridium(I) of stoichiometry [IrCl(CO)(P-P)]$_m$ in which the diphosphine (n = 1, m = 2; n = 3, m = 2; n = 4, m = 3) bridges the iridium atoms. The complex of Ph$_2$PCH$_2$CH$_2$PPh$_2$ has been shown to be the salt [Ir(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][IrCl$_2$(CO)$_2$] contrary to a previous report in which the complex has been formulated as [Ir(CO)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]Cl (ref. 189). The phosphine (Me$_3$CCH$_2$)$_3$P, (L), reacts



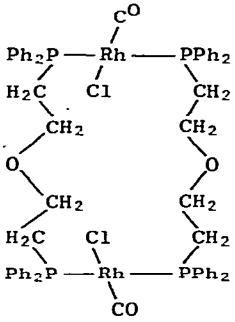
[215]

with hydrated rhodium(III) chloride in ethanol at room temperature to give $[RhCl_2L_2]_2$ but in boiling $ROCH_2CH_2OH$ (R = Me or Et) the carbonyl $[RhCl(CO)L_2]$ is formed. With the phosphine $PPh(CH_2CMe_3)_2$, (L′) the complexes $[Rh_2Cl_4L'_3]$ and $[RhCl_2L'_2]_2$ are formed (ref. 190). Treatment of $[\{Rh(acac)(CO)\}_2L]$, (L = 1,4-bis-(diphenylphosphino)xylylene) with sodium azide in the presence of triphenylphosphine in a water-benzene emulsion gives $[Rh(N_3)(CO)(PPh_3)_2]$. The structures of both of these complexes have been determined by single crystal X-ray structure determinations (ref. 191).

In the series of complexes $[Rh(CO)L]PF_6$ formed by the phosphinoethers L = $Ph_2P(CH_2)_2(OCH_2CH_2)_nPPh_2$, (n = 1-3) striking changes in geometry are observed as the length of the ligand changes. In the complex with n = 1 the ligand is terdentate while that with n = 3 the ligand forms a loose chain with a very strongly held water molecule encapsulated in the large ring. The crystal and molecular structures of the complex with n = 2 [216] has been published and this complex also contains an encapsulated molecule, of ethanol, but this is much less firmly held. The crystal structure of the dimer [217] has also been determined (ref. 192). Cationic complexes of the type $[Rh(CO)_2L_3]ClO_4$, (L = $Ph_3P$, $Ph_3As$) have been shown to react with imidazoles to give four-co-ordinate complexes $[Rh(CO)QL_2]ClO_4$ and five-co-ordinate complexes $[Rh(CO)(N\text{-}N')L_2]ClO_4$, (Q = imidazole, benzimidazole, or substituted benzimidazole; N-N′ = 2-(α-pyridyl)benzimidazole). The complexes $[Rh(CO)_2(N\text{-}N')]ClO_4$ and $[Rh(CO)_2L'_2]ClO_4$, (L′ = 2-phenylbenzimidazole) have also been isolated (ref. 193). The crystal structure of the cationic pyrazine complex $[Rh(CO)(pyrazine)(AsPh_3)_2]ClO_4$ has been reported (ref. 194).

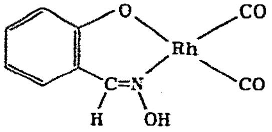


[216]



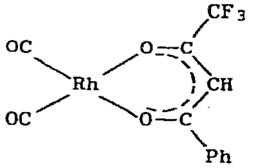
[217]

Addition of salicylaldoxime to the cooled lemon solution obtained by refluxing hydrated rhodium(III) chloride in dimethylformamide gives the dicarbonyl [218] which can also be obtained by the addition of salicyldoxime to $[Rh_2Cl_2(CO)_4]$. Analogous complexes containing α-benzoinoximato and α-furildioximato ligands have also been



[218]

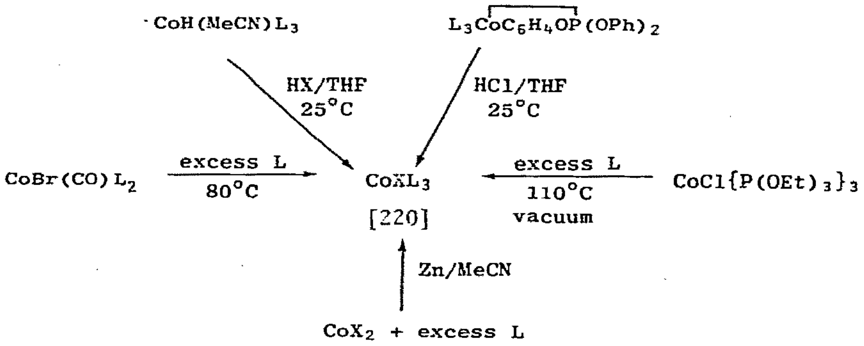
prepared. Treatment of these complexes with triphenylphosphine give the monocarbonyl substituted products (ref. 195). The crystal and molecular structure of [219] has been reported. It is considered that the carbonyl ligand <u>trans</u> to the phenyl group



[219]

would be displaced in substitution reactions with phosphines (ref. 196).

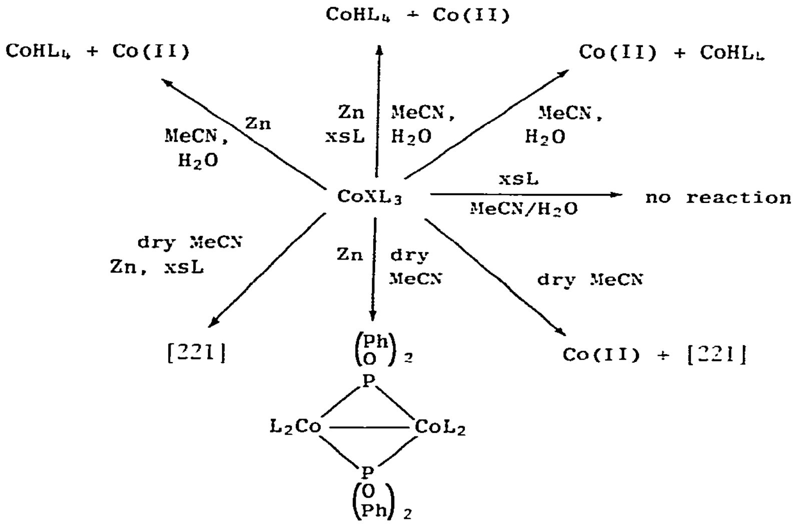
Four-co-ordinate cobalt(I) halide complexes, $CoXL_3$, ($L = P(OEt)_3$, $PMe_3$, $PPh_3$) have previously been described. Three methods of preparation of the analogous paramagnetic triphenyl phosphite complex [220] have now been reported and are outlined in Scheme 34.



($X = Cl$, Br; $L = P(OPh)_3$)

Scheme 34

Treatment of [220] with triethyl phosphite readily gives $[Co\{P(OEt)_3\}_5]Cl$ at room temperature, (a reaction greatly influenced by solvent polarity) and other reactions of [220] have also been reported, (Scheme 35) (refs. 197, 198). The related triisopropyl phosphite complexes $[CoXL'_3]$ have also been described (Scheme 36). The $\eta^3$-allyl complex $[Co(\eta^3\text{-}C_3H_5)L'_3]$ reacts with dihydrogen to give $[CoH_3L'_3]$. This hydride catalyses the selective hydrogenation of α,β-unsaturated ketones and amides to the saturated ketones and amides (ref. 114).

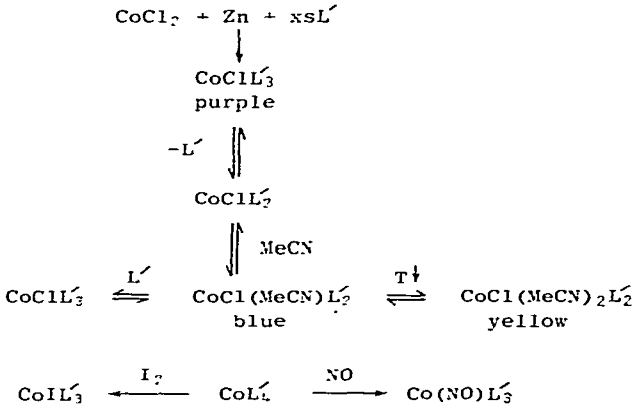


[221]

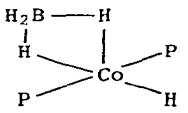
$L = P(OPh)_3$

Scheme 35

A cobalt(II) paramagnetic hydride complex [222] has been prepared and characterised by a single crystal X-ray structure determination. The co-ordination around cobalt is distorted square pyramidal (ref. 199). Tritertiarybutylphosphine has been shown to form an ionic complex $[Bu^t_3PH][CoBr_3PBu^t_3]$. The geometry about the cobalt(II) is pseudotetrahedral; the unexpected formation of an ionic complex is attributed to the bulkiness of the $PBu^t_3$ ligand (ref. 200). The cobalt(II) phosphine complexes $[CoX_2(PR_3)_2]$, (X = Cl, Br; R = Et, Ph, $C_6H_{11}$) react with furoyl azides to give phosphinimine complexes, $[CoX_2(furN{=}PR_3)_2]$. At lower temperatures the intermediate complex $CoBr_2(furN_3PCy_3).Et_2O$ with phosphatriazene ligand can be isolated (ref. 201). The crystal structure of the five-co-ordinate cobalt(III) complex [223] has been determined (ref. 202).

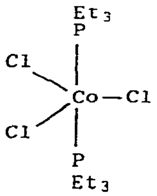


Scheme 56



$P = P(C_6H_{11})_3$

[222]



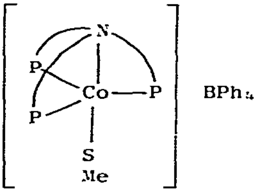
[223]

Soluble metal compounds containing $H_2S$, $SH^-$, and $S^{2-}$ as ligands are rare since the compounds tend to revert to binary sulphides. However, by the reaction of dihydrogen sulphide or methyl mercaptan with cobalt(II) aquo ions in the presence of the poly(tertiaryphosphine) ligands [224] and [225] low-spin mercapto and methylthio

$(Ph_2PCH_2CH_2)_3N$
np$_3$
[224]

$(Ph_2PCH_2CH_2)_3P$
pp$_3$
[225]

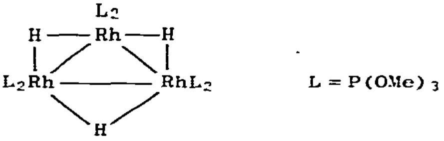
complexes $[Co(SH)L]BPh_4$, ($L = np_3$ or $pp_3$) and [226] have been obtained (ref. 205).



[226]

The crystal structure determination of cis-$[CoCl_2(np_3)]BF_4$ reveals the first example of the ligand $np_3$ forming an octahedral complex (ref. 204).

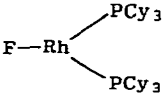
Treatment of the $\eta^3$-allyl complex $[Rh(\eta^3\text{-allyl})\{P(OMe)_3\}_2]$ with dihydrogen affords the trimer $[RhH\{P(OMe)_3\}_2]_3$ [227] which has been the subject of an X-ray study. The positions of the hydrogen atoms have not been located but they appear to be bridging



[227]

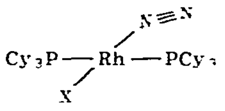
In contrast, the isopropyl phosphite derivative, $[RhH\{P(OPr^i)_3\}_2]_2$ is a dimer. Both these complexes are exceedingly active hydrogenation catalysts (ref. 205). The structure of $[RhBr(PPh_3)_3]$ has been determined by extended X-ray absorption fine structure (EXAFS) (ref. 206).

Three-co-ordinate species of the type $[RhCl(PR_3)_2]$ are often invoked in catalytic processes but evidence for such complexes is lacking. However, the complexes $[RhX(PCy_3)_2]$, ($X = F$, Cl, Br, I; Cy = cyclohexyl) have been prepared from rhodium(I) cyclo-octene compounds. The chloro compound is in equilibrium with its dimer. The magnitude of $^2J(F\text{-}P)$ found for the fluoride complex [228] strongly suggests trigonal three-co-ordination for $[RhF(PCy_3)_2]$. The complexes $[RhX(PCy_3)_2]$ form dinitrogen

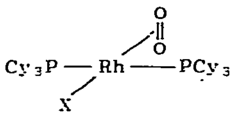


[228]

[229] and dioxygen [230] complexes. Carbonyl, ethylene, and diphenylacetylene complexes, trans-$[RhX(L)(PCy_3)_2]$, ($X = F$, Cl, Br, I, $N_3$, NCO, NCS; $L = CO$, $C_2H_4$, $C_2Ph_2$; $X = CN$, $NO_3$, OCOMe; $L = CO$) have also been prepared (ref. 207). A three-co-ordinate

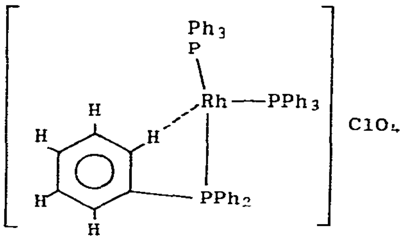


[229]



[250]

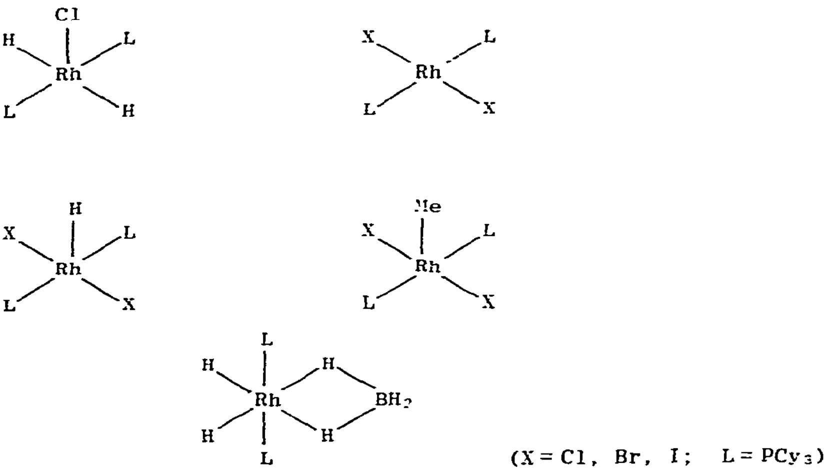
complex $[Rh(PPh_3)_3]ClO_4.CH_2Cl_2$ [251] has also been obtained from the reaction of $[RhCl(PPh_3)_3]$ with $TlClO_4$ in donor solvents followed by recrystallisation from methylene chloride. An X-ray study of [251] reveals a near T shape geometry about the rhodium and a weak ortho-hydrogen interaction. However, on heating [251] no



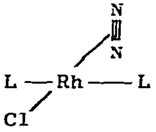
[251]

ortho-metallation reaction takes place. The complex [251] like $[Pt(PPh_3)_3]$, does not oxidatively add dihydrogen but it reacts with carbon monoxide to give $[Rh(CO)_2(PPh_3)_3]ClO_4$ (ref. 208). The three-co-ordinate compounds $[RhX(PCy_3)_2]$ (X = Cl, Br, I) can be oxidised by halogens $Cl_2$, $Br_2$, and $I_2$ to give the paramagnetic rhodium(II) compounds $[RhXY(PCy_3)_2]$, (X = Cl; Y = Br, I; X = Y = Br). Hydrogen halides, HY, add to give the hydrides $[RhHXY(PCy_3)_2]$ and depending on the reaction conditions methyl iodide reacts to give either $[RhClIMe(PCy_3)_2]$ or $[RhI_2Me(PCy_3)_2]$. The compounds $[RhH_2Cl(PCy_3)_2]$ and $[RhH_2(BH_4)(PCy_3)_2]$ have also been isolated. Structures of these complexes are illustrated in Scheme 37 (ref. 209).

The four-co-ordinate dioxygen complexes [250] exhibit unusually high ν(O = O) stretching frequencies at about 990 $cm^{-1}$. This high frequency is attributed to the four-co-ordination found for this complex. In three-co-ordinate complexes of the type $[PtO_2(PPh_3)_2]$ and five-co-ordinate complexes of the type $[IrCl(CO)(O_2)(PPh_3)_2]$ there is more back-bonding from metal to $O_2$ than is observed in [250]. An analogous four-co-ordinate dioxygen complex trans-$[RhCl(O_2)(PPr^i_3)_2]$ has also been prepared and its structure has been determined by an X-ray study. The dinitrogen complex [252] has also been the subject of an X-ray study which reveals the presence of a side-bonded dinitrogen ligand. This is a most unusual bonding mode for dinitrogen and the complex warrants further study. The ethylene complex trans-$[RhCl(C_2H_4)(PPr^i_3)_2]$ has a C-C bond distance of 1.319(4) Å which is one of the



Scheme 57

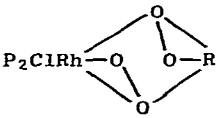


(L = PPr$^i{}_3$)

[232]

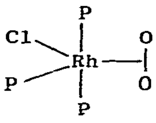
shortest reported for co-ordinated ethylene (ref. 210).

Two crystalline materials, [233] and [234] have been isolated from the reaction o dioxygen with $[RhCl(PPh_3)_3]$ and each of these complexes has been characterised by a



(P = PPh$_3$)

[233]



[234]

single crystal X-ray study (refs. 211, 212). Spectral changes observed for the oxidation of the dimer $[RhCl(PPh_3)_2]_2$ by dioxygen indicate that the reaction proceeds via rapid formation of [233] which then slowly decomposes to form $Ph_3PO$ and

Rh-$O_2$-$Ph_3PO$ complexes, Scheme 58. The spectral changes observed during the oxida-

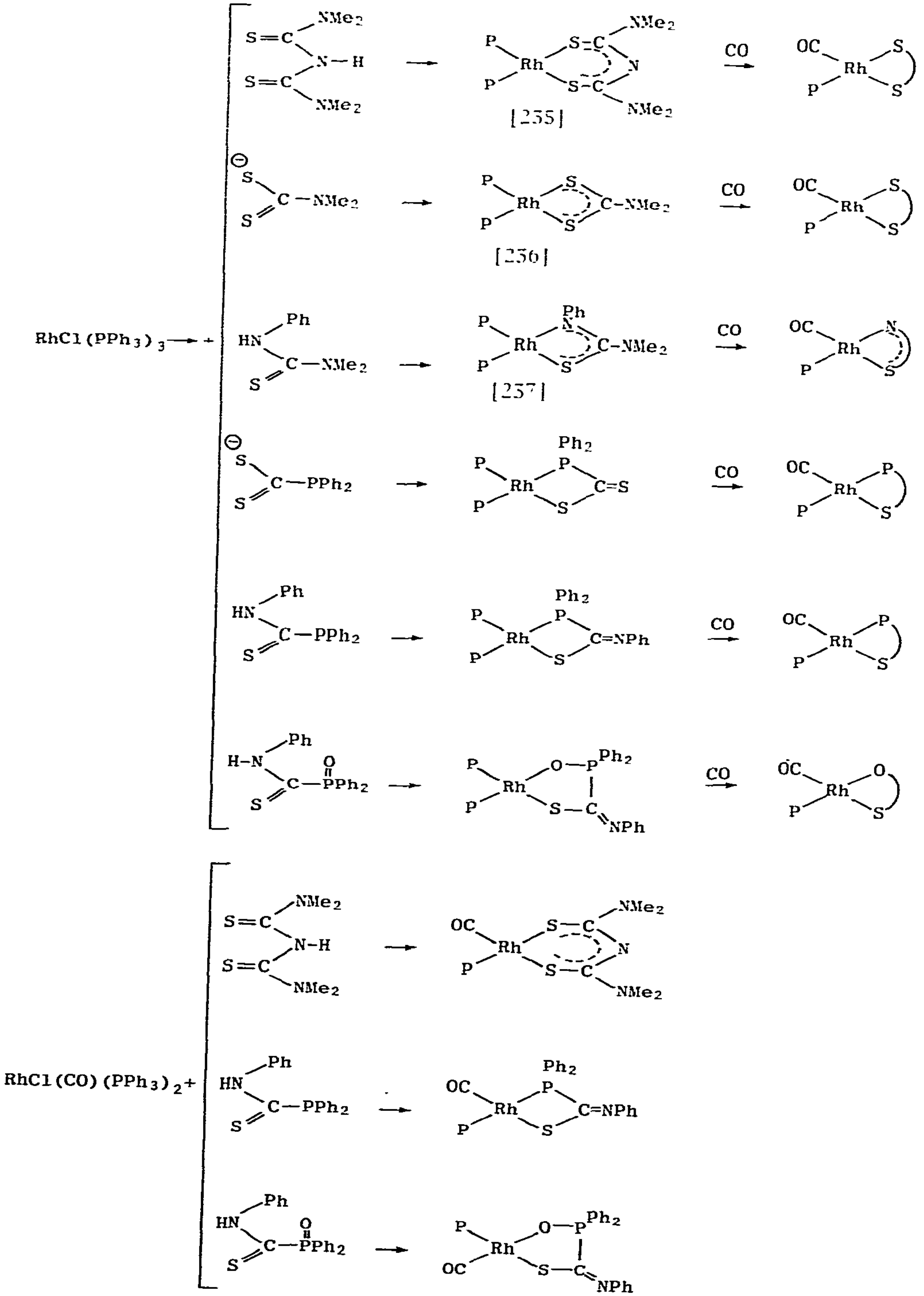
$$\begin{tikzcd}
{[RhClP_2]} \arrow[r, "O_2", "fast"'] & {[RhCl(O_2)P_2]_2} \arrow[d, "O_2"', "slow"] \\
& PO + Rh\text{-}O_2\text{-}PO \text{ complexes}
\end{tikzcd}$$

$(P = PPh_3)$

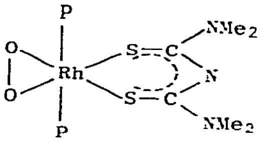
Scheme 58

tion of $[RhCl(PPh_3)_3]$ are similar to those observed for the dimer, $[RhCl(PPh_3)_2]_2$ but some differences are observed suggesting that the oxidation pathways may not be entirely similar. The oxidation products of $[RhCl(PPh_3)_3]$ and $[RhCl(PPh_3)_2]$ can be readily converted back to $[RhCl(PPh_3)_3]$ by refluxing ethanol solutions of the products with excess triphenylphosphine under a dinitrogen atmosphere (ref. 213). A kinetic study on the reactions of $H_2$, $O_2$, $C_2H_4$, $CHCl{=}CCl_2$ and $CH_3I$ with $[RhCl(PPh_3)_3]$ has been published (ref. 214).

Various rhodium(I) complexes containing bidentate unsaturated thio ligands have been prepared from $[RhCl(PPh_3)_3]$ and trans-$[RhCl(CO)(PPh_3)_2]$ in the presence of triethylamine (Scheme 59). In the carbonyl derivatives the CO ligand is trans- to the chelate donor atom with the lowest trans-influence (ref. 215 and see ref. 196). The rhodium(I) complexes [235], [236], and [237] react with dioxygen to give 1:1 adducts. In solution only the trans-isomer [238] is observed but with the complexes [239]-[242] cis- and trans-isomers are observed. For [241], [242] there is a solvent effect on the initial cis-trans ratio. In benzene solution, the formation of $Ph_3PO$ from [241] is inhibited by addition of triphenylphosphine. The reaction of [243] with dioxygen in the presence of $PPh_3$ gives $Ph_3PO$ and [244]. The complex [244] can also be obtained from $[Rh\{Ph_2P(O)C(S)NPh\}(PPh_3)_2]$ and dioxygen. Only [245] reacts with dihydrogen to give [246] which is a catalyst for cyclohexene hydrogenation (ref. 216). The influence of the anionic ligand X on the polarographic behaviour of the complexes trans-$[MX(CO)(PPh_3)_2]$, (M = Rh, Ir; X = $NO_2$, I, Br, NCS, OCOH, Cl, SPh, $N_3$, OCOPh, NCO, OCOMe, OPh, SH, F, OH) has been investigated and the half wave potentials obtained have given a kinetic scale for the electron donor properties of the anionic ligands which can be related to the stability of the dioxygen adduct, formed by the four-co-ordinate complex (ref. 217). The interactions of rhodium atoms with dioxygen have given the species $Rh(O_2)$ and $Rh(O_2)_2$. Small, well-defined rhodium clusters, $Rh_n$ (n = 2 or 3) also react with dioxygen to give dinuclear complexes, $Rh_2(O_2)_n$ (n = 1, 2, 3 and 4) together with a trinuclear species $Rh_3(O_2)_m$ (m is probably 2 or 6) (refs. 218, 219). The action of light and

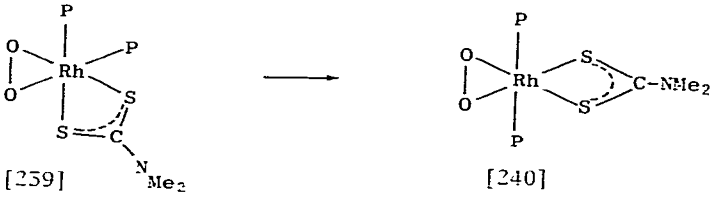


Scheme 39

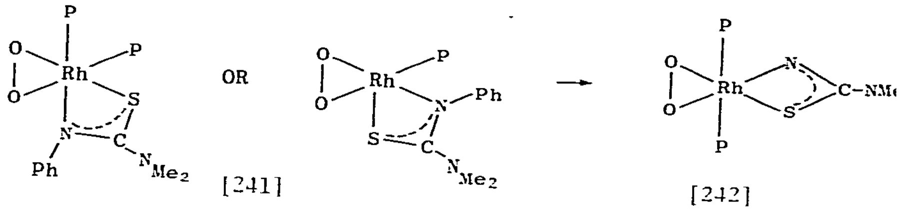


[238]

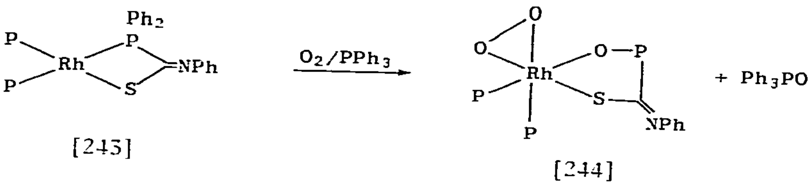
(P = PPh$_3$)



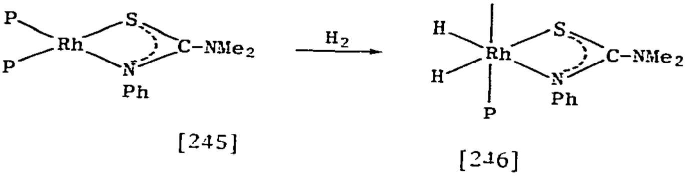
[239] [240]



[241] [242]



[243] [244]



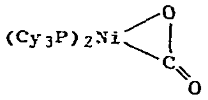
[245] [246]

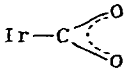
dioxygen upon [247] gives the monomeric superoxo-rhodium species [248] which is relatively stable in water (ref. 220).

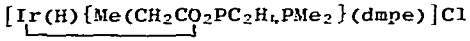
$$\underset{[247]}{(+)\ [Rh(NO_2)_2(en)_2]} + O_2 \xrightarrow{h\nu} \underset{[248]}{[Rh(NO_2)(O_2)(en)_2]^+}$$

The compound $[RhCl(PPh_3)_3]$ is known to be an active decarbonylation agent for aldehydes and acyl halides. The rhodium compound has now been shown to react with the hexacarbonyls $[M(CO)_6]$ (M = Mo and W) to give $[M(PPh_3)(CO)_5]$ and trans-$[RhCl(CO)(PPh_3)_2]$ (ref. 221). Thermodynamic and kinetic data for the reversible carbonylation of $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ reveal that contrary to previous reports the rôle of the solvent is zero (ref. 222).

Activation of carbon dioxide by co-ordination to transition metals continues to attract attention. Treatment of $[Ir(Me_2PCH_2CH_2PMe_2)_2]^-$ with carbon dioxide gives an adduct $Ir(dmpe)_2Cl.CO_2$. The i.r. bands of the co-ordinated $CO_2$ are significantly different to those observed in [249] and it is suggested that the carbon dioxide may be monodentate in the iridium complex as illustrated in [250]. Heating a solution or suspension of $Ir(dmpe)_2Cl.CO_2$ at ca. 120°C gives an isomer considered to be [251] in which a co-ordinated dmpe has been metallated and carboxylated. An analogous adduct

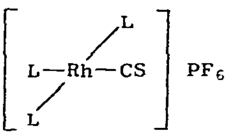

[249]


[250]


$$[Ir(H)\{Me(CH_2CO_2PC_2H_4PMe_2\}(dmpe)]Cl$$
[251]

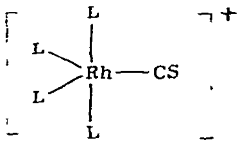
$Ir(diars)_2Cl.CO_2$ can also be isolated but increasing the bulk of the compounds $[IrL_4]^+$ reduces their reactivity towards $CO_2$. The co-ordinated $CO_2$ in $Ir(dmpe)_2Cl.CO_2$ can be displaced by small molecules, L, to yield $[IrL(dmpe)_2]Cl$, (L = CO, $PMe_3$, $CS_2$) or cis-$[IrH_2(dmpe)_2]Cl$ (ref. 223). Although the corresponding rhodium complexes react with difficulty with $CO_2$ (ref. 223) treatment of $[Rh_2Cl_2(C_2H_4)_4]$ with two mole equivalents of $PBu^n_3$ under an atmosphere of $CO_2$ gives $[RhCl(CO_2)(PBu^n_3)_2]$ which on standing in solution gives the phosphine oxide complex $[RhCl(CO)(OPBu^n_3)(PBu^n_3)]$. With $PEtPh_2$ the bis-phosphine complex, $[RhCl(CO)_2(PEtPh_2)_2]$ and tris-phosphine complex, $[RhCl(CO_2)(PEtPh_2)_3]$ can be obtained. Similar bis- and tris-phosphine complexes are formed with $PEt_2Ph$. The complexes $[RhCl(CO_2)(PMe_2Ph)_2]$ and $[RhCl(CO_2)(PMePh_2)_3]$ are also reported. The bis-phosphine complexes are considered to contain bidentate $CO_2$ as in [249] while the tris-phosphine complexes are believed to contain unidentate $CO_2$ as in [250]. All the rhodium complexes lose $CO_2$ when treated with sulphuric acid or when heated at temperatures above 80°C (ref. 224). The reaction of COS with $[RhCl(PPh_3)_3]$ gives *trans*-$[RhCl(CO)(PPh_3)_2]$ and $[Rh_2Cl_2S(CO)(PPh_3)_3]$ (ref. 225).

Carbon disulphide is known to react with $[RhCl(PPh_3)_3]$ to give *trans*-$[RhCl(CS)(PPh_3)_2]$. Using this complex a range of cationic thiocarbonyl complexes $[Rh(CS)L_3]^+$, ($L = PMePh_2$, $PEt_2Ph$, $PPh(OPh)_2$), $[Rh(CS)L_4]^+$, ($L = PMe_2Ph$, $PPh_2OMe$, $PPh(OMe)_2$, $PPh(OEt)_2$, $P(OMe)_3$, $P(OEt)_3$), and $[Rh(CS)L_2]^+$, ($L = Ph_2PCH_2CH_2PPh_2$) have now been isolated. Preliminary X-ray studies on [252] and [253] confirm the illustrated structures (ref. 226). The reaction of dihydrogen with $[IrH(CS)(PPh_3)_3]$



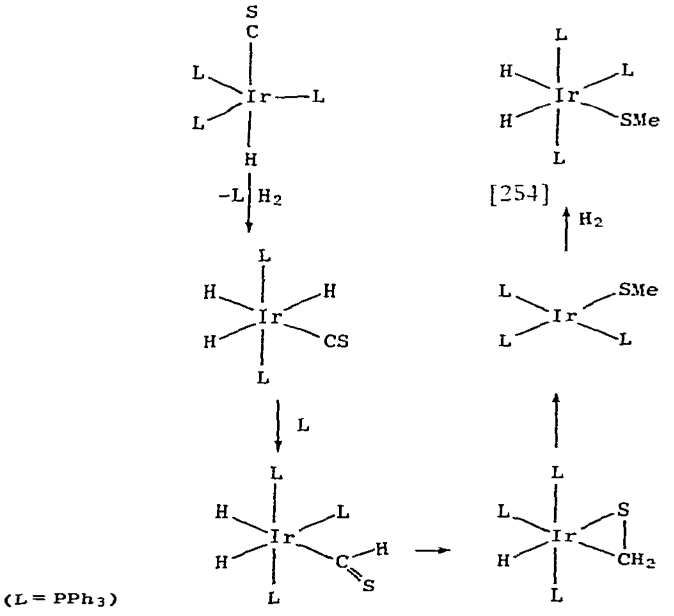
($L = PMePh_2$)

[252]



($L = PMe_2Ph$)

[253]

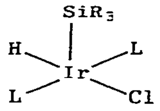


Scheme 40

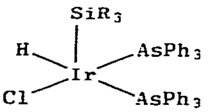
gives the methanethiolato complex [254]. This reduction of the thiocarbonyl ligand is considered to occur via thioformyl and thioformaldehyde complexes (Scheme 40). That a thioformyl complex of iridium(III) is a plausible intermediate is shown by the isolation of $[Ir(CHS)Cl_2(CO)(PPh_3)_2]$ via the sodium borohydride reduction of the cationic thiocarbonyl complex, $[IrCl_2(CS)(CO)(PPh_3)_2]I_3$ (ref. 227).

The single crystal X-ray structures of the sulphur dioxide complex, $[RhCl(SO_2)(PPh_3)_2]_2$ and disulphur dioxide complex $[Ir(S_2O_2)(Ph_2PCH_2CH_2PPh_2)_2]Cl$ and the ESCA spectra of $[Ir(S_2)(P\text{-}P)_2]Cl$, $[Ir(S_2O)(P\text{-}P)_2]PF_6$, and $[Ir(S_2O_2)(P\text{-}P)]Cl$, $(P\text{-}P = Ph_2PCH_2CH_2PPh_2)$ have been reported (refs. 228-230).

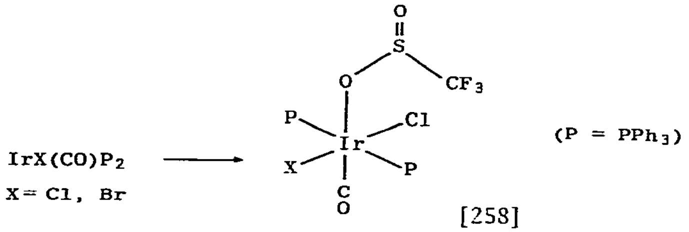
During the past year various studies on oxidative-addition reactions of square planar rhodium(I) and iridium(I) complexes have been published. The ability of low-valent $d^8$-metal complexes to homogeneously catalyse the hydrosilation of alkenes has stimulated further interest in the reactions of monosilanes with planar iridium(I) complexes. The silanes $R_3SiH$, $(R_3 = Cl_3$, $MeCl_2$, $(EtO)_3$, $Ph_3)$ undergo oxidative addition to $[IrClL_3]$, $(L = PPh_3$, $PMePh_2$, and $AsPh_3)$ to give silyliridium(III) hydrides $[IrHCl(SiR_3)L_n]$, $(n = 2$ or $3)$ which unlike the corresponding rhodium(III) compounds show no tendency to lose silane. The five-co-ordinate complexes are considered to have the square pyramidal structure [255] although the triphenylarsine derivative [256] may have hydrogen cis to chlorine. The five-co-ordinate complexes are formed mainly when $L = PPh_3$ or $AsPh_3$, and also in the example of $L = PMePh_2$, $R = Ph$ but six-co-ordinate adducts are formed predominantly when $L = PMePh_2$. However, both five- and six-co-ordinate adducts can be isolated by addition of $MeSiHCl_2$ to $[IrCl(AsPh_3)_3]$. Most of the adducts react with carbon monoxide to give the carbonyls $[IrHCl(SiR_3)(CO)L_2]$ which may undergo complete or partial reductive-elimination to form $R_3SiH$ and $[IrCl(CO)L_2]$. The ease of this reaction depends on $L(PPh_3 > PMePh_2 > AsPh_3)$ and on $R_3\{Ph_3 > (EtO)_3 > Cl_3\ MeCl_2\}$ (ref. 231). Addition of $CF_3SO_2Cl$ to [257] gives [258]. This is in contrast to the analogous reaction of



[255]



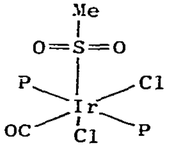
[256]



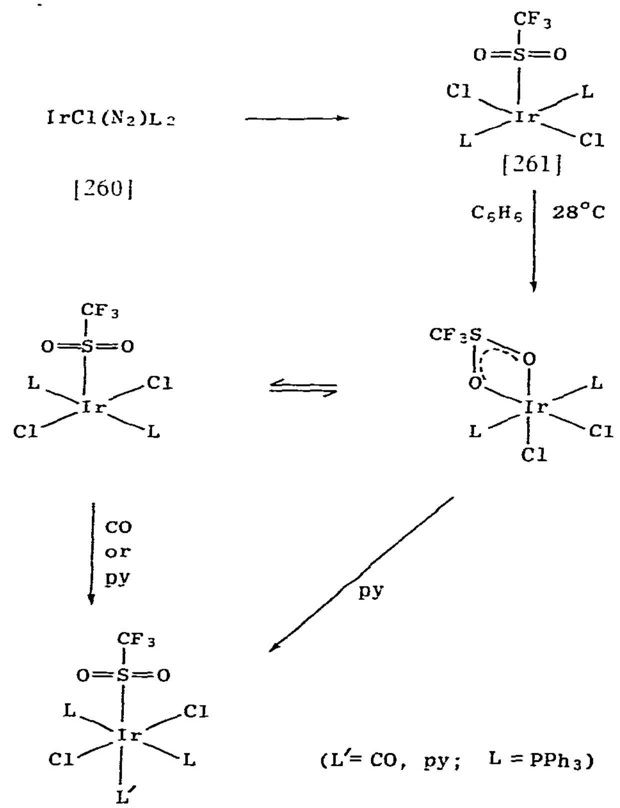
[257]

[258]

MeSO$_2$Cl with (257; X = Cl) which gives the S-bonded compound [259]. The reaction of CF$_3$SO$_2$Cl with [260] gives the co-ordinatively unsaturated complex [261] which undergoes the transformations outlined in Scheme 41. The compound [261] does not readily undergo trifluoromethyl migration reactions and the reported transformation of [IrCl$_2${S(O)$_2$C$_6$F$_5$}(PPh$_3$)$_2$] to [IrCl$_2$(C$_6$F$_5$)(SO$_2$)(PPh$_3$)$_2$] appears to be incorrect (ref. 232). The transformation is probably a rearrangement of the S-sulphinato com-

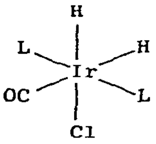


[259]



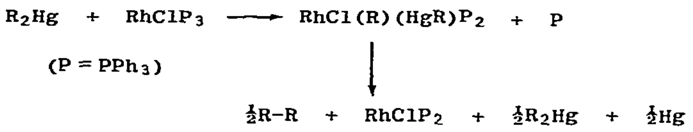
Scheme 41

plex to the bidentate O,O -sulphinato isomer. The secondary phosphine, $Ph_2HPS$ reacts with *trans*-$[IrCl(CO)(PPh_3)_2]$ to give $[IrHCl(SPPh_2)(CO)(PPh_3)_2]$ which reacts with MeI or EtI to give $[IrHClI(CO)(PPh_3)_2]$. However, reaction of $Ph_2HPS$ with *trans*-$[RhCl(CO)(PPh_3)_2]$ gives a mixture of $[Rh(SPPh_2)(CO)(PPh_3)_2]$ and the starting complex (ref. 233). In an attempt to obtain a neutral transition metal-formyl complex the reaction of acetic formic anhydride, HC(O)OC(O)Me, with *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ has been investigated. However, the expected oxidative-addition product, $[IrCl(CHO)(OCOMe)(CO)(PMe_2Ph)_2]$ was not observed and the reaction leads, via a series of intermolecular anion (hydrido, formato and chloro) ligand exchange reactions to [262] (ref. 234).



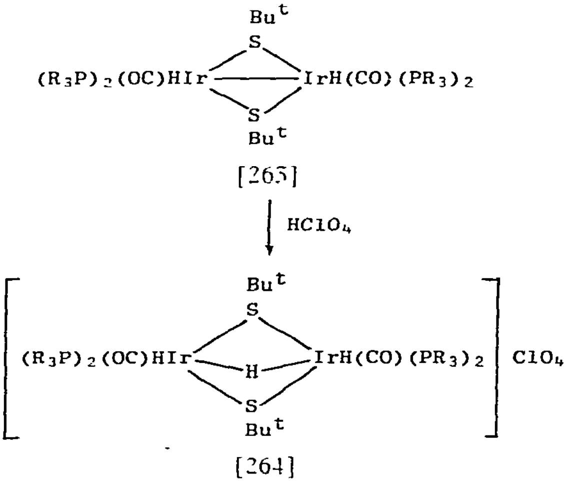
[262]

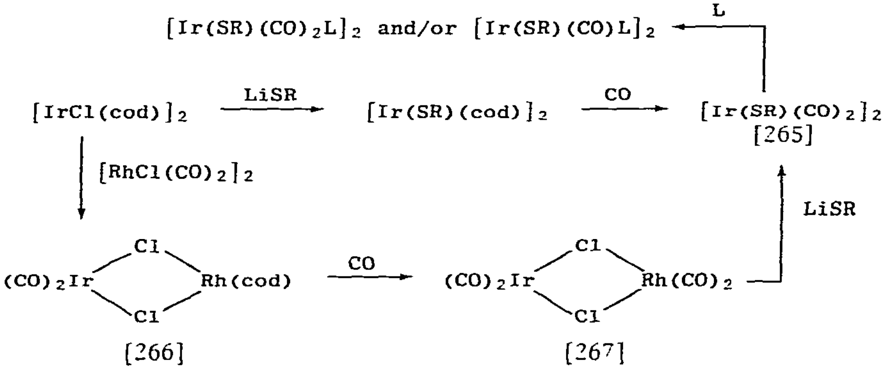
Mercury(II) halides, $HgX_2$, have long been known to oxidatively add to the complex *trans*-$[IrY(CO)(PPh_3)_2]$ to give the iridium-mercury bonded compounds $[IrXY(HgX)(CO)(PPh_3)_2]$, (X,Y = Cl, Br, I). It has now been observed that these six-co-ordinate complexes are decomposed by the presence of halide ions to regenerate the Vaska complexes. In reactions involving different halides the iridium(I) product tends to preferentially co-ordinate to the halide in the sequence $I < Br < Cl$. The iridium(III) complexes can also be reduced electrochemically (ref. 235). The decomposition of organomercurials occurs only at elevated temperatures (generally above 300°C). However, $[RhCl(PPh_3)_3]$ has been shown to be an effective catalyst for the formation of the coupling product R-R from $HgR_2$, (R-R = conjugated diyne, conjugated diene, biaryl, and alkane). The proposed reaction sequence, which involves an initial oxidative-addition reaction is outlined in Scheme 42 (ref. 236).



Scheme 42

Although the oxidative-addition of dihydrogen to Vaska type complexes has been extensively studied there have been few studies on dinuclear complexes. It has now been found, however, that the complexes $[Ir(SBu^t)(CO)(PR_3)]_2$, (R = Me, Ph, $NMe_2$ and OMe) homolytically cleave dihydrogen to give the iridium-iridium bonded complexes [265]. Protonation of these complexes gives the bridged hydrides [264] (refs. 257, 258). The thiolato-bridged iridium(I) carbonyl complexes [265] have been prepared by the reaction of carbon monoxide with $[Ir(SR)(1,5\text{-cod})]_2$ and reactions of the complexes are outlined in Scheme 43. The crystal structure of $[Ir(SPh)(CO)_2]_2$ suggests the existence of intra- and inter-molecular metal-metal interactions. The compounds [266] and [267] are only the second examples of dinuclear complexes with two different $\underline{d}^8$ metals in a square-planar environment (ref. 259). The crystal

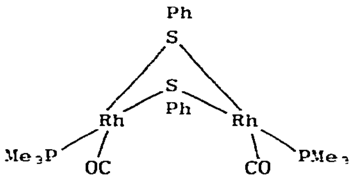




[R = $Bu^t$, Ph; L = $PMe_3$, $P(NMe_2)_3$, $PPh_3$, $P(OMe)_3$]

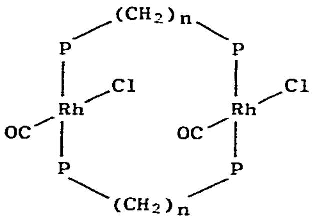
Scheme 43

structure of [268] reveals a "bent" geometry with a dihedral angle of 115° between the square planes about each rhodium. There is a solvent-dependent equilibrium between the *cis*- and *trans*-isomers of [268] (ref. 240). By altering the bridging



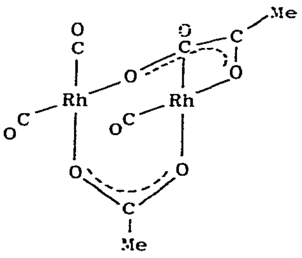
[268]

groups present in dimeric rhodium(I) complexes both the distance between the rhodium centres and the relative orientation of the two co-ordination planes can be varied. Thus by comparing the electronic spectra of solutions of *trans*-[RhCl(CO)(PPh$_3$)$_2$] with those of the dimers [269], [270] and [271] it is revealed that only [269] shows

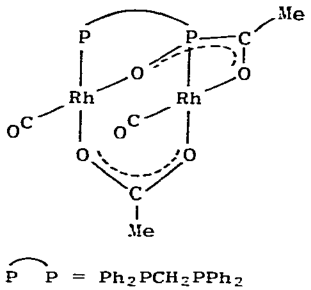


[269], n = 1
[270], n = 3
[271], n = 4

a significant shift of the low energy absorption. The shift in this absorption can be explained in terms of overlap of the two filled metal $d_{z^2}$ orbitals in the dimer and of the two empty ligand $\pi_z$ orbitals which results in a narrowing of the energy gap between the highest filled metal orbital and the lowest empty ligand $\pi_z$ orbital. The lack of a proximity shift in [270] and [271] is due to the larger rhodium-rhodium separations involved in these complexes. Comparison of the electronic spectra of [Rh(acac)(CO)$_2$] with that of [272] also reveals the presence of a rhodium-rhodium interaction and addition of Ph$_2$PCH$_2$PPh$_2$ to [272] produces [273] which also exhibits effects due to the close proximity of the rhodium centres. Both [Rh(OCOCF$_3$)(CO)$_2$]$_2$ and [274] again appear to have structures which contain rhodium-rhodium interactions but the electronic spectra of [275] and [276] show no pronounced proximity shift. Neither *trans*-[RhCl(CO)(PPh$_3$)$_2$] nor the dimers [269], [270] and [271] react with dihydrogen, dioxygen, or diphenyl disulphide. However, some of the

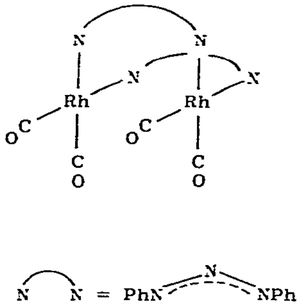


[272]



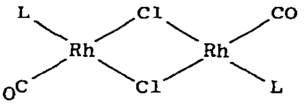
P P = $Ph_2PCH_2PPh_2$

[273]



N N = PhN N NPh

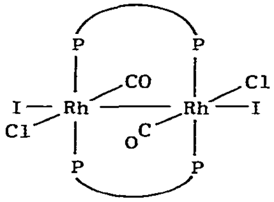
[274]



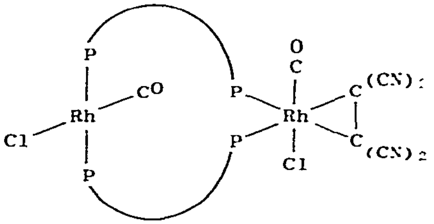
[275], L = CO

[276], L = $PPh_3$

complexes do react with di-iodine, tetracyanoethylene, and sulphur dioxide. Treatment of [269] with di-iodine gives [277] while reactions of di-iodine with [270] an [271] give polymeric products of stoichiometry $[RhClI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}]_n$, (n = 3-4) and $[RhClI_2(CO)\{Ph_2P(CH_2)_4PPh_2\}]_n$ respectively. Tetracyanoethylene does not react with [269] at room temperature but with [270] the complex [278] is formed. A yellow polymeric product $[RhCl(CO)(TCNE)\{Ph_2P(CH_2)_4PPh_2\}]_n$ is formed with [271].



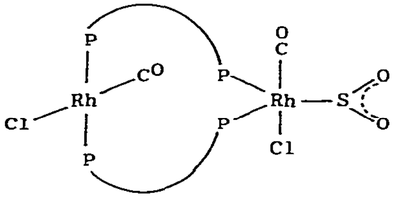
[277]



P⌒P = $Ph_2P(CH_2)_3PPh_2$

[278]

Addition of sulphur dioxide to [270] gives [279]. However, with [271] sulphur

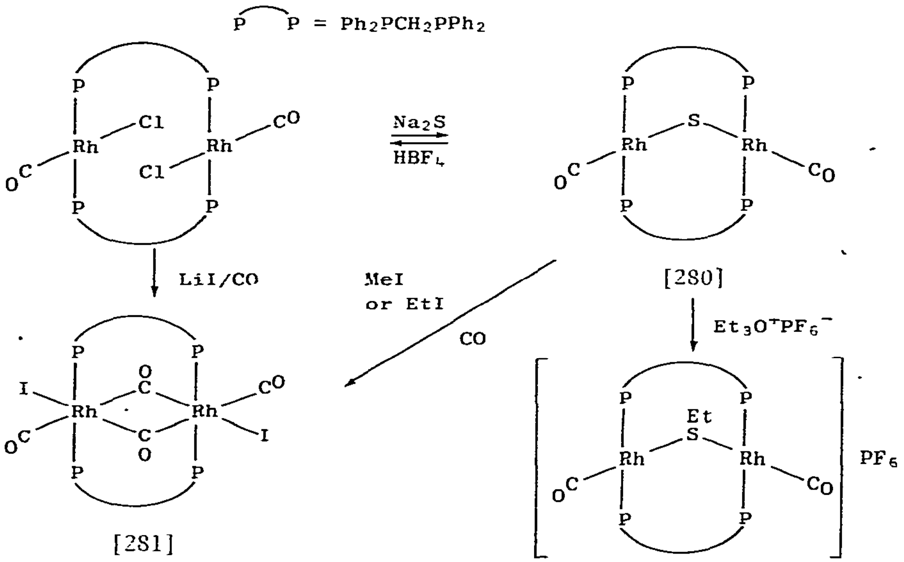


P⌒P = $Ph_2P(CH_2)_3PPh_2$

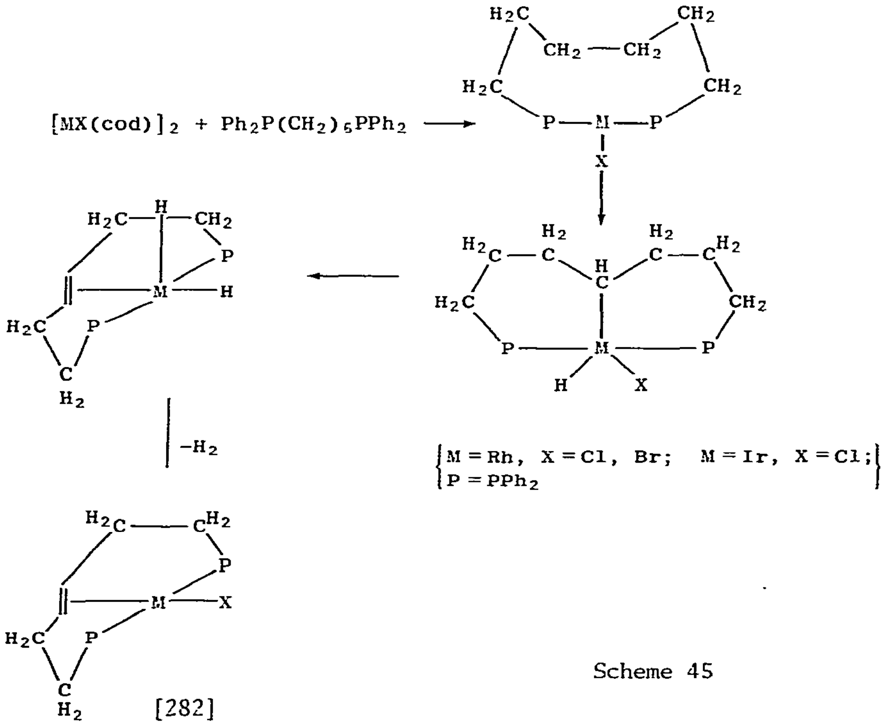
[279]

dioxide gives an adduct which is thermally less stable than [279] and with [269] sulphur dioxide gives an adduct which cannot be isolated in a pure form (ref. 241). The addition of sodium sulphide to $[Rh_2Cl_2(CO)_2\{Ph_2PCH_2PPh_2\}_2]$ produces red crystals of [280] which contains a novel "A-Frame" type structure and it has been characterised by an X-ray study. Some reactions of this complex are illustrated in Scheme 44. Treatment of [280] with methyl isocyanide gives $[Rh_2(\mu\text{-}S)(CNMe)_2\{Ph_2PCH_2PPh_2\}_2]$ The complex [280] also absorbs reversibly sulphur dioxide and catalyses the hydrogenation of ethylene. The bridged carbonyls in [281] may be unsymmetrical in view of their high ν(CO) stretching frequency (ref. 242).

The ligand $Ph_2P(CH_2)_6PPh_2$ undergoes a dehydrogenation reaction with $[MX(cod)]_2$ in refluxing mesitylene (M = Rh, X = Cl or Br; M = Ir, X = Cl) to give the complexes [282] and a suggested mechanism for this reaction is outlined in Scheme 45. However, in no case is metallation or dehydrogenation observed on reacting the ligands $Ph_2P(CH_2)_nPPh_2$, (n = 5, 7, or 8) and the diarsine $Ph_2As(CH_2)_6AsPh_2$ with rhodium(I) or iridium(I) complexes in refluxing mesitylene. Upon reacting the ligands $Ph_2P(CH_2)_6PPh_2$ or $Ph_2As(CH_2)_6AsPh_2$ with $[MCl(cod)]_2$, (M = Rh or Ir) in methylene

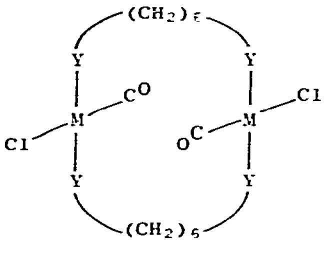


Scheme 44



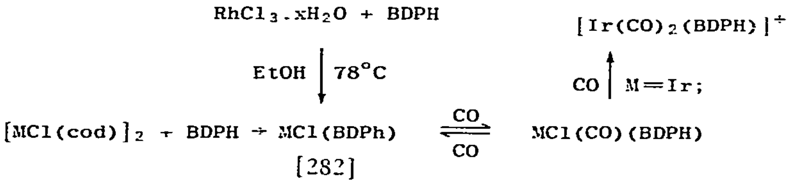
Scheme 45

chloride solution in the presence of carbon monoxide the dimeric complexes [283] are formed which do not undergo dehydrogenation reactions. The ligands 1,6-bis(diphenylphosphino)-trans-hex-3-ene and 1,6-bis(diphenylarsino)-trans-hex-3-ene undergo normal substitution reactions with rhodium(I) and iridium(I) complexes as outlined in Scheme 46 (ref. 243). Treatment of the heterocyclic compounds [284] with



[283]

Y = P or As
M = Rh or Ir



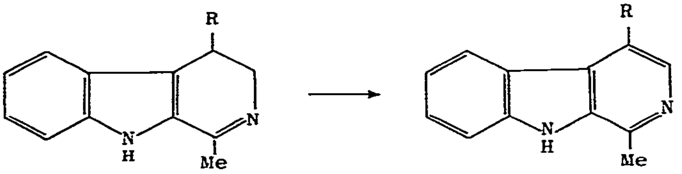
$[RhCl(cod)]_2 + BDAH \longrightarrow RhCl(BDAH)$

(BDPH = $Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2$)

(BDAH = $Ph_2As(CH_2)_2CH=CH(CH_2)_2AsPh_2$)

Scheme 46

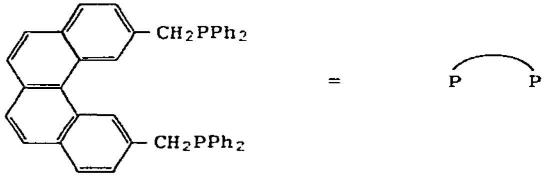
$[RhCl(PPh_3)_3]$ also results in a dehydrogenation reaction to give [285] (ref. 244).



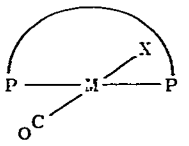
[284] [285]

[R = H, Me, Pr, $Me_2CHCH_2$, Ph, $PhCH_2$, 2-pyridylmethyl, 3-pyridylmethyl, 4-pyridylmethyl, and (1-methyl-4-pyrazolyl)methyl]

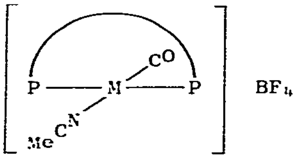
The bidentate phosphine [286] forms the mononuclear square planar complexes [287] and [288]. The tendency of these complexes to form adducts with carbon monoxide,



[286]



[287]

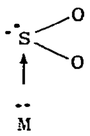


[288]

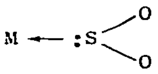
(M = Rh, Ir; X = Cl, Br, I, NCS)

dioxygen and sulphur dioxide is significantly lower than that of the corresponding triphenylphosphine complexes. The oxidative-addition reactions of the complexes trans-$[IrX(CO)(P\text{-}P)]$ with hydrogen halides give the species $[IrHX_2(CO)(P\text{-}P)]$ showing that this bidentate phosphine ligand [286] does allow the formation of six-co-ordinate complexes although the presence of the ligand [286] does tend to reduce the ability of the metal to undergo oxidative-addition reactions. Reactions of the appropriate square planar complexes with dihydrogen give the complexes $[IrH_2I(CO)(P\text{-}P)]$ and $[IrH_2L(CO)(P\text{-}P)]BF_4$, ($L = CO$ or MeCN). The static requirements of the ligand [286] are similar to those of bis-$Ph_2PCH_2Ph$ metal compounds (ref. 245).

Sulphur dioxide is known to bond to a metal atom through the sulphur atom in one of two spatial arrangements i.e. bent [289] with approximately tetrahedral geometry around the sulphur atom and coplanar [290] with the metal atom. In general, in the

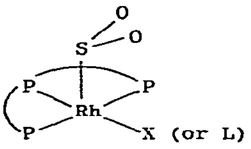


[289]

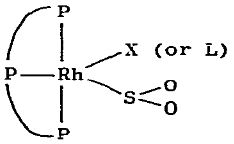


[290]

"bent" geometry, the S = O stretching frequencies occur near 1200 and 1050 $cm^{-1}$, the $SO_2$ is labile, and the co-ordinated $SO_2$ reacts with dioxygen to form sulphate complexes. However, if the metal-$SO_2$ groups are coplanar, the S = O stretching frequencies appear near 1300 and 1100 $cm^{-1}$, the $SO_2$ is not labile and sulphates are not formed upon oxidation. Some exceptions to these generalisations have been noted previously and in order to determine factors which influence the reactivity of co-ordinated sulphur dioxide a series of rhodium-$SO_2$ adducts of the type $Rh(ttp)XSO_2$, [ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$, X = Cl, $N_3$, CN] and $[Rh(ttp)L(SO_2)]^+$, (L = MeCN, $PPhMe_2$, $PEt_3$, CO) have been prepared. All of these complexes have S = O stretching frequencies in the region associated with "bent" $SO_2$ but there are major differences in the reactivity of these complexes towards dioxygen and in their lability in solution. The structures of these $SO_2$ complexes are not known with certainty and the three geometries [291], [292] and [293] have been proposed. It is clear that further work is required in order to determine factors which control the chemistry of bonded sulphur dioxide (ref. 246). The complexes $[Rh(L\text{-}L)_2]PF_6$, (L-L = [294], [295], and [296]) also react with sulphur dioxide to give 1:1 adducts. The S = O stretching frequencies of these adducts are in the range associated with the "bent" geometry and they react with dioxygen to give sulphato complexes. These sulphur dioxide complexes are formulated as square-pyramidal species with apical $SO_2$. By contrast $SO_2$ reacts with $[Rh(diars)_2]Cl$ to give an extremely insoluble 1:1 adduct which has low values of ν(SO) at 1099 and 984 $cm^{-1}$. It is suggested that in this adduct $[Rh(diars)_2(SO_2)]^+$ units stack so that weak interactions occur between one metal and the $SO_2$ co-ordinated to the adjacent one. The complexes $[Rh(L\text{-}L)_2]PF_6$ also react with dioxygen to give 1:1 adducts which contain "side-on" bonded dioxygen. The $^1H$ n.m.r. spectrum of $[Rh(O_2)(Ph_2AsCH{=}CHAsPh_2)_2]PF_6$ indicates the presence of a



[291]



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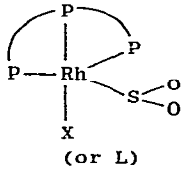
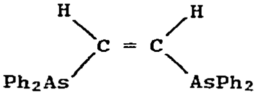
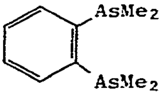


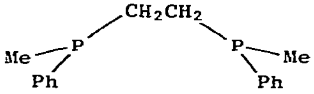
[293]



[294]

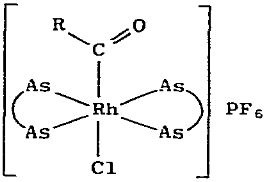


[295]



[296]

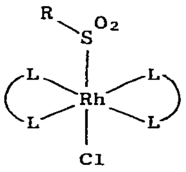
significant interaction between the ortho hydrogens of two ligand phenyl groups and the dioxygen molecule as has been observed in $[Ir(O_2)(Ph_2PCH_2CH_2PPh_2)_2]Cl$. The three rhodium(I) complexes also react with $S_8$ but only the complexes $[Rh(S_2)(Ph_2AsCH{=}CHAsPh_2)_2]Cl$ and $[Rh(S_2)(Ph_2AsCH{=}CHAsPh_2)_2]PF_6$ could be isolated in a pure state. There are also interactions between the ortho ligand hydrogens and the co-ordinated $S_2$ molecule in these complexes. The $[RhO_2(L\text{-}L)_2]X$, $(X = Cl, PF_6)$ complexes react with nitrogen dioxide to yield a variety of nitrate derivatives including $[Rh(OH)(NO_3)(MePhPCH_2CH_2PPhMe)_2]PF_6$, $[RhCl(NO_3)(diars)]PF_6$, and $[Rh(NO_3)(NO_2)(Ph_2AsCH{=}CHAsPh_2)_2]Cl$. While only $[Rh(diars)_2]PF_6$ reacts with acyl chlorides to give [297], sulphonyl halides react with all three complexes to give



[297]

= diars

[R = Me, Et, Ph, 3,5-$(NO_2)_2C_6H_3$]

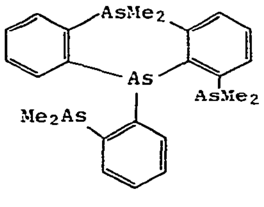


[298]

= [294], [295], [296]

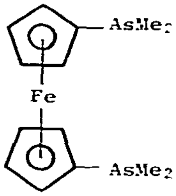
[R = Me, Et, Ph, *p*-$BrC_6H_4$, *m*-$(NO_2)C_6H_4$, *p*-$MeC_6H_4$, 1-naphthyl]

the sulphinato- S bonded complexes [298]. For L-L = [296] and R = *m*-$(NO_2)C_6H_4$, *p*-$MeC_6H_4$, or 1-naphthyl, O-sulphinate complexes are also produced. The rhodium(I) complexes also undergo oxidative-addition reactions with halogens (ref. 247). Attempts to prepare $[Rh(Qas)]PF_6$ (Qas = [299]) have been unsuccessful although from



[299]

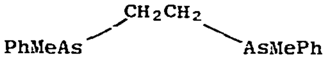
the reactions of Qas with $[RhCl(CO)_2]_2$ or $[RhCl(cod)]_2$ followed by metathesis with $AgPF_6$ the compounds $[Rh(CO)(Qas)]PF_6$ and $[Rh(cod)(Qas)]PF_6$ can be isolated. Treatment of the cyclo-octa-1,5-diene derivative with p-toluenesulphonyl chloride or methyl iodide gives the cis-complexes $[RhCl\{S(O_2)p\text{-}MeC_6H_4\}(Qas)]PF_6$ and cis-$[RhIMe(Qas)]PF_6$ respectively. The complex $[Rh(fdma)_2]PF_6$, (fdma = [500]) adds a



[500]

variety of small molecules L to produce five-co-ordinate adducts $[RhL(fdma)_2]PF_6$, (L = CO, $SO_2$, $CNCMe_3$, $O_2$, $S_2$, $CF_3C{\equiv}CCF_3$) and it oxidatively adds molecules XY to give octahedral complexes $[RhXY(fdma)_2]PF_6$, (XY = $H_2$, $Br_2$, $I_2$, HCl, HBr, HI, $MeSO_2Cl$, MeI, MeSSMe). Several of these adducts are stereochemically non-rigid in solution (ref. 248). The crystal structure and absolute configuration of an optically active dioxygen complex of cobalt(III) $(+)_{546}$-Λ-cis-β-$[Co\{R,R\text{-}Me_2As(CH_2)_3AsPh(CH_2)_2AsPh\text{-}(CH_2)_3AsMe_2\}O_2]ClO_4$ have been determined. This is one of the few cobalt complexes in which there is definitive evidence for a side-bonded dioxygen ligand (ref. 249).

Cobalt(II) perchlorate readily reacts with the diarsine ligand [501] to give $[Co(dase)_2]ClO_4$ which contains planar cobalt(II). However, attempts to isolate the



(dase)

[501]

$PhMeAs(CH_2)_3AsMePh$

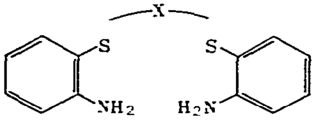
(dasp)

[502]

analogous compound with dasp [502] fails. Cobalt(II) halides readily form complexes of empirical formula $Co(dase)X_2$, (X = Cl, Br, I) which are formulated as the salts $[Co(dase)_2][CoX_4]$. In solution the following isomerism occurs:

$$[Co(dase)_2][CoX_4] \rightleftharpoons 2[CoX_2(dase)]$$

The ligand dasp, however, forms only pseudo tetrahedral compounds $[CoX_2(dasp)]$ (ref. 250). Treatment of hydrated rhodium(III) chloride with the tetradentate ligands [503]-[506] does not give simple monomeric adducts and only the compounds $Rh_4L_3Cl_{12}$, (L = [503]-[506]) can be isolated (ref. 251). In an attempt to obtain new planar



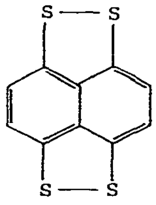
[503] —X— = $-(CH_2)_2$ - ($eS_2N_2$)

[504] —X— = $-(CH_2)_3$ - ($pS_2N_2$)

[505] —X— = $-(CH_2)_4$ - ($bS_2N_2$)

[506] —X— = cis-CH=CH - ($V_2N_2$)

organometallic complexes which will form multiparallel chains bridged by a highly delocalised π-system, tetrathionaphthalene [507] has been treated with several metal carbonyls. Reaction of [507] with a stoichiometric amount of $Co_2(CO)_8$ in benzene



(TTN)

[507]

... $Co_2(CO)_2TTNCo_2(CO)_2TTN$ ...

[508]

gives an insoluble red precipitate formulated as [508]. Thus in contrast to the dithiolene ligand $S_2C_2(CF_3)_2$ TTN does not lead to complete displacement of carbon monoxide from the cobalt. The compound [508] behaves as a one-dimensional conducting system (ref. 252).

### Metal nitrosyl and aryldiazo compounds

Treatment of $[Co(NO)(CO)_3]$ with dimethyl arsine gives [509] which can be oxidised by air to the dinuclear complex [510] which can also be obtained from $[Co(NO)(CO)_3]$

$$Co(NO)(CO)_2(AsMe_2H) \longrightarrow (CO)_2(NO)Co\text{-}AsMe_2\text{-}AsMe_2Co(NO)(CO)_2$$

[509] [510]

and $Me_2AsAsMe_2$ (ref. 253). The organometallic Lewis base [511] reacts with $[Co(NO)(CO)_3]$ to give [512] and a monosubstituted complex, [CoCp(CO)L] can be

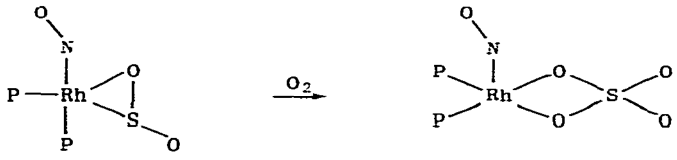
$(CO)_4Fe\text{-}PMe_2\text{-}PMe_2$ [511]

$(CO)_2(NO)Co\text{-}PMe_2\text{-}PMe_2\text{-}Fe(CO)_4$ [512]

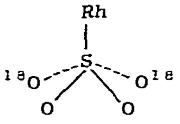
obtained by the reaction of [511] with $[CoCp(CO)_2]$, (ref. 254). The n.m.r. spectra of these complexes of [511] exhibit line broadening which has been attributed to variable interactions of the quadrupolar nuclei with different spin states of the $X_6ABY_6$ spin system (ref. 255). The species $[Co(NO)(CO)_2]$ is considered to participate in photochemical and thermal substitution reactions of $[Co(NO)(CO)_3]$. Evidence for this intermediate has been provided by the isolation of $[Co(NO)(CO)_2]$ in argon and methane matrices. The primary photolysis steps which lead to this species are readily reversed by irradiation with visible light and by annealing the matrix in the case of the reaction of $[Co(NO)(CO)_2]$ with CO. The formation of $[Co(NO)(CO)_2(N_2)]$ and possibly $[Co(NO)(CO)(N_2)_2]$ has been observed in dinitrogen matrices (ref. 256).

Although phosphines of the type $PR_2R'$ ($R'$ = alkyl or H) react with $Co(NO_3)_2.6H_2O$ in $Pr^iOH$ to give $[Co(NO)(PR_2R')_3]$ complexes, the phosphite $P(OCH_2)_3CMe$ (L) induces disproportionation of divalent cobalt to form $[CoL_5]_2[Co(NO_3)_4]$. However, the isomeric phosphine $P(CH_2O)_3CMe$ does form a nitrosyl $[Co(NO)\{P(CH_2O)_3CMe\}_3]$. The disproportionation of cobalt(II) by phosphites is probably associated with the strong ligand field stabilisation afforded by ligands which are able to accept π-electron density from the cobalt. Attempted recrystallisation of $[CoL_5]_2[Co(NO_3)$ from methyl cyanide gives $[CoL_5]NO_3$ and $[CoL_5][Co(NO_3)_3(NCMe)]$ which contains a near-perfect trigonal-bipyramidal array of phosphorus atoms around cobalt(I). The anion $[Co(NO_3)_3(NCMe)]^-$ has a heptaco-ordinate cobalt(II) geometry formed by three bidentate nitrates and a methyl cyanide ligand (ref. 257).

The crystal structure of the tetrahedral compound $[Rh(NO)(PPh_3)_3]$ has been reported (ref. 258). Solutions of this compound saturated with sulphur dioxide afford crystals of [513] which has been characterised by a single crystal X-ray study. The complex [513] reacts readily with dioxygen to give [514] which again contains a bent nitrosyl ligand and this complex has also been characterised by an X-ray study (refs. 259, 260). The mechanism of the reaction of this side-bonded sulphur dioxide compound [513] with dioxygen has been studied using oxygen-18 substitution and infrared analysis. The data are consistent with a mechanism which involves formation of an intermediate [515] which contains square pyramidal co-ordination about the sulphur. The oxygen atoms thus become equivalent in the basal plane allowing the metal to move to each of the four basal edges with equal



[513] P = $PPh_3$ [514]



[315]

probability. This would predict a 1:2:1 ratio corresponding to $^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$ for the isotopic content in the terminal oxygen of the sulphato group respectively. Three infrared peaks in this ratio are observed in the $\nu_3$ region of the infrared spectrum. In studies with S-bonded sulphur dioxide a different distribution of labelled oxygen is observed suggestive of a peroxysulphite intermediate (ref. 259).

Studies on the carbonylation of $[Ir(NO)(PPh_3)_3]$ are consistent with the stepwise mechanism outlined in Scheme 47 (ref. 261). Some nitrosyl carbonyl derivatives of

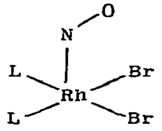
$$Ir(NO)L_3 \underset{-S}{\overset{+S}{\rightleftharpoons}} Ir(NO)(S)L_2 + L$$

$$Ir(NO)(S)L_2 + CO \longrightarrow Ir(NO)(CO)L_2 + S$$

$(S = \text{solvent}, P = PPh_3)$

Scheme 47

the type $[RhXCl(NO)(CO)L_2]$ can be obtained by treating trans-$[RhX(CO)L_2]$, (X = Cl, Br I; L = $PPh_3$, $AsPh_3$) in either dimethylformamide or chloroform with solid sodium nitrite and moderately concentrated hydrochloric acid. The action of silver nitrate on the compounds $[RhXCl(NO)(CO)L_2]$ results in loss of the carbonyl ligand to give $[Rh(NO_3)_2(NO)L_2]$ (ref. 262). An X-ray study of a related compound [316] has been



L = $P(OPh)_3$

[316]

reported (ref. 263). The action of sodium nitrite on trans-$[IrCl(CO)(PPh_3)_2]$ leads to $[Ir(NO)(CO)(PPh_3)_2]$ probably via the sequences of reactions outlined in Scheme 48. Treatment of $[Ir(NO)(CO)(PPh_3)_2]$ with $NOPF_6$ gives $[Ir(NO_2)(PPh_3)_2]PF_6$ and this cationic complex can also be obtained by the action of nitrogen monoxide upon

$$IrCl(CO)P_2 + NaNO_2 \longrightarrow Ir(NO_2)(CO)P_2 + NaCl$$

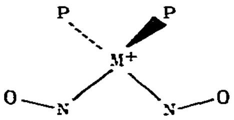
$$Ir(NO_2)(CO)P_2 + CO \rightleftharpoons Ir(NO_2)(CO)_2P_2$$

$$Ir(NO_2)(CO)_2P_2 \longrightarrow Ir(NO)(CO)P_2 + CO_2$$

$$(P = PPh_3)$$

Scheme 48

$[Ir(CO)_3(PPh_3)_2]PF_6$. The dinitrosyl rhodium cation $[Rh(NO)_2(PPh_3)_2]PF_6$ can be obtained from NO and $[Rh(diene)(PPh_3)_2]PF_6$. The black cobalt salts $[Co(NO)_2L_2]PF_6$ can be obtained by the action of $NOPF_6$ upon $[Co(NO)(CO)L_2]$, ($L = PPh_3$, $P(OPh)_3$). The structures of the three cationic complexes (317; M = Co, Rh, Ir) are known and study of some of their reactions has been reported. With tertiary phosphines or chloride ion the reactions fall into three classes.

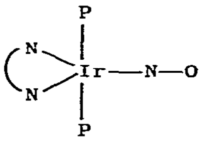


[317]

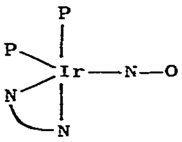
(a) For M = Co, reaction with phosphine or chloride occurs via the 16-electron intermediate $[Co(NO)_2(PPh_3)]^+$.

(b) For M = Rh or Ir, reactions with phosphines occur via an associative path with the formation of a 20-electron intermediate formally containing $NO^+$ and $NO^-$. This leads to coupling of the two nitrosyl ligands and formation of $N_2O$, phosphine oxide and the cations $[RhL_4]^+$. However, when L is $PPh_3$, $NO^+$ and $[M(NO)(PPh_3)_3]$, (M = Rh, Ir) are produced.

(c) For M = Rh or Ir reaction with HCl produces $[MCl_2(NO)(PPh_3)_2]$, $N_2O$ and water. The reaction of $[Ir(NO)_2(PPh_3)_2]^+$ with 2,2 -bipyridyl gives $[Ir(NO)(bipy)(PPh_3)_2]^{2+}$ and evolution of $N_2O$. This five-co-ordinate dication may have the structure [318] or [319]. Treatment of the cations $[M(NO)_2(PPh_3)_2]^+$ with $NaBH_4$ or $N_2H_4$ in tetra-



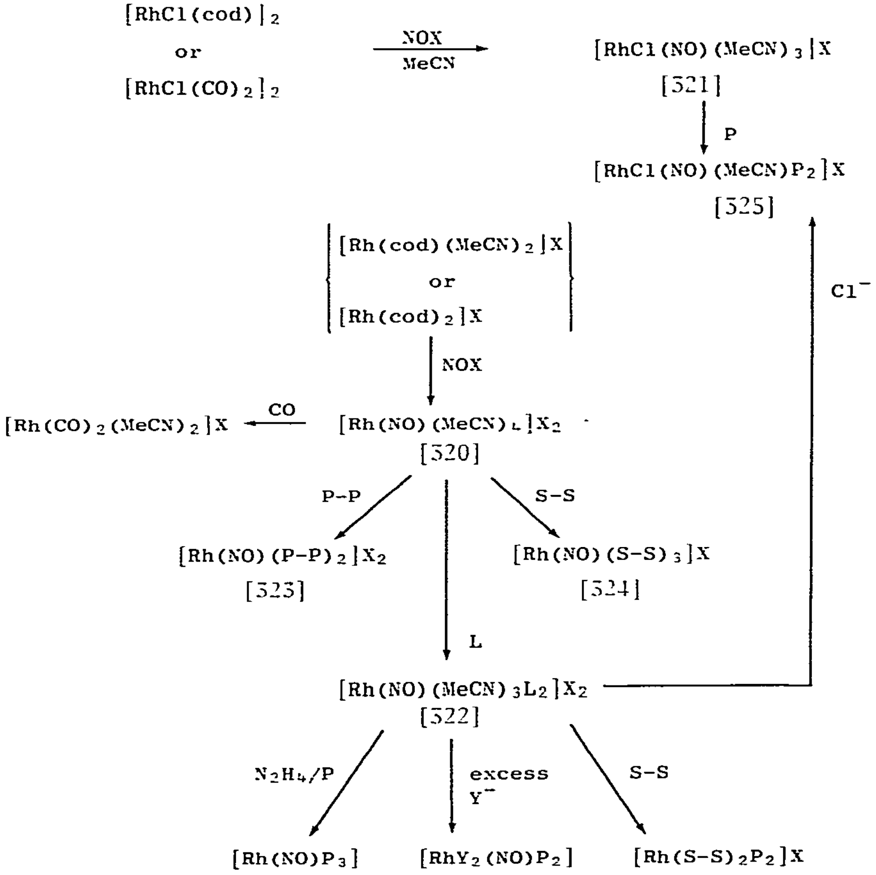
[318]



[319]

hydrofuran in the presence of $PPh_3$ gives $[M(NO)(PPh_3)_3]$. In the reactions with $NaBH_4$ attack of $H^-$ on co-ordinated NO occurs to generate ammonia (ref. 264). A series of cationic cobalt nitrosyl complexes $[Co(NO)_2L_2]Y$, ($L = RCN$, ROH, $Me_2CO$; $L_2$ = cod, nbd: $Y = PF_6$, $BF_4$, $ClO_4$) have been prepared by the reaction of $[CoCl(NO)_2$ with AgY in the presence of the ligand L, (ref. 265), and the crystal structure of the compound $[Co(NO)_2(Ph_2PCH_2CH_2PPh_2)]PF_6$ has been determined (ref. 266).

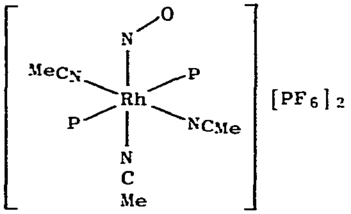
A number of dicationic nitrosyl compounds of rhodium have been obtained by reactions of rhodium(I) compounds with either $NOPF_6$ or $NOBF_4$ as outlined in Scheme 49. The compound [522], which was originally incorrectly formulated as a bis-



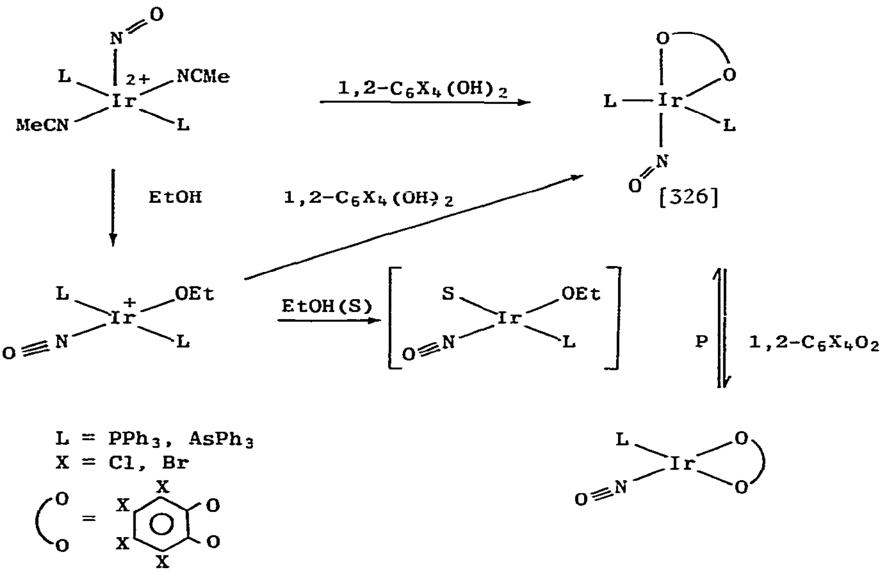
($P = PPh_3$; $P\text{-}P = Ph_2PCH_2CH_2PPh_2$; $L = PPh_3$, $AsPh_3$; $S\text{-}S = S_2CNR_2$; $Y^- = Cl^-$, $I^-$; $X = BF_4$, $PF_6$)

Scheme 49

acetonitrile compound, has been shown by an X-ray study to contain a bent nitrosyl ligand and the compounds [320], [321], [324], and [325] are also considered to contain bent nitrosyl ligands. The compound [323] probably contains linear $NO^+$ (refs. 267, 268). The dication $[Rh(NO)(MeCN)_4][BF_4]_2$, dissolved in nitromethane, is an effective catalyst for the di-, tri-, and tetra-merisation of isobutylene at room temperature (ref. 269). In view of the reformulation of the dication $[Rh(NO)(MeCN)_2(PPh_3)_2][PF_6]_2$ as the tris-methylcyanide compound [322] it seems likely that the ions $[M(NO)(MeCN)_2L_2]^{2+}$, (M = Rh, Ir; L = $PPh_3$, $AsPh_3$), (ref. 270) may also have analogous octahedral structures to [322]. Treatment of these dicati with ortho-benzoquinones or ortho-catechols in ethanol or diethyl ether gives the compounds [326], (Scheme 50), (ref. 270) and similar four- and five-co-ordinate ortho-catecholato rhodium and iridium compounds have been obtained with catechols



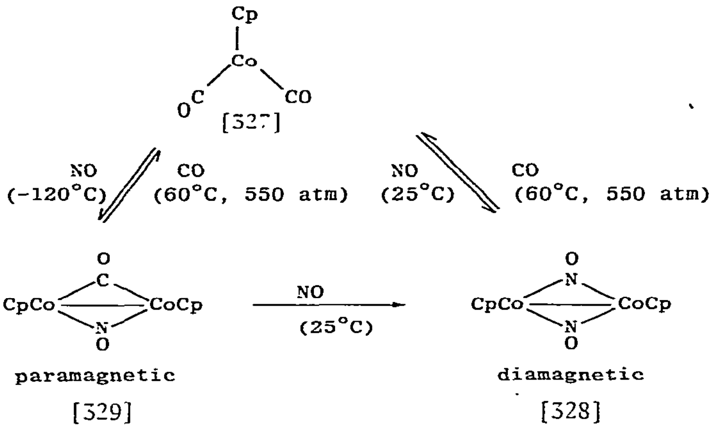
[322]



Scheme 50

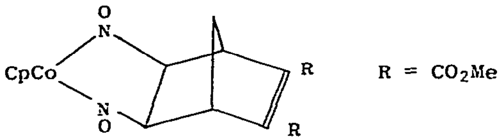
with both electron-releasing or -withdrawing substituents (ref. 271).

$[CoCp(CO)_2]$ [327] reacts at room temperature with nitrogen monoxide to give [328] Partial nitrosylation of [327] has now been accomplished either by reducing the reaction temperature or by using N-methyl or N-ethyl-N-nitrosourea (Scheme 51) (ref. 272). The crystal and molecular structures of [328] and [329] have been determined



Scheme 51

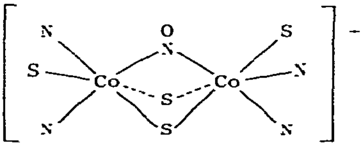
together with the e.s.r. spectrum of [329]. The compound [328] undergoes reversible oxidation to its cation and [329] undergoes reversible reduction to its anion (ref. 273). Nitrosyl chloride reacts with [327] and with $[Co(NO)(CO)_3]$ to give $[CoCl(NO)_2]_2$ (ref. 274). The reaction of [327] with the Diels-Alder adduct of cyclopentadiene with $MeO_2CC{\equiv}CCO_2Me$ in the presence of NO gives [330] and the structure of this product has been confirmed by an X-ray study (ref. 275). The



[330]

reaction of $NO^+$ with the cobalt compound $[CoL]_2$, where L is the tetradentate $N_2S_2$ donor ligand derived from N,N′-dimethyl-N,N′-bis(2-mercaptoethyl)ethylenediamine ($LH_2$) affords $[(CoL)_2NO]^+$ [331] which has been characterised by an X-ray study. Unlike the corresponding iron compound there is no metal-metal bond. The reaction has been interpreted in terms of an oxidative-addition reaction of the $NO^+$ ion to the bimetallic species (ref. 276).

$$[Co^{II}L]_2 + NO^+ \longrightarrow [(Co^{III}L)_2(NO^-)]^+$$



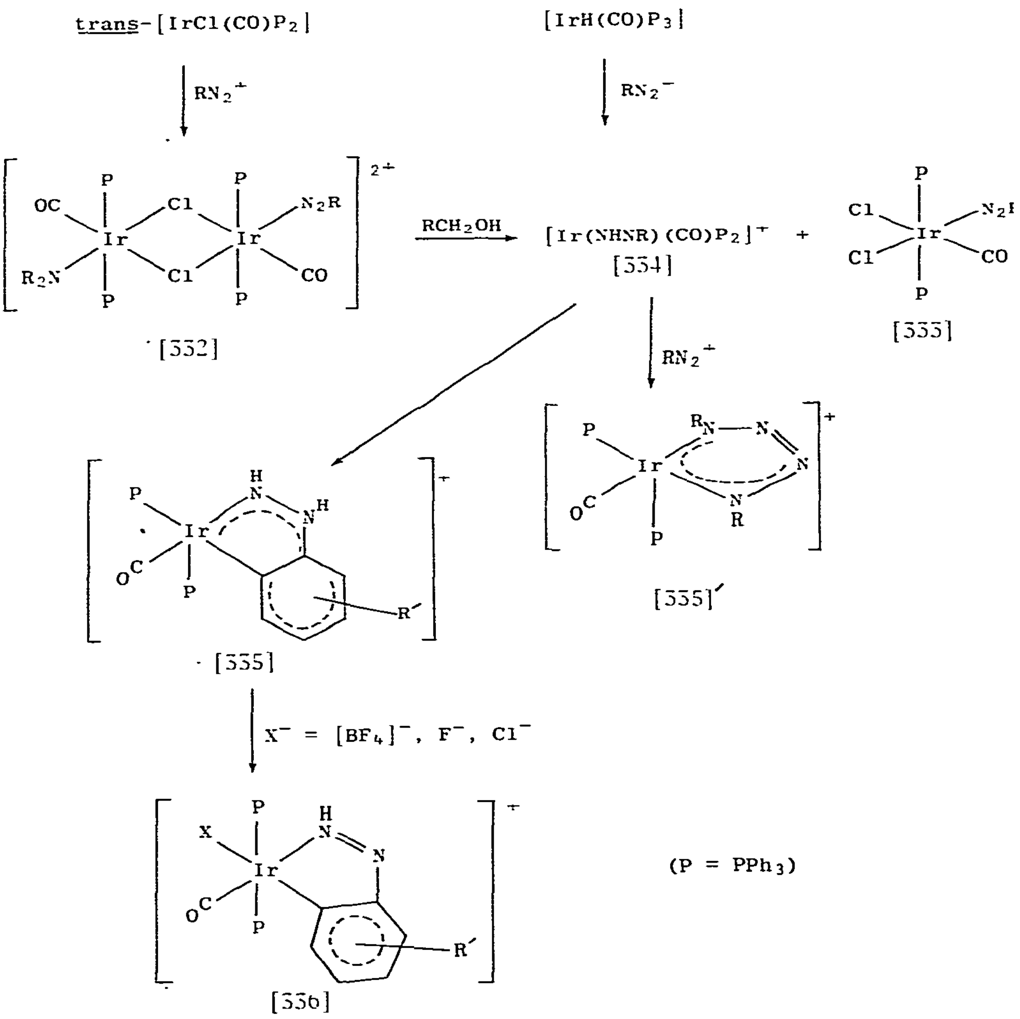
[551]

The products of the metathetical reactions of $[CoCl(NO)_2]_2$ with $Na[Fe(NO)(CO)_3]$, $Na[FeCp(CO)_2]$, and $Na[Co(CO)_4]$ are active catalysts for the selective dimerisation of butadiene to 4-vinylcyclohexene (ref. 277). Ethanolic solutions of $[RhCl_2(CO)_2]^-$ containing aqueous acid catalyse the reduction of NO by carbon monoxide under mild conditions. Further studies on this system indicate that the catalytically active species is best formulated as a rhodium(III) carbonyl dinitrosyl complex in which both nitrosyl ligands are bent (ref. 278). The relative stabilities of the anions $[M(NO)Cl_5]^{n-}$, (M = Ir, n = 1; M = Ru, Os, Re, n = 2) have been compared (ref. 279).

The reactions of Vaska's complex trans-$[IrCl(CO)(PPh_3)_2]$ with diazonium salts, $RN_2{}^+BF_4{}^-$, are critically dependent on the conditions employed and the suggested mechanisms for the reactions in benzene-ethanol together with those of diazonium salts with $[IrH(CO)(PPh_3)_3]$ are outlined in Scheme 52. The chloride-bridged aryldiazenido complex [552] is formed initially in benzene-ethanol as it is in acetone. This reacts with the alcohol at one iridium centre causing asymmetric cleavage of the chloride bridges to give [553], [554] being formed via hydrogen abstraction from the alcohol. In reactions with $[IrH(CO)(PPh_3)_3]$, [554] is formed initially followed by insertion to give [555′]. The intermediate [554] rearranges to the orthometallated complex [555] which can be isolated from reactions in benzene-ethanol when R′ = o or p-$NO_2$. However, [555] usually undergoes oxidation to an orthometallated iridium(III) aryldiazene complex [556] (refs. 280-283). ESCA spectra have been obtained for nitrosyl, aryldiazo, and aryldiimine complexes of rhodium and iridium. A good correlation is observed between the N 1s binding energies of the nitrosyl complexes and those of their aryldiazo analogues and provides further evidence that nitrosyl and aryldiazo ligands possess similar co-ordination properties. It is also found that aryldiazo and aryldiimine ligands possess low overall charges and are appreciably less polar than dinitrogen ligands co-ordinated in similar situations (ref. 284).

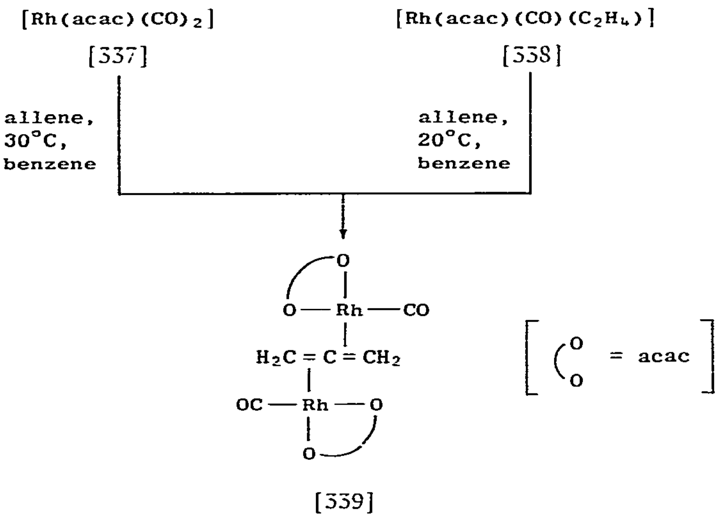
### Metal-alkene compounds

Several rhodium(I) compounds are known to be catalysts for the polymerisation of

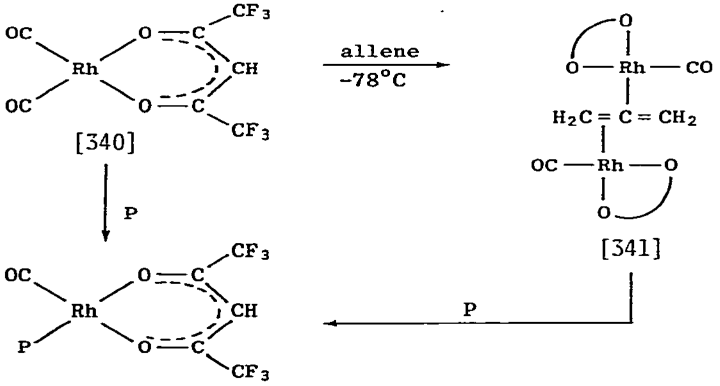

trans-[IrCl(CO)P2]
[IrH(CO)P3]
RN2+
RN2−
RCH2OH
[Ir(NHNR)(CO)P2]+
+
[332]
[333]
[334]
[335]
[335]′
[336]
RN2+
X− = [BF4]−, F−, Cl−
(P = PPh3)
OC
R2N
Cl
Ir
P
N2R
CO
N2R
H
N
R′
X

Scheme 52

allene. Studies on the reaction of allene with [337] and [338] reveal that at 30°C



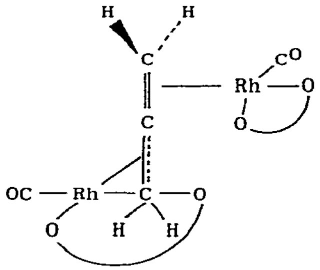
rapid reaction occurs to give [339] which has been characterised by an X-ray study. An analogous reaction does not occur with [Rh(PhCOCHCOPh)(CO)$_2$] between -78 and +30°C, but liquid allene reacts with [340] at -78°C to give [341] analogous to [339], (Scheme 53). Three diastereoisomeric structures are to be expected for [341



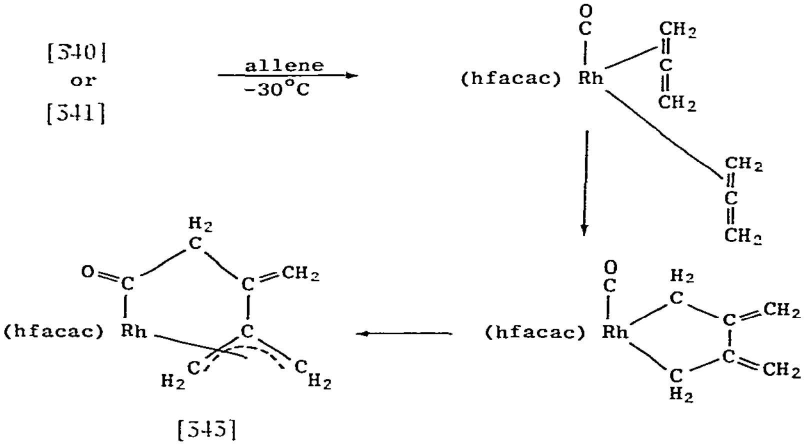
(P = PPh$_3$)

Scheme 53

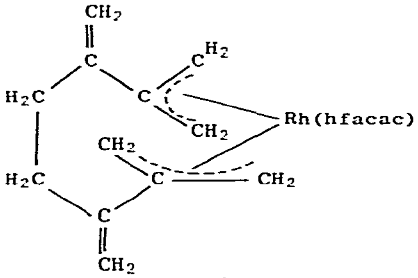
and n.m.r. studies reveal the presence of two in solution. However, the configuration [342] is probably the major isomer present in solution and is the favoured configuration in the solid state in view of the known structure of [539]. The reaction of allene with [540] at -30°C gives the allyl compound [543] and it is considered to be formed via the mechanism outlined in Scheme 54. When the reaction between [540] and allene is carried out between -20 and +20°C in pentane [544] is obtained in high yield together with varying amounts of [543] which is not an intermediate in the formation of [544] (ref. 285). Compounds [545], analogous to [544], are formed from the reactions of allene with the iridium compounds, [Ir(β-diketonato)(cyclo-octene)$_2$], the hexafluoroacetylacetonato derivative of [545] being characterised by an X-ray study. These bis-allyl compounds are considered to be formed via metallacyclopentane intermediates. A compound containing this ring system [546] is formed by the action of allene on [Ir(acac)(cyclo-octene)$_2$] at



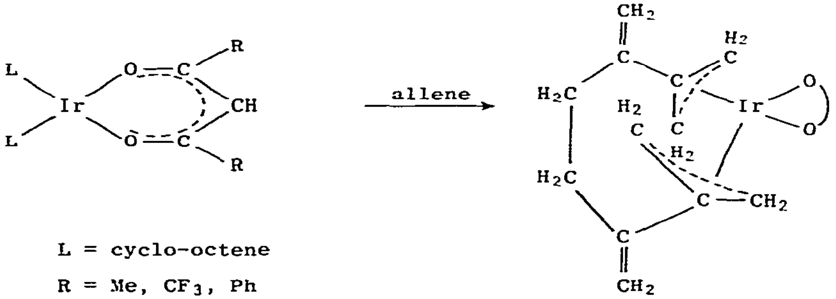
[542]



Scheme 54



[344]



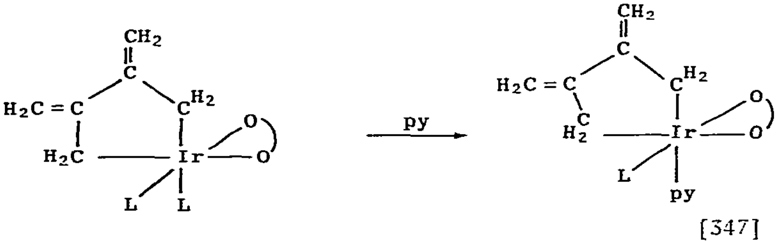
L = cyclo-octene

R = Me, $CF_3$, Ph

[345]

[Ir(acac)(cyclo-octene)$_2$]

allene
-78°C



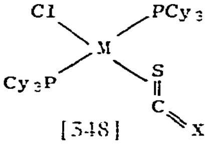
[346]

(L = $CH_2=C=CH_2$)

[347]

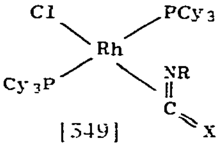
-78°C and treatment of [346] with pyridine results in displacement of one of the allene ligands to give [347] which has been characterised by an X-ray study (ref. 286). Compounds of rhodium(I) and iridium(I) containing co-ordinated pseudo-allene

X=C=Y, (X, Y = S, NR, O) have also been prepared, e.g. [348], [349]. Most of these



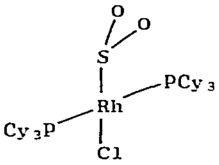
[348]

M = Rh; X = S, O, NMe, Nallyl, NPh, N(p-tol);
M = Ir; X = S, NPh

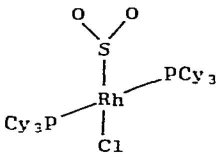


[349]

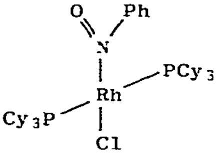
X = NR, O



[350]



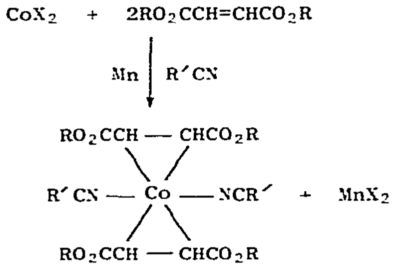
[351]



[352]

products can be prepared by simple addition of the pseudo-allene to $[RhCl(PCy_3)_2]$. *Compounds of phenyl isocyanate and sulphur dioxide (structure either [350] or [351])* may also be prepared using solutions of $[RhCl(cyclo\text{-}octene)_2]_2$ and the required amount of $PCy_3$. However, addition of S=C containing heterocumulenes to $[RhCl(PCy_3)_2]$ results in decomposition of the heterocumulene but the required compounds can be obtained by addition of the ligands S=C=X, (X = S, O, NR) to $[RhH_2Cl(PCy_3)_2]$. The reaction of $[IrCl(cyclo\text{-}octene)_2]_2$ with $PCy_3$ leads to the formation of an oily product. However, $PCy_3$ reacts with $[IrCl(C_2H_4)_4]$ to give an orange solution which reacts with carbon disulphide, carbonyl sulphide and phenyl isocyanate but not with methyl and allyl isocyanate to give the compounds (348; M = Ir). The carbon disulphide complexes decompose in solution by sulphur-abstraction and addition of $PCy_3$ gives the complexes trans-$[MCl(CS)(PCy_3)_2]$. No sulphur abstraction from the isothiocyanate complexes has been observed. However, in the presence of light, solid $[RhCl(PhNCO)(PCy_3)_2]$ decomposes to trans-$[RhCl(CO)(PCy_3)_2]$. The nitrene fragment has not been detected. $[RhCl(PCy_3)_2]$ does not co-ordinate carbon dioxide although $[IrCl(PMe_3)_3]$ does. Nitrosobenzene gives [352] (ref. 287).

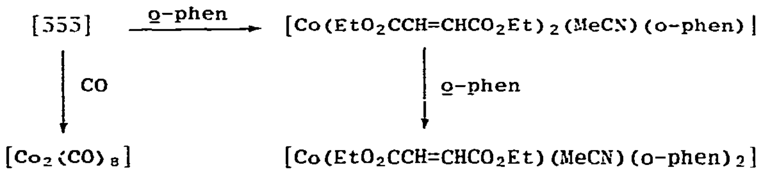
Some cobalt(0) complexes prepared "in situ" can catalyse the dimerisation and cyclisation of co-ordinated alkenes. Some zerovalent cobalt alkene complexes of general formula $[Co(ROOCCH{=}CHCOOR)_2(R'CN)_2]$ [553] have now been obtained by reducing anhydrous cobalt(II) chloride, bromide, or iodide with manganese powder in the presence of fumaric esters and organic nitrile. The compounds are paramagnetic and



R= Et, R′= Me;
R= Pr, R′= Me;
R= Bu, R′= Et.

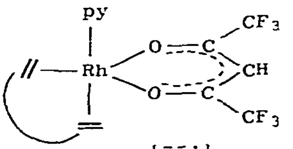
[553]

the structure of the compound (553; R =Et, R′ =Me) has been determined by an X-ray study. The four co-ordination about the cobalt as based on a distorted trigonal pyramid. Some reactions of these air-sensitive bis-alkene compounds are illustrated in Scheme 55 (ref. 288).

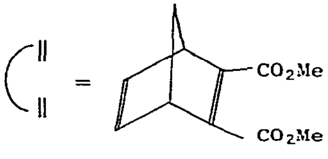


Scheme 55

A number of four-co-ordinate square-planar diene complexes of rhodium(I) exhibit temperature-dependent $^1H$ n.m.r. spectra which have been interpreted in terms of an intramolecular exchange of alkene protons between non-equivalent sites. The rate of this site exchange is enhanced by the addition of donor ligands and an associative mechanism involving formation of a five-co-ordinate intermediate and an intramolecular rearrangement of the intermediate provide a mechanism for the reaction. Such an intermediate [554] has now been isolated and its structure has been determined by

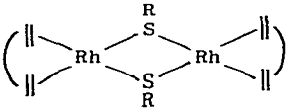


[554]

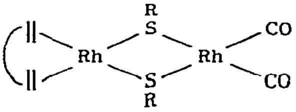


[555]

an X-ray study. The $^{13}$C n.m.r. spectra of [554] and of the compounds [RhX(diene)]$_2$, [RhX(diene)py] and [Rh(acac)(diene)], (X = Cl, Br, I; diene = [555]) have been studied. Pyridine reacts with [Rh(hfacac)(cod)] or [Rh(hfacac)(nbd)] to give [Rh(cod)py$_2$][hfacac] or [Rh(nbd)py$_2$][hfacac] respectively (ref. 289). Variable temperature n.m.r. studies of the compounds [556] and [557] reveal the existence of both an alkene rotation and an inversion of non-planar $Rh_2S_2$ rings, the non-planarity of a $Rh_2S_2$ ring being established by an X-ray study of [$Rh_2(CO)_2(\mu\text{-SPh})_2(C_8H_8)$]. Confirmation of the high temperature alkene rotation process has been achieved by a study of compound [558] which also exhibits co-ordinated alkenic proton changes analogous to that of [$Rh_2(SBu^t)_2(C_8H_8)_2$]. Only a rotation of the alkenes of [558] can explain this observation (ref. 290).



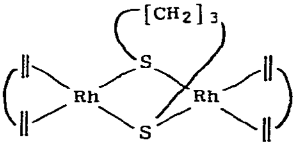
[556]



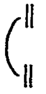
[557]


= cyclo-octa-tetraene, cyclo-octa-1,5-diene

R = Me, Et, $Pr^i$, $Bu^t$, Ph



[558]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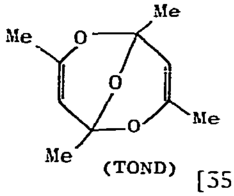
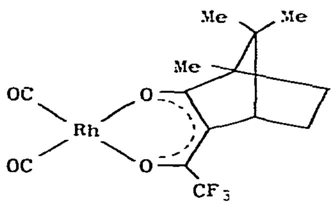
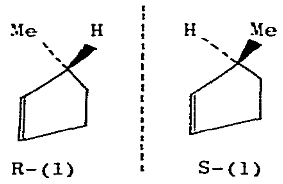


(TOND) [559]

Treatment of [$RhCl(C_2H_4)_2]_2$ with TOND [559] gives the stable diene compound [RhCl(TOND)]$_2$. Reaction of this binuclear compound with (S)-α-methylbenzenemethaneamine (S-Am) gives a mixture of the diastereoisomeric compounds [RhCl(TOND)(S-Am)] which can be separated by fractional crystallisation. The enantiomers of $[RhCl(1OND)]_2$ can be obtained by treatment of the diastereoisomers $[RhCl(1OND)(\underline{S}\text{-Am})]$ with HCl. Optically active 1OND can then be obtained by reaction of $[RhCl(1OND)]_2$ with cyanide ion (ref. 291). Resolution of a chiral alkene by complexation chromatography on an optically active rhodium(I) complex has been achieved by using a high-resolution capillary column loaded with optically active [360]. Using this column chiral 3-methylcyclopentene [361] can be resolved quantitatively into its antipodes (refs. 292, 293). Rhodium(I) complexes of optically active trans-cyclo-octene, $[Rh(acac)L_2]$, $[Rh(PhCOCHCOPh)L_2]$ and $[Rh_2Cl_2L_4]$, ($L = (+)_D$-trans-$C_8H_{14}$) have been prepared and absorption and CD spectra have been measured (ref. 294).



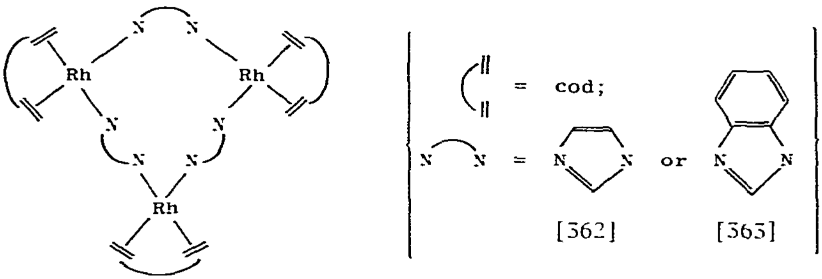
[360]



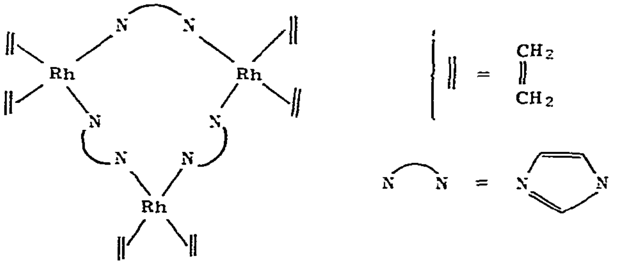
[361]

The cyclo-octa-1,5-diene compounds $[RhCl(cod)]_2$ react with $NaO_2CR$, (R = Me, Ph) or $AgO_2CR$, (R = Me, Ph, $CF_3$) to give the dimers $[Rh(O_2CR)(cod)]_2$. Attempts to obtain cationic compounds $[Rh(cod)_2][O_2CR]$ give the dimers $[Rh(O_2CR)(cod)]_2$ (ref. 295). Passage of carbon monoxide gas through anhydrous solutions of $[RhX(cod)]_2$, (X = Br, solvent = hexane, chloroform; X = I, solvent = benzene; X = $O_2CMe$, $O_2CPh$, $O_2CCF_3$, solvent = benzene, chloroform or ethylacetate) gives $[RhX(CO)_2]_2$. Treatment of $[Rh(O_2CR)(cod)]_2$ in a 30:1 methanol-water solvent mixture gives a 70% yield of $[Rh_6(CO)_{16}]$. Thallium(I) phenoxide cleaves the chloride bridges in $[RhCl(cod)]_2$ to give $[Rh(OPh)(cod)]_2$ which in chloroform solution reacts with carbon monoxide to give $[Rh_4(CO)_{12}]$. However, in aqueous methanol $[Rh_6(CO)_{16}]$ is formed. The bridged bromo and iodo compounds $[RhX(cod)]_2$, (X = Br, I) do not give $[Rh_6(CO)_{16}]$ when treated with carbon monoxide in aqueous solution (ref. 296). Some trinuclear imidazole complexes [362], [363], and [364] have been reported in a patent. The compound [362] is reported to be formed by the addition of imidazole to a mixture of $[RhCl(cod)]_2$ and butyl lithium and the compounds [363] and [364] can be similarly prepared (ref. 297).

A number of papers have been published during the year concerning cationic complexes of the type $[Rh(diene)(donor\ ligand)_2]^+$. Complexes containing tertiary phosphine ligands are highly effective asymmetric hydrogenation catalysts but the highest optical yields have been achieved with cationic rhodium catalysts containing chiral chelating diphosphine ligands. In the light of these observations the basic



[362] [363]



[364]

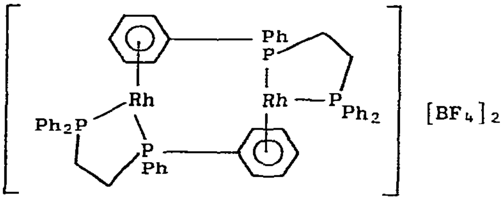
co-ordination chemistry and catalytic properties of $[Rh(nbd)(Ph_2PCH_2CH_2PPh_2)]^+$ have been examined. In methanol, this cation rapidly reacts with dihydrogen according to the equation:

$$[Rh(nbd)(diphos)]^+ + 2H_2 \longrightarrow \underset{[365]}{[Rh(diphos)]^+} + C_7H_{12}$$

This reaction should be contrasted to the corresponding reaction of $[Rh(nbd)(PPh_3)_2]^+$ with dihydrogen:

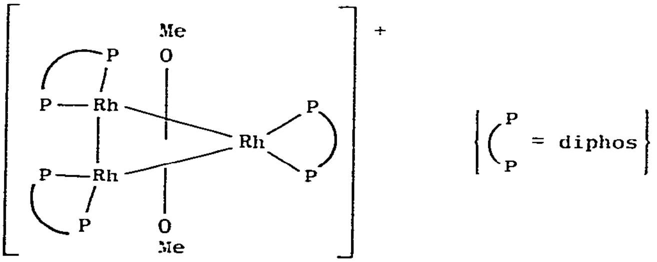
$$[Rh(nbd)(PPh_3)_2]^+ + 3H_2 \longrightarrow [RhH_2(PPh_3)_2(solvent)_2]^+ + C_7H_{12}$$

A single crystal X-ray structure determination shows that the cation [365], isolated as its tetrafluoroborate salt, to have the structure [365]. In methanol

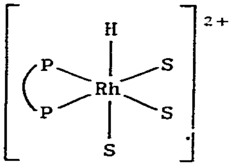


[365]

$[Rh_2(diphos)_2][BF_4]_2$ dissociates into mononuclear $[Rh(diphos)]^+$ and treatment of the cation with methoxide gives [366] which has also been the subject of a single crystal X-ray study. The cation $[Rh(diphos)]^+$ forms 1:1 adducts with a variety of alkenes and arenes. The binding constants of arenes are significantly higher than those of simple alkenes, thus styrene co-ordinates to the rhodium via its phenyl ring. Treatment of [365] with $HBF_4$, $HPF_6$, or $HClO_4$ gives the cation [367]. The cation $[Rh(diphos)_2]^+$ catalyses the hydrogenation of alkenes according to the Scheme 56. The inability of $[Rh(diphos)]^+$ to oxidatively add dihydrogen is considered to be related to the instability of the resulting dihydride which would have hydrogen ligands *trans* to phosphorus ligands (ref. 298). Species similar to $[Rh(diphos)]^+$ have also been detected in rhodium(I) compounds containing the diphosphines 1,3-bis(diphenylphosphino)propane (dppp) and isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop), Scheme 57. The species $[Rh(dppp)(Me_2CO)_2]BF_4$ may well be similar to [365]. Results with diop appear to be similar to those of (dppp) (ref. 299). The crystal structure and absolute configuration of $[Rh(cod)(2S,3S\text{-}2,3\text{-}Ph_2PCHMeCHMePPh_2)]ClO_4$ have been determined by an X-ray study

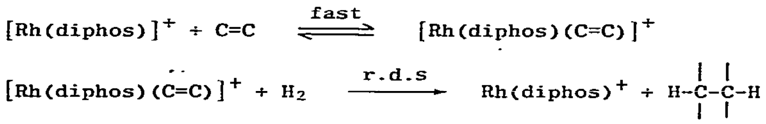


[366]



(S = solvent, P⁀P = diphos)

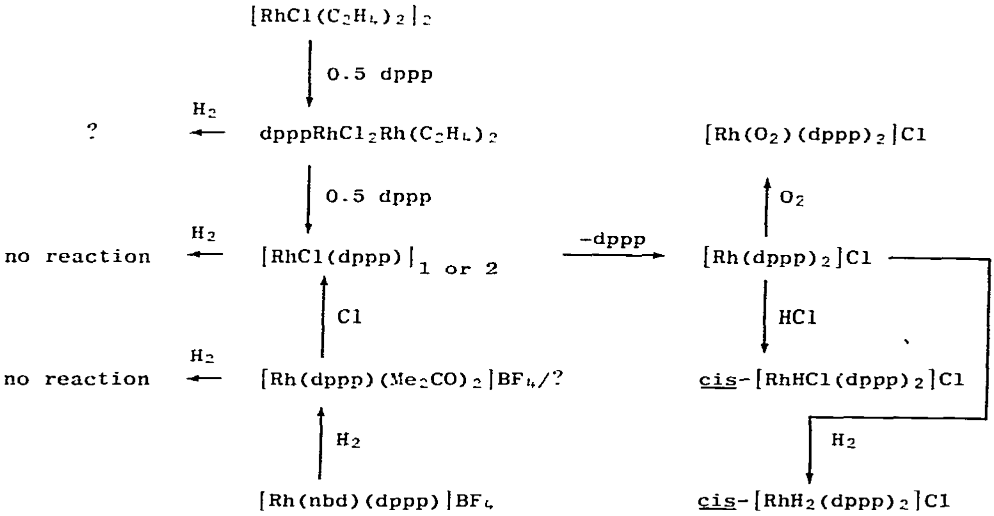
[367]



$$[Rh(diphos)]^+ + C{=}C \underset{}{\overset{fast}{\rightleftharpoons}} [Rh(diphos)(C{=}C)]^+$$

$$[Rh(diphos)(C{=}C)]^+ + H_2 \xrightarrow{r.d.s} Rh(diphos)^+ + H\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}H$$

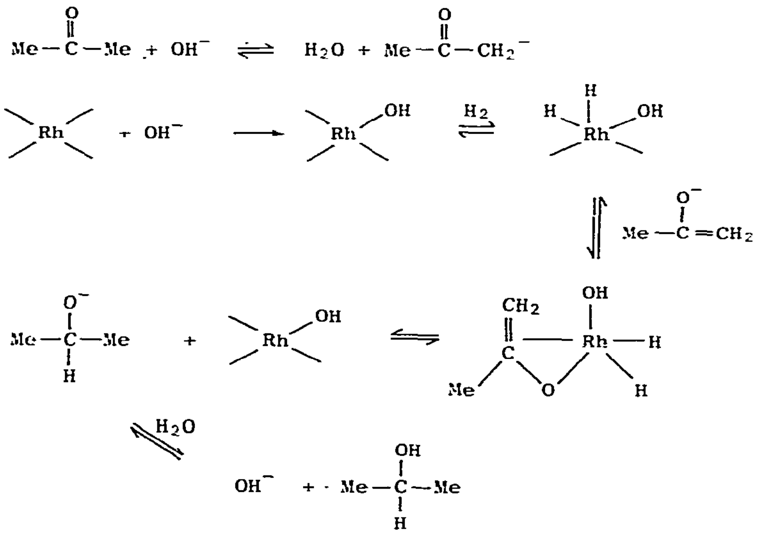
Scheme 56



Scheme 57

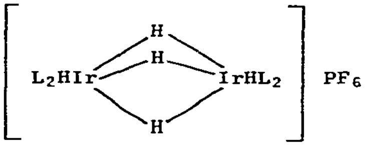
(ref. 500).

In addition to the above studies with chelating diphosphines a variety of other neutral and cationic rhodium(I) and iridium(I) compounds have been prepared and have been shown to be hydrogenation catalysts. These include [RhX(cod)]$_2$, (X = OCOPh, SPh), [Rh(S$_2$CNEt$_2$)(cod)], [RhCl(cod)L], (L = PBu$^n_3$, PPr$^i_3$, PCy$_3$, 2-picoline, imidazole), [Rh(OCOPh)(cod)(PPh$_3$)], [Rh(cod)(PBu$^n_3$)$_2$]PF$_6$, [Rh(cod)(imidazole)$_2$]PF$_6$, [Rh(cod)(PPh$_3$)(imidazole)]PF$_6$, [Rh(cod)(py)L]PF$_6$, (L = PPh$_3$, PPr$^i_3$, PCy$_3$) (ref. 501). The compounds [Rh(N—N)(diene)]X (N—N = 2,2′-dipyridyl, 1,10-phenanthroline, methyl substituted phenanthrolines; diene = hexa-1,5-diene; X = Cl, PF$_6$, BPh$_4$) are good catalysts for the hydrogenation of ketones in an alkaline medium at room temperature and atmospheric pressure. In the presence of an excess of the chelating nitrogen donor ligand they selectively catalyse the reduction of C=O in the presence of C=C bonds (ref. 502). In the presence of strong alkali the complexes [RhCl(cod)(PPh$_3$)] and [Rh$_2$H$_2$Cl$_2$(cod)(PPh$_3$)$_2$] readily promote the hydrogenation of acetone. However, a better homogeneous system can be obtained by treating the rhodium complexes with a stoichiometric amount of NaBH$_4$ in toluene and methanol and this system will reduce an aromatic ketone such as benzophenone. The hydrogenation of acetone has been interpreted in terms of the mechanism shown in Scheme 58 (ref. 503). The complexes [M(cod)L$_2$]ClO$_4$, (M = Rh, Ir; L = tertiary phosphine), in co-ordinating solvents such as acetone, ethanol, or tetrahydrofuran are known to be active hydrogenation catalysts for alkenes, the iridium complexes being less active. It has now been



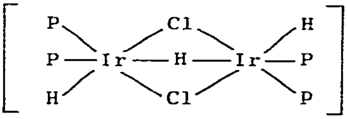
Scheme 58

found, however, that the use of non-co-ordinating solvents enhances the catalytic activity of these complexes. Thus in dichloromethane the complexes $[Ir(cod)L_2]PF_6$ and $[Ir(cod)L(py)]PF_6$, (L = tertiary phosphine) became very active homogeneous hydrogenation catalysts for alkenes, reducing even tri- and tetra-substituted alkenes. However, when the alkene has been consumed, or in some cases partly consumed the catalyst is irreversibly deactivated and when the catalysts are $[Ir(cod)L_2]PF_6$ the compounds [368], (L = $PPh_3$, $PMePh_2$) can be isolated. The compound



[368]

(368; L = $PPh_3$) has been the subject of a single crystal X-ray study but due to disorder in the crystal only atom positions of iridium, phosphorus and those carbons directly bonded to phosphorus could be located. A triple metal-metal bond has been previously assigned to this complex but it has now been suggested that the short iridium-iridium bond (2.52 Å) found for this compound results from the geometrical requirement of the $IrH_3Ir$ bridged system and that a three 3 centre, 2-electron bridge bonding system with no additional iridium-iridium bond is a better descriptio of the $IrH_3Ir$ unit. Treatment of (568; $L = PPh_3$) with hydrochloric acid gives [569]. The catalyst system from $[Ir(cod)L_2]PF_6$ gives the hydride compounds



[569]

$[IrH_5L_2]$ upon addition of triethylamine while that from $[Ir(cod)L(py)]PF_6$ gives $[IrH_5L_2]$ in the presence of L and triethylamine (ref. 504). Displacement of the labile acetone ligand from $[Rh(diene)(PPh_3)(acetone)]X$, (diene = cod, nbd; $X = PF_6$, $SbF_6$) by dialkyl or alkyl aryl sulphoxides gives the cations $[Rh(diene)(PPh_3)(sulphoxide)]^+$, (sulphoxide = dimethyl sulphoxide, tetramethylene sulphoxide, di-n-propyl sulphoxide, (S,S;S,R)-(+)-2-methylbutyl methyl sulphoxide, methyl phenyl sulphoxide, (R)-(-)-methyl-p-tolyl sulphoxide and (R)-t-butyl p-tolyl sulphoxide). Diaryl sulphoxide co-ordinate in solution but no solid compounds can be isolated. The sulphoxide compounds are all O-bonded and the infrared frequency shift of ν(SO) upon O-co-ordination is roughly proportional to the strength of the metal-oxygen bond (ref. 505).

The voltammetric behaviour of cationic complexes of the type $[M(diene)(N\text{-}N)]^+$, (M = Rh, Ir; N-N = 2,2′-dipyridyl; 1,10-phenanthroline; diene = cyclo-octa-1,5-diene, norbornadiene) and $[Rh(N\text{-}N)_2L]$, (L = fumaronitrile, acrylonitrile) have been studied in methyl cyanide. The reduction of these $d^8$ complexes proceeds in two one-electron steps, leading to $d^{10}$ anionic species according to Scheme 59. The $d^9$ species are

$$\underset{d^8}{M^I} \overset{e}{\rightleftharpoons} \underset{d^9}{M^0} \overset{e}{\rightleftharpoons} \underset{d^{10}}{M^{-1}}$$

Scheme 59

stable intermediates, the π-acceptor ligands stabilising the zerovalent metal. In contrast $d^8$ complexes with weaker π-acceptor ligands e.g. $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[MX(CO)L_2]$, (M = Rh, Ir; X = Cl, Br, I; L = tertiary phosphine) are reduced in a single two-electron step. All the complexes, with the exception of $[Rh(N\text{-}N)(cod)]^+$ undergo oxidation at the mercury electrode, the main products of the electro-oxidation being compounds which contain mercury-metal bonds, (Scheme 60) (ref. 506).

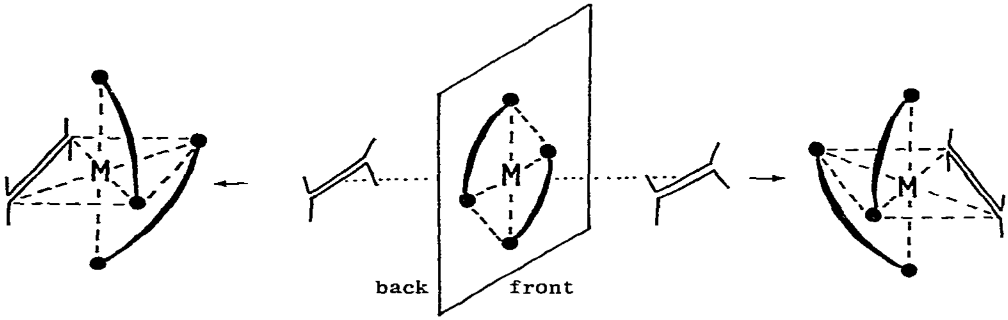
When an alkene or an alkyne add to a bis-chelated rhodium complex the metal centre is converted to a chiral species (Scheme 61). In addition, a pair of diastereomeric complexes is formed when a chiral chelate such as $2C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh$ is used.

$$Hg \longrightarrow Hg^{2+} + 2e$$

$$Hg^{2+} + n[M(N\text{-}N)_xL]^{+} \longrightarrow [Hg\{M(N\text{-}N)_xL\}_n]^{(n+2)+}$$

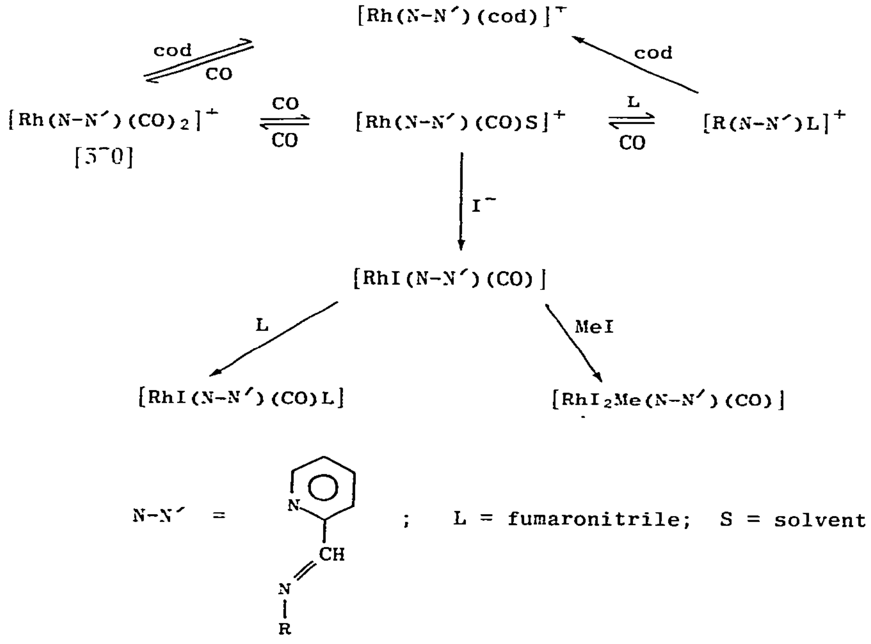
$n$ = 3 or 2 with $[Rh(bipy)_2(CHCN{=}CHCN)]^+$
$x$ = 1; L = nbd, cod
$x$ = 2; L = fumaronitrile, acrylonitrile

Scheme 60



Scheme 61

Complexes of this ligand type, e.g. $[Rh(2\text{-}C_5H_4NCH{=}NR)_2]ClO_4$, (R = (S)-CHMePh, $CH_2Ph$, $Bu^t$), have been prepared and their adducts with fumaronitrile, maleic anhydride and dimethyl fumarate have been prepared. A stereoselectivity is observed in the formation of the maleic anhydride adduct of $[Rh(2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh)_2]ClO_4$. One of the diastereomers of the maleic anhydride and dimethyl fumarate adducts have been isolated by fractional crystallisation. The rates of epimerisation of these adducts have been determined and the interconversions appear to occur via an $S_N1$ mechanism. This is in contrast to the alkene complexes of platinum(II) whose interconversion have been reported to take place via an $S_N2$ mechanism. The slower rate of epimerisation of the maleic anhydride adduct as compared to the rate found for the dimethyl fumarate adduct is considered to be a consequence of a stronger rhodium-alkene bond in the maleic anhydride adduct (ref. 307). Cationic cyclo-octa-1,5-diene and dicarbonyl compounds of rhodium(I) and iridium(I) containing Schiff bases of pyridine-2-aldehyde have also been reported and some reactions of these compounds are illustrated in Scheme 62. The 1,10-phenanthroline and 2,2′-dipyridyl dicarbonyl complexes, $[Rh(N\text{-}N)(CO)_2]^+$, analogous to [370] have been reported to form tricarbonyl compounds $[Rh(N\text{-}N)(CO)_3]^+$ on the basis of the appearance of an extra carbonyl band in the infrared spectrum of the dicarbonyl compounds. However, it has now been found



Scheme 62

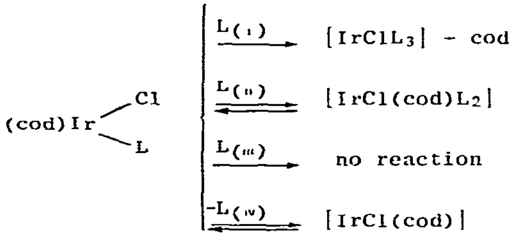
that this band, which also appears in the infrared spectrum of [570], is due to a reaction of the dicarbonyl with the NaCl infrared cell to give [RhCl(CO)(N-N)] (ref 508). In the solid state the compounds [IrX(cod)(phen)], (X = SCN, I), are pentaco-ordinate. The substitution reaction of these compounds with ethylenediamine (en)

$$[\mathrm{IrX(cod)(phen)}] \xrightarrow[\mathrm{en}]{\mathrm{MeOH}} [\mathrm{Ir(cod)en}]^+ + \mathrm{phen} + \mathrm{X}^-$$

has been shown to proceed via a dissociative mechanism but the reaction between [Ir(cod)(phen)]$^+$ and ethylenediamine shows the involvement of either a four- or five-co-ordinate intermediate [Ir(cod)(phen)en]$^+$ (ref. 509).

A high yield (90-95%) preparation of [IrCl(cod)]$_2$ has been described. This method is a two-step synthesis from $H_2IrCl_6$ and cyclo-octa-1,5-diene in refluxing isopropanol to give [IrHCl$_2$(cod)]$_2$ followed by removal of co-ordinated HCl with aqueous sodium acetate. In non-polar solvents, a wide variety of ligands L cleave the halide bridge of [IrCl(cod)]$_2$ to give the compounds [IrCl(cod)L]. The $^1$H and $^{13}$C n.m.r. spectra of a number of compounds [IrCl(cod)L] have been interpreted in terms of a *trans*-influence series $Cl^- <$ *sym*-collidine $<$ 2-picoline $<$ $PCy_3 <$ $PPr^i_3$

> $PEt_3$ > $AsPh_3$ > $PMe_2Ph$ > $PMePh_2$ > $PPh_3$ > $PPh_2(OMe)$ > $PClPh_2$ > $P(OPh)_3$ > $PCl_2Ph$. The compound $[IrCl(cod)AsPh_3]$ is known to dissociate $AsPh_3$ rapidly and reversibly on the $^1H$ n.m.r. time scale and the exchange reactions of a range of complexes $[IrCl(cod)L]$ have been examined. The results of these studies are summarised in Scheme 63.

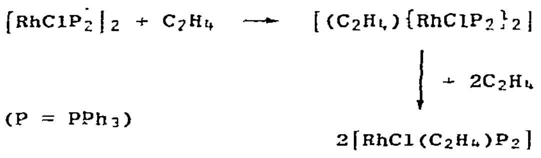


$L_{(i)}$ = $PCl_2Ph$, $P(OPh)_3$, $PClPh_2$, $P(OMe)Ph_2$
$L_{(ii)}$ = $PPh_3$, $PMePh_2$, $PMe_2Ph$, $PEt_3$
$L_{(iii)}$ = $PPr^i_3$, $PCy_3$, 2-picoline, sym-collidine
$L_{(iv)}$ = $AsPh_3$, pyridine

Scheme 63

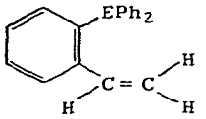
number of cationic complexes of the type $[Ir(cod)L_n]PF_6$ (n = 2; L = $PMePh_2$, $PEtPh_2$, $P(OMe)Ph_2$, $PPh_3$; n = 3; L = $P(OMe)_3$, $P(OEt)_3$, $PMe_2Ph$) have been prepared by the addition of L to $[IrCl(cod)]_2$. From further studies it appears that phosphorus ligands having a cone angle below 130° give a colourless $[Ir(cod)L_3]^+$ cation, e.g. $P(OMe)_3$, 118°; $P(OEt)_3$, 109°; $PMe_2Ph$, 127°; and above 130° a red $[Ir(cod)L_2]^+$ cation, e.g. $PBu^n_3$, 130°; $PMePh_2$, 136°; $PPh_3$, 145°. Very bulky ligands do not appear to form $[Ir(cod)L_2]^+$ cations and only the compounds $[IrCl(cod)L]$ are isolated e.g. $PPr^i_3$, 160°; $PCy_3$, 179°. An equimolar mixture of $[Ir(cod)(PPh_3)_2]PF_6$ and $[Ir(cod)(py)_2]PF_6$ in solution at room temperature rapidly gives $[Ir(cod)(PPh_3)(py)]$-$PF_6$ and a number of similar complexes can also be obtained (ref. 310). Kinetic studies on the oxidative-addition reaction of HCl in methanol to $[IrCl(cod)(PEtPh_2)]$ to give $[IrCl_2H(cod)(PEtPh_2)]$ reveal that this reaction occurs via initial nucleophilic attack of chloride at the iridium centre to give the intermediate $[IrCl_2(cod)(PEtPh_2)]^-$ followed by attack of $H^+$. This is an unusual and interesting result since it has generally been found that in oxidative addition reactions of this type electrophilic attack at the metal occurs first (ref. 311).

Kinetic studies on the addition of ethylene to $[RhCl(PPh_3)_2]_2$ reveal that the reaction proceeds in two successive steps (Scheme 64) (ref. 312). Kinetic studies on the hydrogenation of cyclohexene catalysed by $[RhCl(PPh_3)_3]$ have also been reported. There is an equilibrium constant of $3.4 \times 10^{-4}$ between $[RhH_2Cl(PPh_3)_3]$ and $[RhH_2Cl(PPh_3)(cyclohexene)]$. The rate determining step involves the migratory



Scheme 64

insertion of the co-ordinated cyclohexene into the rhodium-hydrogen bond (ref. 313) Studies on the co-ordinating properties of the ligands [371] and [372] reveal

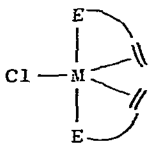


[371] spp, E = P

[372] spas, E = As

that both spp and spas promote five-co-ordination for rhodium(I) and iridium(I) far more readily than their more flexible aliphatic counterparts 3-butenyldiphenylphosphine (mbp) and 4-pentenyldiphenylphosphine (mpp). Thus although [RhCl(mbp)$_2$] is five-co-ordinate in the solid state and is four-co-ordinate in solution any four-co-ordinate compound of [RhCl(spp)$_2$], which might be involved in the fluxional behaviour of the spp compound, is not observed. Similarly, although the double bonds of [RhCl(mbp)$_2$] are saturated by dihydrogen this is not observed with [RhCl(spp)$_2$]. The five-co-ordinate rhodium(I) and iridium(I) compounds of spp and spas can be obtained by reactions of the ligands with [MCl(C$_8$H$_{14}$)$_2$]$_2$, (M = Rh, Ir) and the resulting compounds are considered to have the structures [373] and [374].

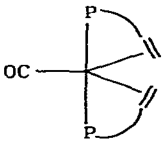
= [371] or [372]



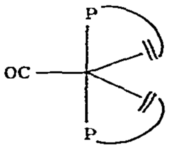
M = Rh; [373]

M = Ir; [374]

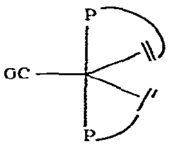
Cationic complexes [ML(spp)$_2$]$^+$ and [ML(spas)$_2$]$^+$ can be obtained by the action of AgBF$_4$, NH$_4$PF$_6$, or NaBPh$_4$ on [373] or [374] in the presence of the ligand L, (M = Rh, L = CO, PF$_3$, C$_2$H$_4$, PPh$_3$, PMePh$_2$; M = Ir, L = CO, PF$_3$, PMePh$_2$, pyridine). These cationic derivatives have similar five-co-ordinate geometries to [373] but the $^1$H and $^{31}$P n.m.r. spectra show that many of the complexes contain two isomers, a symmetric isomer having equivalent vinyl groups, and an unsymmetrical isomer having inequivalent vinyl groups. There are, in fact, three conceivable isomers for these compounds due to the different possible mutual orientations of the vinyl groups, i.e. head-to-head [575], tail-to-tail [576], and head-to-tail [577]. The isomers can



[575]

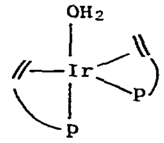


[576]

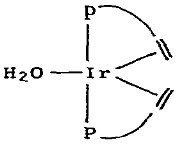


[577]

interconvert if one of the double bonds dissociates from the co-ordination sphere and the observation that the rhodium(I) isomers interconvert more rapidly on the n.m.r. time scale than the iridium isomers is in line with the general tendency of these <u>d</u>$^8$ metals to increase their co-ordination number from four to five, i.e. Ir(I) ≫ Rh(I). The ethylene complexes $[Rh(C_2H_4)(spp)_2]^+$ and $[Rh(C_2H_4)(spas)_2]^+$ undergo rapid intermolecular exchange with free ethylene at room temperature. Treatment of $[RhCl(spp)_2]$ with $AgBF_4$ or $NaBPh_4$ gives the planar cation $[Rh(spp)_2]^+$ which contains varying amounts of <u>cis</u>- and <u>trans</u>-isomers, depending on the solvent. Attempts to obtain the corresponding planar iridium cation $[Ir(spp)_2]^+$ have only met with limited success since this species has a very high affinity for water and other ligands. The aquo adduct is formed as a mixture of two isomers considered to have the structures [578] and [579]. Ammonia forms similar adducts (ref. 514). In

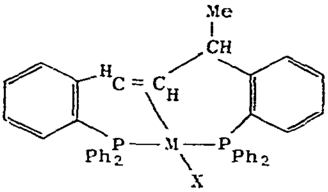


[578]



[579]

contrast to the reaction of [571] with $[RhCl(C_8H_{14})_2]_2$, which gives the five-co-ordinate compound (573; E = P), the reaction of the phosphine spp [571] with hydrated rhodium(III) chloride in refluxing 2-methoxymethanol leads to a coupling reaction of the ligand, via a mechanism analogous to the rhodium(III) chloride catalysed dimerization of ethylene to but-1-ene, to give the planar chlororhodium(I) compound [580]. The corresponding bromo compound [581] can be similarly prepared starting from rhodium(III) bromide. Treatment of the compound [580] with sodium cyanide in aqueous 2-methoxyethanol liberates the bidentate phosphine ligand, 1-bdpb and reaction of this ligand with $[IrCl(cod)]_2$ gives the air-sensitive complex [582].



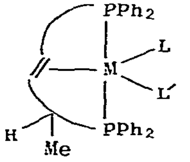
[580]; X = Cl, M = Rh

[581]; X = Br, M = Rh

[582]; X = Cl, M = Ir

[583]; X = CO, M = Rh$^+$

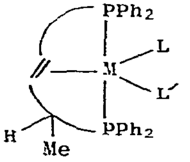
The n.m.r. spectra of [580], [581], and [582] show the presence of two isomers in solution. The isomers of [580] interconvert rapidly on the n.m.r. time scale in solution above 122°C ($\Delta G^{\ddagger}$ = 20.5 kcal mol$^{-1}$). The process is slower for the corresponding iridium complex even at 122°C ($\Delta G^{\ddagger} > 20.5$ kcal mol$^{-1}$) and the process is considered to be associated with a conformational change of the ligand leading to net rotation of the co-ordinated double bond from a position in which it is perpendicular with the $MP_2Cl$ co-ordination plane into an orientation approximately parallel with the $MP_2Cl$ co-ordination plane. The rhodium and iridium compounds [580] and [581] react with carbon monoxide to give five-co-ordinate adducts [584] and [585] and an ethylene adduct [586] can be obtained from the iridium compound [582]. These five-co-ordinate adducts also exhibit temperature-dependent n.m.r. spectra which are caused by intermolecular exchange of carbon monoxide or ethylene between the isomers [584a]-[584b], [585a]-[585b], or [586a]-[586b]. The five-co-ordinate carbonyl compounds [584] and [585] react with hydrogen chloride to give the chelate 2-butyl compounds [587] and [588] respectively, the addition being reversible in the case of rhodium. In the absence of other ligands [RhCl(1-bdpb)]



[584a]

[585a]

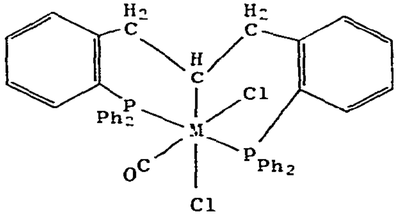
[586a]



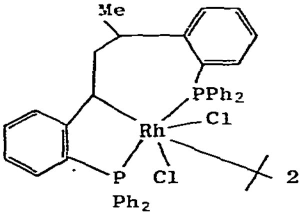
[584b], M = Rh, L = CO, L′ = Cl

[585b], M = Ir, L = CO, L′ = Cl

[586b], M = Ir, L = $C_2H_4$, L′ = Cl

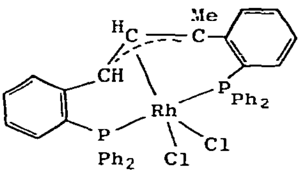


[387; M = Rh]
[388; M = Ir]

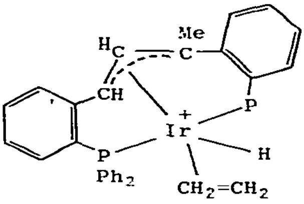


[389]

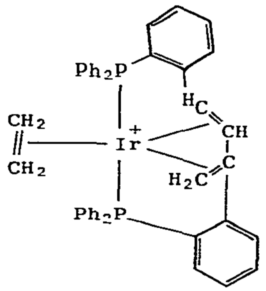
[380] adds hydrogen chloride slowly to give a 1:1 mixture of the chlorine bridged dimer [389] and the compound [$RhCl_3$(1-bdpb)]. However, the presence of triphenylphosphine in this reaction promotes protonation of the double bond the product being exclusively [389]. In the absence of auxiliary ligands the four-co-ordinate iridium(I) compound [382] undergoes irreversible oxidative-addition at the iridium atom with chlorine and hydrogen chloride and reversible oxidative-addition with dihydrogen to give the chelate alkene complexes of iridium(III), [$IrCl_3$(1-bdpb)], [$IrHCl_2$(1-bdpb)] and [$IrH_2Cl$(1-bdpb)] respectively. Each isomer of [382] gives rise to one corresponding isomer in the case of [$IrCl_3$(1-bdpb)] and to two corresponding isomers in the cases of the iridium hydride compounds. The octahedral rhodium(III) compound [$RhCl_3$(1-bdpb)] loses hydrogen chloride irreversibly in solution to give the $\eta^3$-allyl compound [390]. Five-co-ordinate dicarbonyl cations [$M(CO)_2$(1-bdpb)]$^+$ can be isolated as tetrafluoroborate salts but analogous ethylene compounds cannot be obtained. In reactions with iridium, the tertiary C-H bond of co-ordinated 1-bdpb oxidatively adds to the metal atom to give the $\eta^3$-allyl hydrido-ethylene compound [391] and a minor by-product [392]. The cation [391] contains ethylene cis to hydride and its stability and reluctance to undergo migratory insertion is probably a consequence of the high stability of octahedral iridium(III) (ref. 315).



[590]

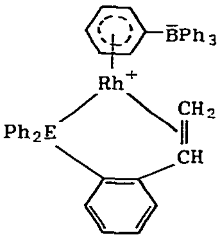


[591]



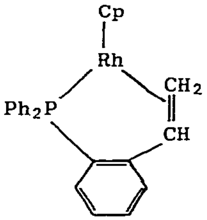
[592]

The tetraphenylborate salts of the square planar rhodium(I) cations, $[Rh(spp)_2]^+$ and $[Rh(spas)_2]^+$ absorb one mole of dihydrogen per mole of complex forming the $\eta^6$-tetraphenylborate complexes [593] and [594]. The cyclopentadienyl compound [595]



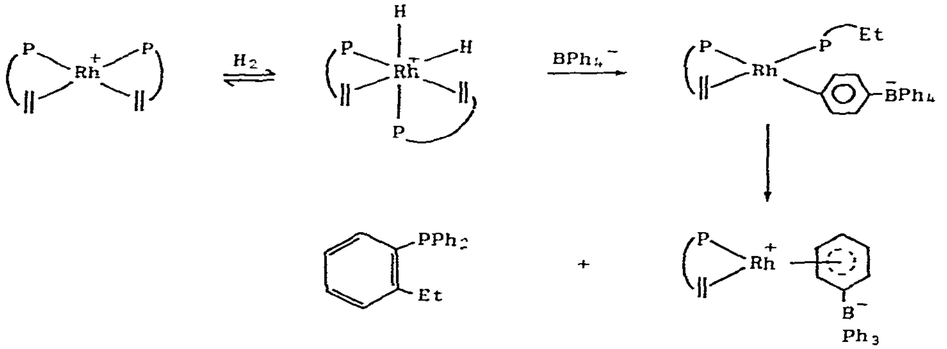
[593], E = P

[594], E = As



[595]

has also been prepared. A proposed mechanism for the formation of [593] is outlined in Scheme 65. The report that hydrogenation of $[Rh(spp)_2]BPh_4$ affords $[Rh(\eta^6\text{-}C_6H_5BPh_3)(\underline{o}\text{-}C_2H_5C_6H_4PPh_2)_2]$ has not been confirmed (ref. 316). However, the complexes $[RhCl(CO)[PPh_2\{(CH_2)_nCH{=}CH_2\}]_2]$ and $[RhCl(CO)\{PPh_2(CH_2CH_2CH\overset{c}{=}CHMe)\}_2]$ add



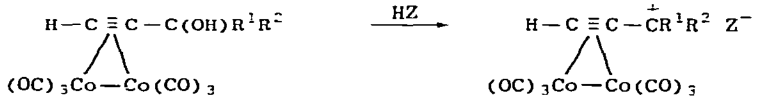
Scheme 65

hydrogen in methanol solution saturating the double bonds to give $[RhCl(CO)[PPh_2\{(CH_2)_{n+1}Me\}]_2]$, (n = 0-3). Carbon monoxide inhibits the reaction and the reaction does not proceed in non-protic solvents. The rate of reaction depends mainly on steric factors and follows the order $[RhCl(CO)\{PPh_2(CH_2CH_2CH{=}CH_2\}_2]$ > $[RhCl(CO)\{PPh_2(CH_2CH_2CH\overset{c}{=}CHMe)\}_2]$ ~ $[RhCl(CO)\{PPh_2(CH_2CH_2CH_2CH{=}CH_2)\}_2]$ > $[RhCl(CO)\{PPh_2(CH_2CH{=}CH_2)\}_2]$ > $[RhCl(CO)\{PPh_2(CH{=}CH_2)\}_2]$ (ref. 317).

### Metal alkyne compounds

The reactions of the dihaloalkynes $XC{\equiv}CX$, (X = Cl, Br, I) with dicobaltoctacarbonyl afford the alkyne cobalt compounds $[Co_2(C_2X_2)(CO)_6]$. Treatment of the iodo compound with the donor ligands L, ($L = PBu^n_3$, $SbEt_3$, $PPh_3$, $AsEt_3$) gives the monosubstituted compounds $[Co_2(C_2I_2)(CO)_5L]$ while reaction of $[Co_2(C_2I_2)(CO)_6]$ with either $[Co_2(CO)_8]$ or $Na[Co(CO)_4]$ gives $[Co_3(CO)_9C]_2$ (ref. 318). The $^1H$ and $^{13}C$ n.m.r. spectra of the alkyne complexes $[Co_2(RC_2R')(CO)_6]$ exhibit downfield shifts of the ligand resonances upon complexation but upfield shifts are observed for the alkyne carbons when one carbonyl ligand is replaced by a tertiary-phosphine or -arsine ligand. Variable temperature $^{13}C$ n.m.r. spectral studies reveal that the carbonyls are rapidly interchanging (ref. 319). The Raman spectra of cobalt carbonyl alkyne compounds $[Co_2(C_2R_2)(CO)_6]$ have been interpreted (ref. 320).

The enhanced stability of carbonium ions adjacent to organotransition metal moieties has been demonstrated in a number of systems. Stable carbonium ion salts of the type [396] have now been isolated by treatment of the corresponding alcohol complexes with $HF.SbF_5$ or $HBF_4.Et_2O$ at -45°C. Extensive charge delocalisation onto the $Co_2(CO)_6$ group present in the cations occurs since there is an increase in $\nu(CO)$ values and the $^1H$ n.m.r. spectra of the cations exhibit very small downfield shifts relative to the alcohol precursors. The $pK_{R+}$ values for the cations are essentially the same regardless of the other substituents at the carbonium ion centre and are



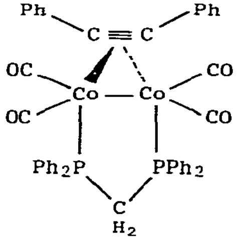
$R^1 = R^2 = Me$
$R^1 = R^2 = Ph$
$R^1 = Me,\ R^2 = H$
$R^1 = R^2 = H$

$(Z = BF_4,\ SbF_6)$

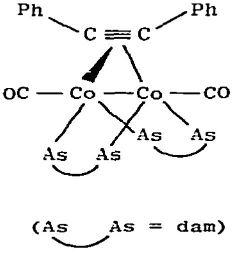
[596]

approximately equal to that of the triphenylmethyl carbonium ion (ref. 321).

One or two carbonyl ligands can be readily displaced from compounds of the type $[Co_2(alkyne)(CO)_6]$ by a range of ligands. However, further displacement of carbon monoxide is only usually achieved by ligands which have good π-acceptor properties. Thus phosphites or trifluorophosphine can replace a maximum of four carbonyl groups. Studies on the reaction of the ligands $Ph_2PCH_2PPh_2$ (dpm) and $Ph_2AsCH_2AsPh_2$ (dam) with $[Co_2(PhC{\equiv}CPh)(CO)_6]$ have resulted in the isolation of both 1:1 and 1:2 complexes, $[Co_2(PhC{\equiv}CPh)(CO)_4(L\text{-}L)]$ and $[Co_2(PhC{\equiv}CPh)(CO)_2(L\text{-}L)_2]$, (L-L dpm or dam). The crystal structures of [597] and [598] have been reported (ref. 322).

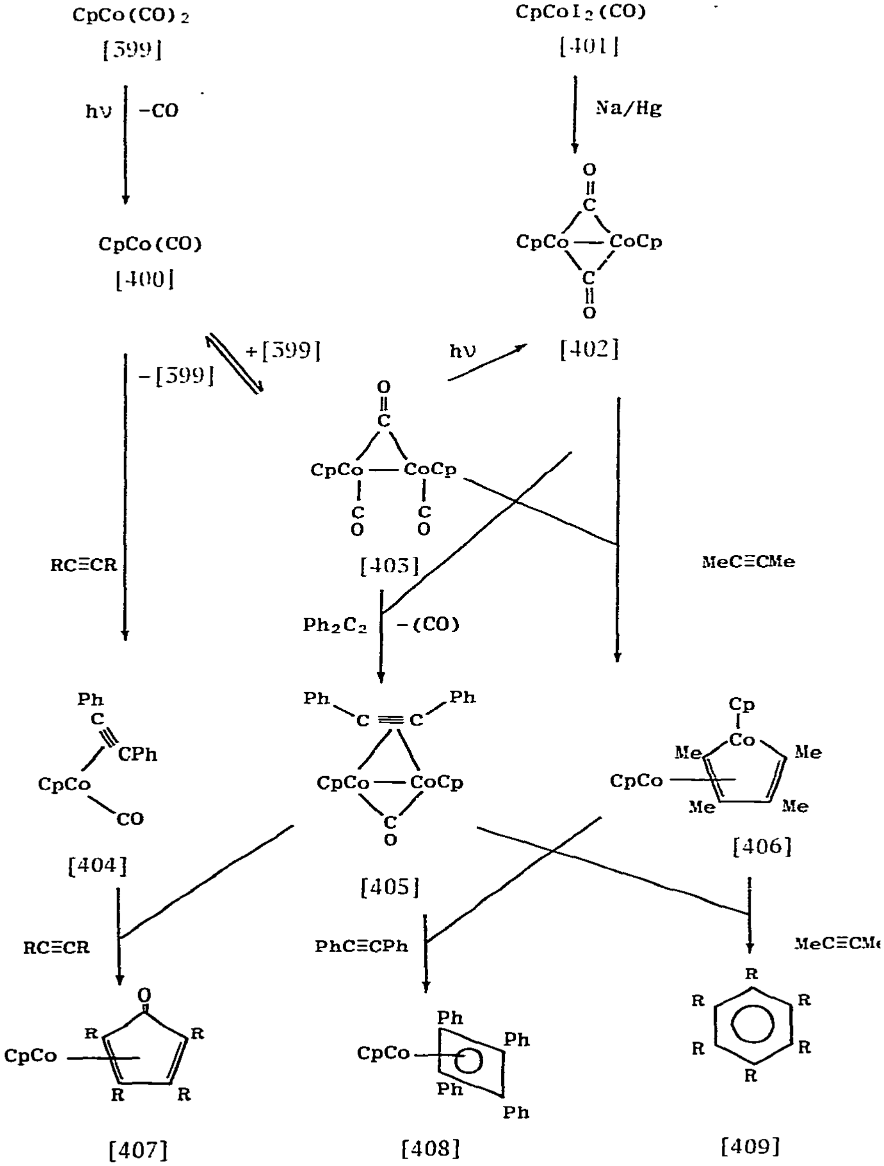


[597]



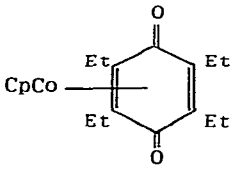
[598]

The reactions of various alkynes with $[CoCp(CO)_2]$ are known to give a large number of products depending on the reaction conditions and on the alkyne derivatives involved. Detailed studies on the photochemical and thermal reaction sequences, through which alkynes are transformed by $[CoCp(CO)_2]$ into cyclobutadiene and cyclopentadienone complexes and hexasubstituted benzenes, have been carried out and the results are summarised in Scheme 66. A primary intermediate identified by its i.r. spectrum in low-temperature photochemical reactions of [399] with diphenyl alkynes $RC{\equiv}CR$ is the mixed mononuclear species [404]. At room temperature this species is converted by excess alkyne into [407]. The important binuclear intermediate [405] has been isolated in this study and in the presence of excess alkyne this compound is converted thermally either to the cyclobutadiene complex

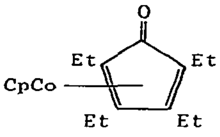

CpCo(CO)2
[399]
hν
-CO
CpCo(CO)
[400]
CpCoI2(CO)
[401]
Na/Hg
O
C
CpCo
CoCp
C
O
[402]
hν
-[399]
+[399]
O
C
CpCo
CoCp
C
O
C
O
[403]
Ph2C2
-(CO)
RC≡CR
MeC≡CMe
Ph
C
CPh
CpCo
CO
[404]
Ph
C
C
Ph
CpCo
CoCp
C
O
[405]
Cp
Co
Me
Me
Me
Me
CpCo
[406]
RC≡CR
PhC≡CPh
MeC≡CMe
O
R
R
R
R
CpCo
[407]
Ph
Ph
Ph
Ph
CpCo
[408]
R
R
R
R
R
R
[409]

Scheme 66

[408] or to the cyclopentadienone complex [407], depending on the partial pressure of carbon monoxide in the reaction system. The compound [405] also forms a catalys for the cyclotrimerisation of excess but-2-yne. The fluxional metallacycle [406] is a true catalyst for alkyne cyclotrimerisation (ref. 523). Thermal reactions of hex-3-yne with $[CoCp(CO)_2]$ at 100-150°C give the *p*-benzoquinone complex [410] and the cyclopentadienone complex [411]. The thermal reactions of hex-3-yne with

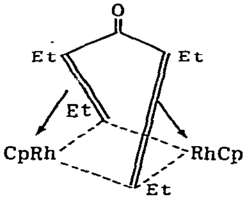


[410]



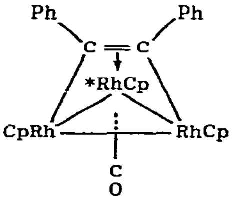
[411]

$[RhCp(CO)_2]$ give a rhodium cyclopentadienone complex analogous to [411] and a binuclear complex [412] (ref. 524). The characterisation of the complex [412] is

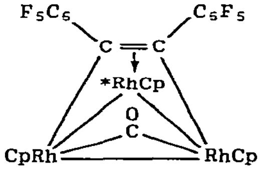


[412]

strongly supported by an X-ray determination of the structure of the closely related complex $[Cp_2Rh_2(Me_2C_2Me)(CF_3C_2CF_3)CO]$ (ref. 525). The structures of two compounds [413] and [414], isolated from the reactions of $[RhCp(CO)_2]$ with the

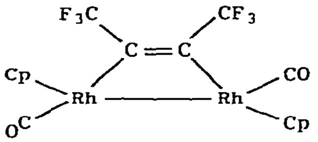


[413]

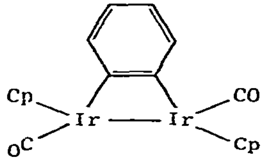


[414]

appropriate alkyne, have been determined by X-ray structural studies. The differences observed in the positioning of the bridging carbonyl ligand in these two compounds is a consequence of the differing σ-donor and π-acceptor interaction of the alkyne ligand with $Rh^*$ in competition with the relative π-acceptor ability of the carbonyl as a triply bridging ligand in its interaction with $Rh^*$ (ref. 326). The crystal structure of [415], isolated from the reaction of hexafluorobut-2-yne with [$RhCp(CO)_2$], has also been reported (ref. 327). An iridium compound [416]

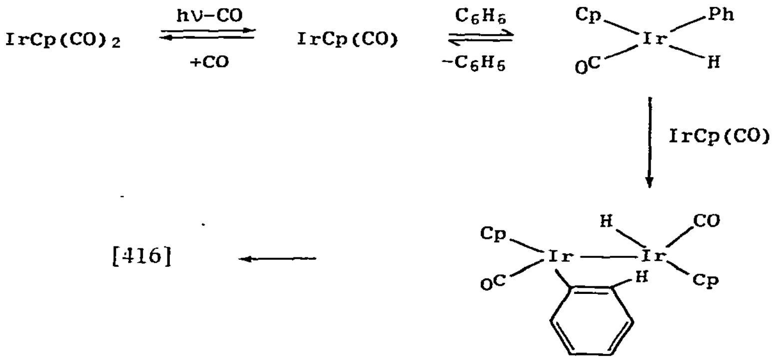


[415]



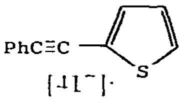
[416]

which is related to [415] has been isolated in low yield during a study of the reaction of [$IrCp(CO)_2$] with photo-2-pyrone in benzene solution. Subsequent studies have shown that [416] can also be isolated in low yield from the photolysis of [$IrCp(CO)_2$] in benzene. A mechanism for the formation of [416], which involves an initial oxidative-addition of benzene to iridium, is outlined in Scheme 67 (ref.

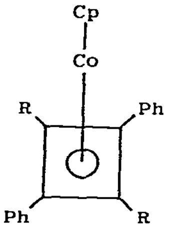


Scheme 67

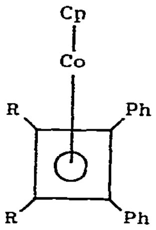
328). The reaction of [417] with [$CoCp(CO)_2$] gives mainly the substituted cyclobutadiene complex [418] together with lesser amounts of a cyclotrimerisation product, triphenyltri-2-thienylbenzene and three isomeric cyclopentadienone cobalt complexes. Attempts to determine the position of the groups in the cyclobutadiene ring of [418] by an X-ray study have not been successful since there is disorder of these groups in the crystalline lattice. The compound is probably a mixture of [418a] and [418b]. A minor by-product [419] has also been isolated from the reactio



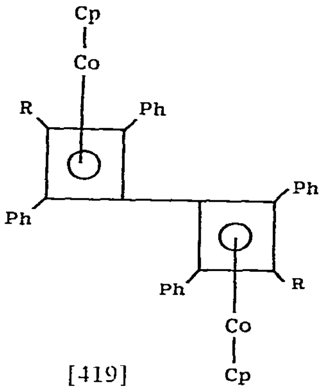
[417].



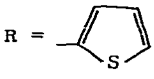
[418a]



[418b]

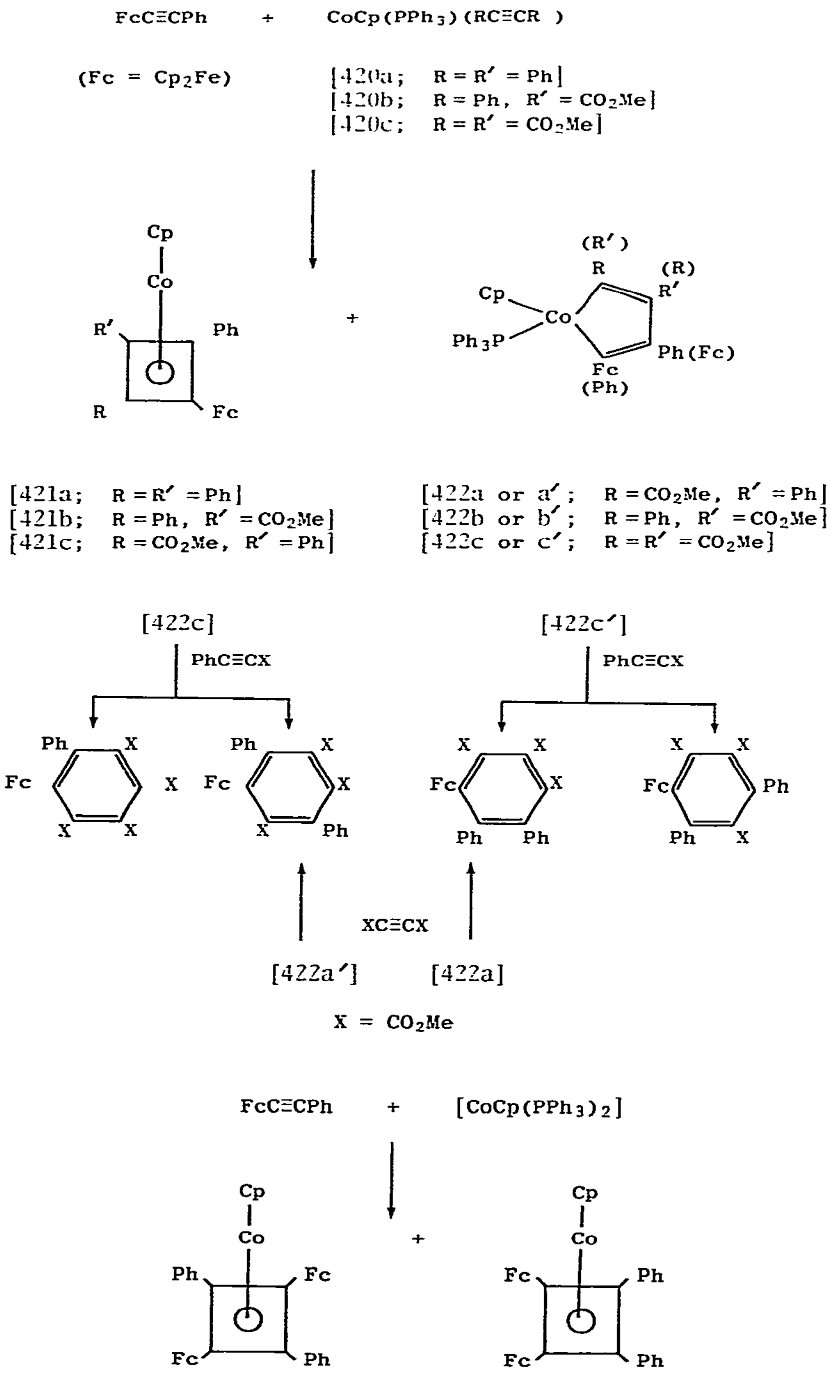


[419]

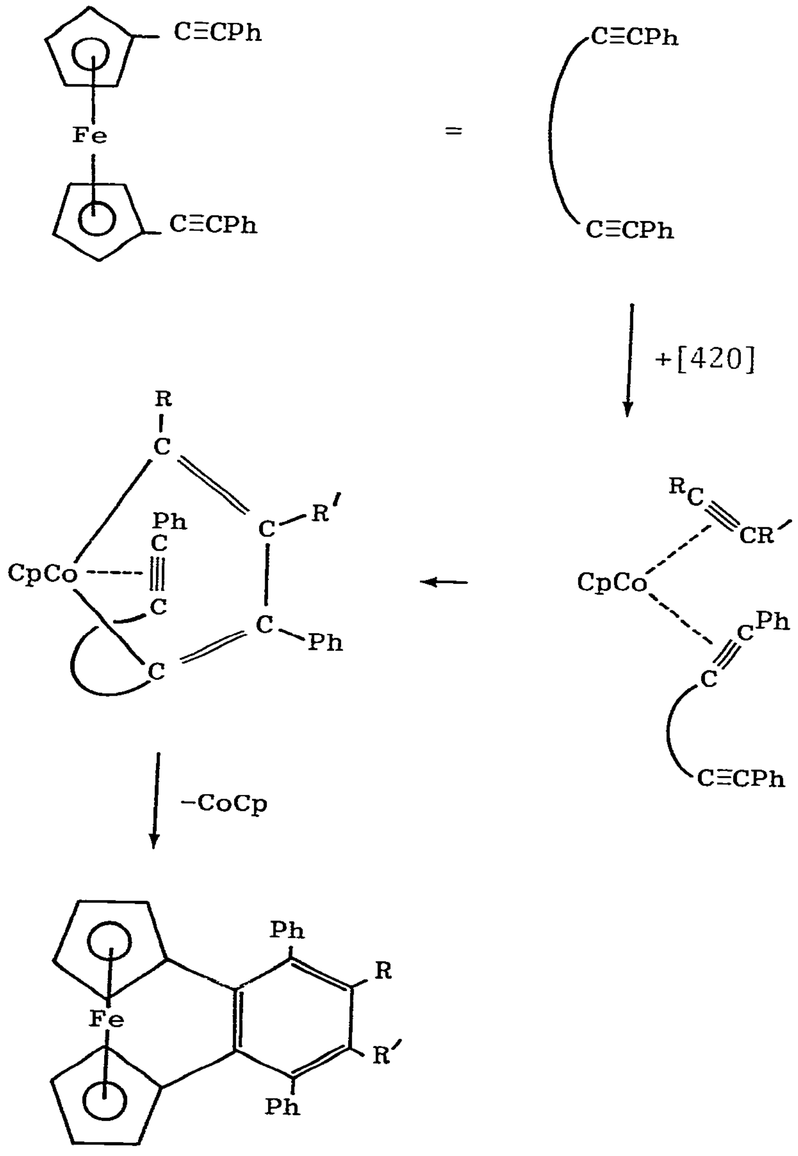


and has been identified by X-ray studies (ref. 529). Some ferrocene substituted cyclopentadienone- and cyclobutadiene-cobalt complexes have been isolated by the reaction of mono-(phenylethynyl)ferrocenes with [CoCp(PPh$_3$)(RC≡CR′)] [420] or [CoCp(PPh$_3$)$_2$], and the results of these studies are summarised in Scheme 68. Reactions of bis-(phenylethynyl)ferrocenes with [420] give ferrocene derivatives [421] bridged with o-phenylene groups (Scheme 69) (ref. 530).

A new synthesis of substituted benzocyclobutenes, indans, tetralins and anthraquinones has been described which utilises the catalytic ability of [CoCp(CO)$_2$] to co-oligomerise α,ω-diynes with substituted monoalkenes. Using this cobalt compoun a steroid synthesis and a catalytic one-step synthesis of annelated pyridines have been developed and the various reactions are outlined in Scheme 70. Quinoid

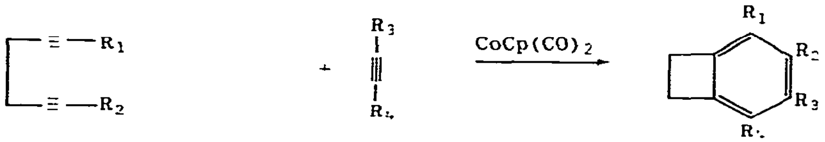

FcC≡CPh + CoCp(PPh3)(RC≡CR )
(Fc = Cp2Fe)
[420a; R = R′ = Ph]
[420b; R = Ph, R′ = CO2Me]
[420c; R = R′ = CO2Me]
Cp
Co
R′
Ph
R
Fc
+
(R′)
R
(R)
R′
Cp
Co
Ph3P
Ph(Fc)
Fc
(Ph)
[421a; R = R′ = Ph]
[421b; R = Ph, R′ = CO2Me]
[421c; R = CO2Me, R′ = Ph]
[422a or a′; R = CO2Me, R′ = Ph]
[422b or b′; R = Ph, R′ = CO2Me]
[422c or c′; R = R′ = CO2Me]
[422c]
PhC≡CX
[422c′]
PhC≡CX
Ph
X
Fc
X
X
X
Ph
X
Fc
X
X
Ph
X
X
Fc
X
Ph
Ph
X
X
Fc
Ph
Ph
X
XC≡CX
[422a′]
[422a]
X = CO2Me
FcC≡CPh + [CoCp(PPh3)2]
Cp
Co
Ph
Fc
Fc
Ph
+
Cp
Co
Fc
Ph
Fc
Ph

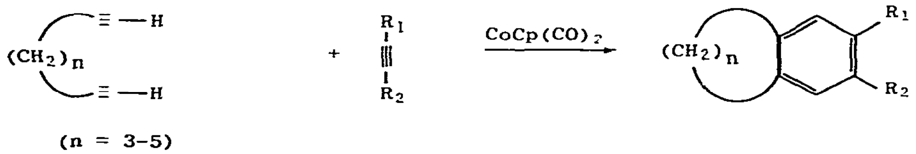
Scheme 68

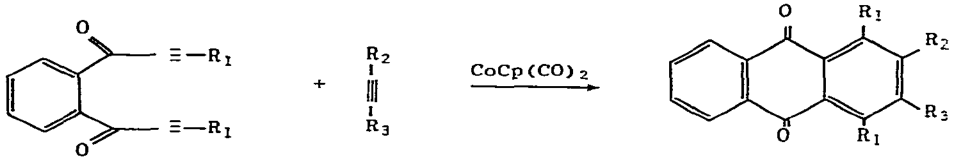


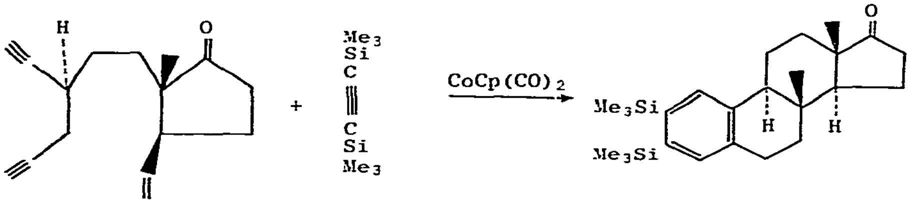
[421]

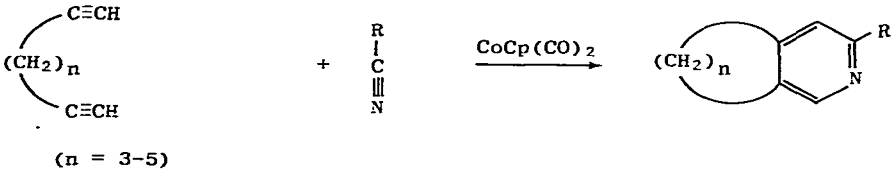
Scheme 69

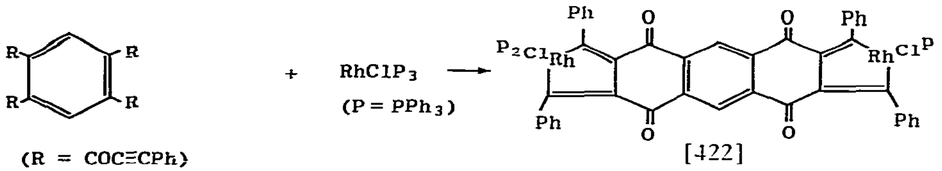

R1
R2
R3
R4
CoCp(CO)2

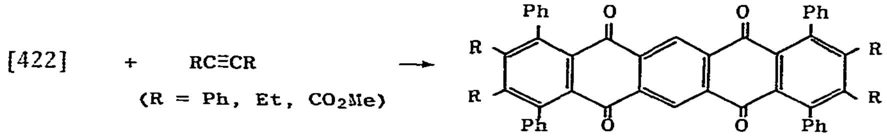

(CH2)n
H
R1
R2
CoCp(CO)2
(n = 3-5)

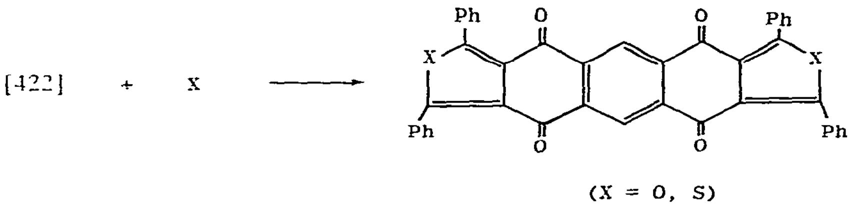

O
R1
R2
R3
CoCp(CO)2


H
O
Me3Si
C
CoCp(CO)2
Me3Si
H


C≡CH
(CH2)n
R
C
N
CoCp(CO)2
(n = 3-5)


R
(R = COC≡CPh)
RhClP3
(P = PPh3)
Ph
O
P2ClRh
RhClP
[422]

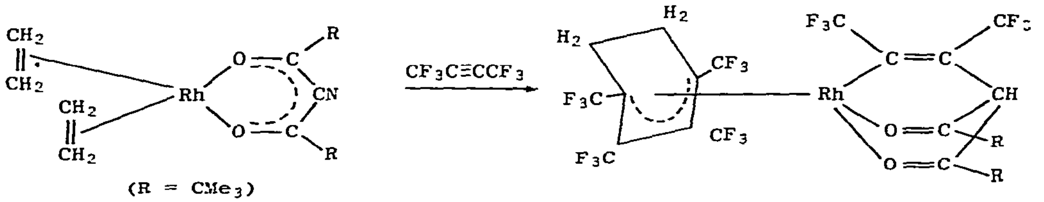

[422]
RC≡CR
(R = Ph, Et, CO2Me)
Ph
O
R



Scheme 70

derivatives have also been obtained using $[RhCl(PPh_3)_3]$ (Scheme 70) (refs. 331, 332, 333, 334). These novel syntheses have prompted a study of the reactions of the diynes $MeC{\equiv}C(CH_2)_nC{\equiv}CMe$, (n = 2-4) with $[CoCp(CO)_2]$. A p-benzoquinone complex $[CoCp\{C_8H_{10}(CO)_2\}]$ and three isomers of the cyclopentadienone complex $[CoCp\{(C_8H_{10})_2CO\}]$ are formed in the reaction of octa-2,6-diyne with $[CoCp(CO)_2]$. The corresponding reactions with nona-2,7-diyne and deca-2,8-diyne give complexes $[CoCp\{(C_9H_{12})CO\}]$ and $[CoCp\{(C_{10}H_{14})CO\}]$ in which a bicyclic cyclopentadienone has been formed by intramolecular condensation of the diyne (ref. 335).

Cyclocotrimerisation reactions of two alkynes and one alkene are observed in reactions of alkynes with bis-alkene complexes of rhodium(I). Thus hexafluorobut-2-yne reacts with [423] to give the substituted cyclohexadiene compound [424].

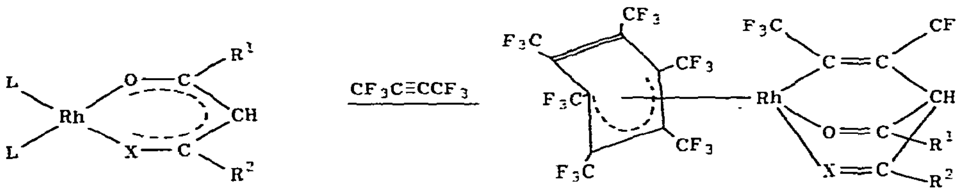


[423]

[424]

However, the reactions of the related compounds [425] with excess hexafluorobut-2-yne give the hexakistrifluoromethylbenzene compounds [426] (ref. 336). Cyclohexadiene compounds [427], [428] and [429] have also been shown to result from the reactions of $Bu^tC{\equiv}CH$ with $[Rh(\eta^5\text{-indenyl})(C_2H_4)_2]$, $Bu^tC{\equiv}CH$ with $[Rh(\eta^5\text{-indenyl})(CH_2{=}CHCN)_2]$, and hexafluorobut-2-yne with $[Rh(\eta^5\text{-indenyl})(isoprene)]$. The structure of [429] has been determined by an X-ray study. The formation of these cyclohexadiene complexes would appear to proceed via a mechanism in which the incorporated alkene remains co-ordinated to the metal throughout the reaction (Scheme 71) (ref. 337).

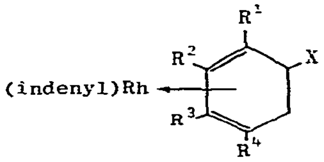
Treatment of the hydrides $[MH(CO)(PPh_3)_3]$ with stoichiometric amounts of diphenylacetylene afford the alkenyl compounds [430] which have a trans-arrangement of



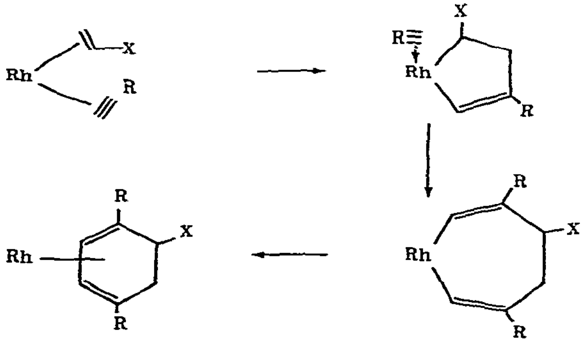
[426]

$L_2$ = cod; X = O; $R^1 = R^2$ = Ph
$L_2$ = cod; X = O; $R^1$ = Me, $R^2$ = NHPh
$L_2$ = nbd; X = O; $R^1$ = Me, $R^2$ = NHPh
L = $C_2H_4$; X = O; $R^1$ = Me, $R^2$ = NHPh
$L_2$ = cod; X = NH; $R^1$ = Me, $R^2$ = Me
$L_2$ = nbd; X = NH; $R^1$ = Me, $R^2$ = Me
L = $C_2H_4$; X = NH; $R^1$ = Me, $R^2$ = Me

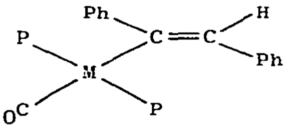
[425]



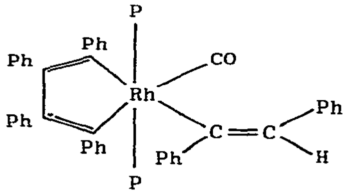
[427; X = H; $R^1 = R^4 = Bu^t$, $R^2 = R^3$ = H]
[428; X = CN; $R^1 = R^4 = Bu^t$, $R^2 = R^3$ = H]
[429; X = C(Me)=$CH_2$; $R^1 = R^2 = R^3 = R^4 = CF_3$]



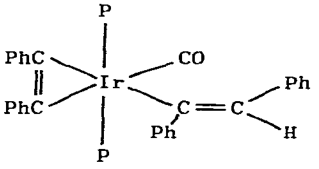
Scheme 71



[430]



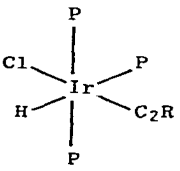
[431]



[432]

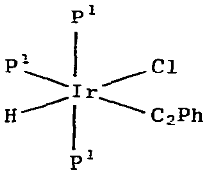
(P = $PPh_3$)

phenyl groups about the double bond. In the presence of an excess of diphenylacetylene the compounds [431] and [432] can be isolated (ref. 538). Alk-1-ynes $RC_2H$, (R = Ph, $CO_2Me$, H, Pr, Bu or $CH_2CH_2OH$) react rapidly and irreversibly with $[IrCl(PPh_3)_3]$ to give six-co-ordinate acetylide complexes of iridium(III) having the configuration [433]. However, the first isolated product in the reaction of PhC≡CH with $[IrCl(PMePh_2)_3]$ has the configuration [434] which rapidly isomerises to configuration [433]. It seems likely that the thermodynamically more stable isomers [433] result from the initial formation of compounds with configuration [434]. Since in both the compounds [433] and [434] the hydride and acetylide ligands are mutually *cis*, the oxidation addition of alk-1-ynes to $[IrClL_3]$ complexes proceeds in a *cis*, concerted manner probably via an intermediate π-complex analogous to the complex $[IrCl(PhC_2Ph)(PPh_3)_2]$ which can be isolated from the reaction of diphenylacetylene with $[IrCl(PPh_3)_3]$. The reaction of $[IrCl(PPh_3)_3]$ with $MeO_2CC{\equiv}CCO_2Me$



(P = $PPh_3$)

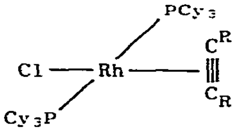
[433]



($P^1$ = $PMePh_2$)

[434]

gives the iridiacyclopentadiene complex $[IrCl(MeO_2CC_2CO_2Me)_2(PPh_3)_2]$. Carbonylation of the acetylides $[IrHCl(C_2R)(PPh_3)_2]$ give $[IrHCl(C_2R)(CO)(PPh_3)_2]$, which can be isolated only when R = H, Ph or $CO_2Me$; when R = Pr, Bu, or $CH_2CH_2OH$, the complexes immediately decompose to trans-$[IrCl(CO)(PPh_3)_2]$ and the alkyne (ref. 339). The alkyne compounds [455] have been prepared by the reactions of RC≡CR with $[RhCl(PCy_3)_2]$, (ref. 287), and addition of $MeO_2CC{\equiv}CCO_2Me$ to $[Rh(2\text{-}C_5H_4N.CH{=}NR)_2]ClO_4$,

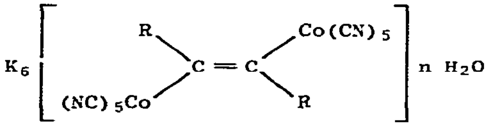


(R = H, Et, or Ph)

[455]

(R = (S)-CHMePh, $CH_2Ph$, $Bu^t$) yields two diastereomeric complexes (ref. 307).

The integrated molar absorption coefficients of the C≡C stretching vibration of alkynes co-ordinated to rhodium(I) have been measured. The order of decreasing acceptor and increasing donor interaction strength is: hexafluorobut-2-yne → diphenylacetylene → hex-3-yne. It is also found that rhodium(I) is a better back-bonding metal with $PCy_3$ than with the less basic $PPh_3$ as a ligand. Iridium(I) is also a better backbonding metal than rhodium(I) (ref. 340). The Raman and i.r. spectra of the compounds [456] have been recorded (ref. 341).



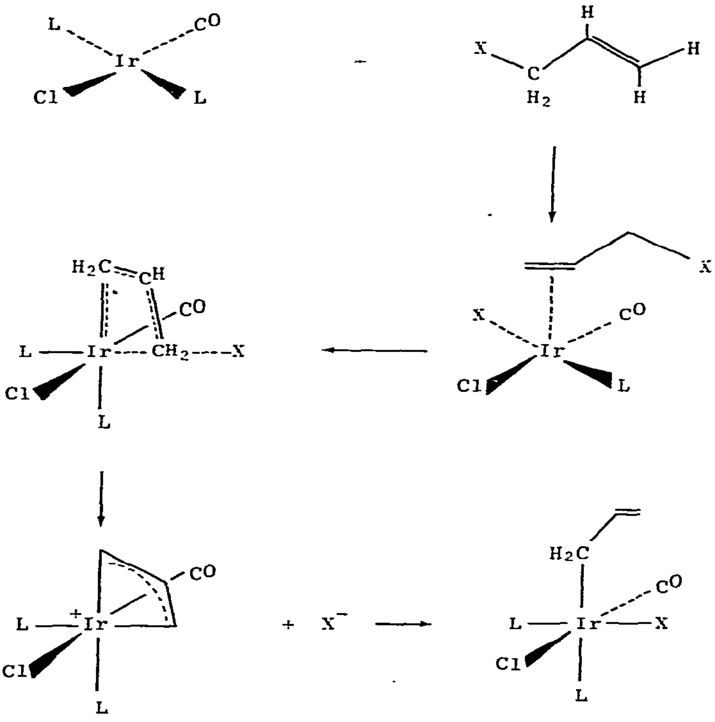
(R = H, $CO_2Me$, $CO_2Et$)

[456]

## Metal allyl compounds

Although $\eta^3$-allyl-$\eta^5$-cyclopentadienylchlororhodium complexes $[RhCl(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5R'_5)]$ have been well characterised, the related salts $[Rh(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5R'_5)L]^+X^-$ have only received brief attention in the literature. Treatment of the complexes $[RhCl(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5R'_5)]$ (R = 1-Me, R′ = H, Me; R = 2-Me, R′ = H) with $AgBF_4$ in acetone followed by addition of a stoichiometric amount of a donor ligand L affords the cationic complexes $[Rh(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5R'_5)L]BF_4$ (L = py, $PPh_3$, $AsPh_3$) which have been studied by $^{1}H$ and $^{13}C$ n.m.r. spectral measurements (ref. 542). Some related iridium compounds [IrCl($\eta^3$-methallyl)Cp] and [IrCl($\eta^3$-methallyl)Cp] have been obtained by reaction of $[IrI_2Cp]_2$ with [HgCl(methallyl)] to give [$IrHgI_2Cl$($\eta^3$-methallyl)Cp] followed by reduction with sodium thiosulphate (ref. 543).

It is known that the addition of allyl halides to trans-[IrCl(CO)$(PMe_2Ph)_2$] in benzene affords the cis compounds [437] and kinetic and product studies are consistent with the idea of alkene co-ordination to the iridium atom in the rate-determining step (Scheme 72) leading to [438] followed by attack of the displaced halide to give



[438]

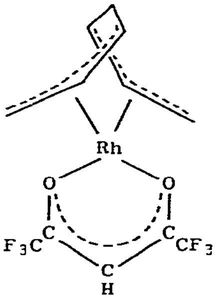
[437]

(L = $PMe_2Ph$)

Scheme 72

the cis-adduct. The tetrafluoroborate salt of [438] has been isolated and its structure has been determined by an X-ray study. Treatment of this salt with bromide ion gives the cis-compound [437] and suggests that [438] can be an intermediate in the oxidative-addition reaction (ref. 544).

The reaction of trans-divinyl-cyclopropane with [Rh(CF$_3$COCHCOCF$_3$)(C$_2$H$_4$)$_2$] results in opening of the cyclopropane ring and conversion of a bis(vinyl) to a bis(allyl) hydrocarbon which is co-ordinated to rhodium. The single crystal X-ray structure determination of this product [438a] has been reported (ref. 545).

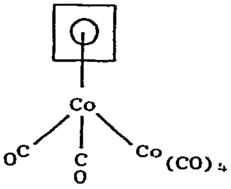


[438a]

Extended CNDO/studies on [Co($\eta^3$-C$_3$H$_5$)(CO)$_3$] have been reported (ref. 546), and electronic, far-infrared and n.m.r. spectra of the allylic rhodium(III) compounds [RhX$_2$(allyl)] (X = Cl, Br) have been studied (ref. 547).

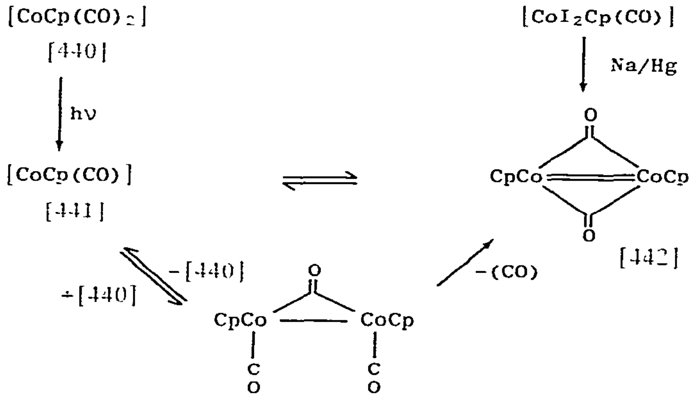
### Metal carbocyclic and carbaborane compounds

A review on cyclobutadienemetal complexes contains information on the cobalt triad (ref. 548). The dicobalt compound [Co$_2$(C$_4$H$_4$)(CO)$_6$] [439] is an intermediate in the synthesis of [Co(C$_4$H$_4$)Cp]. The structure of [439] has now been determined by a single crystal X-ray study. In order to decrease repulsion between the cyclobutadiene ring and the bulky Co(CO)$_4$ group, the four-membered ring is tilted and as a consequence the Co-cyclobutadiene interaction is not symmetrical (ref. 549).



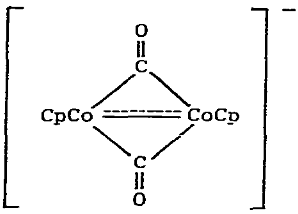
[439]

Photolysis of [CoCp(CO)$_2$] [440] in toluene or petroleum spirit at -78°C generates the monocarbonyl species [441]. At room temperature this monocarbonyl can associate with excess [CoCp(CO)$_2$] to give [Co$_2$Cp$_2$(CO)$_3$] or dimerize to [Co$_2$Cp$_2$(CO)$_2$] [442]. The dimer [442] is stable as a solid, but in solution it is slowly converted to the insoluble trimer $[Co_3Cp_3(CO)_3]$ (Scheme 73). The dimer [442] is cleaved by phosphines to give $[CoCp(CO)(PR_3)]$ while dienes cause unsymmetrical cleavage to give [CoCp(diene)] and $[CoCp(CO)_2]$ (ref. 550). Reduction of $[CoCp(CO)_2]$ with sodium-



Scheme 73

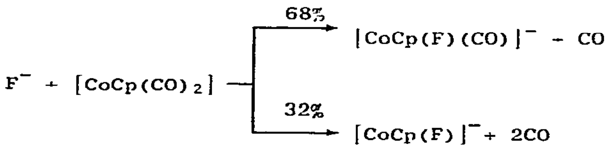
amalgam in tetrahydrofuran at room temperature under anhydrous and air-free conditions gives $Na[Co(CO)_4]$ and the pyrophoric binuclear paramagnetic complex $Na[Co_2Cp_2(CO)_2]$. Infrared studies indicate that this complex is contacted ion-paired in tetrahydrofuran, but exists as dissociated ions or possibly solvent-separated pairs in tetrahydrofuran containing 18-crown-6. An air stable salt of this paramagnetic binuclear anion [443] can be obtained with the cation $(Ph_3P)_2N^+$ and an X-ray



[443]

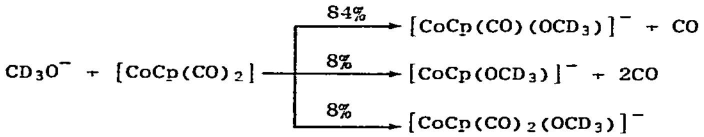
diffraction study of this salt reveals an unusually short Co-Co bond consistent with the presence of a partial double metal-metal bond. Oxidation of [443] with anhydrous $FeCl_3$ gives the dimer $[Co_2Cp_2(CO)_2]$ (442; Scheme 73) which presumably contains a complete Co-Co double bond. Reduction of $[CoCp(CO)(PPh_3)]$ occurs more slowly than $[CoCp(CO)_2]$ to give a dark oligomeric cobalt complex which gives

Na[Co(CO)$_4$] and [445] upon carbonylation (ref. 551). The first-step in the reduction of [CoCp(CO)$_2$] is probably the formation of 19-electron complex [CoCp(CO)$_2$]$^-$. The gas-phase negative ion chemistry of [CoCp(CO)$_2$] leads to the formation of this anion, [CoCp(CO)$_2$]$^-$, and [CoCp(CO)]$^-$. The anion [CoCp(CO)]$^-$ reacts with [CoCp(CO)$_2$] to give the dimer [Co$_2$Cp$_2$(CO)$_2$]$^-$ [445]. Phosphorus trifluoride displaces carbon monoxide from [CoCp(CO)]$^-$. It is also apparent from these studies that PF$_3$ is a stronger $\pi$-acceptor than CO toward [CoCp]$^-$ in the gas phase. Nitrogen monoxide reacts with both [CoCp(CO)]$^-$ and [CoCp(CO)$_2$]$^-$ to give the very stable anion [CoCp(NO)]$^-$ which is isoelectronic with [NiCp(NO)]. $\pi$-Acids weaker than CO ($C_2F_4$, HCN, ethylene oxide, MeCN, NH$_3$, NMe$_3$ and PMe$_3$) have not been observed to react with [CoCp(CO)]$^-$. Fluoride anion, produced by the dissociative attachment of electrons to NF$_3$, reacts with [CoCp(CO)$_2$] to give a carbonyl fluoride anion, (Scheme 74). Analogous reactions to those outlined in Scheme 74 occur in a mixture



Scheme 74

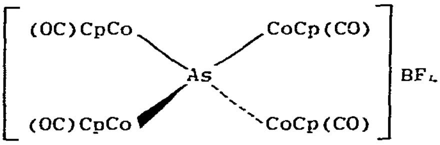
of [CoCp(CO)$_2$] and CD$_3$ONO (Scheme 75). The anions CN$^-$, NO$_2^-$, Cl$^-$, and I$^-$ are not



Scheme 75

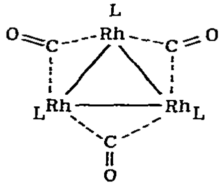
observed to react with [CoCp(CO)$_2$] in the gas phase (ref. 552). The reaction of arsenic trifluoride with a benzene solution of [CoCp(CO)$_2$] produces the complex [444] which has been characterised by a single crystal X-ray study. The complex contains a tetrahedral like arsenic atom co-ordinated to four cobalt atoms and is structurally analogous to [{Fe$_2$(CO)$_8$}$_2$($\mu_4$-Sn)]. The boron atom in the BF$_4^-$ anion of [444] apparently originates from the pyrex glass of the reaction vessel (ref. 553).

Although [RhCp(C$_2$H$_4$)$_2$] does not react with carbon monoxide, the $\eta^5$-indenyl analog reacts instantly at room temperature to give [Rh($\eta^5$-C$_9$H$_7$)(CO)$_2$] in quantitative yield. This enhanced reactivity of the $\eta^5$-indenyl compound is explicable in terms



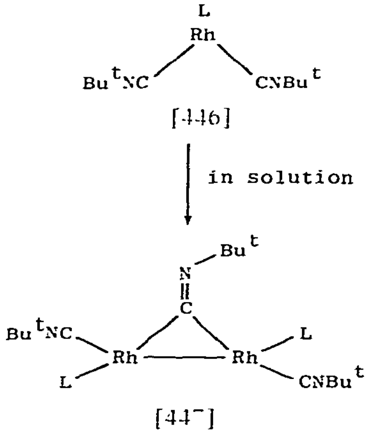
[444]

of the "slippage" of the indenyl ligand ($\eta^5$-$C_9H_7$ → $\eta^3$-$C_9H_7$) thereby creating a vacant co-ordination site at the rhodium(I). In refluxing heptane [Rh($\eta^5$-$C_9H_7$)(CO)$_2$] is converted selectively in high yield into the dark-green trimer [445]. Prolonged photolysis of [RhCp(CO)$_2$] is known to produce two isomers of [Rh$_3$Cp$_3$(CO)$_3$] in low yield. Ethylene is rapidly displaced from [Rh($\eta^5$-indenyl)($C_2H_4$)$_2$] by two mole equivalents of Bu$^t$NC to give [446] which in solution is slowly converted to the dinuclear complex [447]. Excess Bu$^t$NC gives [Rh($\eta^1$-$C_9H_7$)(Bu$^t$NC)$_4$]. Ethylene can also be readily displaced at room temperature by methylenecyclopropane, acrylonitrile and 1,3-dienes such as isoprene, cyclohexadiene, or cyclohepta-1,3,5-triene (ref. 537).



L = $\eta^5$-indenyl

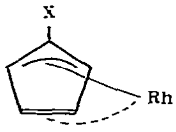
[445]



[446]

[447]

The $^1$H and $^{13}$C n.m.r. spectra of the monosubstituted $\eta^5$-cyclopentadienylrhodium complexes [Rh($\eta^5$-$C_5H_4X$)$L_2$] (L = ethylene, CO; $L_2$ = 1,3-, 1,4-, or 1,5-diene; X = Me, CMe$_3$, CO$_2$Me, CO$_2$Et, CO$_2$Pr$^i$, CHO, COCO$_2$Et, or CN) exhibit a temperature dependence of the cyclopentadienyl ring protons when X is an electron-withdrawing substituent and the neutral ligand is ethylene or a non-conjugated diene. In contrast, the n.m.r. behaviour of the conjugated diene complexes are normal. The temperature-dependent spectra observed for the non-conjugated dienes are attributed to restricted rotation of the cyclopentadienyl ring. A single crystal X-ray structure determination of [Rh($\eta^5$-$C_5H_4CO_2Me$)(1,5-cod)] suggests that the preferred rotamer in solution may be one in which the $C_5$ ring is bonded to the π-allyl as indicated in [448] and that



[448]

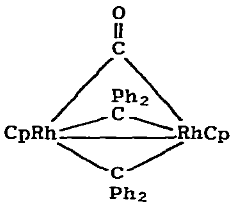
this localised bonding structure accounts for the temperature-dependent n.m.r. spectra. The occurrence of the localised bonding structure in those complexes where the neutral ligands are isolated double bonds and a delocalised structure in the case of the conjugated dienes can be explained in terms of the different symmetries of the π-acceptor orbitals of the neutral ligands with respect to the $C_5H_4X$ moiety (ref. 354).

The reaction of diphenylphosphine with $[RhCp(CO)_2]$ in refluxing heptane in the presence of air produces the dioxygen compound $[Rh(PPh_2)(O_2)(PHPh_2)_3]$. However, in the absence of dioxygen the compound $[Rh(PPh_2)(PHPh_2)]_3$ is formed which does not take up dioxygen or carbon monoxide. An attempt to prepare the compound $[Rh(PPh_2)(PHPh_2)]_3$ by the reaction of $[RhCl(CO)_2]_2$ with $PHPh_2$, however, gives trans-$[RhCl(CO)(PHPh_2)_2]$. Halogens and methyl iodide react with the dioxygen compound according to the equations:

$$[Rh(PPh_2)(O_2)(PHPh_2)_3] + X_2 \longrightarrow [RhX(O_2)(PHPh_2)_3] + PXPh_2$$
$$[Rh(PPh_2)(O_2)(PHPh_2)_3] + MeI \longrightarrow [RhI(O_2)(PHPh_2)_3] + PMePh_2$$

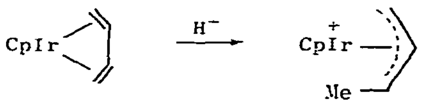
The dioxygen compounds are stable to air (ref. 355).

The reaction of $[RhCl(CPh_2)_2(CO)]_n$ with sodium cyclopentadienide gives [449] which has been the subject of a single crystal X-ray study (ref. 356). The compound



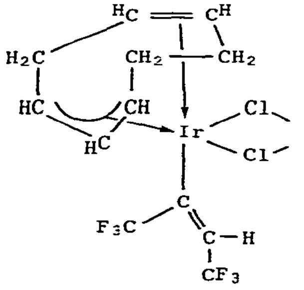
[449]

[IrCp(carvone)] can be obtained by the reaction of $[IrCl(cyclo\text{-}octene)_2]_2$ with carvone and thallium cyclopentadienide (ref. 357) and [IrCp(butadiene)] [450] can be obtained from [IrCl(butadiene)$_2$] and thallium cyclopentadienide. Protonation of



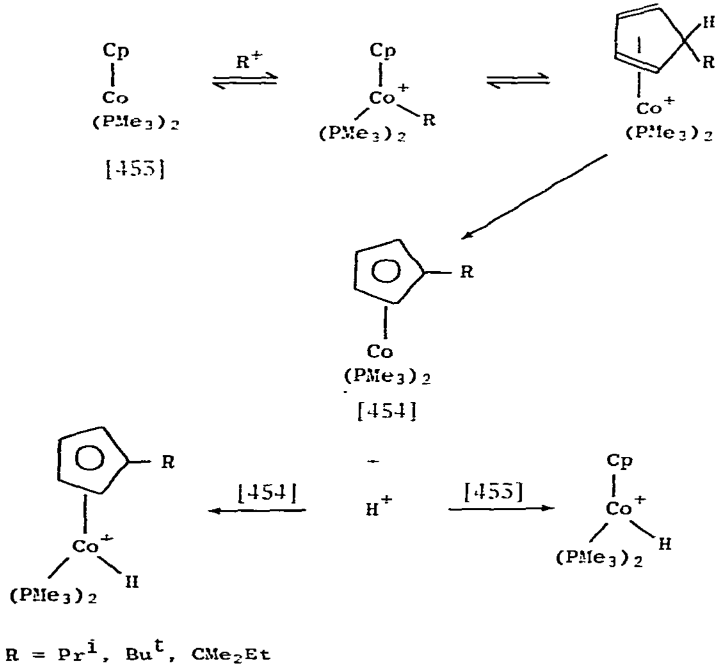
[450] [451]

[450] with trifluoroacetic acid gives the antimethallyl cation [451]. Initial protonation at the metal is postulated (ref. 358). Studies on the protonation of the cyclo-octa-1,5-diene complexes [MCp(cod)], (M = Co, Rh, or Ir) reveal that these neutral diene complexes are also susceptible to electrophilic attack. On protonation no stable 16-electron cobalt cations are observed but rhodium and iridium provide a balance of stability: $[MCp(\eta^3\text{-enyl})]^+ \rightleftharpoons [MCp(\eta^4\text{-diene})H]^+ \rightleftharpoons [MCp(\eta^5\text{-dienyl})]^+$. The 16-electron $\eta^3$-enyl cations are more favoured by rhodium, and the 18-electron dienehydrido-cations more so by iridium. The observation that the iron(0) compounds [Fe(CO)$_3$(diene)] and cobalt(I) compounds [CoCp(diene)] are susceptible to electrophilic attack is a consequence of the electron donor ability of the cyclopentadienyl ligand while carbonyl groups have both donor and acceptor properties. Thus the electron density available to the dienemetal fragment may be similar in both the tricarbonyliron and cyclopentadienylcobalt triads (ref. 359). Treatment of [IrCl(cod)]$_2$ with the electrophilic alkyne, hexafluorobut-2-yne, is known to give the enyl complex [452] which has been the subject of an X-ray study (ref. 360).



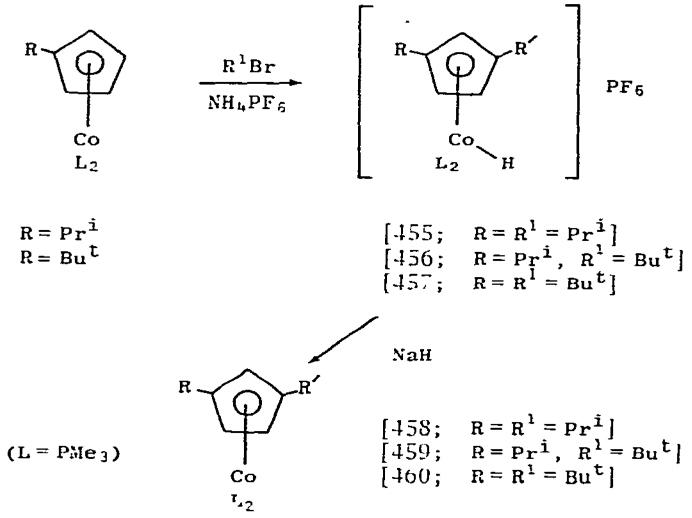
[452]

The compound [CoCp(PMe$_3$)$_2$] contains an extraordinarily nucleophilic metal centre. Thus it reacts with both methyl iodide and ethyl iodide to give [CoMeCp(PMe$_3$)$_2$]I and [CoEtCp(PMe$_3$)$_2$]I respectively. In contrast reactions of [CoCp(PMe$_3$)$_2$] with alkyl bromides which carry at least two methyl or ethyl groups on the $C_\alpha$ atom leads to an alkyl-substituted cyclopentadienyl ring cationic hydridocobalt complex. The mechanism of the reaction is outlined in Scheme 76. On using equimolar amounts of



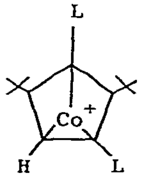
Scheme 76

[453] and RX product ratios $[CoH(\eta^5\text{-}C_5H_4R)(PMe_3)_2]^+$ : $[CoH(Cp)(PMe_3)_2]^+$ = 70 : 30 ($R = Pr^i$) and 50 : 50 ($R = Bu^t$) are observed. The reaction of [453] with $Me_3SiCl$ gives a paramagnetic product but $Me_3SiOSO_2CF_3$ gives the cation $[CoH(\eta^5\text{-}C_5H_4SiMe_3)(PMe_3)_2]^+$. Treatment of the cationic hydrido complexes $[CoH(\eta^5\text{-}C_5H_4R)(PMe_3)_2]^+$ with sodium hydride gives the neutral compounds $[Co(\eta^5\text{-}C_5H_4R)(PMe_3)_2]$. The mild reaction conditions observed for the ring substitution of [453] differ markedly from those which are necessary for electrophilic substitution of $[FeCp_2]$ or $[MnCp(CO)_3]$ (ref. 361). Using the method outlined in Scheme 77 disubstituted cyclopentadienylcobalt complexes can also be obtained. N.m.r. studies on [457] and [460] indicate the presence of rigid rotamers even at 100°C. The rotamers of [457] and [460] obtained in the synthesis are [461] and [462] respectively (ref. 362). The pronounced Lewis basic character of the cobalt atom in $[CoCp(PMe_3)_2]$ is further demonstrated by its reactions with $ZnCl_2/PMe_3$, $[CuCl(PMe_3)_2]_2$, $SnCl_4$, $SnClR_3$, ($R = Me$, Ph) and $HgCl_2$ which lead to Lewis acid-base adducts containing Co-Zn, Co-Cu, Co-Sn and Co-Hg metal-metal bonds (ref. 363). The metal atom of the phosphite compounds $[MCp\{P(OR)_3\}_2]$, ($M = Co$, $R = Me$, Et; $M = Rh$, $R = Me$, Et, Ph, o-tolyl) also exhibit

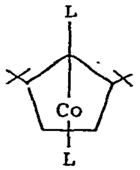


Scheme 7

Lewis base properties reacting with $H^+$ and $Me^+$ to give $[MH(Cp)\{P(OR)_3\}_2]^+$ and $[MMe(Cp)\{P(OR)_3\}_2]^+$ respectively (ref. 564).



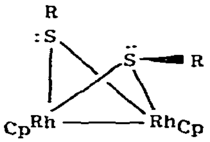
[461]



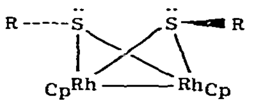
[462]

(L = PMe3)

The compound $[RhCp(CO)_2]$ with $R^1SSR^1$ or $[Rh(SR^1)(CO)_2]_2$ with $C_5H_5R^2$, in refluxing toluene afford a mixture of two isomers of $[Rh(SR^1)(\eta^5\text{-}C_5H_4R^2)]_2$ ($R^1$ = Ph or $C_6H_4Me$-p, $R^2$ = H or Me). For $R^1 = C_6H_4Me$-p and $R^2$ = H, the hexane-soluble isomer has the *anti* structure [463], while the hexane-insoluble isomer has the structure [464]. The structure of (463; R = Ph) has been confirmed by an X-ray study. Although both [463] and [464] are static, the isomerisation of [464] to [463] may be followed by visible and $^1H$ n.m.r. spectroscopy. This conversion can only involve cleavage of one of the Rh-S-Rh bridges, rotation about the terminal Rh-S bond, and regeneration of the $Rh_2S_2$ ring. The conversion of [464] to [463] can also be studied electrochemically. The complex [463] reacts rapidly at room temperature with di-p-tolyl disulphide and $NOPF_6$ as oxidising agent to give [465], and with $[(C_6H_4Br\text{-}p)_3N]SbCl_5$ to give [466]. Electrochemical and chemical studies indicate



[463]



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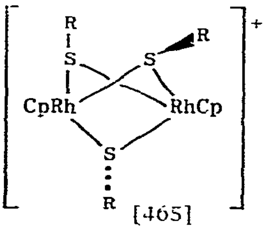
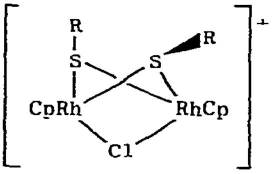


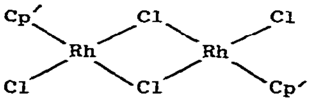
[465]



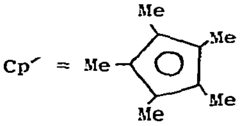
[466]

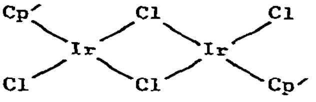
that the formation of [465] or [466] from [463] involves an initial one-electron oxidation followed by insertion of RS• or Cl• into the metal-metal bond of the radical cation $[Rh(SR^1)(\eta^5\text{-}C_5H_4R^2)]_2^+$ species (ref. 365).

The results of X-ray structural analyses of the compounds [467], [468], and [469]

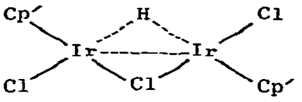


[467]





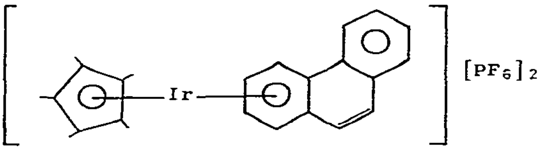
[468]



[469]

have been published. The metal-metal distances in [467] and [468] vary significantly with values of 3.769(1) Å for Ir----Ir and 3.719(1) Å for Rh----Rh but there is no significant difference between the Ir—Ir [2.903(1) Å], distance of [469] and the Rh—Rh, [2.906(1) Å], distance of the corresponding rhodium compound. The results suggest that the Ir(μ-H)Ir and Rh(μ-H)Rh systems are held together by closed two-electron three-centre bonds in which there is substantial direct metal-metal bonding (refs. 366, 367).

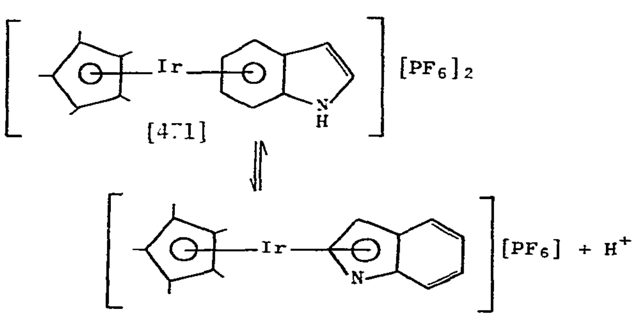
Treatment of $[MCl_2(\eta^5-C_5Me_5)]_2$ with $AgPF_6$ in acetonitrile, dimethylsulphoxide, or pyridine yields the dicationic salts $[M(\eta^5-C_5Me_5)L_3][PF_6]_2$, (M = Rh or Ir, L = MeCN, $Me_2SO$, pyridine). Similar reactions occur in acetone, dichloromethane or methanol but attempts to isolate these materials have not been successful. Studies on the dimethylsulphoxide compounds indicate that dimethylsulphoxide is always O-bonded to rhodium but that it is S-bonded in solution and both O- and S-bonded in the solid to iridium. Presumably $C_5Me_5Rh(III)$ is a harder centre than $C_5Me_5Ir(III)$. A range of arene compounds $[M(\eta^5-C_5Me_5)(\eta^6-arene)][PF_6]_2$, (M = Rh, arene = benzene, toluene, m-xylene, mesitylene, fluorene, or indole; M = Ir, arene = toluene, m-xylene, naphthalene, phenanthrene, indene, indole, or fluorene) can be obtained by addition of the arene to the acetone complex $[M(\eta^5-C_5Me_5)(acetone)_3][PF_6]_2$. The naphthalene- and the phenanthrene-iridium complexes are very labile but do not exhibit fluxional behaviour. The phenanthrene complex has the structure [470]. Bonding to a terminal rather than to the central ring is probably due to the bond-delocalisation energy being lowest for an end ring; i.e. less resonance energy is lost if this is taken out of conjugation and complexed. The reaction of $[Rh(\eta^5-C_5Me_5)(Me_2CO)_3][PF_6]_2$ with indene gives the $\eta^5$-indenyl complex $[Rh(\eta^5-C_5Me_5)(C_9H_7)][PF_6]$ which is protonated to give the $\eta^6$-indene complex. Similar reversible protonation-deprotonation reactions occur for the iridium complexes:



[470]

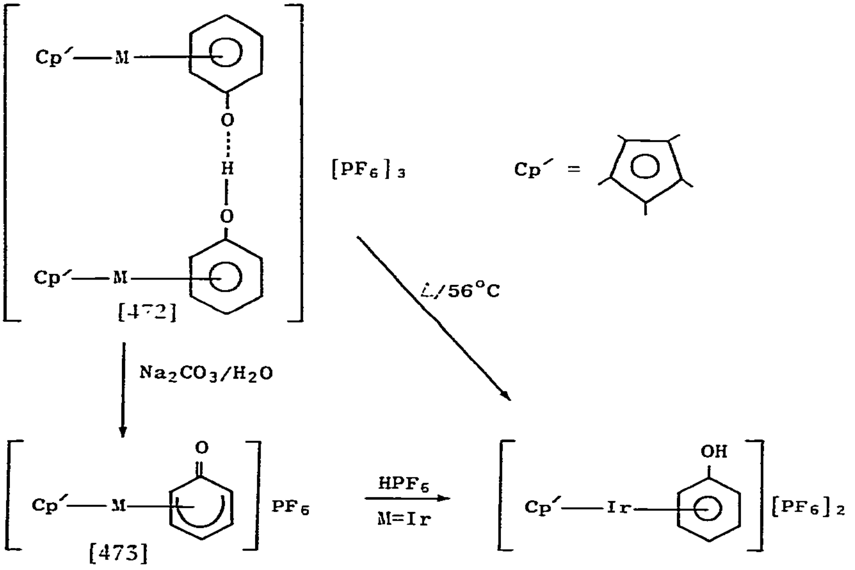
$$[Ir(C_5Me_5)(\eta^6-C_9H_8)]^{2+} \rightleftharpoons [Ir(C_5Me_5)(\eta^5-C_9H_7)]^{+} + H^{+}$$

The iridium (but not the rhodium) indole complex [471] also undergoes reversible

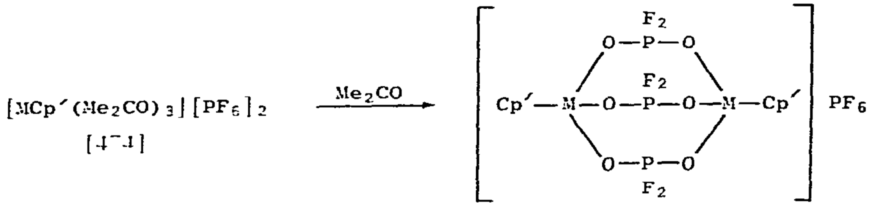


[471]

deprotonation. From exchange studies with $CF_3CO_2D$ on $[Ir(\eta^5-C_5Me_5)(\eta^6-C_9H_8)]^{2+}$ it appears that protonation-deprotonation is rapid and that the rate-determining step in the overall reaction is the movement of the metal from the five- to the six-membered ring and <u>vice versa</u>. Exchange reactions indicate an increasing stability of arene ligand in the order: $\eta^6$-naphthalene < $\eta^6$-phenanthrene < $\eta^6$-benzene < $\eta^6$-alkylbenzenes < $\eta^6$-indole < $\eta^5$-indenyl > $\eta^6$-indene, $\eta^5$-indolyl (ref. 368). Treatment of the acetone complexes $[M(\eta^5-C_5Me_5)(Me_2CO)_3][PF_6]_2$, (M = Rh or Ir) with phenol gives the hydrogen bonded dimeric phenol complexes [472]. These are easily

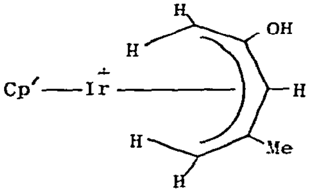


deprotonated to give the $\eta^5$-oxocyclohexadienyl complexes [473] (ref. 369). When the complex [474] is heated in acetone partial solvolysis of the hexafluorophosphate anion occurs to give (475; M = Rh). This is the first definitive example of the partial hydrolysis of $PF_6^-$ to $PO_2F_2^-$. The iridium acetone complex [474] on standing in acetone gives (475; M = Ir) in solution but the product isolated from the solution as the tetraphenylborate salt is [476]. Treatment of (474; M = Ir) with mesityl oxide gives [477] which in the presence of acid gives [476]. The complex [477] is probably an intermediate in the formation of [476] and the formation of [477] may be an example of a metal-catalysed aldol condensation (ref. 370). The co-ordination of ligands to $[M(C_5Me_5)]^{2+}$ is subject to strong steric restraints and only one or two molecules of the bulkier phosphines and phosphites can co-ordinate. Thus $[Rh(\eta^5-C_5Me_5)(MeCN)_3][PF_6]_2$ and triphenylphosphine give $[Rh(\eta^5-C_5Me_5)(MeCN)_2(PPh_3)][PF_6]_2$ and triphenylphosphite gives orthometallated products [478]. Treatment of $[M(\eta^5-C_5Me_5)(Me_2CO)_3][PF_6]_2$ with the phosphorus donor ligands L (L = $P(OMe)_3$,

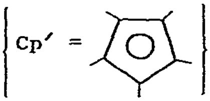


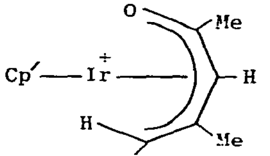
[474]

[475]

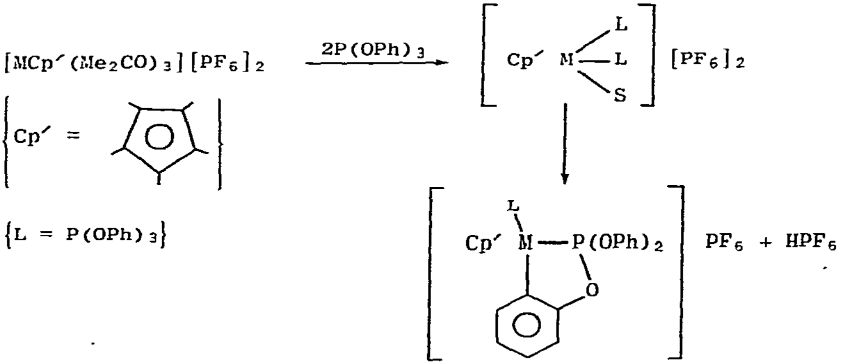


[476]





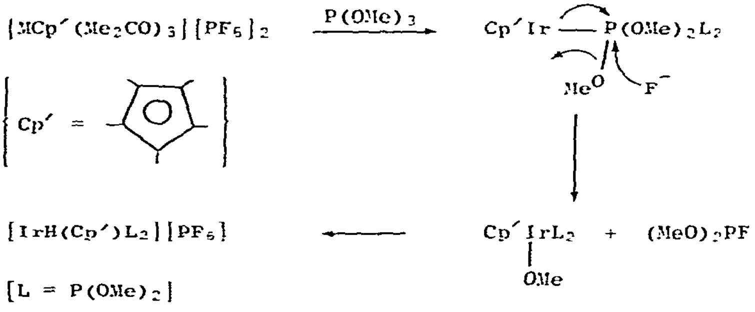
[477]



[478]

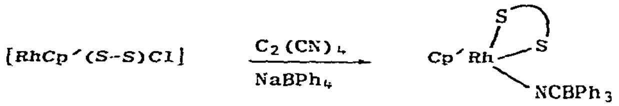
P(OEt)$_3$, or PMe$_2$Ph) gives [M($\eta^5$-C$_5$Me$_5$)L$_3$][PF$_6$]$_2$. Trimethylphosphite reacts further with [Ir($\eta^5$-C$_5$Me$_5$)(Me$_2$CO)$_3$][PF$_6$]$_2$ to give [479], Scheme 78 (ref. 371). The reaction of tetracyanoethylene with [Rh($\eta^5$-C$_5$Me$_5$)(S-S)Cl] in methanol followed by addition of NaBPh$_4$ gives the triphenylcyanoborate complexes [480], (S-S = S$_2$PMe$_2$, S$_2$PPh$_2$, S$_2$CNMe$_2$), (ref. 372).

Treatment of a dichloromethane solution of [RhCl(cyclohexa-1,3-diene)$_2$] or [IrCl(cyclohexa-1,3-diene)$_2$] with a molar equivalent of AgBF$_4$ in the presence of excess cyclohexa-1,3-diene gives the benzene complexes [481]. The reactions involve a disproportionation of co-ordinated cyclohexa-1,3-diene to benzene and cyclohexene. Reactions of [481] with 1,3,5-trimethylbenzene result in displacement

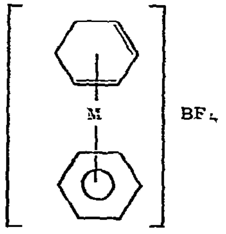


[479]

Scheme 78



[480]

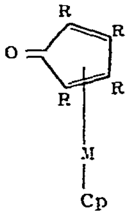


(M = Rh, Ir)

[481]

of benzene and the formation of the corresponding arene cations. In contrast, MeCN pyridine, $PMe_3$, or $PMe_2Ph$ displace benzene to form the cations $[ML_3(\text{cyclohexa-1,3-diene})]^+$. When the rhodium(I) and iridium(I) chloro-complexes of cyclohepta-1,3-diene and cyclo-octa-1,3,5-triene are treated with $AgBF_4/CH_2Cl_2$ the cations $[M(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]^+$ and $[M(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{10})]^+$, are formed, the latter complex being a hydrogenation catalyst for alkenes. If the reaction of $AgBF_4$ with the cyclohepta-1,3-diene chloro-complexes is conducted in the presence of dimethylsulphoxide, pyridine or triethylphosphine the cations $[ML_3(\text{cyclohepta-1,3-diene})]^+$ are produced. The cations $[ML_3(\text{cyclohexa-1,3-diene})]^+$ and $[ML_3(\text{cyclohepta-1,3-$

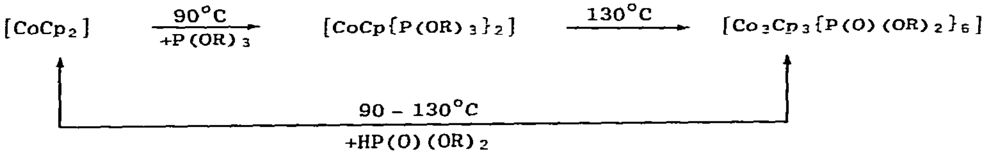
diene)$]^-$ exhibit dynamic behaviour in solution (ref. 373). The cyclopentadienone complexes [482] undergo a reversible one-electron reduction but only the cobalt complexes give anions stable enough to allow e.s.r. studies (ref. 374).



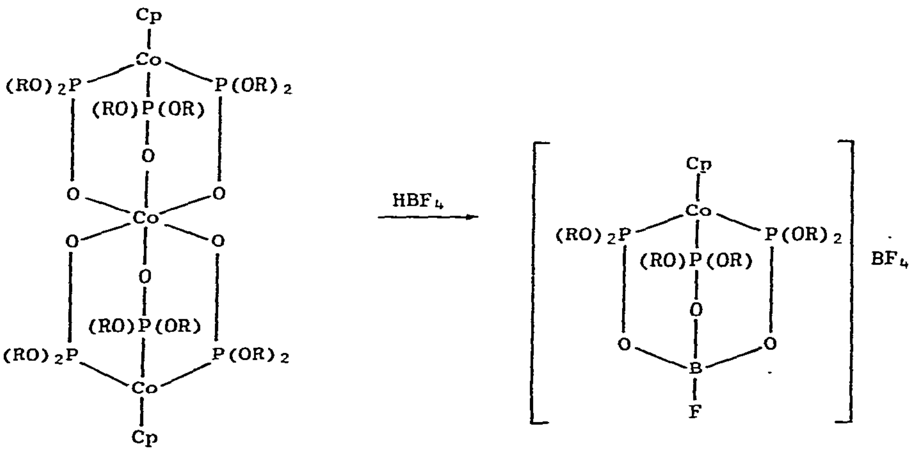
M = Co, Rh, R = Ph, $C_6F_5$

[482]

Thermolysis of the compounds $CoCp[P(OR)_3]_2$, (R = Me, Et) or treatment of cobaltocene with $HP(O)(OR)_2$, Scheme 79, gives the "supersandwiches" [483], and the formati



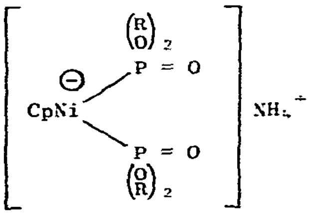
Scheme 79



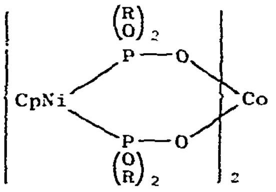
[483]

[484]

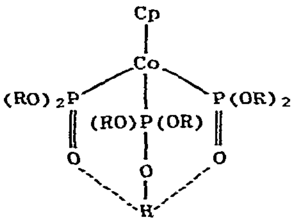
of these compounds has been reviewed (ref. 375). Treatment of [483] with fluoroboric acid in propionic anhydride gives [484] the structure of which has been confirmed by a single crystal X-ray study (ref. 376). The nickel compound [485] has been shown to react with cobalt(II) chloride to give [486], (ref. 377), while the cobalt compound [487] reacts with lanthanum(III) and europium(III) compounds to give [488] (ref. 378).



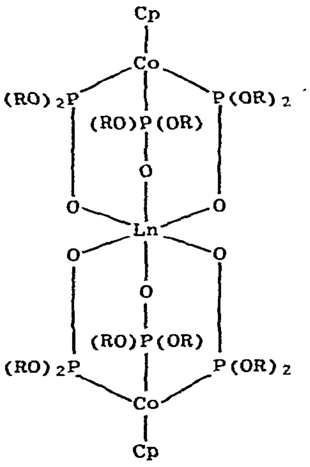
[485]



[486]



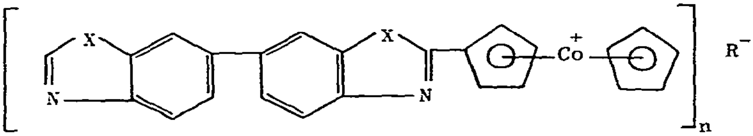
[487]



[488]

A kinetic equation for the (first order) decomposition of cobaltocene at 450-500° C and 45-280 mm mercury pressure has been developed. The decomposition of 1 mol. of cobaltocene gives 0.53 H, 0.32 $CH_4$, 0.43 cyclopentadiene, 0.20 cyclopentene, 0.05 $C_6H_6$, 0.04 cyclopentane, 0.02 methylcyclopentene, 0.003 PhMe, 0.03 $C_2H_4$ and 0.06 mol. of unidentified products (ref. 379). Values of the thermodynamic functions and crystallographic parameters of cobaltocene in the temperature range 77 to 300 K have been determined. There are no phase transitions in this range for this ordered metallocene in contrast to the disordered metallocenes $MCp_2$, (M = Fe, Ni, Cr) (ref. 580).

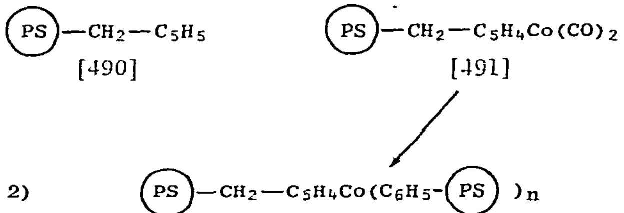
Treatment of $[Co(NH_3)_6]Cl_3$ with the organo sodium compounds $(CH_3)_nC_5H_{6-n}Na$ followed by oxidation leads to a series of *sym*-polymethylcobalticenium bromides and hexafluorophosphates of the general formula $[(Me_n(C_5H_{5-n})_2Co]X$, {X = $PF_6$, Br; $Me_n$ = $CH_3$, 1,3-$(CH_3)_2$, 1,2,4-$(CH_3)_3$, $(CH_3)_4$} (ref. 581). A comparison of the $^{13}C$ n.m.r. spectra of substituted cobalticenium ions and ferrocene show a similarity in the effect of alkyl substitution (ref. 582). The cobalticenium bridged polymers [489] have been prepared but their thermal stability and solubility are inferior to those of phenylene-bridged bibenzimidazoles (ref. 583).



X = NH, R = Cl or $PF_6$
X = S, R = Cl or $PF_6$

[489]

Treatment of a $(C_5H_5)CH_2$-substituted polystyrene-divinylbenzene (18%) copolymer [490] with $[Co_2(CO)_8]$ gives cobalt cyclopentadienyl dicarbonyl attached to a cross-linked polystyrene [491]. Photolysis of [491] forms unsaturated cobalt centres whic interact with aromatic rings of the polymer support to form species of the type [492] (ref. 584).

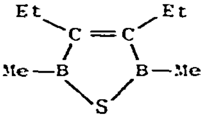


(n= 1 or 2)

[492]

Microcalorimetric measurements at elevated temperatures of the heats of thermal decomposition and of iodination of arene metal carbonyls have given values for the standard enthalpies of formation of the crystalline compounds at 25°C: $[Co_4(C_6H_6)(CO)_9]$ = -(1313 ± 13); $Co_4(C_6H_3Me_3)(CO)_9$ = -(1444 ± 13); $Co_4(C_6Me_3)(CO)_9$ = -(1555 ± 17) K J $mol^{-1}$. From these and other data, the bond-enthalpy contributions of the various ligand-metal bonds, D(L-M), in the gaseous metal complexes have been determined: $D(C_5H_5)$-Co = 270; $D(C_5Me_4H)$-Co = 285; $D(C_5Me_5)$-Co = 310 kJ $mol^{-1}$ (ref. 385).

The triple-decker sandwich compounds which have been previously reported in the literature are constructed with two cyclopentadienyl metal fragments bridged by homocyclic $C_5H_5$ or heterocyclic $C_2B_3$, $C_2B_2S$ and $C_4B$ ligands. A triple-decker sandwich with three heterocyclic ligands, [493] however, has now been obtained from $[Co_2(CO)_8]$ and [494] (ref. 386). The reaction of the difunctional Lewis acid 1,3-diborolene [495] with a mixture of $[CoCp(CO)_2]$ and $[FeCp(CO)_2]_2$ gives a triple decker sandwich [496] which contains two different metal atoms (ref. 387).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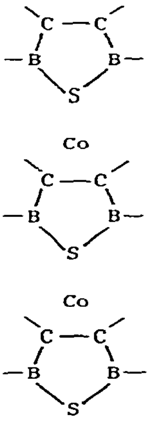
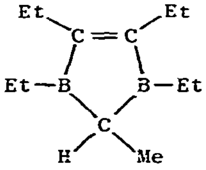

[493]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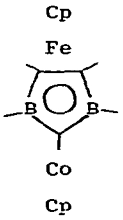
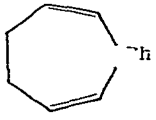
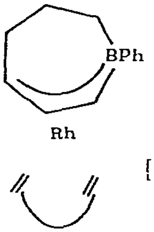

[496]

Derivatives of borabenzenes are known to form sandwich complexes with certain transition metals. A novel 1-4η-1-borato-1,3-butadiene type structure [497] has now been obtained from the reaction of [498] with $LiCMe_3$ and $[RhCl(cod)]_2$ (ref. 388).

An important development in inorganic chemistry has been the realisation of a



[498]

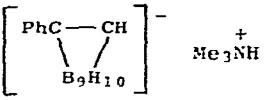


[497]

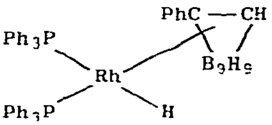
close structural and electronic relationship between the polyhedral boranes and other types of cage compounds such as the metal clusters. A series of cobaltaborane cage compounds, which exhibit a variety of structures, compositions and stereochemically novel features, have been obtained from the reaction of $Na^+B_5H_8^-$, $CoCl_2$ and $Na^+Cp^-$. The major products of this reaction are [2-$CpCoB_4H_8$] (an analogue of $B_5H_9$ and [CoCp(cyclohexa-1,3-diene)]. Pyrolysis of [2-$CpCoB_4H_8$] gives [1-$CpCoB_4H_8$]. The other structurally characterised products are 5-$CpCoB_9H_{13}$ (an analogue of $B_{10}H_{14}$), [1,2-$Cp_2Co_2B_4H_6$] and its 3- and 4-cyclopentyl derivatives, [1,2,3-$Cp_3Co_3B_3H_5$], [$Cp_3Co_3B_4H_4$], [$Cp_4Co_4B_4H_4$], [μ(2,3)-1,3-$C_3H_4$-1,7,2,3-$Cp_2Co_2C_2$-$B_3H_3$] (refs. 389, 390, 391). Using the metal atom technique a number of cobaltaborane clusters containing 3- and 4-boron can also be obtained, but in addition a series of new complexes, many of which contain 5-boron fragments can be prepared. Thus the reaction of cobalt atoms with pentaborane-(9) and cyclopentadiene give a variety of new metalloborane clusters including [$Cp_3Co_3B_5H_5$] and [cyclopentyl-$B_5H_4Co_3Cp_3$] (ref. 392). The crystal structure of [CpCo(2,3-$Me_2C_2B_4H_4$)], one of the products from the reaction of $Na^+Me_2C_2B_4H_5^-$, $CoCl_2$ and $Na^+Cp^-$, has been reported (ref. 393). Treatment of $FeH_2$(2,3-$Me_2C_2B_4H_4$) with cobalt(II) chloride and cyclopentadiene in ethanolic potassium hydroxide produces a mixture of cobaltaferracarboranes, cobaltacarboranes, iron(III) ferracarboranes, and a B-diethoxy derivative of the tetracarbon system $Me_4C_4B_8H_8$. The new products isolated are [σ-EtO(Cp)Fe(III)$Me_2C_2B_4H_3$], [CpFe(III)$Me_2C_2B_4H_4$], σ-EtO(Cp)$CoMe_4C_4B_7H_6$], (a distorted icosahedron related to $Me_4C_4B_8H_8$ with CoCp replacing an apex BH group), [CpCo($Me_2C_2B_3H_3$)$FeH_2$($Me_2C_2B_4H_4$)], [1,2,4,5-[CpCo($Me_2C_2B_3H_3$)FeHCp], [(σ-EtO)$_2Me_4C_4$-$B_8H_6$], and the known [1,7,2,3-$Cp_2Co_2Me_2C_2B_3H_3$] (ref. 394).

Various B- and C-substituted derivatives of [$CpCoC_2B_9H_{11}$] have been described (refs. 395, 396, 397). Infrared data indicate [$CpCoC_2B_9H_{11}$] forms hydrogen bonds with dimethyl sulphoxide not only with the carborane CH groups but also with the cyclopentadienyl CH groups. The energy of both types of CH bond is 1.5 kcal. $mol^{-1}$ (ref. 398).

Treatment of the two enantiomers of [499] with [$RhCl(PPh_3)_3$] in ethanol gives the two enantiomers of [500] (ref. 399) and it is apparent that deuterium exchange at terminal boron-hydrogen bonds, catalysed by low-valent metal complexes, proceeds



[499]



[500]

via oxidative-addition of boron-hydrogen bonds to catalytic species (ref. 400). Th first supported metallocarborane hydrogenation catalyst $[3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}4(\text{polystyrylmethyl})\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$ has been obtained by the reaction of $9\text{-}(\text{polystyrylmethyl})\text{-}7,8\text{-}C_2B_9H_{11})^-$ with $[RhCl(PPh_3)_3]$ (ref. 401).

The solvent extraction behaviour and electrochemical properties of $[Co(1,2\text{-}C_2B_9H_{11})_2]^-$ have been described (refs. 402, 403) and ESCA investigations of various cobaltocarboranes have been reported (ref. 404).

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