COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1976

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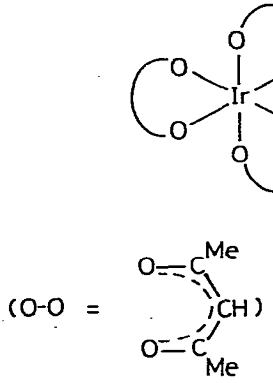
Contents

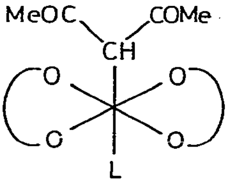
Metal—Carbon σ-Bonded Complexes

Although octahedral iridium(III)-carbon σ-bonded complexes have high thermal and oxidative stability no well characterised γ-C-bonded β-diketone complexes of iridium(III) have hitherto been described. However, on heating chloroiridic acid or hydrated iridium(III) chloride with excess 2,4-pentanedione and sodium bicarbonate, 1 is formed together with a polymeric yellow solid.

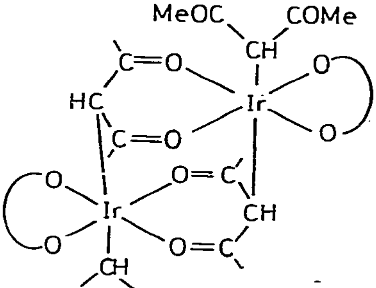


(1)

Treatment of this yellow solid with boiling pyridine gives **2**, (L = py) and a *p*-toluidine complex can similarly be obtained. The yellow solid reacts with boiling water to give a dimer **3** which on treatment with ammonia or n-propylamine gives the adducts **2**, (L = NH_3 or $CH_3CH_2CH_2NH_2$). Similar adducts containing triphenylphosphine, dimethylphenylphosphine, *N*-methylaniline, or *N,N*-dimethylaniline could not be obtained. Complex **3** is the first example of a complex which contains three different types of coordinated acac. On attempted sublimation of **3**, a small amount of **1** is obtained but attempts to convert **1** to γ-bonded acac complexes were not successful [1].

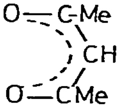


(L = py, NH_3, p-$CH_3C_6H_4NH_2$, $CH_3CH_2CH_2NH_2$) (2)



(3)

(O-O =



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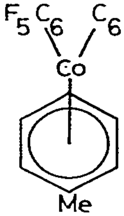
The reaction of cobalt atoms with bromopentafluorobenzene gives $[Co(C_6F_5)_2]$ which on treatment with toluene gives the novel paramagnetic 17-electron complex **4** which on treatment with triethylphosphine gives $[Co(C_6F_5)_2(PEt_3)_2]$ [2]. Some polyfluorophenylcobalt(III) complexes, [RCo(acacen)py] [R = C_6F_5, *p*-HC_6F_4, *o*-HC_6H_4; H_2acacen = *N,N'*-ethylenebis(acetylacetonimine)], and [RCo(salen)py], [R = C_6F_5, *p*-HC_6F_4; H_2salen = *N,N'*-ethylenebis(salicylaldimine)] have been prepared by reaction of the appropriate bromobis(polyfluorophenyl)thallium(III) with [Co(acacen)] or [Co(salen)]. Spectroscopic evidence for the formation of $[C_6F_5Co(salophen)]$ has also been obtained, [H_2salophen = *N, N'*-*o*-phenylenebis(salicylaldimine)]. The reactivity of the cobalt compounds increases in the order [Co(salophen)] < [Co(salen)] < Co(acacen). The reactivity of the thallium compounds increases in the sequence $Ph_2TlBr \ll (o\text{-}HC_6F_4)_2TlBr < (p\text{-}HC_6F_4)_2TlBr < (C_6F_5)_2TlBr$ [3]. A perfluoroalkylcobalt(III) compound, $[C_3F_7Co(S_2CNEt_2)py]$, can be obtained in small yield from the

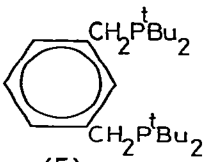


(4)

reaction of C_3F_7I with cobalt(II) acetate, in the presence of pyridine and sodium diethyldithiocarbamate [4].

The five coordinate cobalt(I) perfluoroalkyl compounds $[RCo(PF_3)_x(CO)_{4-x}]$ ($R = CF_3, C_2F_5, C_3F_7; x = 1$—4) are stereochemically non-rigid at room temperature. ^{19}F NMR studies reveal two types of dynamic processes, one occurring between different isomers and the other between nonequivalent sites in a single isomer. The data are consistent with a trigonal bipyramidal structure with an axial perfluoroalkyl group. In the complex $[CF_3Co(PF_3)(CO)_3]$ there are nearly equal proportions of isomers having axial and equatorial PF_3 groups, however, the equatorial isomer is increasingly favoured for $x = 2$ and 3. In the perfluoroethyl and perfluoropropyl compounds $[RCo(PF_3)(CO)_3]$ the isomer with an axial PF_3 group is strongly favoured over the equatorial while for the di- and trisubstituted compounds the isomer with all PF_3 groups equatorial is not observed [5].

Novel *ortho*-metallation reactions continue to produce a variety of rhodium and iridium metal—carbon σ-bonded complexes. The bulky diphosphine 5 undergoes metallation very readily to give a new type of tridentate chelating system. Thus reaction of 5 with hydrated rhodium(III) chloride gives the five coordinate hydride 6 (M = Rh) and an analogous iridium complex can similarly be prepared. Treatment of 6 (M = Ir) with carbon monoxide gives the octahedral complex 7. A similar reaction with the rhodium complex gave an analogous adduct but this readily loses hydrogen chloride to give 8 and possibly other products. Attempts to obtain an analogous iridium(I) carbonyl complex failed. Thus treatment of 6 (M = Ir) with sodium ethoxide and carbon monoxide gives only impure 7 [6]. The reactions of the allylic phosphines, $R_2P(allyl)$ (R = t-Bu, cyclohexyl) with $[IrCl(cyclooctene)_2]_2$ in the presence of γ-picoline at room temperature yield the octahedral metallated complexes 9.



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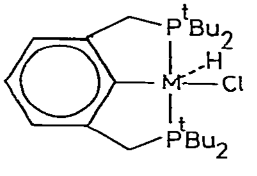
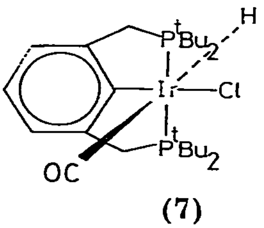


(6)

(M = Rh,Ir)



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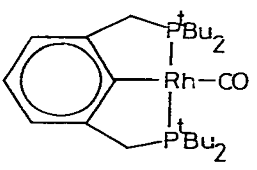

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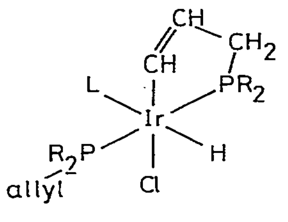
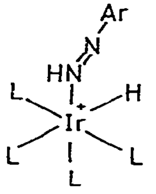


(L = γ-picoline ;
R = ^{t}Bu , cyclohexyl)

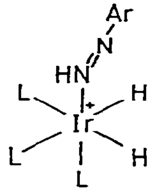
(9)

A five coordinate metallated complex can be obtained with t-Bu_2P-allyl in the absence of γ-picoline. The ease of metallation of these unsaturated ligands may be related to the presence of a double bond which would relieve strain in the five-membered ring formed upon metallation. The presence of bulky groups will also enhance the metallation reaction. The reactions of the same phosphines with [RhCl(cyclooctene)$_2$]$_2$ did not give metallated products [7]. The reaction of [IrH$_3$(PPh$_3$)$_3$] with *p*-anisyldiazonium tetrafluoroborate gives the isomeric cations **10a** and **10b**. Both **10a** and **10b** react with chlorine to give the original diazonium salt while reaction with ethanolic potassium hydroxide or sodium borohydride gives the hydride [IrH$_3$(PPh$_3$)$_3$]. On prolonged boiling in benzene, chloroform or ethanol **10** undergoes *ortho*-metallation to give **11** which is isolated as a mixture of isomers.

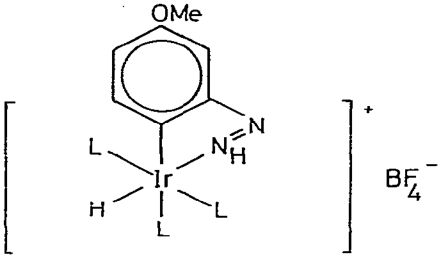


(L=PPh$_3$)

(10a)

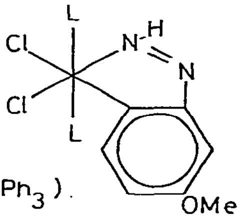


(10b)



(L=PPh$_3$)

(11)

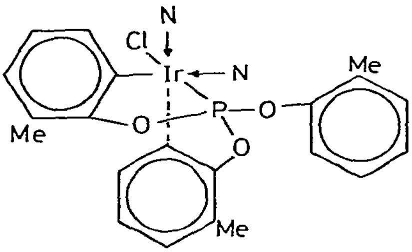


(L=PPh$_3$).

(12)

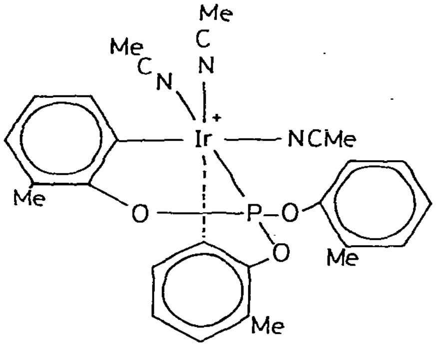
Treatment of **11** with chloride, bromide or iodide results in displacement of a phosphine ligand to give [IrHXNHNC$_6$H$_3$OMe(PPh$_3$)$_2$] (X = Cl, Br, I) and reaction of the halide complexes (X = Br, I) with the corresponding halogen results in substitution of hydrogen by halogen. However, high yields of the chloride complex **12** are best obtained on leaving a chloroform solution of **10** to stand for 15—20 days [8].

Although the reaction of triphenylphosphite with [IrCl(COD)]$_2$ in hot ethanol produces the metallated complex [IrP(OC$_6$H$_4$)(OPh)$_2${P(OPh)$_3$}(COD)], in boiling xylene tri-*o*-tolylphosphite reacts with [IrCl(COD)]$_2$ to give a complex of stoichiometry, [Ir$_2$Cl$_2${P(O-*o*-tolyl)$_3$}$_3$]. This complex has been shown to be a novel precursor for a series of neutral and cationic dimetallated phosphite-iridium(III) complexes. Thus treatment of [Ir$_2$Cl$_2${P(O-*o*-tolyl)$_3$}$_3$] with γ-picoline gives the complex **13** which has been characterised by a single crystal X-ray study. Similar complexes can be obtained with pyridine, PPh$_3$, PMe$_2$Ph and PMePh$_2$. In boiling acetonitrile, [Ir$_2$Cl$_2${P(O-*o*-tolyl)$_3$}$_3$], gives a cationic complex **14** isolated as its hexafluorophosphate salt. In boiling ethanol **14** reacts to



(N = γ-picoline)

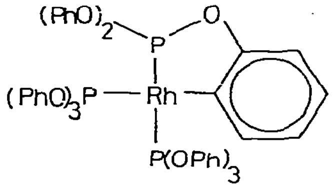
(13)



(14)

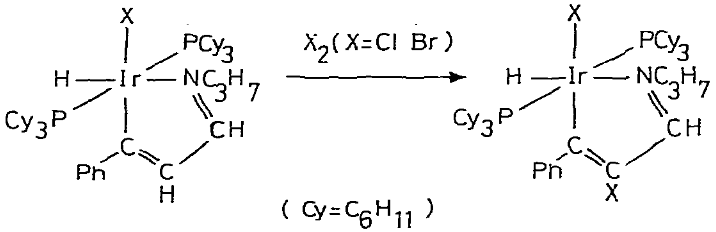
give the dimeric hydride $[IrHCl\{P(OC_6H_3Me)(OC_6H_4Me)_2\}(MeCN)]_2$ [9].

Triphenyl phosphite and $[RhH(CO)(PPh_3)_3]$ heated together in n-heptane give the *ortho*-metallated complex 15 [10].

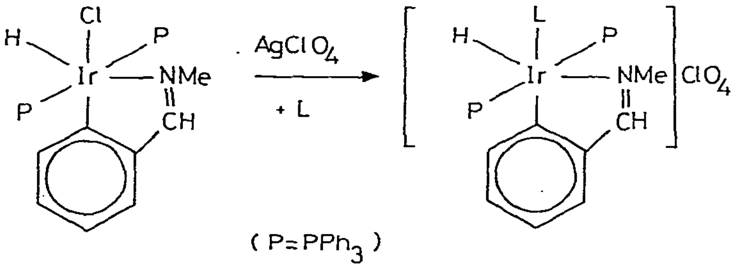


(15)

The cyclometallated complexes 16 react with the appropriate halogen to give the complexes 17 in which a vinylic hydrogen has been replaced by chlorine. No rupture of the iridium—carbon bond is observed. Treatment of 18 with silver



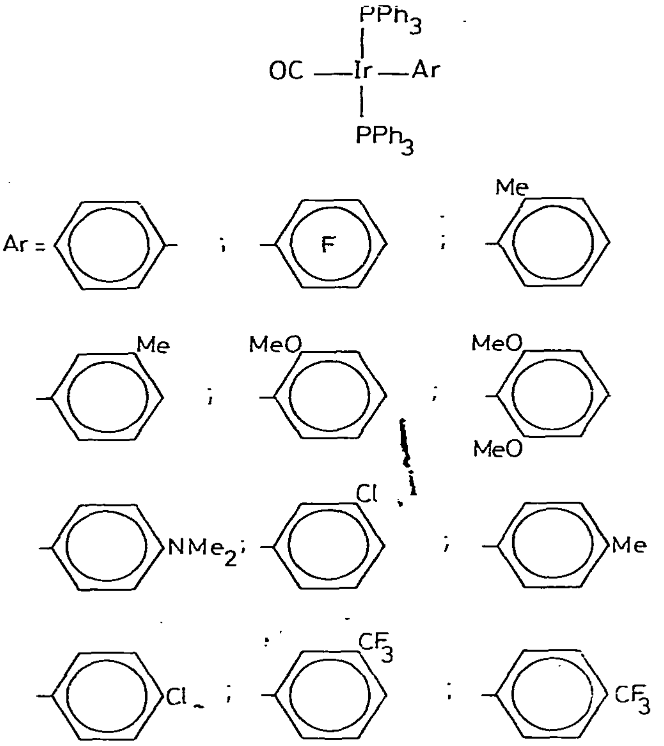
(16) (17)



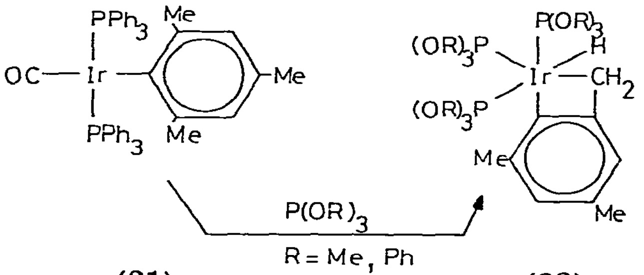
(18) (19)

perchlorate followed by addition of cyclohexyl isocyanide or carbon monoxide gives cationic complexes, the metallocyclic ring remaining intact [11].

Treatment of *trans*-[IrCl(CO)(PPh_3)$_2$] with aryllithium compounds gives the complexes **20**. Some of these complexes react with dioxygen to form adducts [IrAr(O_2)(CO)(PPh_3)$_2$] (Ar = Ph, 3-C_6H_4Me, 4-C_6H_4Me), but complexes with *ortho*-substituted aryl ligands are not oxygenated presumably because the *ortho*-substituents shield the iridium from attack. Sulphur dioxide forms the irreversible addition compound, [Ir(4-C_6H_4Me)(SO_2)(CO)(PPh_3)$_2$]. Sulphur dioxide insertion into the iridium—carbon bond is not observed. Hydrogen chloride oxidatively adds to [Ir(4-C_6H_4Me)(CO)(PPh_3)$_2$] to give [IrHCl(4-C_6H_4Me)(CO)-(PPh_3)$_2$] which only reductively eliminates toluene at elevated temperature [12]. Treatment of the aryl complex **21** with either trimethyl phosphite or triphenyl



(20)



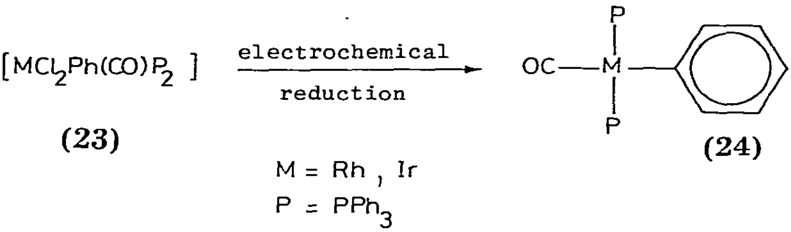
(21) **(22)**

phosphite at room temperature affords the intramolecular oxidative addition product 22 [13].

Although the oxidative addition of alkyl and acyl halides has been extensively studied, the reactions of aryl halides with iridium(I) complexes have not received similar attention. Studies now reveal that aryl halides ArX do oxidatively add to *trans*-[IrCl(CO)(PPh$_3$)$_2$] to give aryliridium(III) complexes [IrCl(X)(Ar)(CO)-(PPh$_3$)$_2$]. The reactivity of the aryl halides decreases in the order I > Br > Cl and electron-withdrawing substituents in the aryl ring accelerate the reaction. The iridium(III) compounds may be used as arylating agents [14], e.g.:

$$\mathrm{PhCH_2COCl} \xrightarrow{\mathrm{IrClPh(CO)(PPh_3)_2}} \mathrm{PhCH_2COPh}$$

Electrochemical reduction of both iridium(III) and rhodium(III) complexes (23) provides a convenient preparation of both aryl- or alkyl-rhodium(I) and -iridium(I) complexes (24). Isolation of the rhodium(III) or iridium(III) complex is not necessary and the complexes 25 can be obtained by oxidative addition of the alkyl or aryl halide to *trans*-[MCl(CO)(PPh$_3$)$_2$] followed by electrochemical reduction [15]. The electrochemical reduction of the rhodium and iridium complexes, [MR(CO)(PPh$_3$)$_2$] (R = alkyl, aryl) occurs via a single two-electron step, there being little difference between the reduction potential of the rhodium and iridium complexes [16].

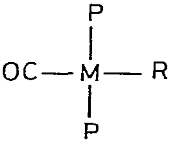


(23)

(24)

M = Rh, Ir

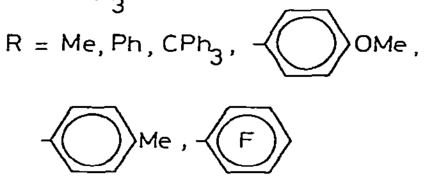
P = PPh$_3$



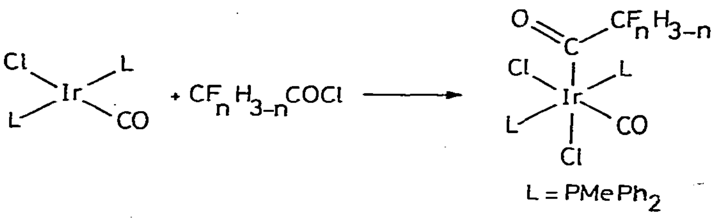
(25)

M = Rh, Ir

P = PPh$_3$



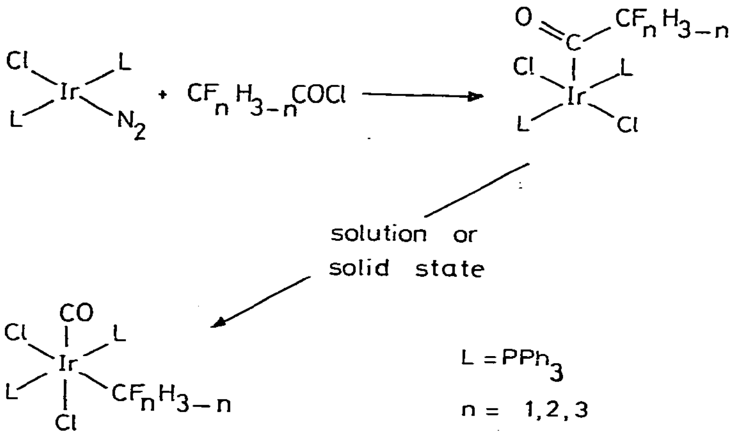
The reactions of *trans*-[IrCl(CO)(PMePh$_2$)$_2$] with acetyl chloride or fluorine substituted acetyl chlorides give the octahedral complexes 26, but five-coordinate complexes 27 are formed upon reaction of an acyl chloride with *trans*-[IrCl(N$_2$)(PPh$_3$)$_2$]. These five-coordinate complexes reversibly add carbon monoxide in solution, form adducts with dimethylformamide and undergo an alkyl group migration reaction upon heating in solution or as a solid to give the six-coordinate complexes 28. The *trans*-influence of acetyl groups, evaluated from ν(Ir—Cl) data, decreases with increasing fluorine substitution. The *trans*-influence of the substituted methyl group decreases in the order CH$_3$



(26)

L = $PMePh_2$

n = 0,1,2,3

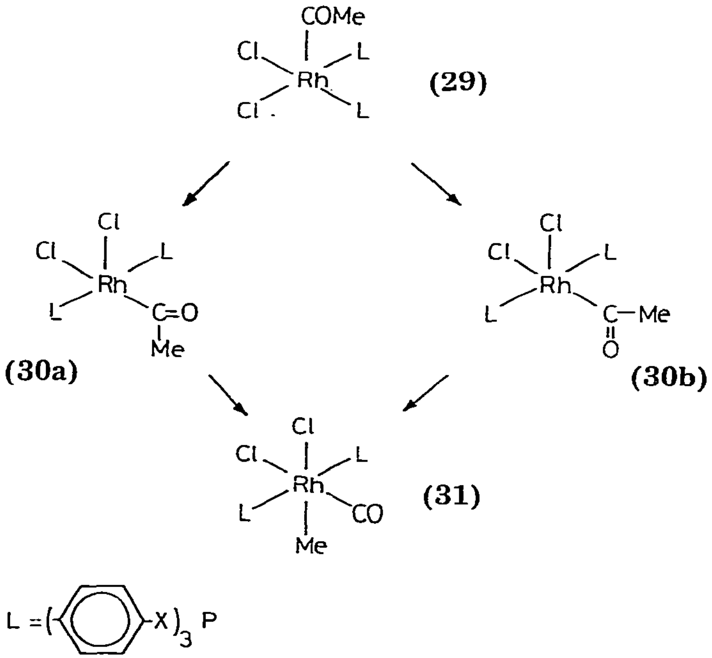


(27)

(28)

L = PPh_3

n = 1,2,3



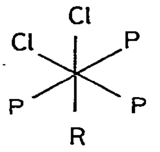
(29)

(30a)

(30b)

(31)

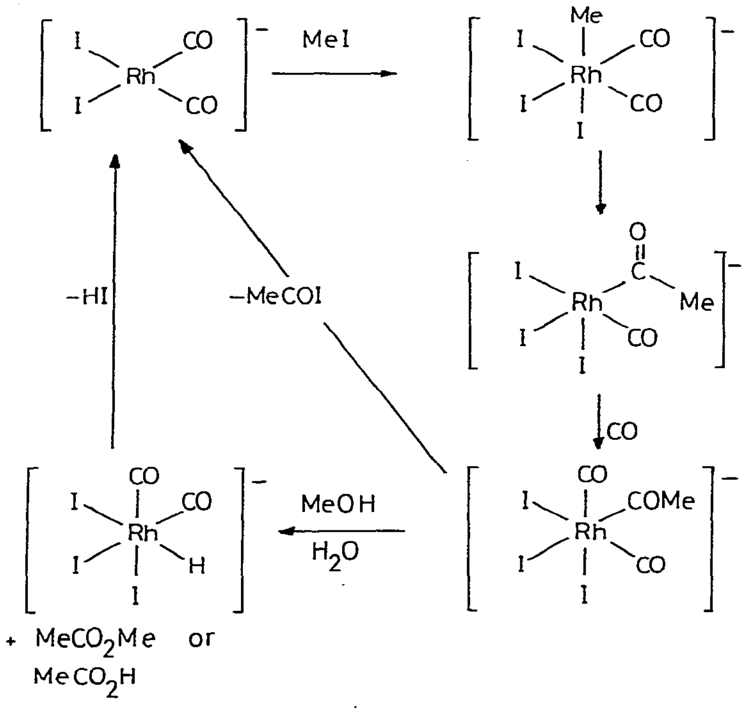
X = F, H, Me



P = PMe$_2$Ph
R = Ph, Me
(32)

$>$ CHF $\simeq$ CH$_2$F $>$ CF$_3$. In the migration reaction the rate decreases in the order CFH$_2$ $>$ CF$_3$ $>$ CF$_2$H and calorimetric measurements establish that the enthalpy change for the migration becomes less exothermic in the order CF$_3$ $>$ CF$_2$H $>$ CFH$_2$. The calorimetric data give an approximate value for the difference between Ir—CF$_3$ and Ir—CH$_3$ bond strengths of at least 57 ± 9 kJ mol^{-1}. The insertion of carbon monoxide into a transition metal—fluorocarbon bond has not been accomplished and a prediction of the activation parameters for this process suggests that the reaction would be very slow [17]. The addition of acetyl chloride to solutions of [RhClL$_3$] in methylene chloride yield the yellow monomeric acetyl complexes **29** which isomerise in chloroform solution to orange monomeric acetyl complexes **30** and thence to methyl complexes **31**. The isomerisation of **29** to **30** to **31** can be followed by using ^{1}H NMR and solution IR spectra. Values for the equilibrium constants for the process **30** $\rightleftharpoons$ **31** are 0.29 ± 0.02 (X = H), 0.35 ± 0.01 (X = F) and 0.38 ± 0.02 (X = Me) and thus there is no correlation with the nature of the *para* substituent in the phosphine ligand. The complexes **32**, which are structurally related to the complexes **31**, can be prepared by addition of either dimethyl- or diphenyl-mercury to refluxing solutions of *mer*-RhCl$_3$(PMe$_2$Ph)$_3$ [18].

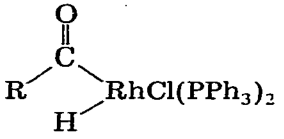
Alkyl migration is an important step in the rhodium-catalysed conversion of



SCHEME 1

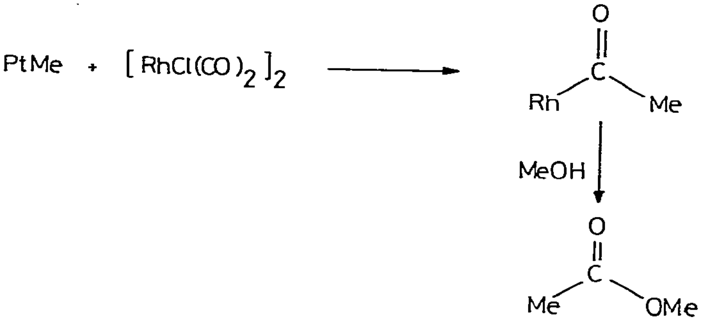
methanol to acetic acid and a pathway for the reaction (Scheme 1) has been proposed which is consistent with the observed independence of the overall reaction rate on carbon monoxide pressure and methanol concentration [19].

Acyl hydride intermediates **33** are thought to be involved in the decarbonylation of aldehydes by [$RhCl(PPh_3)_3$]. It has now been found that the rhodium complexes [$RhCl(PPh_3)_3$] or [$Rh(acac)(C_2H_4)_2$] catalyse aldehyde-alkene addition reactions probably via intermediates similar to **33** [20].



(33)

The transfer of a methyl group from a methylplatinum complex to [$RhCl(CO)_2]_2$ in methanol results in the methyl group being trapped as an ester:



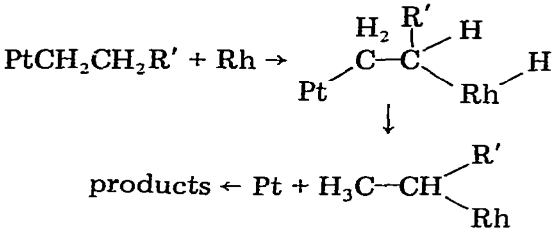
Alkyl isomerisation has now been observed in a study of the reaction of alkylplatinum complexes of the type *cis*-[$PtR_2(PPh_3)_2$] (R = CH_2CD_3, CD_2CH_3, n-Pr, n-Bu, CH_2CHMe_2, n-C_5H_{11}) with [$RhCl(CO)_2]_2$ in CD_3OD (See Table 1).

A large difference observed between ethyl and propyl groups is considered to be related to the difference (about 14 kJ mol^{-1}) in bond energy between a primary and secondary C—H bond of the β-carbon atom of ethyl and propyl. The rapid decrease of isomerisation from propyl to butyl to pentyl is probably a consequence of steric effects. To account for the isomerisation it is proposed that insertion of rhodium into the β-carbon C—H bond occurs (Scheme 2)

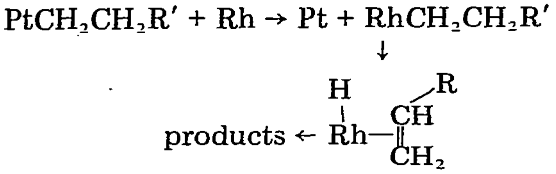
TABLE 1

R	Ester	Yield (%) [a]
CD_2CH_3	$CH_3CD_2COOCD_3$	100
CH_2CD_3	$CD_3CH_2COOCD_3$	100
$CH_2CH_2CH_3$	$CH_3CH_2CH_2COOCD_3$	80
	$CH_3CH(CH_3)COOCD_3$	20
$CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2COOCD_3$	97
	$CH_3CH_2CH(CH_3)COOCD_3$	3
$CH_2CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CH_2COOCD_3$	99
	$CH_3CH_2CH_2CH(CH_3)COOCD_3$	1

[a] % yields refer to the ester product composition at 10% conversion of *cis*-[$PtR_2(PPh_3)_2$].



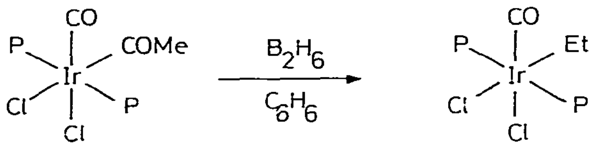
SCHEME 2



SCHEME 3

rather than the normal transfer of propyl to rhodium (Scheme 3) [21]. Alkylcobalt tetracarbonyls prepared under classical oxo conditions [$p(\mathrm{CO}) \geqslant 50$ atm, $p(\mathrm{H_2}) \geqslant 50$ atm, $T \geqslant 80$°C] from alkyl halides and sodium tetracarbonylcobaltate do not isomerise even in the presence of free olefin [22].

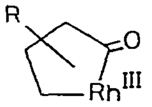
Certain acetyl complexes are rapidly reduced to the corresponding ethyl complexes by $BH_3 \cdot$ THF or B_2H_6/C_6H_6. Thus action of B_2H_6 on **34** in benzene gives the ethyl complex **35** and the acetyl ligand of [Co(COMe)(CO)$_2$(PPh$_3$)-



(34) (P = PMe$_2$Ph) **(35)**

{P(OMe)$_3$}] is also readily reduced. However, the acetyl ligand of [Co(COMe)-(CO)$_2${P(OMe)$_3$}$_2$] is not readily reduced. Substitution of a trimethyl-phosphite ligand for the triphenylphosphine ligand would result in a decrease in electron density in the acetyl ligand, possibly decreasing its susceptibility to reduction. In organic chemistry reduction of an acetyl group by $BH_3 \cdot$ THF yields, after hydrolysis, the expected alcohol. The reductions of these transition metal acetyl groups is unusual in that it involves no hydrolysis stage and results in direct reduction of an acetyl group to an ethyl group [23].

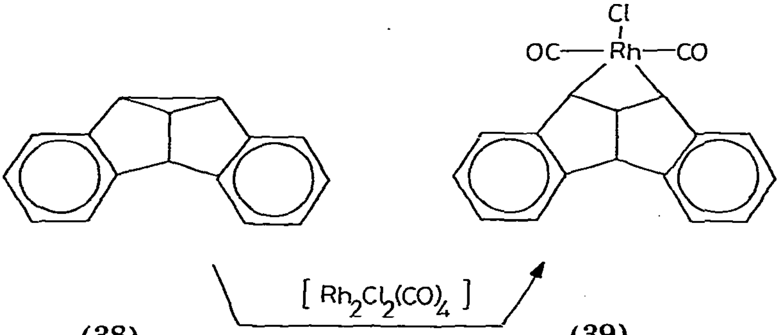
Cyclopropanes and other compounds containing the cyclopropane ring system such as quadricyclane, react readily with [$Rh_2Cl_2(CO)_4$] to give metal acyl complexes of the type **36**. These reactions probably involve intermediates of the



(36)

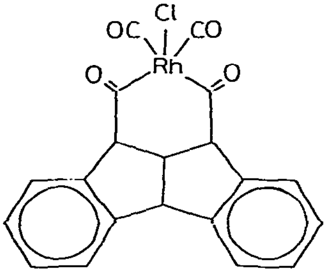
(37)

type **37** and complexes containing 4-membered heterocyclic ring systems have now been obtained as initial products of the reactions of dibenzosemibullvalenes with $[Rh_2Cl_2(CO)_4]$. Thus dibenzosemibullvalene (**38**) reacts with $[Rh_2Cl_2(CO)_4]$ to give the yellow crystalline complex **39**. Passage of carbon monoxide gas

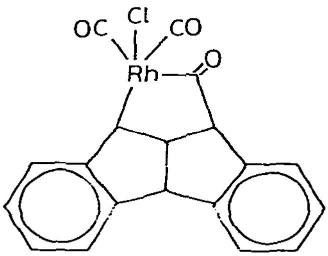


(**38**) (**39**)

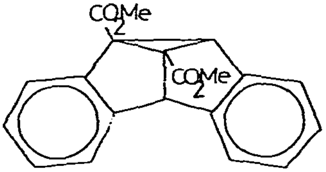
through a suspension of **39** in methylene chloride produces a clear yellow solution which appears to contain **40** but on evaporation the solution yields the monoacyl complex **41**. Similar studies with 1,2-dicarbomethoxydibenzosemibullvalene (**42**) reveal that the presence of two strongly electron-withdrawing



(**40**)



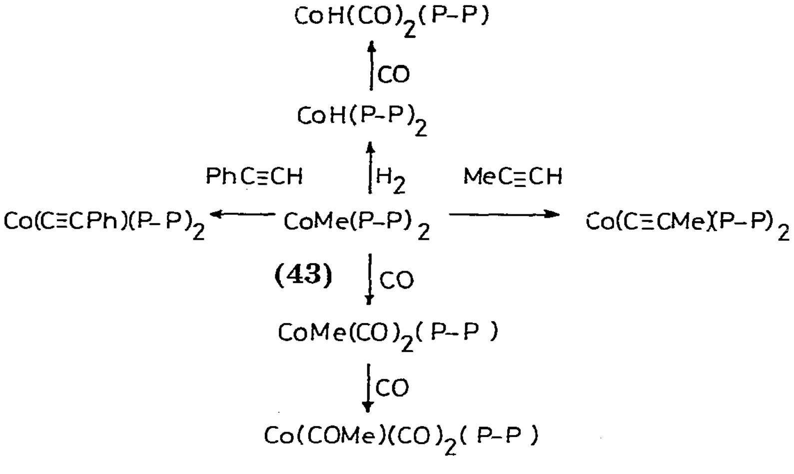
(**41**)



(**42**)

substituents greatly reduces the reaction rate in complex formation and readily generates the free ligand from the acyl-metal complexes [24].

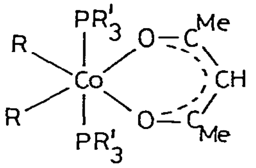
The reaction of $[Co(acac)_3]$ with $AlMe_2OEt$ and $Ph_2PCH_2CH_2PPh_2$ produces the methylcobalt(I) complex **43** and some reactions of this complex are illustrated in Scheme 4. Attempts to prepare similar alkylcobalt(I) complexes using $AlEt_3$, $AlEt_2OEt$, Al-n-Pr_3 and Al-i-Bu_3 give only $CoH(Ph_2PCH_2CH_2PPh_2)_2$. Complex **43** initiates the polymerisation of acrylonitrile at low temperature and under carefully controlled conditions a yellow complex may be isolated which contains a methyl group and coordinated acrylonitrile. Complex **43** reacts with ace-



$(P\text{-}P) = Ph_2PCH_2CH_2PPh_2$

SCHEME 4

taldehyde over a period of a few days releasing methane and carbon monoxide. A carbonyl complex is also formed in this reaction [25]. The reaction of $[Co(acac)_3]$ with alkylaluminium compounds in the presence of monotertiary phosphines produces the complexes 44 [26,27].



$PR'_3 = PEt_3$; R = Me

$PR'_3 = PPhMe_2$; R = Me, Et, ^{n}Pr, ^{i}Bu

$PR'_3 = PPh_2Me$; R = Me

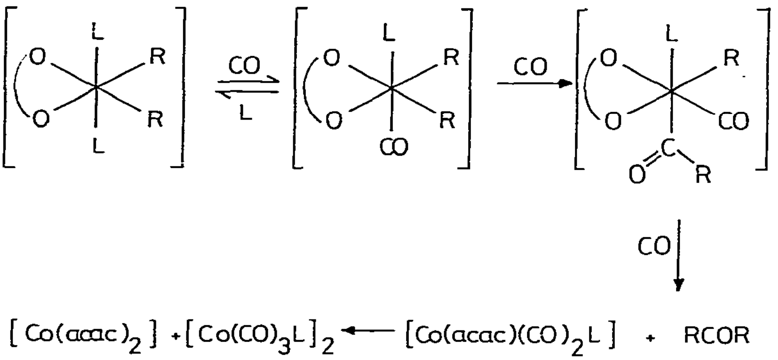
$PR'_3 = P^nBu_3$; R = Me

(44)

The melting point and thermal stability of a series of $[CoR_2(acac)(PPhMe_2)_2]$ complexes decreases with increasing alkyl chain length. The thermal decomposition of the complexes is first order with respect to the complex and addition of free $PPhMe_2$ to the solution of the ethyl complex strongly inhibits its thermal decomposition [28]. For a series of phosphine complexes the decomposition temperature decreases in the order $PPhMe_2 > PPh_2Me > PEt_3 >$ P-n-Bu_3 [27].

The tertiary phosphine ligands in 44 are partly dissociated in solution and one of the phosphine ligands in the complexes can be replaced by pyridine and γ-picoline to give complexes of the type $[CoR_2(acac)(PR_3)L]$ (L = pyridine γ-picoline). However, a similar replacement is not observed with α- and β-picolines. 2,2′-Bipyridyl displaces two tertiary phosphine ligands to give complexes of the type $[CoR_2(acac)(bipy)]$. A similar displacement of the tertiary phosphine ligands with $Ph_2PCH_2CH_2PPh_2$ is not observed. Kinetic and thermodynamic data for the exchange reactions have been obtained [29].

The complexes $[CoR_2(acac)(PPh_2Me)_2]$ react with carbon monoxide even at −50°C to give 1 mol equiv. of dialkyl ketone per cobalt and a complex of composition $[Co(acac)(CO)_2(PPh_2Me)]$. Recrystallisation of this complex from acetone effects a disproportionation reaction to give $[Co(acac)_2]$ and $[Co(CO)_3(PPh_2Me)]_2$, (Scheme 5). This facile insertion of carbon monoxide is a probable consequence of the ability of carbon monoxide to readily displace a phosphine ligand *cis* to an alkyl group and these reactions should be contrasted with the reluctance of alkylcobalt complexes having macrocyclic ligands to readily undergo carbonyl insertion reactions. The alkyl groups in 44 are readily cleaved from the cobalt by mercury(II) acetate and $[CuI(PPh_3)_3]$ (Scheme 6) [27].



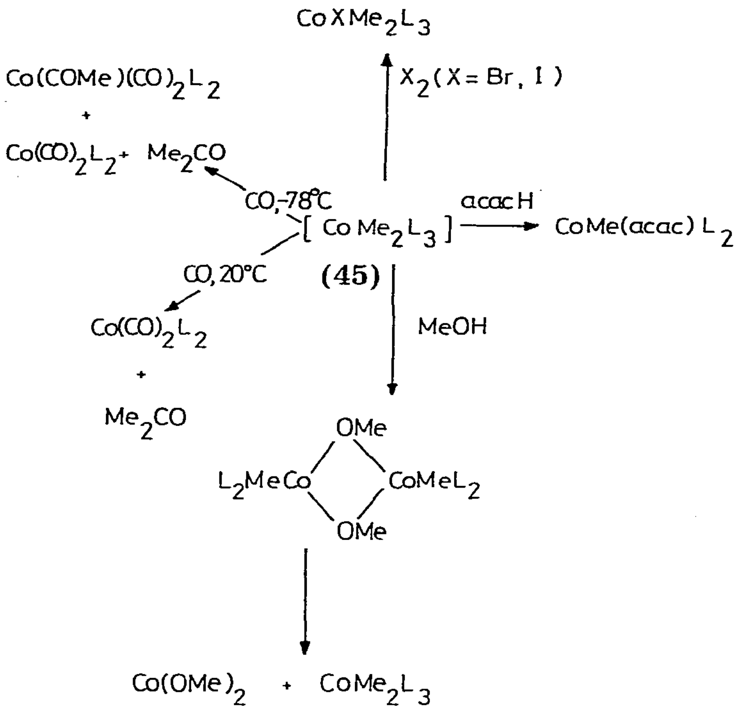
SCHEME 5

$$\underset{(44)}{CoMe_2(acac)(PPhMe_2)_2} + Hg(OAc)_2 \rightarrow HgMe_2$$

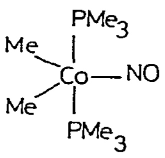
$$\begin{array}{l} CoMe_2(acac)(PEt_3)_2 + 2CuI(PPh_3)_3 \rightarrow 2\ CuMe(PPh_3)_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad Cu^0 + CH_4 + C_2H_6 \end{array}$$

SCHEME 6

A study has also been made on the cleavage of the alkyl groups from $[CoEt_2(acac)(PPhMe_2)_2$, $[CoMe(PPh_3)_3]$, $[CoEt(bipy)_2]$ and $[CoMe(bipy)_2]$ by deuterium gas [30]. A methylcobalt(II) complex $[CoMe_2(PMe_3)_3]$ (45) can be obtained from the reaction of cobalt(II) chloride with trimethylphosphine and methyllithium. Some reactions of this complex are illustrated in Scheme 7. At −30°C nitric oxide reacts with 45 to give 46. The nitrosyl complex 46 rearranges via NO insertion into a Co—C bond at 20°C to give 47 [31].



SCHEME 7



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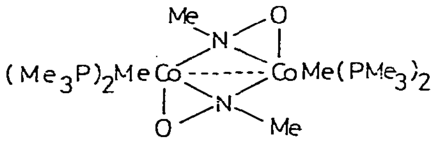
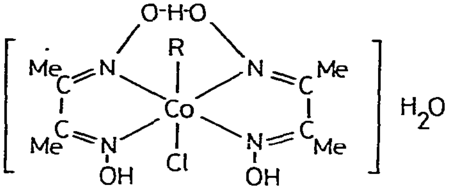


(47)

In an argon atmosphere PhC≡CPh reacts with [$CoCl(PPh_3)_3$] and MeMgBr to give mainly cyclisation products of the acetylene together with very low yields of *cis*- and *trans*-PhCMe=CHPh. Further studies have now shown that dioxygen has a significant effect on this reaction. Thus under dioxygen the consumption of the acetylene through condensation tends to be inhibited while the yield of addition products to the triple bond is increased and dialkylation of the acetylene is observed to give PhCMe=CMePh [32]. Methyltris(triphenylphosphine)cobalt [$CoMe(PPh_3)_3$] reacts with PhC≡CPh to give α-methylstilbene as the sole addition product [33].

Kinetic studies on alkylaquocobaloximes of the type [$CoR(dmgH)_2H_2O$] have demonstrated an acid dependence which was taken as evidence for the existence of an oxime oxygen protonated complex in solution. Such complexes (48) have now been isolated by protonation of the alkylaquocobaloximes (49) in aqueous solution. Protonation under anhydrous conditions yields the complex [CoMeCl-(dmgH)($dmgH_2$)] [34].



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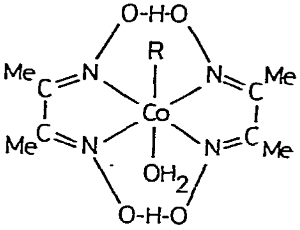
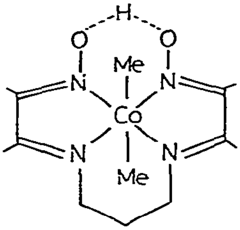


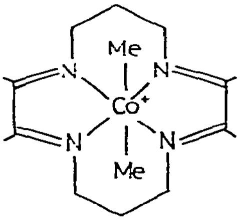
(R=Me, Et, ^{n}Pr, ^{i}Pr, C_6H_{11})

(49)

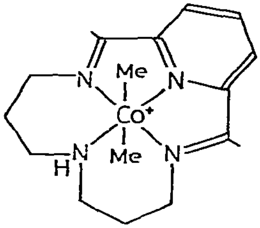
Although the Co—C bond in complexes such as $[CoMe(dmgH)_2(H_2O)]$ is readily cleaved by Hg^{2+} and Pd^{2+}, indeed the topic has been reviewed [35], a number of other reagents such as $H^+(aq)$, $MeHg^+$ and $PhHg^+$ are mainly unreactive toward cleavage of the Co—C bond. In contrast however, reactions of $PhHg^+$ with bis(organo)(chelate)cobalt complexes occur rapidly. Kinetic studies on the methyl-transfer reaction of the complexes **50**, **51** and **52** show that the reactions



(50)

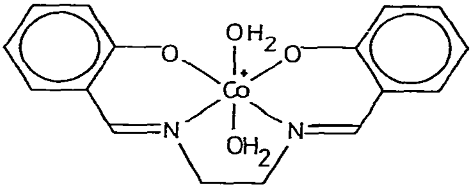


(51)



(52)

follow a second-order rate expression and that the reaction rates for a given $R_2Co(chel)$ complex with different electrophiles follow the order $PhHg^+ > [Co(chel')(H_2O)_2]^+ > H_3O^+$, the complexes $[Co(chel)(H_2O)_2]^+$ being **53**, **54** or **55**.



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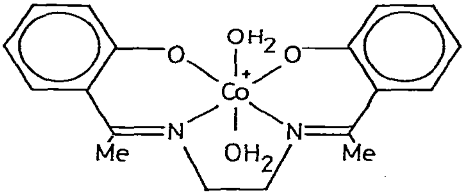

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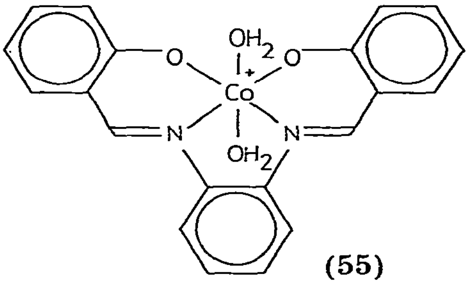


(55)

A kinetic study of the demethylation of **50** by Zn^{2+} and Cd^{2+} reveals the presence of binuclear intermediates of the type **56**. These reactions occur via 1/1

$M^{2+}Me_2Co(BDM\ 1,3\text{-pn})$

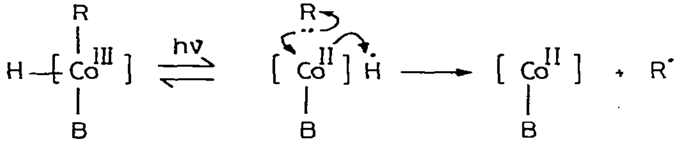
(56)

and 2/1 stoichiometries as illustrated in the following equations [37]:

$$CoMe_2(BDM\ 1,3\text{-pn}) + M^{2+} \xrightarrow{\text{fast}} CoMe(BDM\ 1,3\text{-pn}) + MeM^+$$

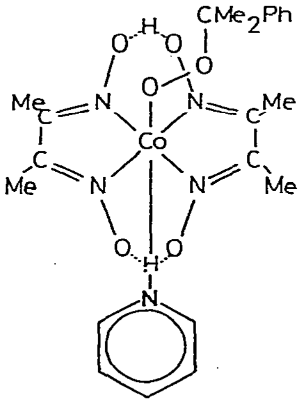
$$CoMe_2(BDM\ 1,3\ pn) + MeM^+ \xrightarrow{\text{slow}} CoMe(BDM\ 1,3\text{-pn}) + Me_2M$$

The photolysis of any alkylcobaloxime proceeds via a mechanism involving an initial electron transfer reaction from an equatorial ligand to the cobalt atom to produce a cobalt(II) species which still retains both axial ligands. This is followed by a rearrangement of the equatorial ligand in which a hydrogen atom is ejected (Scheme 8) [38].



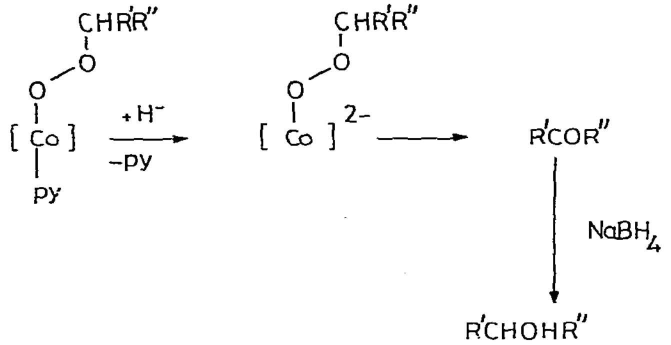
SCHEME 8

Quantum yields for the photolyses of the cobalt complexes $[CoMe(dmgH)_2py]$, $[Co(CH_2Ph)_2(dipy)_2]I$, $[CoMe(salen)py]$, and $[CoMe(salen)quinoline)]$ have been determined [39]. Alkyl(pyridine)cobaloximes irradiated with visible light in the presence of t-butyl or cumyl hydroperoxide give t-butyl- or cumyl-peroxide-(pyridine)cobaloxime via a photochemical substitution reaction and the X-ray structure of one of these complexes (57) has been determined. These photochemical reactions, which do not occur in the dark or even under reflux, appear to proceed via formation of a cobalt(II) complex which subsequently reacts rapidly with the hydroperoxides. Evidence for this mechanism is provided by the obser-



(57)

vation that the cobalt(II) complex, [Co(dmgH)$_2$py$_2$], reacts rapidly with t-butyl or cumyl hydroperoxides to give the same complexes as the alkylcobaloximes. These photo-substitution reactions only occur with very stable hydroperoxides which give rise to long-living free radicals [40]. Various alkyl(tetraphenylporphinato)cobalt(III) compounds [CoR(TPP)] undergo photolytic reactions with dioxygen to give the complexes [Co(OOR)(TPP)] [41]. The preparation of an optically active cobaloxime followed by oxygen insertion and sodium borohydride reduction to the corresponding optically inactive alcohol has been taken as evidence for racemization during oxygen insertion. However, further studies on the sodium borohydride reduction of alkyldioxycobaloximes reveal that the primary products of reduction are ketones and aldehydes which are subsequently reduced to alcohols by excess sodium borohydride (Scheme 9). Further studies are clearly needed on the stereochemistry of oxygen insertion in these systems [42].



SCHEME 9

The first example of homolytic displacement of cobalt(II) from organocobalt(III) complexes by conventional organic radicals has been reported. Thus allylbis(dimethyl glyoximato)pyridinecobalt(III) reacts with bromotrichloromethane at ambient temperature in chloroform to give near quantitative yields of 4,4,4-trichlorobut-1-ene. The reactions of substituted allylcobaloximes with bromotrichloromethane and with carbon tetrachloride each give only a single low molecular weight olefinic product and, in all cases for which a distinction can be made, the reactions were 100% regio-specific (Scheme 10). The reactions are

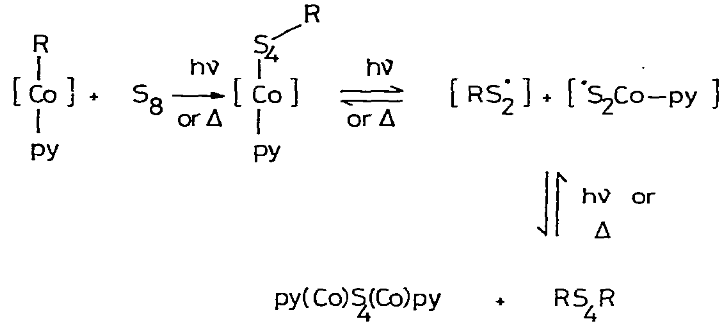
$$\mathrm{R(R')C{=}CR''CH_2Co(dmgH)_2py + XCCl_3\ (X = Br\ or\ Cl)}$$

$$\downarrow$$

$$\mathrm{XCo(dmgH)_2py + CH_2{=}CR''CR(R')CCl_3}$$

R=R'=R''=H
R=Me; R'=R''=H
R=Ph; R'=R''=H
R=R'=H; R'' =Me
R=R'=Me; R''=H

SCHEME 10

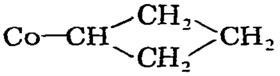


SCHEME 11

inhibited by added galvinoxyl but are faster in the presence of added benzoyl peroxide and in the presence of light. The reactions are believed to involve chain reactions in which trichloromethyl radicals and cobaloxime(II) complexes are the chain carriers. The main initiating species are thought to be allyl radicals and cobaloxime(II) species formed by either thermolysis or photolysis of small quantities of allylcobaloxime [43].

The photoinduced and thermal insertion of sulphur into the Co—C bond of some alkyl- and aryl-cobaloximes has been reported (Scheme 11). Photo-substitution of $(C_6H_{11})S_4(C_6H_{11})$ and organic disulphides on alkylcobaloximes give compounds of the type RS_nR and $[RS_n(Co)Py]$ (n = 1—4) [44].

Enzymes containing coenzyme derivatives of vitamin B_{12} can catalyse rearrangements of the carbon skeleton of the substrate, e.g. the reversible interconversion of certain succinate and methylmalonate derivatives. There is, however, no real evidence to indicate whether the substrate undergoes rearrangement in the form of the carbonium ion, the free radical, or when coordinated to the cobalt. A study on the organocobalamines 58, 59 and 60 has shown while



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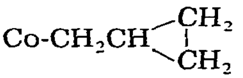


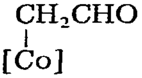
(59)

$Co\text{-}CH_2CH_2CH{=}CH_2$

(60)

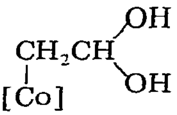
there is no conversion of 58 into 59 or 60, 59 is isomerised to 60 in solution at 60°C, in the presence of dioxygen at a rate which is virtually independent of the dielectric constant of the solvent. A mechanism involving polar intermediates is therefore probably not operative but the reaction could proceed either by a free radical pathway or a pathway involving no cleavage of the Co—C bond [45].

Formylmethylcobalamin 61 as its hydrate 62 or ammoniated form 63 has been suggested as an intermediate in the enzymic conversion of ethylene glycol



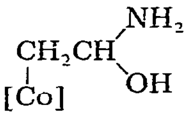
$[Co]CH_2CHO$

(61)



$[Co]CH_2CH(OH)_2$

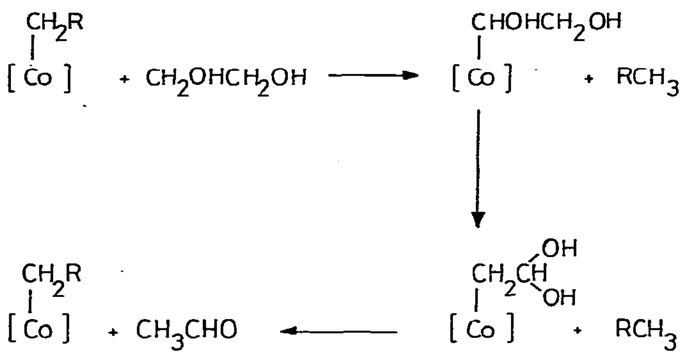
(62)



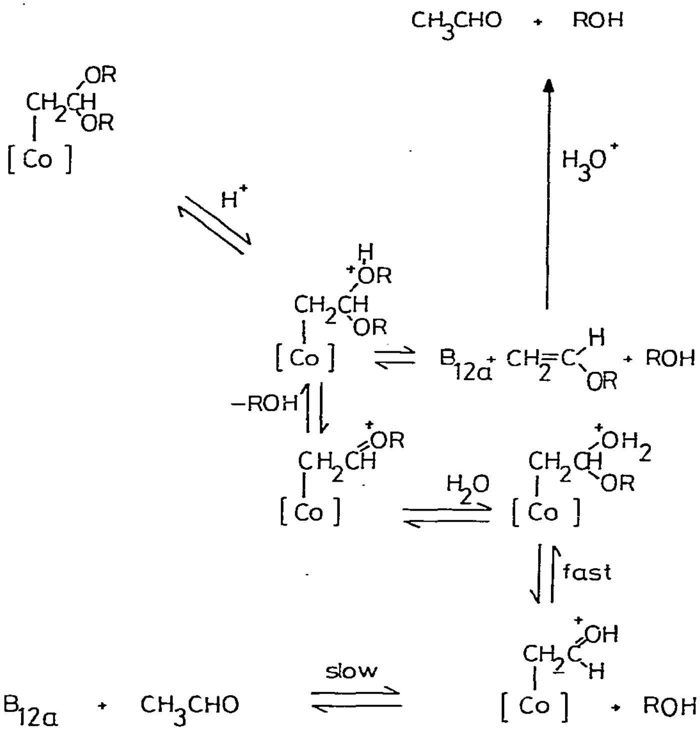
$[Co]CH_2CH(NH_2)OH$

(63)

to acetaldehyde by dioldehydrase and of ethanolamine to acetaldehyde by ethanolamine ammonia lyase (Scheme 12).

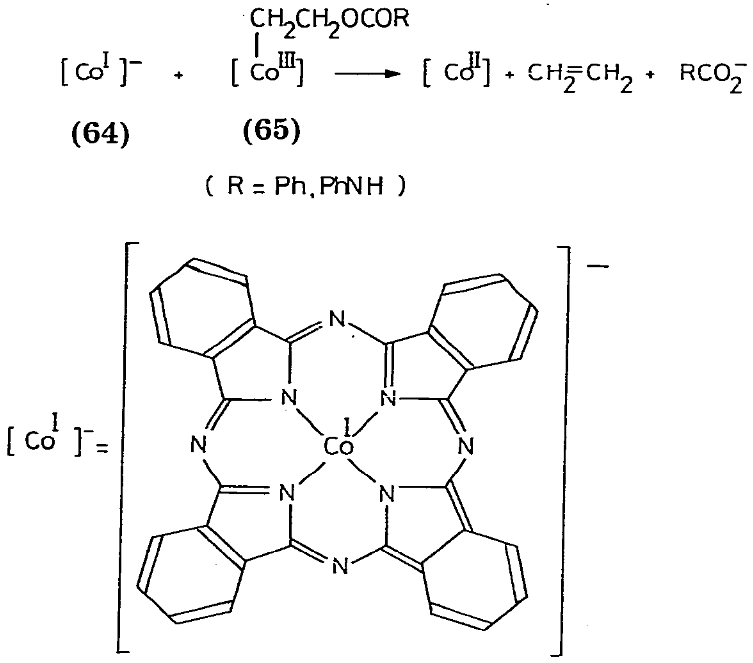


SCHEME 12



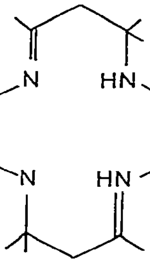
SCHEME 13

A study of the kinetics of the acid-catalysed decomposition of 61 and its acetals has been made in order to determine the relevance of 61 as a possible intermediate in the dioldehydrase and ethanolamine ammonia lyase reactions. These results show, however, that 61 is acid labile and this may be responsible for the inability to observe the compound in these reactions. Two different pathways are observed for the acid-catalysed decomposition of the cobalmin acetals (Scheme 13) [46].



$$[\mathrm{Co^{I}}]^- + [\mathrm{Co^{III}}]\mathrm{CH_2CH_2OCOR} \longrightarrow [\mathrm{Co^{II}}] + \mathrm{CH_2{=}CH_2} + \mathrm{RCO_2^-}$$

SCHEME 14



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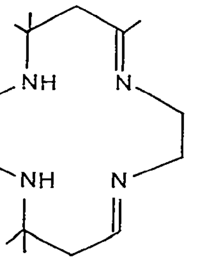

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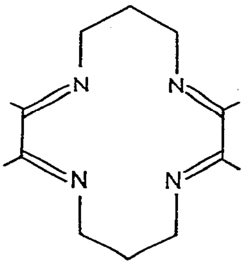

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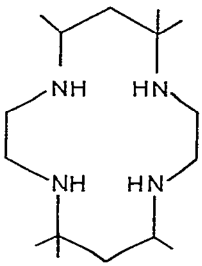

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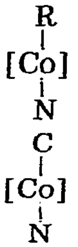

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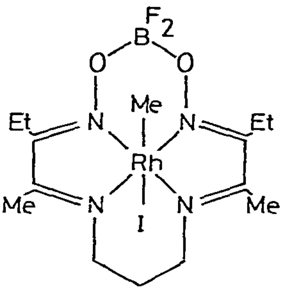


(71)

The cobalt(I) phthalocyanine complex **64** reacts with the complexes **65** releasing ethylene and generating a cobalt(II) phthalocyanine complex (Scheme 14) [47,48].

Cobalt(I) complexes of the unsaturated macrocyclic ligands **66**, **67**, **68** and **69** react rapidly with dinitrogen monoxide, dioxygen and methyl iodide [49].

The reaction of an alkylaquocobaloxime, $[CoR(dmgH)_2(H_2O)]$ with $[CoCN(dmgH)_2N]$, (N = py, py-4-NH_2, py-3-Cl, NH_3 or pip) produce cyano-bridged dicobaloximes of the type **70** [50].

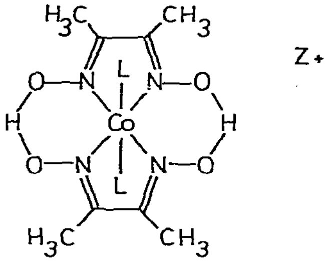
Studies on the oxidation mechanism of organocobalt chelates. [CoR(chel)], reveal that both anodic and homogeneous chemical oxidations of the organocobalt(III) chelates can be interpreted in terms of a single mechanism involving electron transfer with intermediate formation of the organocobalt(IV) chelate followed by Co—C bond cleavage [51]. The paramagnetic radical cations resulting from these oxidations could be represented by either of the limiting electron structures $[Co^{III}R^{\cdot}]$ and $[Co^{IV}R^{-}]$. Evidence derived from EPR measurements support the formulation $[Co^{IV}R^{-}]$ the unpaired electron being predominantly localised on the cobalt atom [52].

The structure of **71** has been determined by single crystal X-ray studies. The BF_2 bridge is bent towards the axial methyl and the ^1H NMR spectrum exhibits spin coupling of the axial methyl protons with ^{19}F in the BF_2 bridge (J(H—F) 2.3 Hz) consistent with CH···F interaction in CD_2Cl_2 solution [53].

Metal—carbene complexes

The cobalt(III) carbene complexes $[Co(dmgH)_2L_2]PF_6$ and $[Co(CH_3)(dmgH)_2L]$ (dmgH = dimethylglyoximato, L = $:C(NHCH_3)_2$) have been prepared by the reaction of $[Co(dmgH)_2(CH_3NC)]PF_6$ and $[Co(CH_3)(dmgH)_2(CH_3NC)]$ with methylamine [54]. The isomeric complexes (L = $:N(CH_3)CH(NHCH_3)$) have also been prepared by the reaction of *N,N'*-dimethylformamidine with either $[Co(CH_3)(dmgH)_2]_2$ or a solution prepared by adding dimethylglyoxime to an ethanolic solution of $CoCl_2 \cdot 6\ H_2O$ followed by aerial oxidation. Specific assignments of the ligand conformations have been made on the basis ^1H NMR parameters. The preparation and interconversion of isomers (a), (b) and (c), (d) in **72** are described.

The reaction of chloro(triphenylphosphine)cobaloxime with arenebisdiazonium sulphates, $[N_2ArN_2](SO_4)_2$ gives complexes **73** [55]:



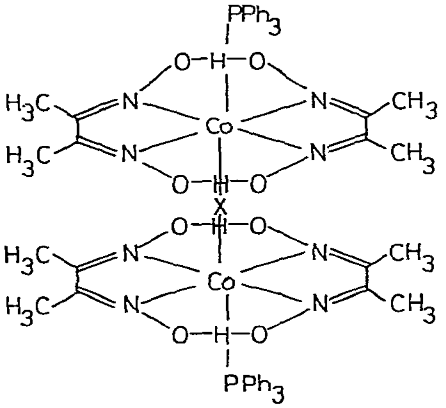
(72)

(a) $L=L'=:C(NHCH_3)_2$ $z=1$

(b) $L=L'=:N(CH_3)CH(NHCH_3)$ $z=1$

(c) $L=CH_3$ $L'=:C(NHCH_3)_2$ $z=0$

(d) $L=CH_3$ $L'=:N(CH_3)CH(NHCH_3)$ $z=0$



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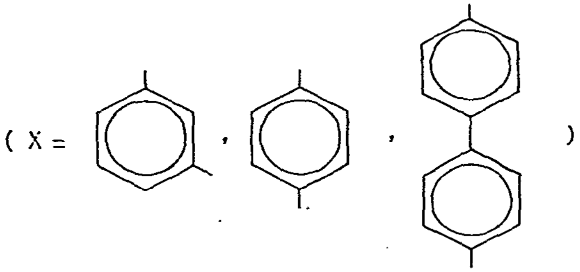
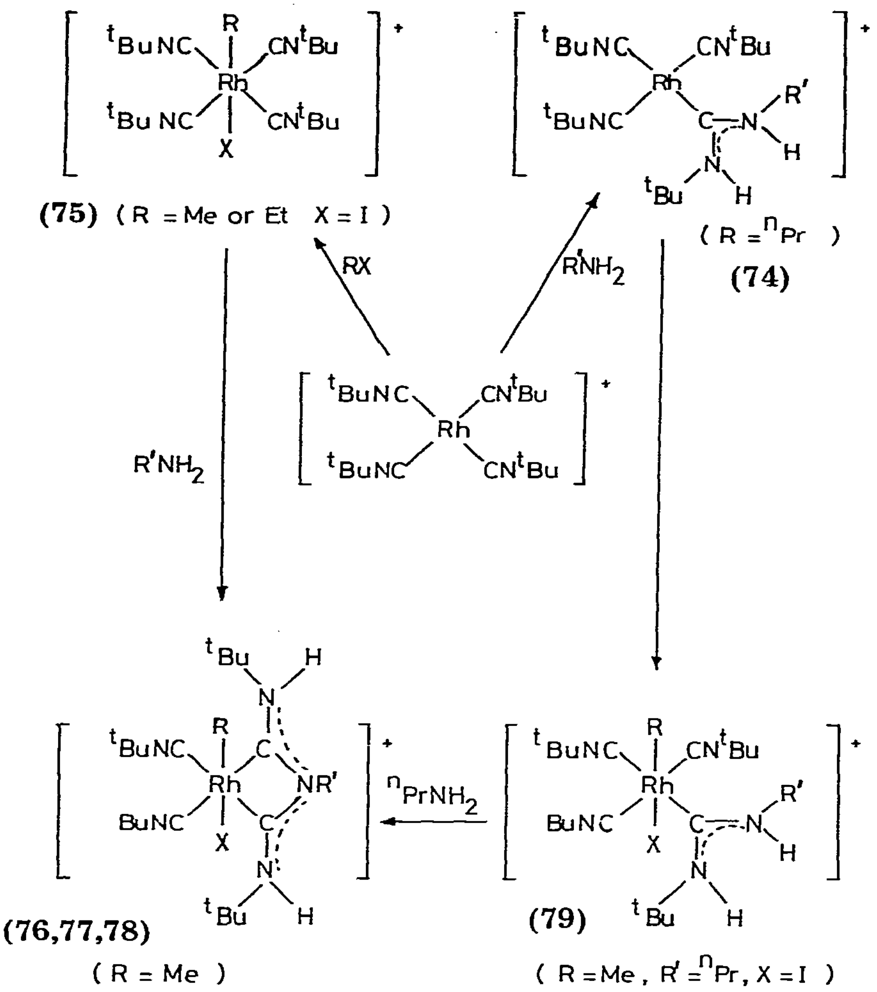
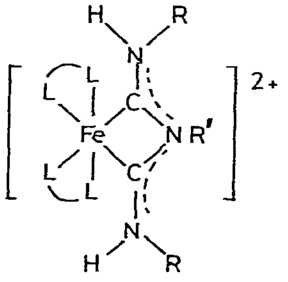


Treatment of $[Rh(X)(R)(CN\text{-}t\text{-}Bu)_4]^+$, formed by *trans*-oxidative addition of alkyl halides to $[Rh(CN\text{-}t\text{-}Bu)_4]^+$, with neat primary amines results in the formation of chelating rhodium(III) dicarbene complexes 74—79 (Scheme 15) [57]. The method of using neat amine as solvent has also been extended to the synthesis of related 2,2'-bipyridyl and 1,10-phenanthroline iron(II) dicarbene complexes 80—82.

A novel ligand 83 formed by the condensation of two benzoyl isothiocyanate molecules and joined together at the sulphur atom of one ligand and the isothiocyanate carbon atom of the other, is produced in the reaction of PhCONCS with $[RhCl(PPh_3)_3]$ in ethoxyethane to give the complex $[RhCl(PhCONCS)_2$-

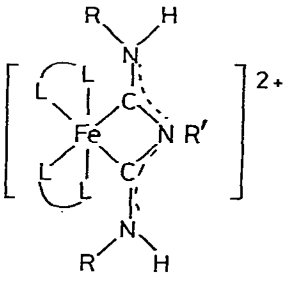


SCHEME 15



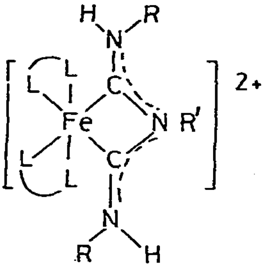
(L-L = 2,2'-bipyridyl
R=R'=Me)

(80)



(L-L = 2,2'-bipyridyl
R = ^{i}Pr R'=Me)

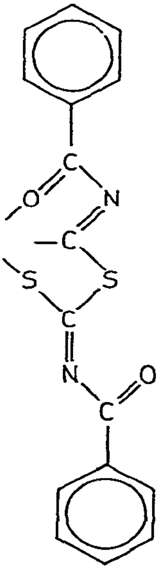
(81)



(L-L = 1,10-phenanthroline
R=^{i}Pr, R′=Me)

(82)

$(PPh_3)_2]$ (84). The crystal structure of this complex is reported [57].



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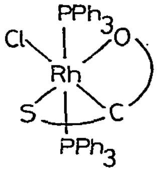
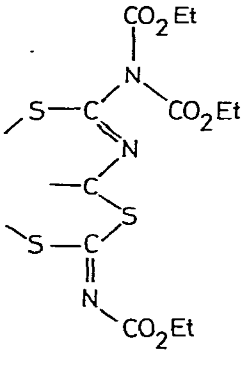
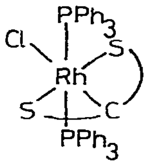


(S⌒C⌒O = 12)

(84)



(85)



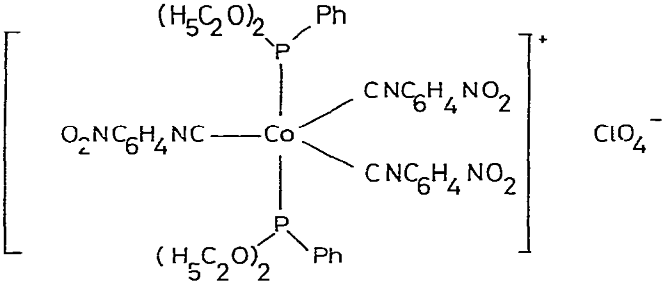
(S⌒C⌒S = 14)

(86)

A related complex (86) is formed between $[RhCl(PPh_3)_3]$ and the tridentate ligand formed by condensation and rearrangement of three ethoxycarbonyl isothiocyanate molecules (85) and the crystal structure data show these complexes to be similar [58].

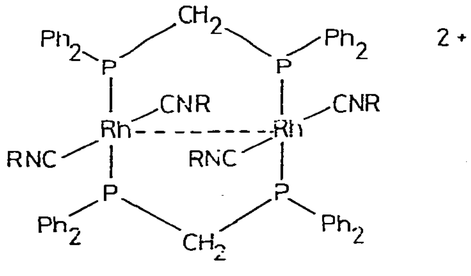
Metal Isocyanide Complexes

Treatment of aromatic isocyanide complexes of cobalt(I) with various trialkyl phosphites results in the ready substitution of two aromatic isocyanide ligands [59]. The resulting complexes of the general type $[Co(CNR)_3\{P(OR')_3\}_2]X$ (R = aromatic, R' = aliphatic and $X = BF_4^-$, ClO_4^-) which showed no sensitivity towards oxygen or water have been characterised by studies of IR, ^1H NMR and ^{59}Co NQR parameters, and have been found to have a regular trigonal bipyramidal structure in solution and a distorted trigonal bipyramidal structure in the solid state. By using 4-nitrophenyl isocyanide as the aromatic cyanide and diethylphenyl phosphonite as the phosphite similar five-coordinate complexes have been prepared having two or three phosphites as ligands. The crystal structure of $[Co(4\text{-}NO_2C_6H_4NC)_3(PhP(OEt)_2)_2]ClO_4$ is reported [60] and the cobalt is found to be in a slightly distorted trigonal bipyramidal environment with the isocyanide ligands in equatorial positions (87).



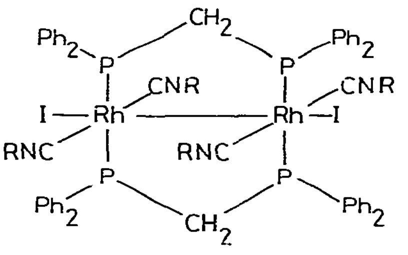
(87)

The synthesis of a new series of phosphine-bridged complexes of rhodium(I) (88) is reported and a study of their conductance parameters over a range of concentrations has confirmed their dimeric nature [61]. Further studies on the ^1H



($R = CH_3, \underline{n}\text{-}C_4H_9$, $\underline{c}\text{-}C_6H_{11}$, $\underline{t}\text{-}C_4H_9$)

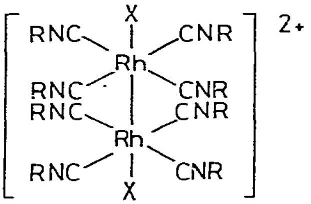
(88)



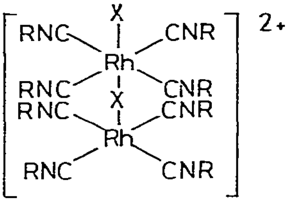
($R = CH_3$
$n\text{-}C_4H_9$
C_6H_{11})

(89)

NMR and IR spectra of these complexes indicate that they have exclusively terminal isocyanide ligands and are diamagnetic. The dimers are readily oxidised by iodine to produce diamagnetic rhodium(II) complexes (89), which have similar conductance values to the initial complexes suggesting that the iodine atoms are firmly bound to the rhodium coordination sphere. The diamagnetic nature of these iodine complexes strongly suggests a direct rhodium—rhodium bond. The ambiguity of interpretation of the ^{1}H NMR signals for the methyl resonances in the complex $[Ir(CNMe)(diphos)_2]ClO_4$ has led to a crystal structure determination of this complex [62]. The solid-state structure is found to be trigonal bipyramidal and this thus eliminates the possibility of a square pyramidal orientation, the alternative suggested by the ^{1}H NMR spectrum. The structure is, however, non-rigid and by analogy to the structurally similar $[Ru(NO)(diphos)_2]^+$ it is suggested that the stereochemical nonrigidity can be considered in terms of Berry pseudorotation involving a square pyramidal transition state with the CNMe ligand in an apical position. The complexes $[IrHI_2(MPh_3)_2]$ (M = P or As) and $[IrH_2I(PPh_3)_3]$ react with the ligand p-MeC_6H_4NC to give $[IrHI_2(MPh_3)_2$-(p-$MeC_6H_4NC)]$ and $[IrH_2I(PPh_3)_2$(p-$MeC_6H_4NC)]$, respectively [63]. *cis*- and *trans*-$[IrHI_2(SbPh_3)_3]$ also react with p-MeC_6H_4NC to give the complexes *cis*- and *trans*-$[IrHI_2(SbPh_3)_2$(p-$MeC_6H_4NC)]$. The action of $[Se_2CNEt_2]^-$ on the hydride $[IrH_3(MPh_3)_2]$ (M = P or As) gives $[IrH_2(MPh_3)_2(Se_2CNEt_2)]$. The association in solution of mixtures of $[(RNC)_4Rh]^+$ and *trans*-$[(RNC)_4RhX_2]^+$ (R = alkyl, X = halide) according to the equilibrium $(RNC)_4Rh^+ +$ *trans*-$(RNC)_4RhX_2^+ \rightleftharpoons (RNC)_8Rh_2X_2^{2+}$ is reported using cyanomethane as solvent [64]. The association is evidenced by the unique electronic spectra which differs from that expected from the sum of the spectra of the reacting species. Similar associations have been observed in other solvents but the equilibrium constant decreases as the dielectric constant of the solution decreases, and no adduct was observed in dichloro- or trichloro-methane. The complex $[(C_6H_{11}NC)_8Rh_2I_2](BPh_4)_2$ has been isolated and it is suggested that it has the structure **90** or **91**.

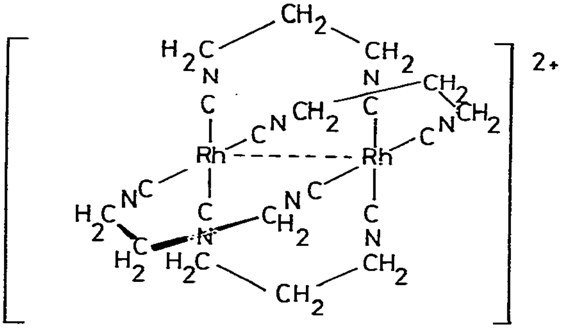


(90)



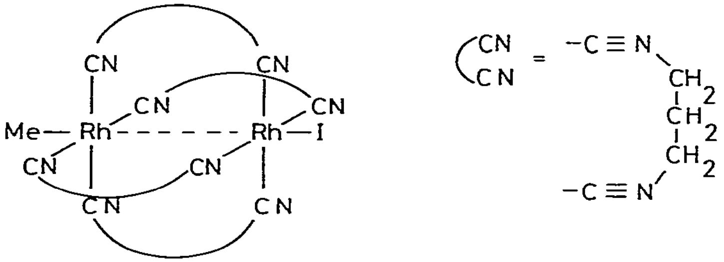
(91)

Non nonexistence of $[(t\text{-}C_4H_9NC)_8Rh_2X_2]^{2+}$ and the observation of a single isocyanide stretching frequency in the infrared spectrum of the adduct strongly indicates that structure **90** is the more likely. Another study of the aggregation of cationic aryl isocyanide complexes of rhodium(I) involves the synthesis of a dimeric rhodium(I) complex containing four 1,3-diisocyanopropane (bridge) ligands (92) and a study of its oligomerisation in varying concentrations in cyano methane according to the equilibria $2D \rightleftharpoons C_2$; $D_2 + D \rightleftharpoons D_3$; $D_n + D \rightleftharpoons_{n+1}$ (D = complex). In dilute cyanomethane solutions treatment of the complex with I_2 or Br_2 results in oxidation to the dihalo adduct probably containing two rhodium(II)—halogen units connected by a single metal—metal bond. The oxidative



(92)

addition was found to be thermally reversible in the case of Br_2. Iodomethane also reacts with 92 giving the complex *trans*-$[Rh_2(bridge)_4(CH_3)(I)]^{2-}$ (93), the structure of which is suggested by the ^1H NMR [65].



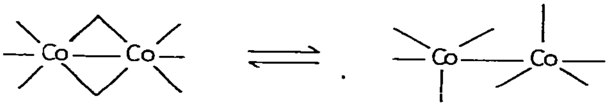
(93)

Metal carbonyls and related compounds.

(a) Zero oxidation state compounds

A review on platinum metal carbonyls and their substituted derivatives contains a number of sections on rhodium and iridium carbonyl compounds [66].

The nature of dicobalt octacarbonyl in solution continues to attract attention. The principal species in solution are those depicted in the equilibrium;

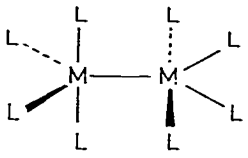


(94)

the bridged form being favoured at low temperatures. In addition a third form is considered to be present based on the observation of two unassignable features in the CO stretching region. Further evidence for a third form has been obtained from Raman studies [67]. The changes observed in the IR spectrum of $[Co_2(CO)_8]$ between —165 and +210°C can also be interpreted in terms of the variation of the relative concentrations of the three isomers if the band at 2031 cm^{-1} is assigned to the third isomer [68]. In a separate study on the IR spectrum of $[Co_2(CO)_8]$ in solution at various temperatures and CO pressures the band at

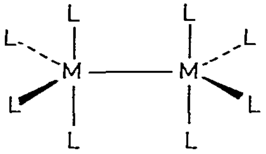
2031 cm^{-1} has been assigned to a species which could be [$CoH(CO)_4$] [69]. At temperatures above 150°C and CO pressures greater than 150 atm, a CO-bridged [$Co_2(CO)_9$] complex which has been previously proposed is probably not present [68,69].

The axially linked bi(trigonal bipyramidal) structure 94, adopted by [$Co_2(CO)_8$] in solution is also adopted by [$Co(CO)_3(P\text{-}n\text{-}Bu_3)$]$_2$ in the solid state and by [$Co_2\{P(OMe)_3\}_8$] and [$Rh_2\{P(OMe)_3\}_8$]. However, ^{19}F and ^{31}P NMR studies on [$Rh_2(PF_3)_8$] and [$Ir_2(PF_3)_8$] reveal that in solution these compelxes adopt the equatorially linked bi(trigonal pyramidal) structure 95 which has been confirmed by an X-ray study of a poor-quality crystal of [$Rh_2(PF_3)_8$]. The other alternative, the eclipsed, D_{2h} microsymmetry, structure 96 would not be favoured on steric grounds. There appears to be no simple reason why [$Rh_2(PF_3)_8$] and [$Ir_2(PF_3)_8$] should adopt the equatorially linked structure 95 in preference to the axially linked structure 94. The compounds [$Rh_2(PF_3)_8$] and [$Ir_2(PF_3)_8$] exhibit temperature dependent ^{19}F and ^{31}P NMR spectra.



(L = PF_3 , M = Rh, Ir)

(95)



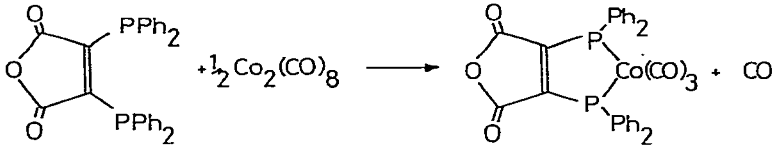
(L = PF_3 , M = Rh, Ir)

(96)

The close similarity in the activation energy parameters found for [$Rh_2(PF_3)_8$], ($\Delta G = 13.21 \pm 0.5$ kcal mol^{-1}) and [$Ir_2(PF_3)_8$] ($\Delta G = 13.0 \pm 0.5$ kcal mol^{-1}) is surprising in view of the general trend toward higher barriers to intramolecular rearrangement processes with increasing atomic weight in a triad, e.g. [$MH(PF_3)_4$], (M = Co, Rh or Ir). The averaging of the PF_3 environments may occur via a Berry mechanism in which the metal—metal bond acts as a pivot and the metal—phosphorus bonds bend until the PF_3 groups are in the equivalent basal positions of a square pyramid about each metal atom. Interestingly, the trimethyl phosphite complexes [$M_2\{P(OMe)_3\}_8$] (M = Co or Rh) are stereochemically rigid up to ~100°C but since these complexes adopt structure 94 the M—M cannot acts as a pivot since this bond occupies the axial position of a trigonal bipyramid. The variable temperature ^{19}F NMR spectrum of [$IrCl(PF_3)_4$] has also been studied [70].

The optimum conditions have been described for the preparation of [$Co_2(CO)_8$] by the reaction of $CoCO_3 \cdot 3\ Co(OH)_2 \cdot H_2O$ and $Co(OAc)_2 \cdot 4\ H_2O$ and a CO and H_2 mixture in an autoclave at 200—220 kg/cm^{-2} and 160—170°C in hexane. The optimum ratio CO/H_2 is 2.66/1 and when 8 volume parts of solvent per 1 weight part of Co in the initial salt are used and the autoclave is 0.4 filled the yield is reported to be 98% [71]. A method has been described for the complete removal of small amounts of [$Co_2(CO)_8$] from liquid mixtures containing [$Co_2(CO)_8$], [$Fe(CO)_5$] and [$Ni(CO)_4$]. The method involves bubbling NH_3 through the mixture at —5 to 23°C to precipitate [$Co_2(CO)_8$] as [$Co(NH_3)_6$][$\{Co(CO)_4\}_2$] [72].

An interesting air-stable paramagnetic five-coordinate complex of cobalt(0) (98), is formed on addition of the phosphine 97 to [$Co_2(CO)_8$]. An X-ray study



(97) (98)

on 98 reveals that the P atoms of the phosphine and the C atoms of the carbonyl groups form a distorted square pyramid with a plane of symmetry around the Co atom [73].

The kinetics and the position of the equilibrium for the reaction:

$Co_2(CO)_8 + H_2 \rightleftharpoons 2\ HCo(CO)_4$

have been studied in the range 80—160°C and 50—100 atmospheres pressure by IR spectroscopy. The reaction is reversible first order with respect to [$Co_2(CO)_8$] and [$HCo(CO)_4$] and the activation energies of the forward and the reverse reac-are 17.3 and 11.0 kcal mol^{-1}, respectively. The reaction is endothermic, $\Delta H =$ 6.6 kcal mol^{-1} and $\Delta S = 14.6$ e.u. The heat of formation of [$HCo(CO)_4$] and the Co—H bond strength are —146.1 and 54.7 kcal mol^{-1}, respectively [74]. The solubility of hydrogen in a toluene solution of [$Co(CO)_3(PBu_3)]_2$ has been studied as a function of pressure of hydrogen (40—180 atm) and concentration of the cobalt complex (1—8%). The ratio of the concentrations of hydrogen and cobalt complex in the solution increased with increased pressure up to 7—9/1 (moles). It is suggested that this high value is a result of association of H_2 with the CO groups through hydrogen bonding and substitution of some of the ligands by hydrogen [75].

The complexes [$Co(CO)_3L]_2$, [$Hg\{Co(CO)_3L\}_2$], and [$HgCo_2(CO)_{8-n}\{P(OMe)_3\}_n$] (L = PEt_3, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(OEt)_3$, $P(OMe)_3$ $P(OMe)Ph_2$, $P(OMe)_2Ph$, $P(OPh)_3$; $n = 0, 2, 4, 6$), have been reduced electrochemically, the reactions occurring being represented by the equations:

$[Co(CO)_3L]_2 + 2e \rightarrow 2[Co(CO)_3L]^-$

$[Hg\{Co(CO)_3L\}_2] + 2e \rightarrow 2[Co(CO)_3L]^- + Hg$

Increasing basicity of the ligand L, increases the electron density of the whole molecule and in consequence the complex is reduced at more negative potential [76].

Although both Ph_4P^+ and Ph_4As^+ react with [$FeCp(CO)_2]^-$ to give 35—45% yields of [$FeCp(C_6H_5)(CO)_2$] and substantial amounts of [$FeCp(CO)_2]_2$ the less nucleophilic [$Co(CO)_4]^-$ is unreactive towards Ph_4As^+ at room temperature and the stable crystalline salt, [Ph_4As] [$Co(CO)_4$] is formed [77].

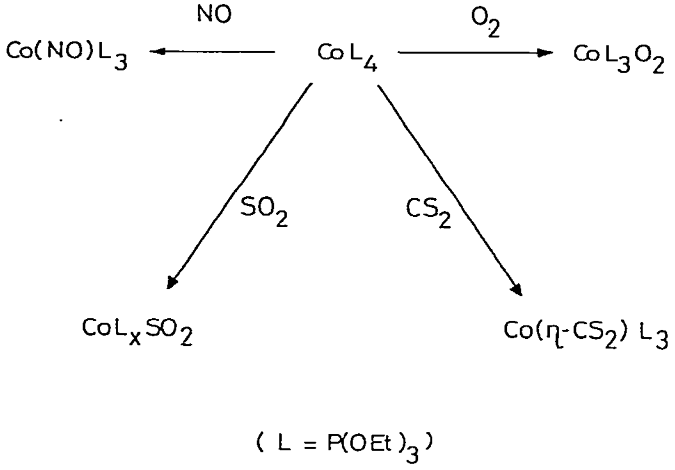
Although paramagnetic phosphine cobalt(0) complexes have been known for some years related phosphite complexes have not been observed. However, paramagnetic [$Co\{P(OEt)_3\}_4$] (99) has now been prepared via electrochemical one-electron oxidation of [$Co\{P(OEt)_3\}_4]^-$.

Magnetic susceptibility measurements of 99 in benzene solution suggest the presence of a metal—metal bonded dimer. Compound 99 may also be obtained

$$2\,Co[P(OEt)_3]_4 \rightleftharpoons Co_2[P(OEt)_3]_8$$

(99)

by the reaction of $[Co\{P(OEt)_3\}_4]^-$ with $[Co\{P(OEt)_3\}_4]^+$. Compound 99 reacts with a variety of small molecules, Scheme 16 [78].



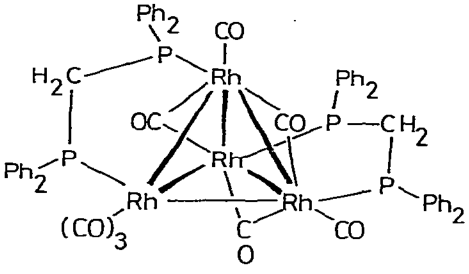
SCHEME 16

The zerovalent rhodium complexes $[Rh(dipy)_2]$ and $[Rh(o\text{-}phen)_2]$ have also been obtained by electrochemical reduction of the rhodium(III) complexes $[Rh(dipy)_3]^{3+}$ and $[Rh(o\text{-}phen)_3]^{3+}$. ESR data are consistent with a distorted square planar structure for these rhodium(0) complexes [79]. The cobalt complex $[Co\{P(OEt)_3\}_5]^+$ undergoes electrochemical reduction via a single, two-electron irreversible step to give $[Co\{P(OEt)_3\}_4]^-$ [78], and it has also been observed that $[Rh\{P(OPh)_3\}_4]^+$ undergoes a similar two-electron irreversible reduction [80]. In view of the one-electron oxidation observed for $[Co\{P(OEt)_3\}_4]^-$ [78] the corresponding rhodium complexes may behave similarly.

Although the structure of $[Co_4(CO)_{12}]$ in solution has been the subject of some dispute, recent IR, ^{13}C and ^{59}Co NMR data indicate that the C_{3v} symmetry found for the solid by X-ray diffraction persists in solution. The X-ray diffraction studies on $[Co_4(CO)_{12}]$ are complicated by disorder but more accurate data on this molecule has now been obtained [81]. The Raman spectrum of $[Co_4(CO)_{12}]$ has also been reported and Co—Co stretching frequencies have been located [67].

The reaction of $Ph_2PCH_2PPh_2$ with $[Rh_4(CO)_{12}]$ gives $[Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2]$ (**100**), which has been the subject of an X-ray study. The structure is derived from the C_{3v} structure of $[Rh_4(CO)_{12}]$ itself [81].

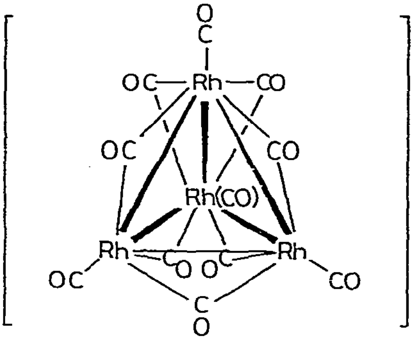
The carbonylation of $[IrCl(CO)_2(p\text{-toluidine})]$ in the presence of zinc provides a convenient preparation of $[Ir_4(CO)_{12}]$ [82]. The addition of a phosphine or



(100)

phosphite ligand to the reaction mixture allows a direct synthesis of $[Ir_4(CO)_{11}L]$ and $[Ir_4(CO)_{10}L_2]$ in moderate yield [83]. Substitution of carbonyl ligands in $[Ir_4(CO)_{12}]$ by phosphine or phosphite ligands requires elevated temperatures and these reactions usually give the final substitution products $[Ir_4(CO)_8L_4]$ or $[Ir_4(CO)_9L_3]$, depending on the size of the entering ligand.

The reaction of $[Rh_4(CO)_{12}]$ with sodium methoxide, or anhydrous sodium carbonate in methanol in an atmosphere of carbon monoxide gas gives the orange anion $[Rh_4(CO \cdot OMe)(CO)_{11}]^-$. A similar reaction is also observed with NaOEt in ethanol and more slowly with NaOPr-i in isopropanol. The reaction of the anion $[Rh_4(COOMe)(CO)_{11}]^-$ with potassium hydroxide gives the red dianion, $[Rh_4(CO)_{11}]^{2-}$ (101) and this dianion can be obtained directly from $[Rh_4(CO)_{12}]$ and potassium hydroxide. Both anions can be isolated as their bis(triphenylphosphine)iminium salts. The methoxy-carbonyl anion reacts with acids to give $[Rh_4(CO)_{12}]$. Solutions of $[Rh_4(COOMe)(CO)_{11}]^-$ in tetrahydrofuran under carbon monoxide gas are stable for a few hours at room temperature but in the presence of traces of water rapid decomposition occurs to give mainly $[Rh_4(CO)_{30}]^{2-}$ together with other unidentified products. The anion $[Rh_4(COOMe)(CO)_{11}]^-$ reacts slowly with $[Rh_4(CO)_{12}]$ in the presence of carbon monoxide gas to give the hexanuclear $[Rh_6COOMe)(CO)_{15}]^-$ anion. The analogous reaction between $[Rh_4(CO)_{11}]^{2-}$ and $[Rh_4(CO)_{12}]$ cannot be carried out under carbon monoxide since the dianion rapidly reacts with carbon monoxide:



(101)

$$2[Rh_4(CO)_{11}]^{2-} + CO \xrightarrow[1\,atm]{25°C} [Rh_6(CO)_{15}]^{2-} + 2[Rh(CO)_4]^-$$

At —70°C a different reaction takes place and ^{13}C NMR spectroscopy indicates that the process may be represented by the equation:

$$5[Rh_4(CO)_{11}]^{2-} + 11\ CO \xrightarrow[-70°C]{THF} [Rh_{12}(CO)_{\sim 34}]^{2-} + 8[Rh(CO)_4]^-$$

Under dinitrogen gas the reaction of $[Rh_4(CO)_{11}]^{2-}$ with $[Rh_4(CO)_{12}]$ is rapid and its path depends on which reagent is in excess. Addition of $[Rh_4(CO)_{12}]$ to $[Rh_4(CO)_{11}]^{2-}$ leads to the sequence of reactions:

$$\begin{tikzcd}
{[Rh_4(CO)_{11}]^{2-}} \arrow[dr, "0.5[Rh_4(CO)_{12}]"', "-2CO"] & & {[Rh_{12}(CO)_{30}]^{2-}} \\
& {[Rh_6(CO)_{15}]^{2-}} \arrow[ur, "1.5[Rh_4(CO)_{12}]", "-3CO"'] &
\end{tikzcd}$$

However, addition of $[Rh_4(CO)_{11}]^{2-}$ to $[Rh_4(CO)_{12}]$ leads to direct formation of $[Rh_{12}(CO)_{30}]^{2-}$.

$$2[Rh_4(CO)_{12}] + [Rh_4(CO)_{11}]^{2-} \rightarrow [Rh_{12}(CO)_{30}]^{2-} + 5\ CO$$

In both cases the evolved carbon monoxide gives rise to the equilibrium:

$$[Rh_{12}(CO)_{30}]^{2-} + 4\ CO \rightleftharpoons [Rh_{12}(CO)_{\sim 34}]^{2-}$$

The dianion $[Rh_4(CO)_{11}]^{2-}$ reacts with $[Rh_6(CO)_{16}]$ to give $[Rh_{12}(CO)_{30}]^{2-}$.

The chemical reactivity of these clusters can be related to the ratio of the number of metal atoms (MA), to the number of negative charges (NC). Thus the sensitivity to atmospheric oxidation increases with a decrease in MA/NC. The sensitivity to hydrolysis decreases in the series: $[Rh_6(CO)_{14}(CO \cdot OMe)_2]^{2-} > [Rh_4(CO)_{11}(CO \cdot OMe)]^- > [Rh_6(CO)_{15}(CO \cdot OMe)]^-$ in keeping with the MA/NC sequence. Further, the lack of evidence for a dicarboalkoxy species in the reaction of $[Rh_4(CO)_{11}(CO \cdot OMe)]^-$ with an excess of MeO^- can also be related to MA/NC ratios [84]. The crystal structure of the salt $[Ph_3PNPPh_3]_2$-$[Rh_4(CO)_{11}]$, **(91)** has been determined [85].

The UV photoelectron spectra of $[Rh_6(CO)_{16}]$ and CO absorbed on a palladium(III) single crystal surface exhibit close similarities. These results can be taken as evidence for the localised character of the chemisorption bond and justifies cluster approximations for its theoretical description [86].

Dicobalt octacarbonyl reacts with $[TiCl_2Cp_2]$ to give the cluster compound $(CO)_9Co_3C$—$OTiClCp_2$ **(102)**, the structure of which has been determined by a single crystal X-ray study [87].

The reaction of $[Co_2(CO)_8]$ with RCX_3 in the presence of the phase transfer catalyst $PhCH_2NEt_3^+\ Cl^-$ provides good yields of the clusters $[Co_3(CR)(CO)_9]$ **(103)**. The first step in the reaction is the formation of $R_4N^+\ OH^-$ which moves into the organic phase and readily reacts with $[Co_2(CO)_8]$ to generate $[Co(CO)_4]^-$ [88].

$$RCX_3 + Co_2(CO)_8 \xrightarrow{PhCH_2NEt^+ Cl^-,\ 3\text{—}5\ M\ NaOH/C_6H_6,\ 0.75\ \text{to}\ 2.5\ h,\ \text{at room temperature}} [RCCo_3(CO)_9]$$

$(R = Cl, Br, Ph, CO_2\ CMe_3, CH_2OH)$

(103)

Methanol is known to react with $[Co_3(CBr)(CO)_9]$ to give $[Co_3(CCO_2Me)(CO)_9]$. With the chloromethylidyne derivative the rate of this reaction is negligible at room temperature but the addition of $AlCl_3$ induces the rapid conversion of this complex to the acylium ion, $[Co_3(COO)(CO)_9]^+$:

$$\begin{tikzcd} {[CO_3(CCl)(CO)_9]} \arrow[dr, "AlCl_3,\ CH_2Cl_2"] & & {[Co_3(CCO_2Me)(CO)_9]} \\ & {[Co_3(CCO)(CO)_9]^+} \arrow[ur, "MeOH"'] & \end{tikzcd}$$

It has now been found this process can be induced by a Lewis base such as a tertiary amine:

$$[Co_3(CBr)(CO)_9] + MeOH \xrightarrow[CO]{Et_2NH} [Co_3(CCO_2Me)(CO)_9]$$

and the reaction can be extended to other alcohols.

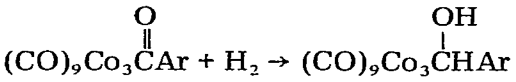
In the absence of methanol amides are produced:

$$[Co_3(CBr)(CO)_9] + Et_2NH \xrightarrow[CO]{C_6H_6,\ 25°C} [Co_3(CCONEt_2)(CO)_9]$$

and amides can be produced with both ammonia and primary amines [89].

The novel cluster complex, $[Co_3(COCOMe)(CO)_9]$ has been obtained by the reaction of CH_3COBr with $Li[Co_3(CO)_{10}]$. The crystal structure of this complex has been determined and the complex provides the first methylidynenonacarbonyltricobalt derivative with a μ_3—C—O—C bond [90]. The first silicon homologue of these cobalt cluster systems $(CO)_9Co_3Si—Co(CO)_4$ (**104**) has been obtained by the reaction of $Na[Co(CO)_4]$ with SiI_4. The crystal structure of **104** has also been reported [91].

Molecular hydrogen reacts with the aroyl complexes $[Co_3(CCOR)(CO)_9]$ at atmospheric pressure in refluxing benzene with no added catalyst to produce the complexes 195. Acyl compounds undergo similar hydrogenation but the



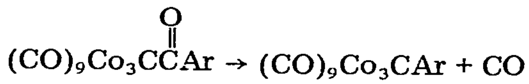
$$(CO)_9Co_3\overset{\overset{O}{\|}}{C}Ar + H_2 \rightarrow (CO)_9Co_3\overset{\overset{OH}{|}}{C}HAr$$

(105)

$(Ar = Ph, 78\%; p\text{-}MeC_6H_4, 83\%; p\text{-}BrC_6H_4, 79\%)$

reactions are more complex and yields of the hydrogenated product are poor.

These reactions may proceed via hydride abstraction from H_2 by the stabilised carbonium ion $(CO)_9Co_3C^+(R)O^-$ (**106**) [92]. Some of the aroyl compounds also readily undergo decarbonylation in refluxing benzene to give the complexes **107** [92].



$$(CO)_9Co_3C\overset{\overset{\displaystyle O}{\|}}{C}Ar \rightarrow \underset{\textbf{(107)}}{(CO)_9Co_3CAr} + CO$$

($Ar = p$-Me_2NPh, 70%; p-MePh, 69%; Ph, 66%; p-BrPh, 0%)

The clusters $[Co_3(CX)(XO)_9]$, (X = halogen, alkyl, aryl) in general undergo a reversible, one-electron reduction in the range —0.7 to —0.9 V vs. SCE, and the ESR spectra of the reduced clusters have been recorded. Irreversible, multielectron oxidation of all the clusters studied occurs around +1.5 V to give unknown products [93].

Various cobalt and rhodium carbonyl cluster systems e.g. $[Co_6(CO)_{15}]^-$, $[FeCo_3(CO)_{12}]^-$, $[Co_4(CO)_{12}]$, $[Co_2(CO)_8]$, $[Co_2(nbd)_2(CO)_4]$, $[Rh_4(CO)_{12}]$, $[Co_3(CY)(CO)_9]$, catalyse the dimerisation of norbornadiene to Binor-S [94,95]. In the systems $[Co_3(CY)(CO)_9]$, the catalytic activity decreases in the series $Y = I > Br > Cl > H > Me > Ph > CF_3$. This order indicates that electronegativity rather than size of the substituent is the overriding factor and although the results for the halo-cluster seem anomalous there is some kinetic evidence that these may proceed via a different mechanism. Substitution of carbonyl ligands in the cluster by phosphines or t-BuNC increases the catalytic activity.

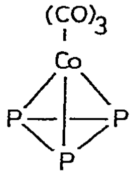
The ^{13}C NMR signals of cobalt carbonyl compounds can be difficult to detect owing to spin—spin coupling of the carbon nuclei with the cobalt nuclei ($^{59}Co/I$ 7/2), which are undergoing moderately rapid quadrupole induced relaxation. Substantial line narrowing is observed as the temperature is lowered and can also be achieved by using viscous solutions [96]. ^{13}C NMR spectra have been recorded for the complexes, $[Co_2(CO)_6(acetylene)]$ [96] and $[Co_3(CY)(CO)_9]$ [96,97].

Solutions of the $[Co_6(CO)_{15}C]^-$ anion in tetrahydrofuran react with carbon monoxide to give a mixture of compounds containing the anion $[Co(CO)_4]^-$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, some $[Co_3(CX)(CO)_9]$ derivatives and the new dark brown paramagnetic anion $[Co_6(CO)_{14}C]^-$. This new anion is more conveniently prepared by reaction of $[Co_3CCl(CO)_9]$ with $Na[Co(CO)_4]$ in diethyl ether. This is the first example of a stable paramagnetic hexanuclear carbonyl and its crystal structure has been determined. The reaction of the dianion $[Co_6(CO)_{15}C]^{2-}$ with $[Co_4(CO)_{12}]$ provides a further example of a redox condensation reaction:

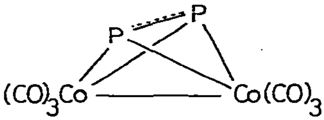
$$2[Co_6(CO)_{15}C]^{2-} + Co_4(CO)_{12} \xrightarrow[i\text{-}Pr_2O]{60^\circ C} 2[Co_8(CO)_{18}C]^{2-} + 6\ CO$$

The crystal structure of the dianion $[Co_8(CO)_{18}C]^{2-}$ has also been determined. The metal atom polyhedron can be described as a tetragonal antiprism elongated along one of the two-fold symmetry axes, resulting in the idealized symmetry D_2. The isoelectronic $[Rh_8(CO)_{19}C]$ has a different structure in which a trigonal prism of rhodium atoms has been capped both along a square face and along one of the triangular edges. The series of anions $[Co_6(CO)_{15}C]^{2-}$, $[Co_6(CO)_{14}C]^-$, and $[Co_8(CO)_{18}C]^{2-}$ provide further examples of the unusual stability of carbido clusters [98].

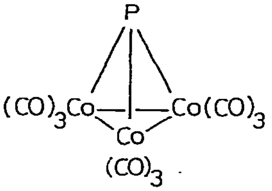
The reactions of white phosphorus or phosphorus trihalides with $[Co_2(CO)_8]$ or $[Co(CO)_4]^-$ under various conditions give the clusters $[CoP_3(CO)_3]$ (**108**), $[Co_2P_2(CO)_6]$ (**109**), $[Co_3P(CO)_9]$ (**110**), and $[Co_3P(CO)_8]_3$. The very unstable cluster **110** can be stabilised as an iron carbonyl adduct **111** [99]. The reaction of AsX_3 with $Na[Co(CO)_4]$ gives the deep-violet $[Co_3As(CO)_9]$ and the deep-green $[Co_3As(CO)_8]_3$, the crystal structure of which has been determined. The reaction:



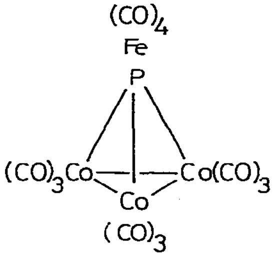
(108)



(109)



(110)



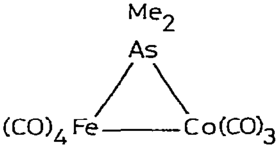
(111)

$$3\ Co_3As(CO)_9 \rightleftharpoons Co_9As_3(CO)_8 + 3\ CO$$

is a reversible process, the position of equilibrium being dependent on the pressure of carbon monoxide [100].

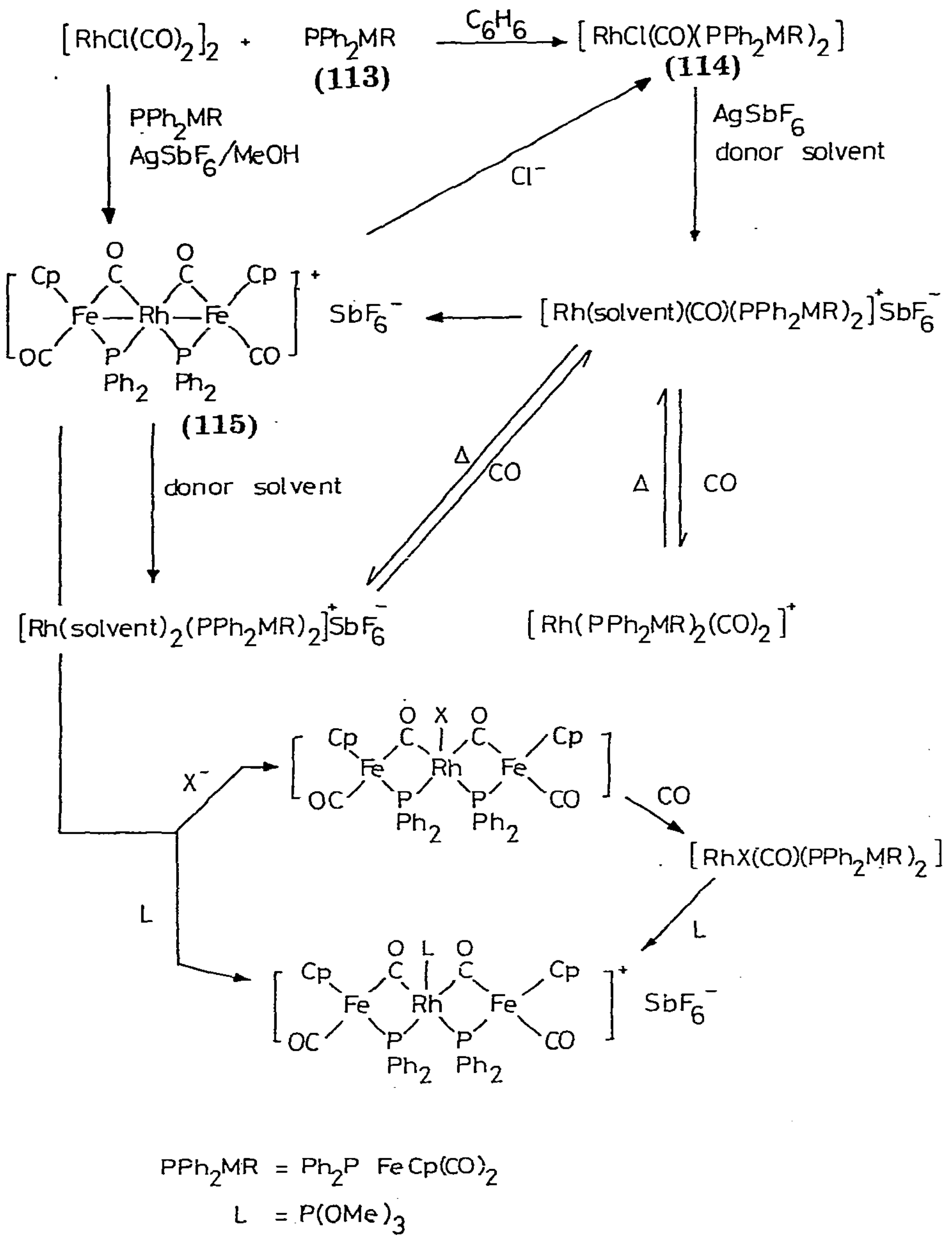
(b) Heteronuclear metal—metal bonded carbonyl compounds

The crystal structure of the iron—cobalt bonded complex **112** has been determined [101]. The reaction of $[RhCl(CO)_2]_2$ with the iron-containing tertiary phosphine **113** affords the neutral compound **114**. However, addition of **113** to $[RhCl(CO)_2]_2$ in methanol in the presence of $AgSbF_6$ affords the novel iron—rhodium bonded complex **115**. The complexes **114** and **115** are readily interconvert-



(112)

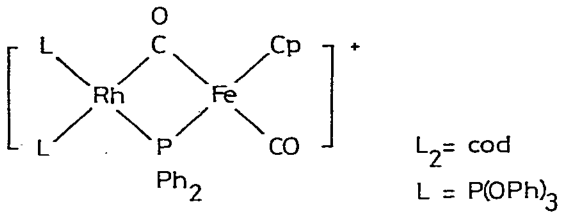
ible, and some reactions of these complexes are illustrated in Scheme 17. Sulph-



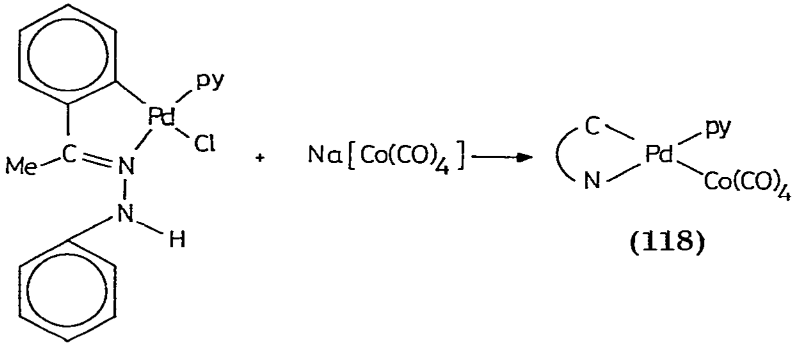
SCHEME 17

ide derivatives analogous to **115** can be obtained by reaction of $[\mathrm{RSFeCp(CO)_2}]$, (R = Et, t-Bu) with $[\mathrm{Rh(cod)(ethanol)}_x]^+$ in ethanol. However, reactions with $[\mathrm{PhSFeCp(CO)_2}]$ give $[\mathrm{Rh(cod)\{SPhFeCp(CO)\}_2}]^+$ which contains terminal carbonyl ligands only. Some dinuclear metal—metal bonded species **116** can be obtained by the reaction of $[\mathrm{RhL_2(solvent)}_x]\mathrm{SbF_6}$ with an equimolar amount of $[\mathrm{PPh_2Fe(CO)_2Cp}]$ [102].

The reaction of $\mathrm{Na[Co(CO)_4]}$ with the chelated palladium compound **117**



(116)

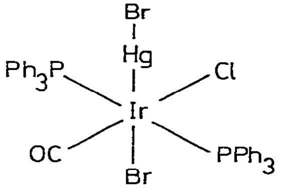


(117)

(118)

gives the palladium—cobalt bonded complex **118**. Analogous reactions of **117** are not observed when the pyridine ligand is replaced either by PEt_3 or PPh_3. Addition of triphenylphosphine to **118** cleaves the cobalt—palladium bond to give $[Pd(C—N)(PPh_3)(py)][Co(CO)_4]$ [103].

Mercury(II) halides oxidatively add to *trans*-$[Ir(C_6F_5)(CO)(PPh_3)_2]$ to give the complexes $[IrX(HgX)(C_6F_5)(CO)(PPh_3)_2]$. The same reaction with *trans*-$[Rh(C_6F_5)(CO)(PPh_3)_2]$ results in the elimination of C_6F_5HgX to give *trans*-$[RhX(CO)(PPh_3)_2]$ which undergo oxidative addition with excess mercury(II) halides [104]. The crystal structure of the iridium—mercury bonded complexes $[IrCl_2(HgCl)(CO)(PPh_3)_2]$ has been determined. The structure of the isomorphous complex **119** indicates that it is formed by *trans*-addition of $HgBr_2$ to *trans*-$[IrCl(CO)(PPh_3)_2]$ [105].



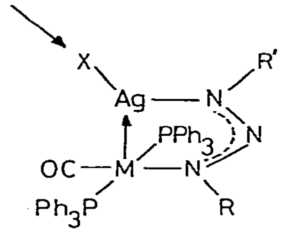
(119)

Treatment of the complexes *trans*-$[MX(CO)(PPh_3)_2]$ (**120**), with Ag(R$\overline{\text{—N—N—N}}$R') gives the metal-to-silver donor bonded complexes **121** [106]. The structure of the complexes **121** appear on the basis of spectroscopic measurements to be analogous to the copper bonded complex **122** which has been characterised by a single crystal X-ray study [106].

Unlike the copper complexes no silver complexes can be obtained in which

$\underline{\text{trans}}$-$MX(CO)(PPh_3)_2$ + $Ag(RNNNR')$

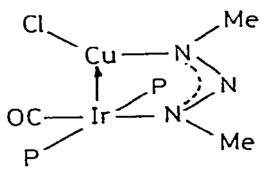
(120)



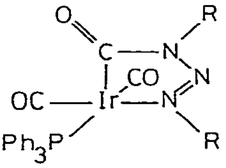
M = Rh X = Xl
Me = lr X = Cl, Br, I
R = Me, *p*-tolyl; R′ = Me

(121)

either $PhMe_2P$ or Ph_3As in place of Ph_3P or *p*-tol_3P are coordinated to the iridium or rhodium. No silver—metal bonded compounds are isolated from the reaction of *trans*-$[MCl(CO)(PPh_3)_2]$ with silver di-*p*-tolyltriazene, and these reactions lead to the triazenido compounds, $[M(RNNNR)(CO)(PPh_3)_2]$. Carbon monoxide reacts rapidly with the iridium triazenido complex and the iridium complexes **121** to give novel acyltriazenido complexes **123** [106]. Treatment of *trans*-[MCl-



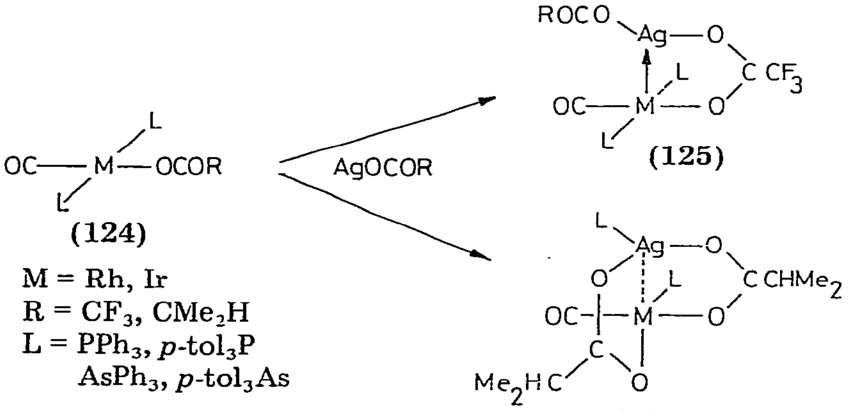
(122)



(123)

(P = PMe_2Ph)

$(CO)L_2]$, under suitable conditions, with a variety of silver salts of oxyacids (one equivalent) gives the complexes **124**. If subsequently a second equivalent of the silver salt is added to the silver—metal bonded complexes **125** or **126** are formed. Similar complexes can be obtained with silver nitrate or silver perchlorate. The silver nitrate complex, $[IrAg(NO_3)_2(CO)(PPh_2)_2]$ has been reported previously and a different type of structure **127** or **128** has been proposed. However, in the light of the present results, reformulation of the complex as a Ag—Ir com-

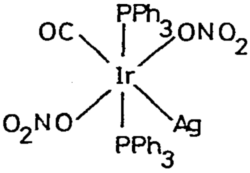


(124)

(125)

(126)

M = Rh, Ir
R = CF_3, CMe_2H
L = PPh_3, *p*-tol_3P
$AsPh_3$, *p*-tol_3As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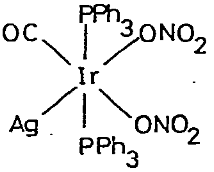
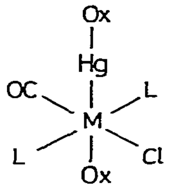

(128)

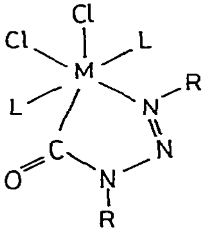
plex analogous to **125** seems appropriate [108]. The complexes **125** and **126** react with carbon monoxide but well defined products could not be obtained. The reactions of $HgOx_2$, ($Ox = O_2CMe$, O_2CCHMe_2, O_2CCF_3), $Hg(RN_3R)_2$ and $XHg(RN_3R^1)$ with *trans*-$[MX(CO)(PPh_3)_2]$ give quite different results and the proposed structures for the compelxes isolated from these reactions are illustrated in the diagrams **129**—**135** [109].


(129)

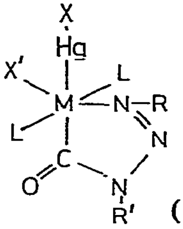
L = PPh M = Rh, Ir

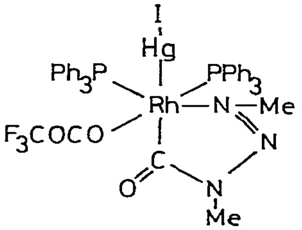
Ox = O_2CMe , O_2CCF_3

O_2CCHMe_2


(130)

M = Rh L = PPh_3 R = Me


(131)

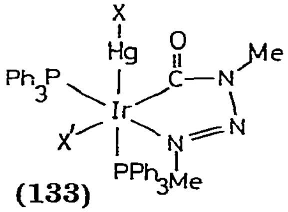

(132)

M = Rh; X′ = Cl; X = I; L = PPh_3, *p*-tol_3P

R = R′ = Me

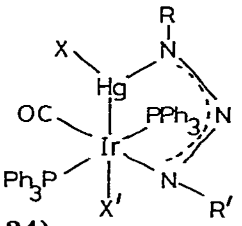
M = Ir; X′ = Cl; X = I; L = PPh_3

R = Me; R′ = p-tol.


(133)

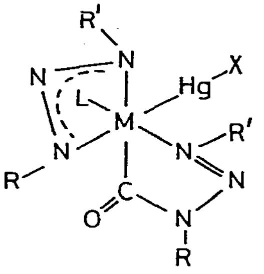
X = Cl I ; X′ = Cl

X = $OCOCF_3$; X′ = I


(134)

R = p-tol ; R′ = Me ; X = X′ = Cl

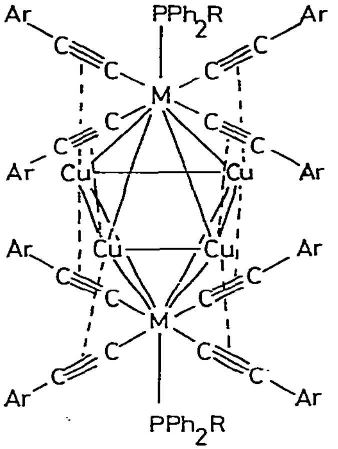
X = O_2CCF_3 ; X′ = Cl, I



(135)

L = PPh_3, p-tol_3P; M = Ir
X = Cl; R = R' = Me:
L = PPh_3; M = Rh; X = Cl
R = R' = Me:
L = PPh_3; M = Rh; X = Cl, O_2CCF_3
R = Me; R' = p-tol

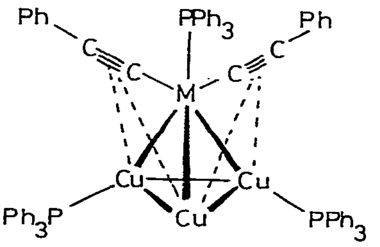
Hexanuclear cluster complexes, $[Ir_2Cu_4(C_2Ar)_8(PPh_2R)_2]$ (**136**) are formed in reactions between *trans*-$[IrCl(CO)(PPh_2R)_2]$ (R = Ph, Me) and $[CuC_2Ar]$.



(136)

M	Ar	R
Ir	Ph	Ph
Ir	C	
M	Ar	R
Ir	Ph	Ph
Ir	C_6H_4Me-p	Ph
Ir	C_6H_4F-p	Ph
Ir	C_6F_5	Ph
Ir	Ph	Me
Ir	C_6F_5	Me
Rh	Ph	Ph
Rh	C_6H_4Me-p	Ph
Rh	C_6H_4F-p	Ph
Rh	C_6F_5	Ph
Rh	Ph	Me
Rh	C_6H_4Me-p	Me
Rh	C_6H_4F-p	Me
Rh	C_6F_5	Me

The corresponding rhodium complexes can be obtained using *trans*-$[RhCl(CO)(PPh_3)_2]$ or $[RhCl(PPh_3)_3]$. From two of the reactions the complexes **137** and **138** can be isolated and these complexes may have the structures illustrated.



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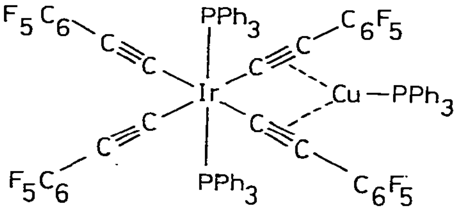
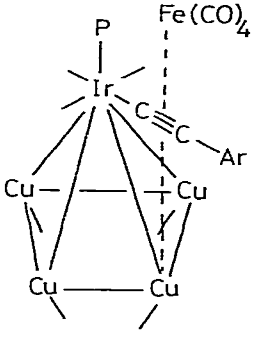


(138)

The iridium clusters **136** (R = Ph, Ar = Ph and R = Ph, Ar = C_6H_4Me-p) react with $Fe_2(CO)_9$ to give the octanuclear complexes $[Ir_2Cu_4Fe_2(C_2Ar)_8(CO)_8(PPh_3)_2]$ (Ar = Ph or C_6H_4Me-p). These clusters probably contain η^2-alkyne-Fe-$(CO)_4$ units as indicated in **139** [110].



(139)

The $[Co(CO)_4]^-$ anion can be displaced by $[Mn(CO)_5]^-$ from germanium—cobalt bonded complexes of the type $[R_3GeCo(CO)_4]$ ($R_3Ge = H_3Ge, H_2MeGe$ or HMe_2Ge):

$$R_3GeCo(CO)_4 + Mn(CO)_5^- \rightarrow R_3GeMn(CO)_5 + Co(CO)_4^-$$

The $[Fe(CO)_4]^{2-}$ anion will also displace $[Co(CO)_4]^-$ from $[H_3GeCo(CO)_4]$ to yield $[(H_3Ge)_2Fe(CO)_4]$ [111]. It is possible that a wide variety of such displacement reactions may occur. An electron diffraction determination of the gas phase structure of $[H_3GeCo(CO)_4]$ has been reported. The difference between axial and equatorial Co—C distances is very small and the equatorial carbonyl groups are bent towards the germyl group [112]. $[Me_3SnCo(CO)_4]$ reacts rapidly with iodine in cyclohexane at room temperature according to the equation:

$$Me_3SnCo(CO)_4 + I_2 \rightarrow CoI(CO)_4 + Me_3SnI$$

The carbonyl iodide $[CoI(CO)_4]$ is unstable and rapidly decomposes. Activation parameters for the iodination reaction are $\Delta H^{\neq}$, 20.8 kJ mol^{-1} and $\Delta S^{\neq}$, 120.8 ± 73 J K^{-1} mol^{-1}. The low activation enthalpy is consistent with the iodination being a multi-step process. The order of reactivities of the first-row transition metals is $[Me_3SnCo(CO)_4] \geqslant [Me_3SnFeCp(CO)_2] > [Me_3SnCrCp(CO)_3] > [Me_3SnMn(CO)_5]$ [113]. The low temperature ^{13}C NMR spectra of the compounds $[X_3SnCo(CO)_4]$, ($X = PhCH_2$, n-Bu, Ph, Me, Cl), reveal the first examples of a stopped exchange between axial and radial carbonyl groups in any compound of the form $[XM(CO)_4]$. It appears that the ability of the X group in $[XCo(CO)_4]$ compounds to act as a π-acceptor is an important factor in determining the barrier to axial-radial interchange [114]. The problem of σ- and π-bonding in compounds of the type $[R_3SnCo(CO)_4]$ has been reviewed [115]. ^{59}Co nuclear quadrupole resonance studies of some gallium- and iridium-cobalt tetracarbonyl compounds suggest that cobalt—iridium(gallium) π-bonding is not a major factor [116]. The fluxional behaviour of the compounds $[Me_2Sn\{Co(CO)_4\}_2]$ and $[Me_2Ge\{Co(CO)_4\}_2]$ has also been reported [117].

The (halomethyl)silanes, XCH_2SiH_3 (X = Cl, Br, I) react with $[Co_2(CO)_8]$ to give the compounds $[XCH_2SiH_2Co(CO)_4]$. The carbonyl stretching frequencies of these and other silyl cobalt tetracarbonyls vary linearly with the summed substituent polarity constants [118]. A linear correlation has also been observed between the Co—Sn and C—O stretching vibrations of the compounds, $[R_nCl_{m-n}Sn\{Co(CO)_4\}_{4-m}]$, (R = Me, Et, Pr, Bu, Ph) [119].

Exposure of $[Ph_3PbCo(CO)_4]$ to ^{60}Co γ-rays at 77 K gives the d^9 species $[Ph_3PbCo(CO)_4]^-$ [120].

An iridium—tin bonded complex $[Et_4N]_2[IrCl(SnCl_3)_2(CO)]$ has been prepared and its reactions with hydrogen and carbon monoxide have been investigated [121].

(c) Oxidation state-(I), -(II) and -(III) compounds

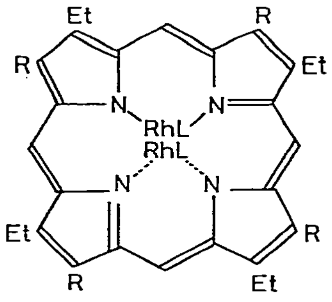
The cobalt(I) d^8 diamagnetic complexes sodium *N,N'*-ethylenebis(salicylideneiminato)cobaltate(I), Co(salen)Na and sodium *N,N'*-*o*-phenylenebis(salicylideneiminato)cobaltate(I), [Co(saloph)Na] in tetrahydrofuran or diglyme solutions reversibly add carbon monoxide at room temperature and atmospheric pressure. The reaction products can be formulated as monocarbonyl species, [Co(salen)(CO)Na] and [Co(saloph)(CO)Na]. However, after an initial very rapid reversible reaction, an additional slower and irreversible absorption of carbon monoxide is observed. The reactions can be represented by the equation:

$$3\ Co(chel)Na + 4\ CO \xrightarrow{L} 2\ Co(chel)_2 + NaCo(CO)_4 + (chel)Na_2$$

(L = THF, chel = salen)
(L = diglyme, chel = saloph)

The THF solution remains green during the first fast step of carbon monoxide absorption but changes to deep red at the end of the second step (four days). Addition of toluene to the red solution precipitates a red crystalline solid, $[Co(salen)_2NaCo(CO)_4]$ which is formulated as a sodium cation complex. In this complex the $[Co(salen)_2]$ and $[Co(CO)_4]^-$ act as bidentate oxygen ligands towards the Na^+ cation [122].

The unusual chemistry of vitamin B_{12} coenzyme has stimulated interest in the related cobalt and rhodium porphyrins. An improved method for the synthesis of dirhodium(I) complexes of porphyrins has been reported which involves addition of $[RhCl(CO)_2]_2$ in chloroform to a solution of the macrocycle in chloroform containing excess anhydrous sodium bicarbonate. Using this method dirhodium complexes **140**, of etioporphyrin, octaethylporphyrin, deuteroporphyrin and protoporphyrin have been obtained [123,124]. However, 8,12-diethyl-2,3,-7,13,17,18-hexamethylcorrole gives a mixture of products one of which is the monorhodium complex **141**. The *meso*-thiaphlorin **142** similarly reacts to give a monorhodium complex **143**. The dirhodium complex (**140**, R = Me) reacts with methyl iodide to give a mixture of the rhodium(III) complexes **144** (R = Me or COMe). Similar results are obtained with ethyl iodide. The acetylrhodium(III) porphyrin complex **143** (R = COMe) is also obtained on heating **140** (R = Me) dissolved in acetic acid containing $CHCl_3$ with excess sodium acetate [123] and acylrhodium(III) complexes **144** (R = COMe, COEt, or CO-n-Pr) are formed in good yield by heating a chloroform solution of **140** (R = Me) with an excess of the appropriate carboxylic acid anhydride [124]. The dirhodium complexes also react with cyclopropanes. Thus **140** (R = Me) reacts with cyclopropyl-4-fluorophenyl ketone at 110°C with ring opening to give **145a**. However, cyclopropyl methyl ketone does not ring open under these conditions but gives the cyclopropyl ketone complex **145b**. It appears that **145b** arises via an oxidative addition of the C—H bond of a methyl ketone to rhodium(I) followed by



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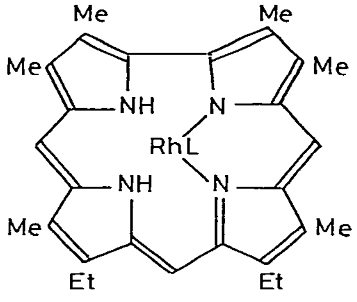
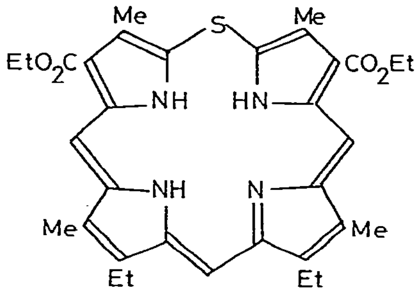


(141)

(RhL = Rh(CO)$_2$)



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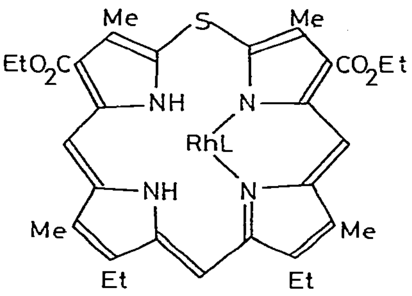
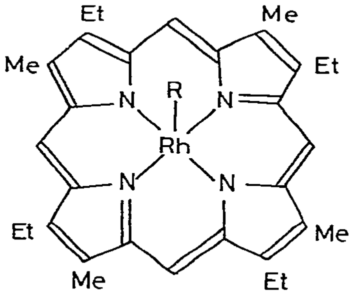


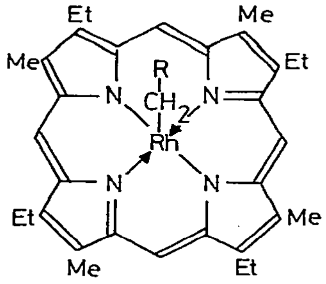
(143)



(144)

collapse of the rhodium(III) species into the centre of the porphyrin ring. The reaction appears quite general for ketones. Thus acetophenone gives **145c** and ethyl phenyl ketone gives **145d** [124].

Bromorhodate(III) species in acidic bromide solutions principally containing $[RhBr_4(OH_2)_2]^-$, catalyse the hydrogen reduction of iron(III) and react with carbon monoxide to give *cis*-$[RhBr_2(CO)_2]^-$. The kinetics of these reactions have been studied and mechanisms have been proposed [125]. The kinetics and mechanisms of reduction of $[RhCl_4(OH_2)_2]^-$ by carbon monoxide in aqueous hydrochloric acid have also been investigated [126]. Rhodium and iridium can be

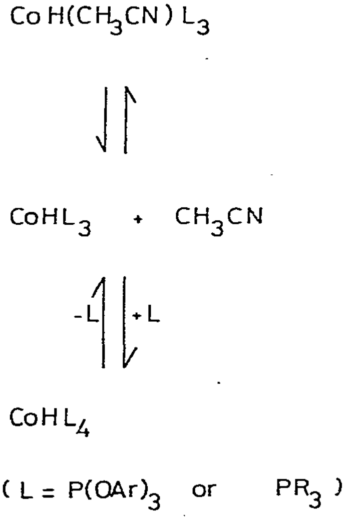


(145)

a ; $R = (CH_2)_2COC_6H_4F$
b ; R = CO—◁
c ; R = COPh
d ; RCH_2 = CHMeCOPh

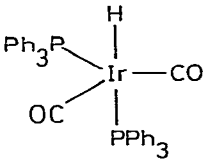
extracted by isopentyl alcohol as $[RhCl_2(CO)_2]^-$ and $[IrCl_2(CO)_2]^-$ after the reduction of rhodium(III) and iridium(IV) chloro complexes with carbon monoxide [127]. Conducting linear chains of *cis*-$[IrX_2(CO)_2]^{0.60-}$ (X = Cl, Br) have been shown to be present in the compounds $K_{0.60}[IrCl_2(CO)_2] \cdot 0.5\ H_2O$, $TTF_{0.61}$-$[IrCl_2(CO)_2]$, (TTF = tetrathiafulvalenium), $K_{0.57}[IrBr_2(CO)_2] \cdot 0.2$ MeCOMe and $Cs_{0.60}[IrBr_2(CO)_2]$. The compounds have been studied by chemical analysis, infrared, ^{193}Ir Moessbauer, and photoacoustic spectroscopy [128—130].

Triaryl phosphite complexes of the type $[CoH(MeCN)\{P(OAr)_3\}_3]$ have been obtained by the reaction of $[Co(C_8H_{13})(C_8H_{12})]$ with mixtures of acetonitrile and phosphorus ligands in a hydrogen atmosphere. Ligand exchange reactions readily occur with these complexes (Scheme 18), and they react with hydrogen chloride or hydrogen bromide to give cobalt(I) halide complexes. The com-



SCHEME 18

plexes are surprisingly active as selective hydrogenation catalysts. Thus $[\mathrm{CoH(MeCN)\{P(OPh)_3\}_3}]$ rapidly catalyses the hydrogenation of but-1-ene to butane with little or no isomeric but-2-enes being produced [131]. It is well established from X-ray studies that hydrides of the form $[\mathrm{MHL_4}]$ (M = Co, Rh, or Ir; L = a phosphorus ligand) are neither trigonal bipyramidal nor square pyramidal but may be considered as pseudo-tetrahedral with an $\mathrm{MP_4}$ skeleton in a nearly tetrahedral array. In some X-ray studies the hydrogen atom position has been located on a face of the tetrahedron. These complexes exhibit stereochemical non-rigidity and variable-temperature NMR studies provide evidence for a C_{3v} symmetry in the low-temperature limit suggesting that the hydrogen is on a tetrahedral face. It is proposed that the lowest-energy path for interchanging the phosphorus environments involves a tetrahedral-jump rearrangement mechanism and further evidence for these conclusions has been obtained from NMR studies of the caged phosphite complexes $[\mathrm{MH\{P(OCH_2)_3CPr\text{-}n\}_4}]$. The increase in rearrangement barrier for the compounds $[\mathrm{MH(PF_3)_4}]$ on going down the triad has been rationalised in terms of increased departure from pseudo-tetrahedral geometry as the size of the metal increases. For the complexes $[\mathrm{MH\{P(OCH_2)_3CPr\text{-}n\}_4}]$ the barrier trend observed is Co < Rh $\simeq$ Ir. It is suggested that with the very small $\mathrm{P(OCH_2)_3CPr\text{-}n}]$ ligand the departure from pseudo-tetrahedral geometry may already be very large for the rhodium complex and little change may occur on going from rhodium to iridium. NMR studies on the complexes $[\mathrm{MH(CO)(PPh_3)\{P(OCH_2)_3CX\}_2}]$ (X = Pr-n, Ph or $\mathrm{NO_2}$) suggest that more than two isomers are involved [132]. The hydrogen atom position has been located in 146, the structure being based on a distorted trigonal bipyramid with the atoms in the equatorial plane bent towards the hydrogen. The Ir—H distance is 1.64(5) Å [133]. An X-ray study of the four-coordinate complex 147 also reveals a slight bending of the phosphine ligands toward the hydrido ligand [134].



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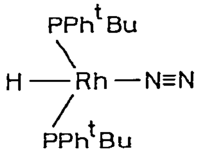
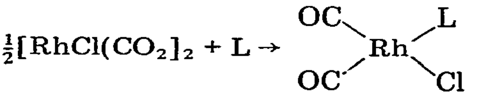


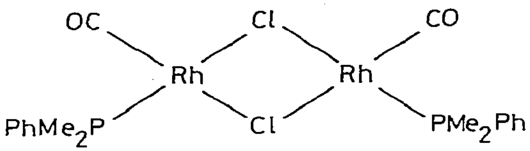
(147)

A large number of ligands containing nitrogen, oxygen and halide donor atoms react with $[\mathrm{RhCl(CO)_2}]_2$ according to the equation:



$$\tfrac{1}{2}[\mathrm{RhCl(CO_2]_2} + \mathrm{L} \rightarrow \mathrm{(OC)_2RhLCl}$$

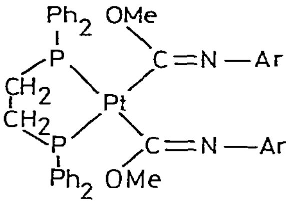
A detailed calorimetric study of the acid—base chemistry of $[\mathrm{RhCl(CO)_2}]_2$ reveals that an enthalpy of 22.6 kcal $\mathrm{mol^{-1}}$ of dimer is required to cleave the chloro bridges [135]. Phosphines can react with $[\mathrm{RhCl(CO)_2}]_2$ to give initial carbon monoxide displacement rather than halide bridge cleavage and the crystal structure of 148 has been reported. Each rhodium is surrounded approximately in a square planar fashion but there is a dihedral angle of 123° between these two planes. In cyclohexane solution 148 undergoes *cis—trans* isomerisation as

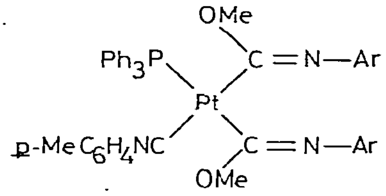


(148)

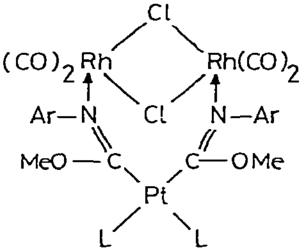
does $[RhCl(CO)(PMe_3)]_2$. Infrared studies suggest that $[RhCl(CO)\{P(NMe_2)_3\}]_2$ has a *trans*-geometry in the solid state [136].

The compounds **149** and **150** react with $[RhCl(CO)_2]_2$ to give adducts formulated as **151** [137].





(149) $(Ar = p\text{-}MeC_6H_4)$ (150)



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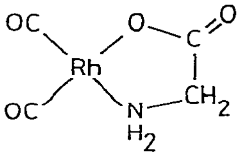


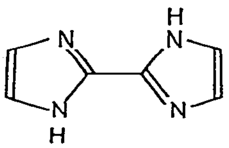
(152)

$(L_2 = Ph_2PCH_2CH_2PPh_2$;

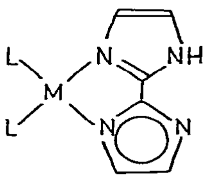
$L = PPh_3$; $L = p\text{-}MeC_6H_4NC)$

The amino acids, glycine, L-alanine, β-alanine, L-leucine and L-histidine react with $[RhCl(CO)_2]_2$ to give amino acid dicarbonylrhodium complexes, e.g. glycine gives **152** [138]. Similar complexes can be obtained with biimidazole **153** and using this ligand the complexes **154** and **155** have been obtained by the action of **154** on $[MCl(cod)]_2$.

The crystal structure of $[Rh_2(COD)_2BiIm]$ (**155**; M = Rh) has been determined. This is the first report of the very weak proton acid **153** functioning as a dianion [139]. The carbonyl complexes **154** can be obtained by the action of carbon monoxide on the corresponding cyclo-octa-1,5-diene complexes, however, the reaction of carbon monoxide with **155** gives the tetranuclear complexes **156**. The reaction of [Rh(acac)(cod)] with **154** (M = Rh, L = CO) gives $[(cod)Rh(BiIM)Rh_2(CO)_4(BiIM)Rh(cod)]$. In the solid state, the molecular complexes **156** are arranged in chains with an intermolecular Rh—Rh separation of 3.25 Å between the terminal rhodium positions [140]. This separation is nearly identical to that



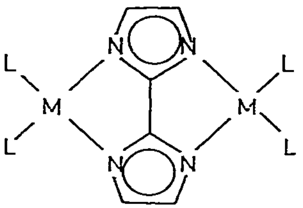
(153)



(154)

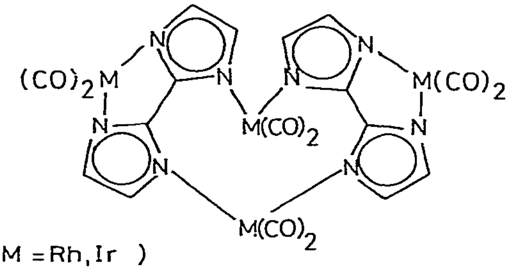
(L = (1,5-COD)$_{1/2}$, CO

M = Rh, Ir)



(155)

(L = (1,5-COD)$_{1/2}$ M = Rh, Ir)



(M = Rh, Ir)

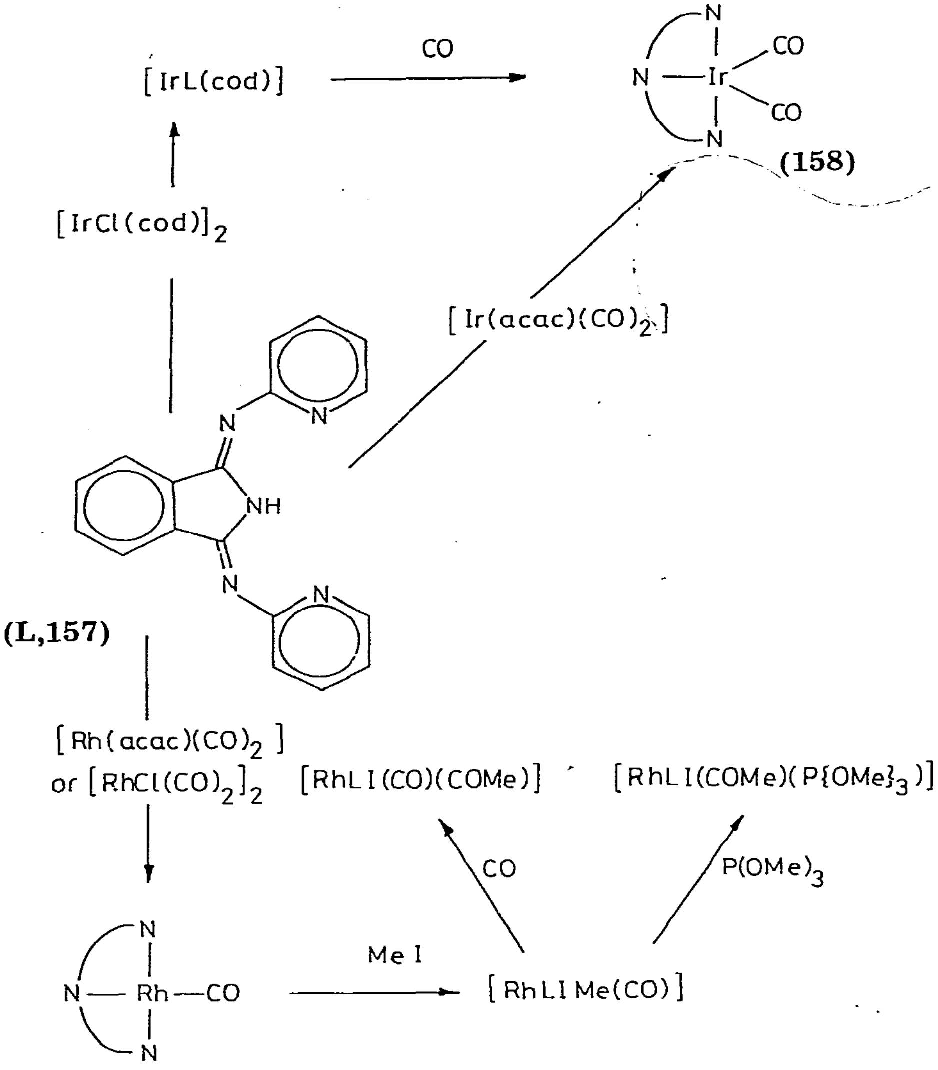
(156)

observed in [Rh(acac)$(CO)_2$], the X-ray crystal structure data of which has been refined [141]. Acetylacetonatodicarbonyliridium has been prepared by heating $K_2[IrCl_6]$ and acetylacetone in dibenzo-18-crown-6-diphenylformamide [142] and a Moessbauer study has been made on the intermolecular Ir—Ir bonding in planar iridium complexes of this type as well as in the complexes [IrCl$(CO)_2$L] [143].

1,3-Bis(2-pyridylimino(isoindoline) (157) readily reacts with [Ir(acac)$(CO)_2$] in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane to give the five coordinate dicarbonyl complex 157. Four-coordinate rhodium complexes can be obtained and some chemistry of these complexes is depicted in Scheme 19 [144].

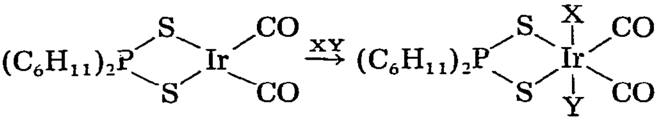
Dithiophosphato complexes of iridium(I) have been obtained by the reactions of $[IrCl(CO)_3]_n$ or $[IrCl(1,5\text{-cod})]_2$ with $(C_6H_{11})_2PSS^- NH_4^+$ or $(PhO)_2PSS^- NH_4^+$, Scheme 20.

The complex 159 undergoes *trans*-oxidative addition with halogens and me-



SCHEME 19

thyl iodide. However, 159 does not react with H_2, O_2 or MeCOCl. The complex

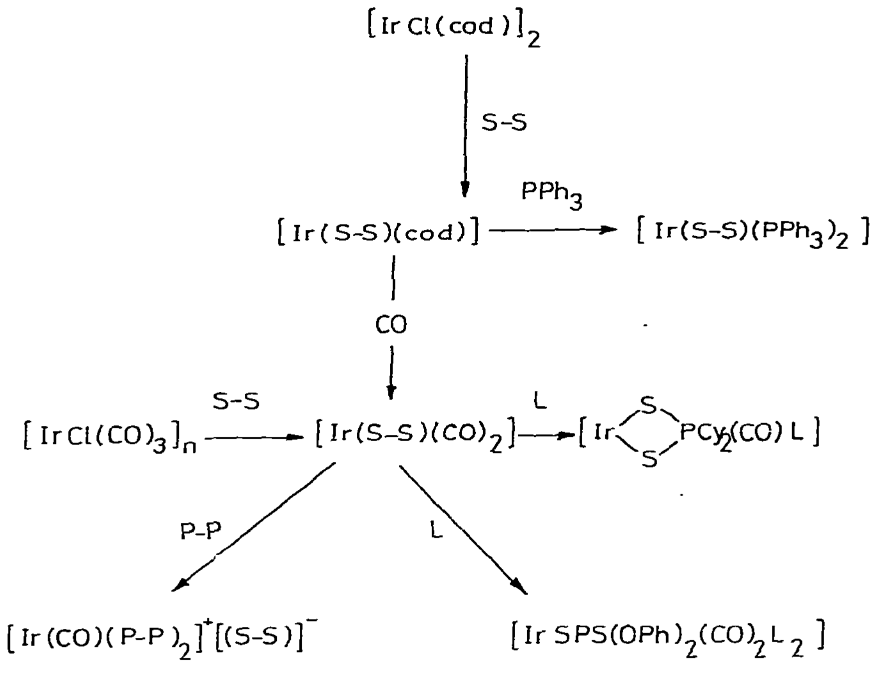


(159)

XY = Cl_2, Br_2, I_2 or MeI

$[IrS_2P(OPh)_2(CO)_2]$ reacts with halogens and methyl iodide but in each reaction more than one compound is obtained [145].

N-Phenyl-*S*-trimethyltinthioacetimidate (160) reacts with $[RhCl(CO)_2]_2$ to



S–S = $S_2P(C_6H_{11})_2$, $S_2P(OPh)_2$; L = PPh_3, PEt_3

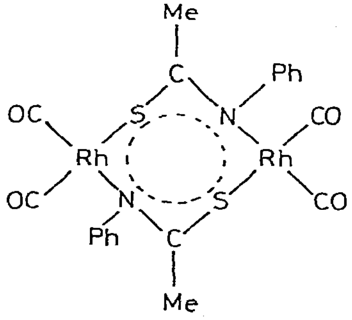
P–P = $Ph_2PCH_2CH_2PPh_2$

SCHEME 20

give the dimer **161** although there seems no reason why a monomeric complex is not obtained [146].

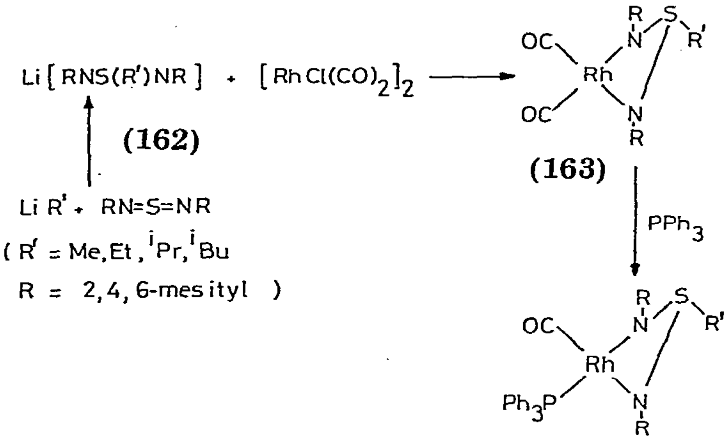
$PhNC(Me)SSnMe_3$

(160)



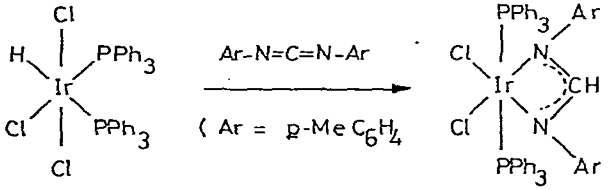
(161)

However, monomeric complexes **163** are obtained on reaction of the lithium compounds **162** with $[RhCl(CO)_2]_2$ [147]. An X-ray study on **163** (R = mesityl,



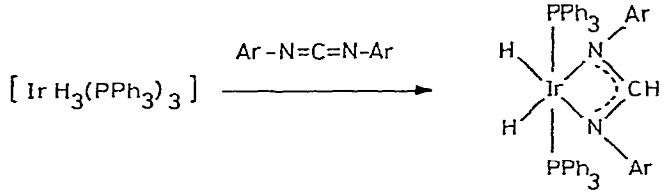
(162)

(163)



(164)

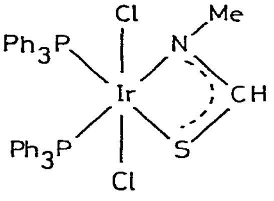
(165)



(166)

R' = t-Bu) indicates that the *S,N,N'*-substituted sulphurdiimine ligand resembles an η^3-allyl group [148]. Bidentate *N,N'*-diarylformamidinate (ArN—CH—NAr) ligands have been obtained by the reaction of **164** or [$IrH_3(PPh_3)_3$], with ArN=C=NAr, (Ar = *p*-tolyl), the complexes **165** and **166** being formed [149] and some related reactions of alkyl- and aryl-isothiocyanates with **164** give the complexes **167** and **168** [150].

Hydrated rhodium(III) chloride in refluxing ethanol reacts with $P(OPr\text{-}i)_3$ in the presence of carbon monoxide to give [$RhCl(CO)\{P(OPr\text{-}i)_3\}_2$]. In acetone solution the rhodium(III) complex, [$RhCl_3(CO)\{P(OPr\text{-}i)_3\}_2$] is obtained. The phosphite ligand in the rhodium(I) complex is easily hydrolysed to $OPH(OPr\text{-}i)_2$. Complexes of $OPH(OR)_2$ and $OPH_2(OR)$ and [$RhCl(CO)\{P(OR)_3\}_2$] are formed on treating [$RhCl(CO)_2]_2$ in aqueous ethanol with $P(OR)_3$, (R = Me,



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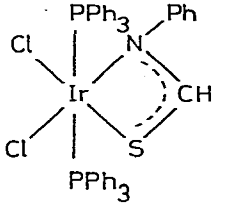
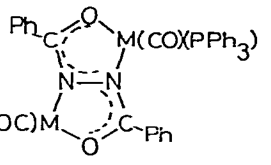
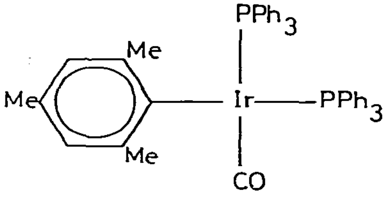


(168)

Et, Pr, Pr-i) [152]. 1,2-Dibenzoyl- and diacetyl-hydrazides react with *trans*-[MCl(CO)(PPh$_3$)$_2$] to give the bridged species [{M(CO)(PPh$_3$)}$_2$RCON$_2$COR] which are thought to have the structure **169**. The complexes oxidatively add chlorine



(169)



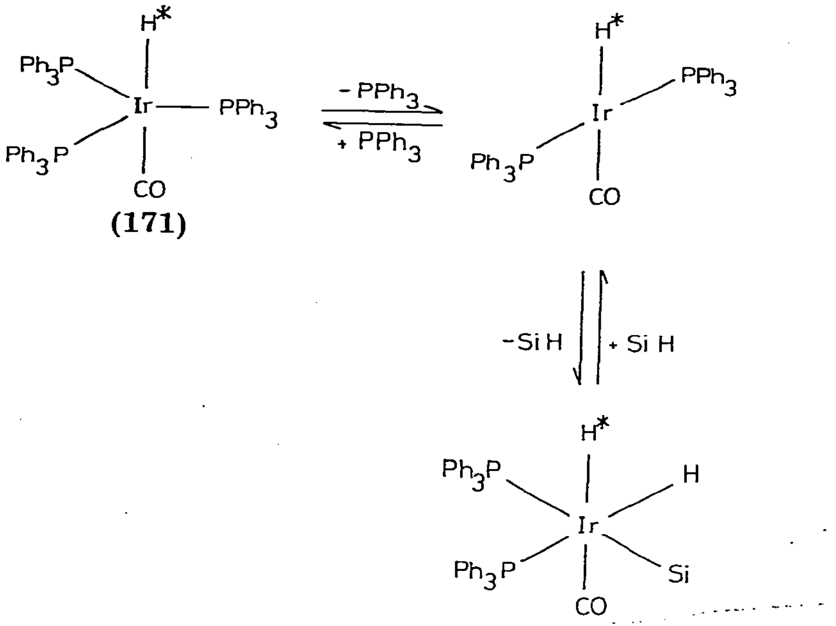
(170)

or bromine and the triphenylphosphine ligands can be replaced by carbon monoxide under high pressure [153]. Complexes of the type [MX(CO)L$_2$] (M = Rh or Ir), invariably have a *trans*-configuration. However, the first example of *cis*—*trans*-isomerism has been observed in the complex **170** [154]. The electronic absorption spectra of a variety of complexes of the type *trans*-[MA(CO)L$_2$], have been measured: M = Rh, L = PPh$_3$, A = OClO$_3$, OReO$_3$, OCO$_2$H, OH, O$_2$P(OH)$_2$, F, ONO$_2$, N$_3$, SH, Cl, Br, NCO, NO$_2$, N(CN)$_2$, I, NCS, NCBH$_3$, SCO$_2$H, CN; M = Rh, A = Cl, L = P(C$_6$F$_5$)$_3$, AsPh$_3$, PEt$_3$, SbPh$_3$, P(*p*-MeOC$_6$H$_4$)$_3$, P(*m*-MeC$_6$H$_4$)$_3$; M = Rh, A = I, L = PCy$_3$, P(*m*-MeC$_6$H$_4$)$_3$, PPh$_3$; M = Ir, L = PPh$_3$, A = OH, F, OCO$_2$H, ONO$_2$, Cl, OReO$_3$, OClO$_3$, N$_3$, NCO, Br, NCS, NO$_2$, I, NCSe, CN; M = Ir, A = Cl, L = P(*o*-MeC$_6$H$_4$)$_3$, PCy$_3$, PEtPh$_2$, PBuPh$_2$, AsPh$_3$, P(*p*-MeOC$_6$H$_4$)$_3$, P(*p*-ClC$_6$H$_4$)$_3$, P(*p*-MeC$_6$H$_4$)$_3$, P(*m*-MeC$_6$H$_4$)$_3$; M = Ir, A = NCBH$_3$, L = PCy$_3$. The principal low-energy bands in the complexes are assigned as metal-to-ligand charge-transfer transitions of the type $d_{z^2} \rightarrow b, \pi$ [155]. Studies on the oxidative addition of Ph$_3$SiD to **171** reveal a pathway involving a stereospecific addition (Scheme 21). The complex **172** undergoes H/D exchange in the presence of excess Ph$_3$SiD [156]. The kinetics of the reaction:

$$[\mathrm{IrH(CO)(PPh_3)_3}] + \mathrm{Ph_3MH} \rightleftharpoons [\mathrm{IrH_2(MPh_3)(CO)(PPh_3)_2}] + \mathrm{PPh_3}$$

have been studied, (M = Si, Ge or Sn). All three reactions proceed by predissociation of the iridium complex and concerted *cis*-addition of Ph$_3$MH to the square-planar intermediate. The relative rate of addition increases in the order Si < Ge < Sn and the difference in rate is due entirely to change in $\Delta S^{\neq}$. It appears that solvation effects related to a change in polarity on passage to the transition state are more important than bond energies or acid—base properties in determining relative reaction rates [157].

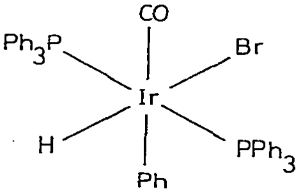
The crystal structure of **173** has been determined. There appears to be no π-interaction in the Ir—Ph bond [158]. The structures of the complexes 174—



(171)

(172)

SCHEME 21



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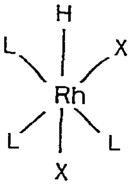

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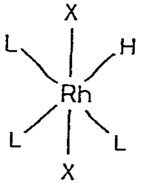

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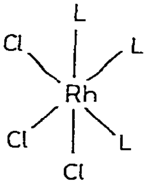

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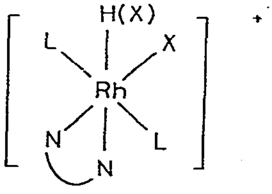
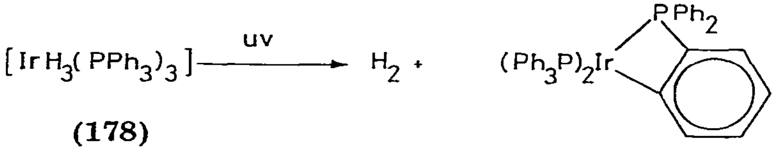


(177)

177 (X = Cl or Br; L = $PEtPh_2$; N-N = 2,2′-bipyridyl or 1,10-phenanthroline) have been assigned on the basis of a study of their metal—halogen stretching frequencies [159].

Irradiation of $[IrClH_2(PPh_3)_3]$ with ultraviolet light or sunlight induces elimination of H_2 with the formation of $[IrCl(PPh_3)_3]$. Similarly the irradiation of the *mer*- and *fac*-isomers of **178** leads to H_2 loss with subsequential formation of the internally metallated complex **179**.



(178)

(179)

The lack of production of HD upon photolysis of an $[IrClH_2(PPh_3)_3]/[IrClD_2(PPh_3)_3]$ mixture demonstrates that the photoelimination of H_2 from $[IrClH_2(PPh_3)_3$ proceeds in a concerted fashion. The $[IrClH_2(PPh_3)_3]/[IrCl(PPh_3)_3]$ system serves as a model system for hydrogen storage and energy storage [160]. The dihydride *cis*-$[CoH_2\{(OMe)_3\}_4]^+$ also slowly loses H_2 in solution and again this reaction is a strictly intramolecular process. The cobalt species resulting is $[Co\{P(OMe)_3\}_5]^+$ and the overall equation is probably:

$$9[CoL_4]^+ \rightarrow 6[CoL_5]^+ + 2\,Co^\circ + [CoL_6]^{3+}$$

$L = P(OMe)_3$

but the octahedral species has not been definitely characterised. Kinetic studies of the reaction of the dihydride with $P(OMe)_3$ are consistent with the mechanism outlined in Scheme 22, $[Co\{P(OMe)_3\}_4]^+$ being an intermediate. Reactions rates

$$\begin{tikzcd}[CoH_2L_4]^+ \arrow[r, phantom, "\rightleftharpoons"] & H_2 + [CoL_4]^+ \arrow[d, "L"] \\ & {[CoL_5]^+}\end{tikzcd}$$

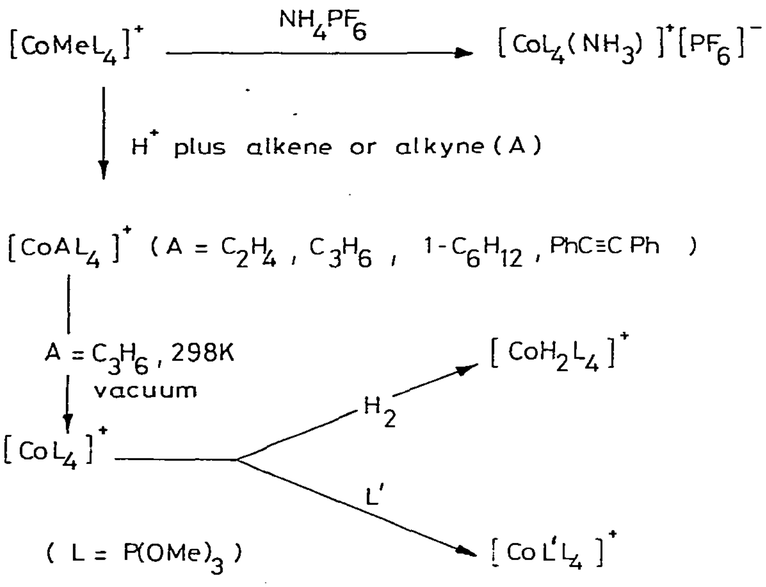
$L = P(OMe)_3$

SCHEME 22

are substantially higher in coordinating solvents indicating that the equilibrium:

$$[CoL_4]^+ + S \rightleftharpoons [CoSL_4]^+$$

must be considered in such solvents. Methylation of $[CoH\{P(OMe)_3\}_4]$ or protonation of $[CoMe\{P(OMe)_3\}_4]$ quantitatively yields methane, the major cobalt products being $[Co\{P(OMe)_3\}_5]^+$ and cobalt metal. The methylhydrido intermediate is too unstable for isolation but studies with $[CoCD_3\{P(OMe)_3\}_4]$ reveal that this elimination is also intramolecular. $[Co\{P(OMe)_3\}_4]^+$ is an intermediate in these reactions and some of its chemistry is outlined in Scheme 23. The dimethylcobalt complex $[CoMe_2\{P(OMe)_3\}_4]^+$ formed in the alkylation of $[CoMe\{P(OMe)_3\}_4]$ by $Me_3O^+\ PF_6^-$ is too unstable for isolation and undergoes an intramolecular reductive elimination. In CD_2Cl_2 there is evidence for a carbene complex (Scheme 24) [161].



SCHEME 23

$$
\begin{array}{l}
[CoMe_2L_4]^+ \rightleftharpoons [CoMe_2L_3] + L \\
\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\
[Co(CH_2)L_3]^+ \xleftarrow[-CH_4]{\text{fast}} [Co(CH_2)(H)MeL_3]^+
\end{array}
$$

SCHEME 24

The radical, $(CF_3)_2NO$ oxidatively adds to the complexes *trans*-$[IrCl(CO)L_2]$ **180** to give the octahedral complexes **181** which contain *trans*-phosphine ligands

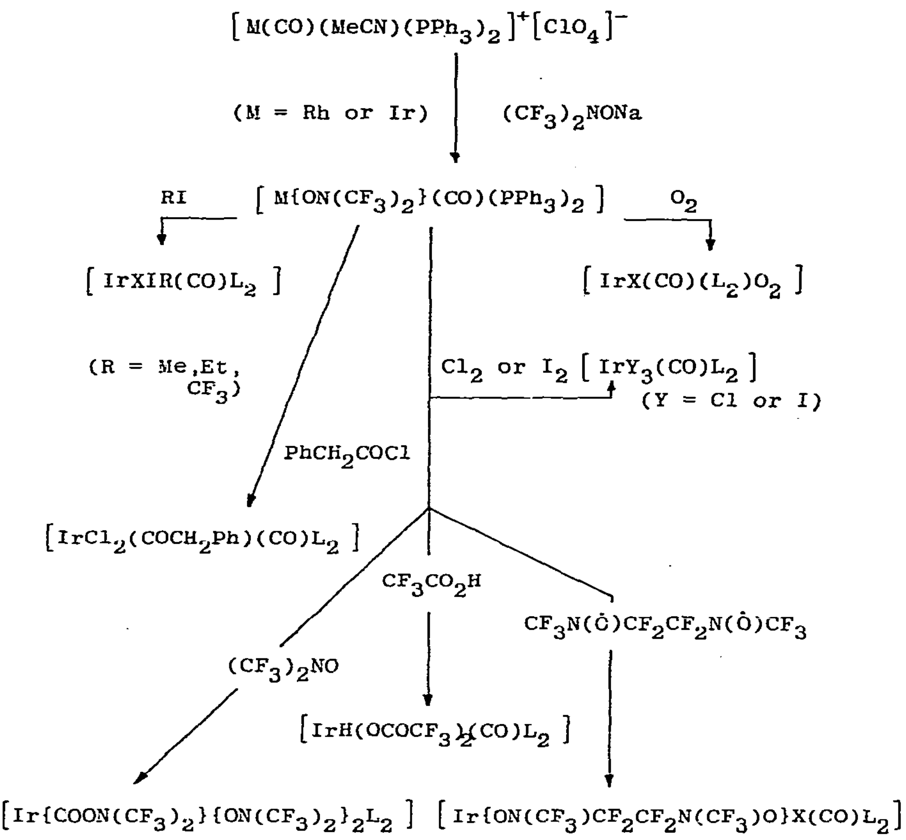
$$
\textit{trans}\text{-}[IrCl(CO)L_2] \xrightarrow{(CF_3)_2NO} [IrCl\{ON(CF_3)_2\}_2(CO)L_2]
$$

$(L = PPh_3, AsPh_3, PMePh_2)$

(180) **(181)**

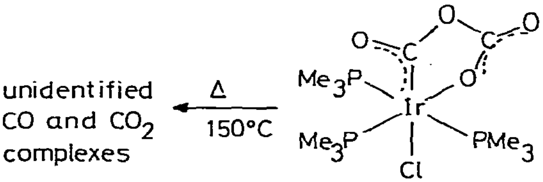
in the case of $L = PMePh_2$. Some four-coordinate rhodium and iridium compounds have been obtained by ligand displacements (Scheme 25) and some reactions of the iridium complex are also illustrated in this scheme [162]. Treatment of *trans*-$[RhCl(CO)(PPh_3)_2]$ with the hydroperoxide t-BuO_2H results in the oxidation of coordinated carbon monoxide to CO_2 and the formation of $[RhCl(PPh_3)_2]_2$. Similarly $[RhCl(CO)_2]_2$ and t-BuO_2H give CO_2 and a brown solid which contains no $\nu(CO)$. The reaction of t-BuO_2H with *trans*-$[IrCl(CO)(PPh_3)_2]$ is more complex, CO_2, Ph_3PO, $[IrCl(O_2Bu\text{-}t)_2(CO)(PPh_3)_2]$ and a blue complex of approximate empirical formula $[IrCl(PPh_3)]_n$ being formed. t-BuO_2H and $[RhCl(PPh_3)_3]$ give $[RhCl(PPh_3)_2]_2$ [163].

The reaction of carbon dioxide with $[IrCl(cyclooctene)(PMe_3)_3]$ gives the novel complex **182**, characterised by an X-ray study. This reaction probably proceeds via an intermediate CO_2 complex, $[IrCl(CO)_2)(PMe_3)_3]$ [164]. The hydride $[RhH(PPh_3)_4]$ is also known to react with carbon dioxide. The complex isolated



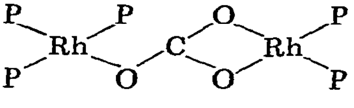
$X = ON(CF_3)_2$ $L = PPh_3$

SCHEME 25



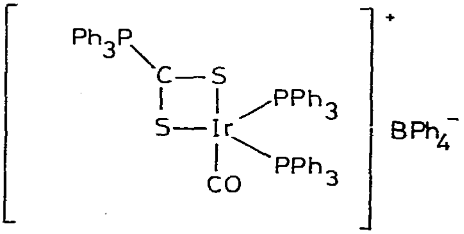
(182)

has been previously formulated as a carbonyl complex, $[Rh_2H_2(CO)_2(PPh_3)_6]$, but an X-ray study shows the complex to be a carbonate complex 183 [165]. It is possible that 183 is formed via a C_2O_4 complex of a type similar to 182.



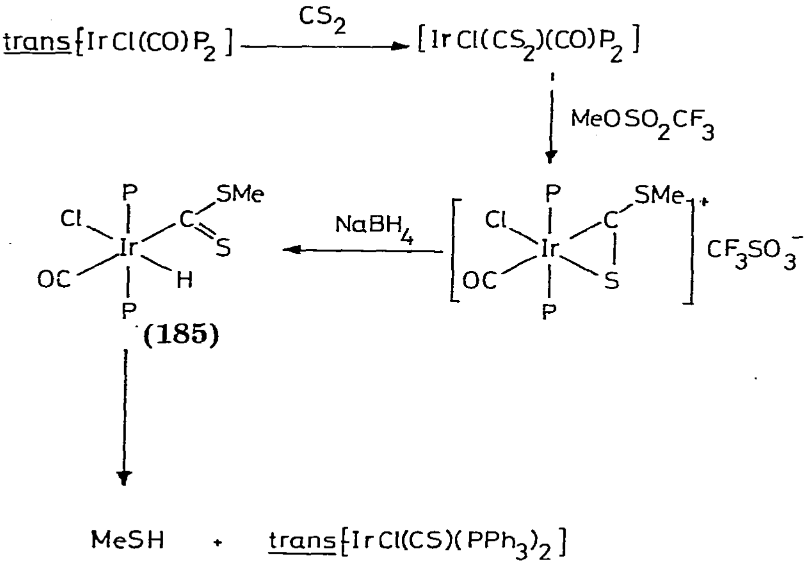
(P = PPh_3)

(183)



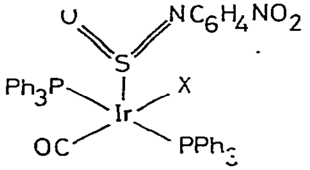
(184)

The reaction of carbon disulphide with *trans*-[$IrCl(CO)(PPh_3)_2$] and excess PPh_3 in methanol followed by addition of $NaBPh_4$ has been suggested to lead to a cationic η-CS_2 complex [$Ir(CS_2)(CO)(PPh_3)_3$][BPh_4]. However, X-ray studies show this complex to be **184** containing the zwitterion, $Ph_3P^+ CS_2^-$ as a ligand [166]. *trans*-[$IrCl(CO)(PPh_3)_2$] can be converted to the thiocarbonyl complex *trans*-[$IrCl(CS)(PPh_3)_2$] in high yield via a hydrido-dithiomethylester complex **185** (Scheme 26) [167].

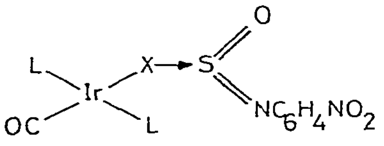


SCHEME 26

trans-[$IrCl(CO)(PPh_3)_2$] has been reported to react with PhNSO to give [$IrCl(CO)(SO_2)(PPh_3)_2$] and aniline. However, it has now been found that while PhNSO does not react with *trans*-[$IrCl(CO)(PPh_3)_2$] under anhydrous conditions, *trans*-[$IrX(CO)(PPh_3)_2$] ($X = Cl$ or Br), does react with p-$O_2NC_6H_4NSO$ to give 1/1 adducts which may have the structure **186a** or **186b** [168]. Sulphur dioxide



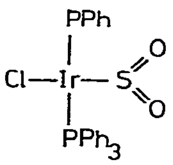
(186a)



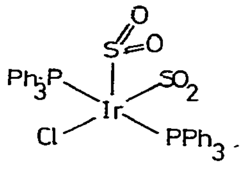
(186b)

reacts with *trans*-[$IrCl(N_2)(PPh_3)_2$] to give **187** which reacts with more SO_2 to give **188**, a complex which contains two SO_2 molecules bonded to a metal in different ways [169].

Both thiocyanogen and selenocyanogen oxidatively add to [$Ir(Ph_2PCH_2CH_2PPh_2)_2$]Cl to give the complex ions [$Ir(SCN)_2(Ph_2PCH_2CH_2PPh_2)_2$]$^+$ and [$Ir(SeCN)_2(Ph_2PCH_2CH_2PPh_2)_2$]$^+$ isolated as their BPh_4^- salts. Selenocyanogen is less effective than thiocyanogen in the oxidative addition reactions with



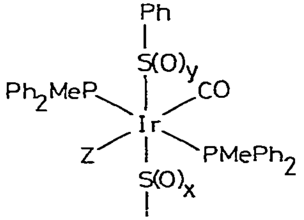
(187)



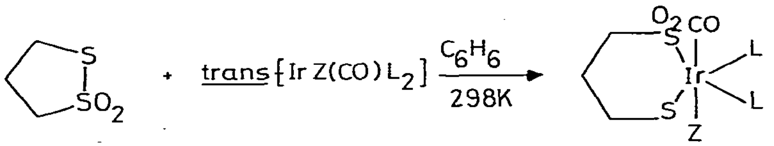
(188)

rhodium(I) and iridium(I). Thus $(SeCN)_2$ does not react with *trans*-$[RhCl(CO)(PPh_3)_2]$ and *trans*-$[IrCl(CO)(PPh_3)_2]$ gives $[IrCl(SeCN)_2(CO)(PPh_3)_2]$ by an equilibrium reaction. Both $(SeCN)_2$ and $(SCN)_2$ oxidatively add to *trans*-$[IrCl(N_2)(PPh_3)_2]$ to give $[IrCl(XCN)_2(PPh_3)_2]$, (X = Se or S) [170]. S—S bond cleavage also occurs in reactions of PhSSPh, $PhSSO_2Ph$ and $PhS(O)SO_2Ph$ with *trans*-$[IrZ(CO)(PMePh_2)_2]$, the complexes **189** being obtained. The cyclic compound 1,2-dithiolane-1,1-dioxide (**190**) reacts with *trans*-$[IrZ(CO)(PMePh_2)_2]$ to give **191** whilst reactions with thionyl chloride produce the complexes **192**. The coordinated S(O)Cl group remains reactive and offers the possibility of introducing other substituents at the S—Cl bond. Thus reaction with methanol produces the complexes **193** [171].

x=y=0; Z=Cl
x=y=0; Z=Br
x=0; y=2; Z=Cl
x=1; y=2; Z=Cl
x=1; y=2; Z=Br



(189)

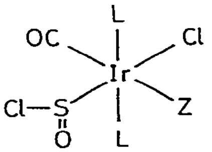


(190)

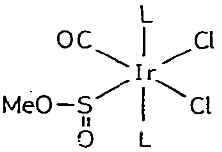
L = $PMePh_2$
Z = Cl or Br

(191)

L=PPh_3; Z=Cl
L=$PMePh_2$; Z=Cl
L=PPh_3; Z=Br

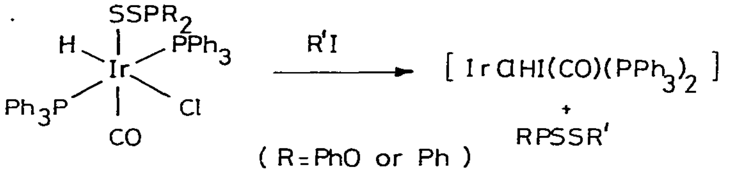


(192)



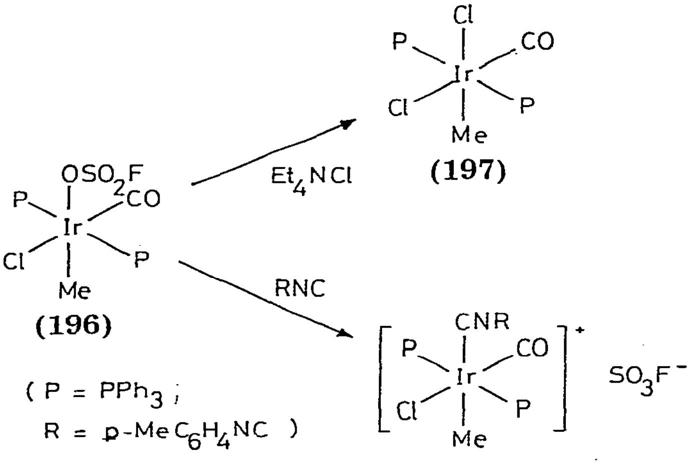
(193) (L = PPh_3 or $PMePh_2$)

Diphenyldithiophosphoric acid, $(PhO)_2PSSH$ and diphenyldithiophosphinic acid, Ph_2PSSH oxidatively add to *trans*-$[IrCl(CO)(PPh_3)_2]$ to give **194**. These



(194) **(195)**

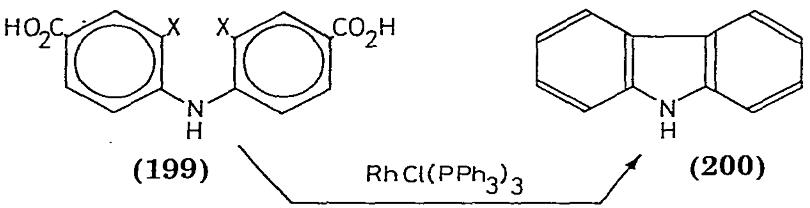
complexes react with both methyl and ethyl iodide to give the esters **195** and $[IrClHI(CO)(PPh_3)_2]$ [172]. A further report on the oxidative addition of methylfluorosulphate, $MeOSO_2F$, to Vaska's complex to give **196** has appeared. The ligand in the complex is labile and is displaced by chloride ion and isocyanide to give **197** and **198**, respectively. Interestingly, the complex **196** is also formed



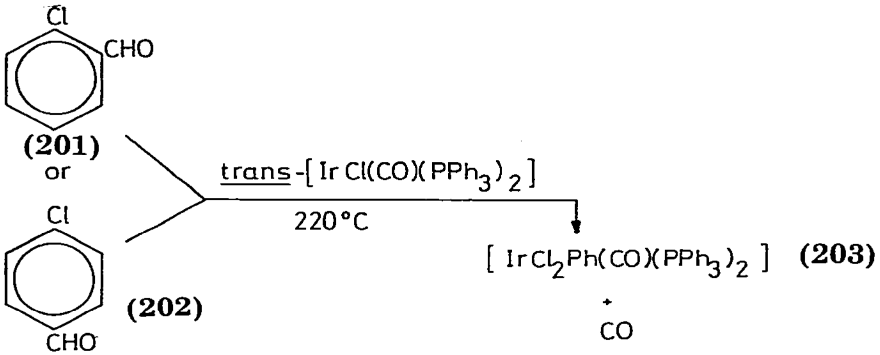
(198)

in reactions of methyl fluorosulphate with $[IrCl(CO)(L)(PPh_3)_2]$ ($L = O_2$, SO_2 or C_2F_4) and products in which the dioxygen, sulphur dioxide or tetrafluoroethylene ligands have been methylated have not been observed [173].

Chlorotris(triphenylphosphine)rhodium(I) catalyses the conversion of some 2,2'-dihalodiphenylamine-4,4'-dicarboxylic acids (**199**) to carbazoles (**200**). Such



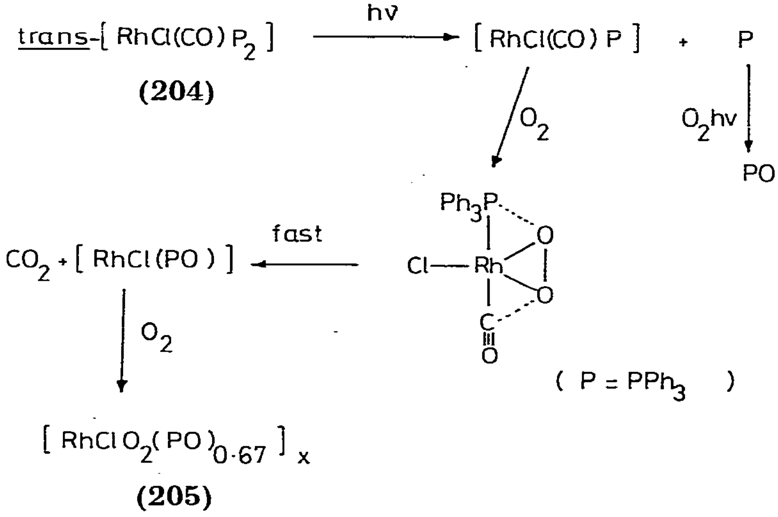
reactions probably proceed via oxidative addition of the phenyl—halogen bond to the rhodium and a phenyl iridium complex **203** has been obtained from reactions of the chlorobenzaldehydes **201** or **202** with *trans*-$[IrCl(CO)(PPh_3)_2]$.



2-Bromo-4-tolualdehyde and 2-iodobenzaldehyde similarly react with Vaska's complex to give $[IrBr_2(p\text{MeC}_6H_4)(CO)(PPh_3)_2]$ and $[IrI_2Ph(CO)(PPh_3)_2]$, respectively. Chlorobenzene does not oxidatively add to the iridium under these conditions but both iodo- and bromo-benzene form $[IrClXPh(CO)(PPh_3)_2]$ (X = I or Br) [147]. The decarbonylation of aldehydes by $[RhCl(PPh_3)_3]$ are usually stoichiometric reactions because the rhodium product *trans*-$[RhCl(CO)(PPh_3)_2]$ is not an active decarbonylating agent and does not lose carbon monoxide thermally to regenerate the active reagent.

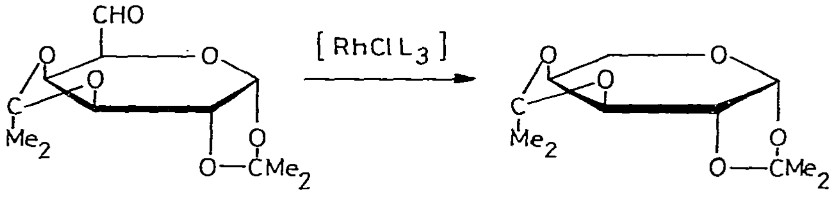
$$RCHO + [RhCl(PPh_3)_3] \rightarrow RH + PPh_3 + trans\text{-}[RhCl(CO)(PPh_3)_2]$$

Since metal carbonyl complexes are known to dissociate CO upon irradiation an attempt to reform the active catalysts $[RhCl(PPh_3)_2]$ or its dimer, via photo-induced loss of carbon monoxide has been made. However, no net photochemical reaction is observed when *trans*-$[RhCl(CO)(PPh_3)_2]$ is irradiated and in the presence of O_2, carbon monoxide and PPh_3 are oxidised to CO_2 and Ph_3PO (Scheme 27). The reaction of the dioxygen complex **205** with PPh_3 does regenerate $[RhCl(PPh_3)_3]$ which can be used for further decarbonylations but the sensitivity of $[RhCl(PPh_3)_3]$ toward oxygen and the need of oxygen to remove CO

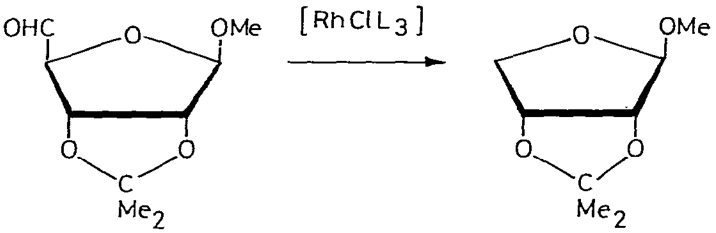


SCHEME 27

from **204** require separate steps in the decarbonylation cycle (Scheme 28) and the reaction cannot be made truly photocatalytic [175]. The aldehyde sugar derivative **206** cannot be decarbonylated with [$RhCl(PPh_3)_3$]. However, decarbonylation of **206** can be achieved using [$RhCl(PMePh_2)_3$], to give **207**. Similarly **208** can be converted to **209** using this reagent. The difference in behaviour of **206** towards the complexes [$RhCl(PPh_3)_3$] and [$RhCl(PMePh_2)_3$] is possibly attributable to less steric hindrance in the approach of the aldehyde to the metal atom in the case of the $PMePh_2$ complex [176]. In the past, there have been some disputes regarding the structures of the complexes [$RhClL_3$] (L = triarylphosphine) in solution, the dissociation or the dimerisation equilibria being proposed (Scheme 29). The monomer-dimer equilibrium of [$RhCl(PPh_3)_3$] in benzene has been studied with a stopped-flow apparatus under He gas pressure. The kinetic results are consistent with the mechanism outlined in Scheme 30 [177].



(206) (L = $PMePh_2$) **(207)**



(208) **(209)**

$$\begin{tikzcd}[RhCl(PPh_3)_3] + RCHO \arrow[r, "N_2"] & trans\text{-}RhCl(CO)(PPh_3)_2 + PPh_3 + RH \arrow[d, "O_2,\ h\nu"] \\ & {[RhClO_2(OPPh_3)_{0.67}]_x} + CO_2 + 1.33\ Ph_3PO \arrow[ul, "N_2,\ PPh_3"]\end{tikzcd}$$

SCHEME 28

$$[RhCl_3] \rightleftharpoons [RhClL_2] + L$$

$$2\ RhCl_3 \rightleftharpoons [RhClL_2]_2 + 2\ L$$

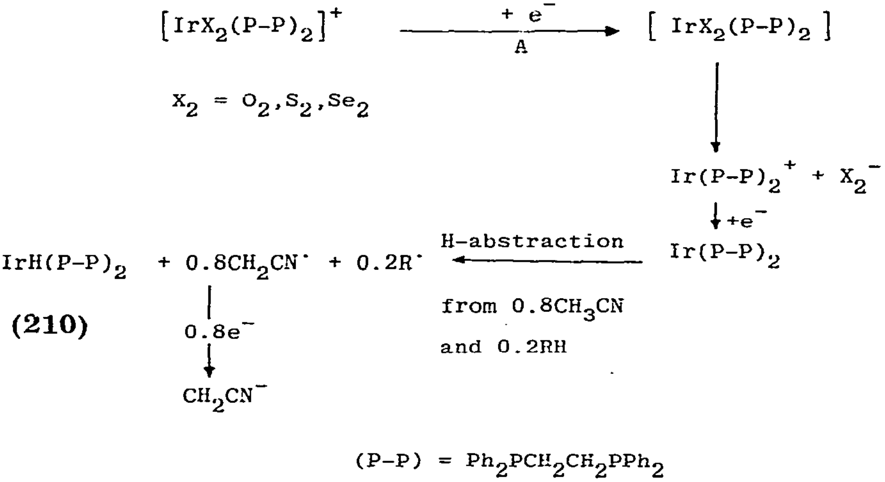
SCHEME 29

$$\begin{tikzcd}2\ RhClL_3 \arrow[r, leftrightharpoons] & RhClL_2 + RhClL_3 + L \arrow[d, leftrightharpoons] \\ & {[RhClL_2]_2} + 2\ L\end{tikzcd}$$

$(L = PPh_3)$

SCHEME 30

Some novel electrochemical behaviour of the adducts $[IrX_2(diphos)_2]^+$, (X = O_2, S_2 or Se_2; diphos = $Ph_2PCH_2CH_2PPh_2$) has been reported and the mechanism in Scheme 31 is proposed for the electrolytic reduction of these complexes. Two important implications of the research are:

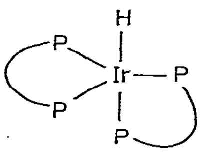


SCHEME 31

(a) The lowest unoccupied molecular orbital, to which one electron is added at wave A, must be strongly antibonding between the metal and the X_2 group, this molecular orbital arising from interaction between a metal *d* orbital and the π^* orbital of X_2 which lies in the MX_2 plane:

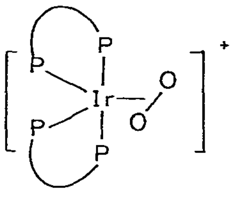
(b) π-back-bonding interaction increases in the order $Se_2 < S_2 < O_2$. These conclusions are supported by Molecular Orbital calculations on model complexes of the type $[RhX_2(PH_3)_4]^+$. A single crystal X-ray study on the hydride **210**, formed by a hydrogen abstraction reaction in the electrochemical work, reveals a trigonal bipyramidal like structure [178].

(210)



(P-P = $Ph_2PCH_2CH_2PPh_2$)

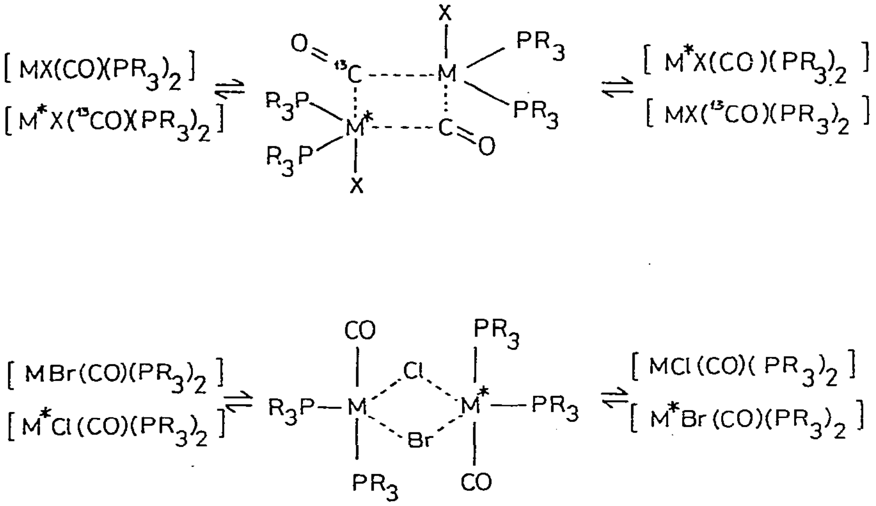
(211)



(P-P = $Ph_2PCH_2CH_2PPh_2$)

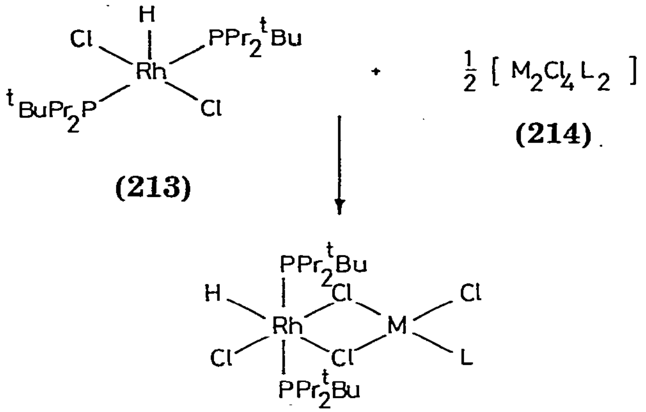
The crystal structures of the PF_6 and ClO_4 salts of **211** have been determined. Although the packing in the two compounds differs greatly, the geometry of the cation in each remains the same. These and other studies reveal that the O—O bond length is constant irrespective of the metal or other ligands, there is no correlation between O—O bond length and the reversibility of metal-dioxygen "uptake" properties and that the dioxygen ligand in rhodium and iridium dioxygen complexes has peroxo character [179]. Similar structures have been found for the complexes $[M(O_2)(PMePh_2)_4][BPh_4]$ (M = Rh or Ir) [180,181]. High pressure liquid chromatography has been used to separate *trans*-$[RhCl(CO)(PPh_3)_2]$, *trans*-$[IrCl(CO)(PPh_3)_2]$, $[IrCl(CO)(O_2)(PPh_3)_2]$, and PPh_3 [182]. The temperature variation of the mechanism of thermal decomposition of $[IrCl(CO)(O_2)(PPh_3)_2]$ has previously been studied at 379—425 K. Studies have now been reported in the range 426—433 K [183].

Transition metal organometallic redistribution reactions are beginning to receive attention. Halide, carbon monoxide and organophosphines undergo intermolecular exchange between four-coordinate species of the type *trans*-$[MX(CO)(L_2)]$ (M = Rh; X = Cl, Br; L = PPh_3, $P(m\text{-}MeC_6H_4)_3$, $PEtPh_2$, PEt_2Ph, PEt_3, $PMePh_2$, $AsPh_3$, $Sb(o\text{-}MeC_6H_4)_3$, $P(OPh)_3$; M = Ir; X = Cl, Br; L = PPh_3, PEt_2Ph, $P(OPh)_3$). The exchange of CO and X appears to be random, a four-centre associative mechanism being proposed (Scheme 32).



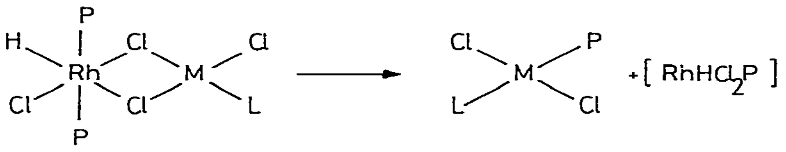
SCHEME 32

The lack of exchange between *trans*-$[RhCl(^{13}CO)(PPh_3)_2]$ and $[RhCl_3(CO)(PPh_3)_2]$ suggests that coordination unsaturation is a prerequisite for fast carbonyl exchange. Organophosphine exchange is proposed to occur via a dissociative process, the exchange between rhodium complexes again being a random process. However, phosphine—phosphite exchange between rhodium and iridium favours the mixed species, *trans*-$[MCl(CO)(PR_3)\{P(OR)_3\}]$ [184] consistent with the previous observation that *trans*-$[IrCl(CO)(PPh_3)_2]$ and *trans*-$[IrCl(CO)\{P(OPh)_3\}_2]$ react in toluene at 25°C to give *trans*-$[IrCl(CO)(PPh_3)\{P(OPh)_3\}]$ [187]. Biheterometallic, chloro-bridged hydrido-species of type **212** are formed on mixing toluene solutions of the square-pyramidal complex **213** and a chloro-bridged dimeric palladium or platinum complex **214**. On allowing the reaction solution to stand for several hours further changes are observed in the ^1H and ^{31}P NMR spectrum of the mixture consistent with the formation of **215** and an uncharacterised complex **216**. The marked difference in reaction rate observed on going from $[RhCl_2(PPr_2Bu\text{-}t)_2]$ to $[RhHCl_2(PPr\text{-}t\text{-}Bu_2\text{-}t)_2]$ may be rationalised in terms of steric strain. Thus considerable relief of steric strain would result in



L = PEt_3, PBu_3 or $PPr_2{}^tBu$; M = Pt

L = PBu_3 and M = Pd

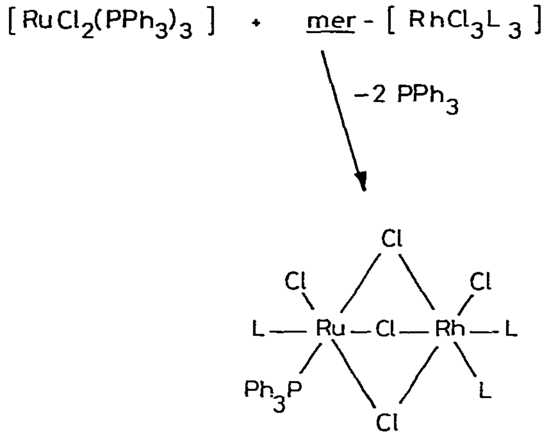


P = $PPr_2{}^tBu$

transfer of one of the t-butyl-substituted phosphines from the rhodium centre to the less crowded palladium or platinum centre. This relief will be more marked for the PPr-t-Bu_2 complex than for the PPr_2Bu-t complex. The increase in reaction rate observed on going from a platinum to a palladium chloro-bridged dimer may be rationalised in terms of a decrease in bridge strength in going from platinum to palladium [186]. A series of triple chloro-bridged heterobimetallic complexes of the type 217 have also been obtained via phosphine—ligand exchange reactions [187].

The lability of the chloride ligand *trans* to phosphorus in *mer*-$[RhCl_3(PMe_2Ph)_3]$ has been previously established and it now appears that this ligand is abstracted in reactions with alkylating agents (Scheme 33) [173].

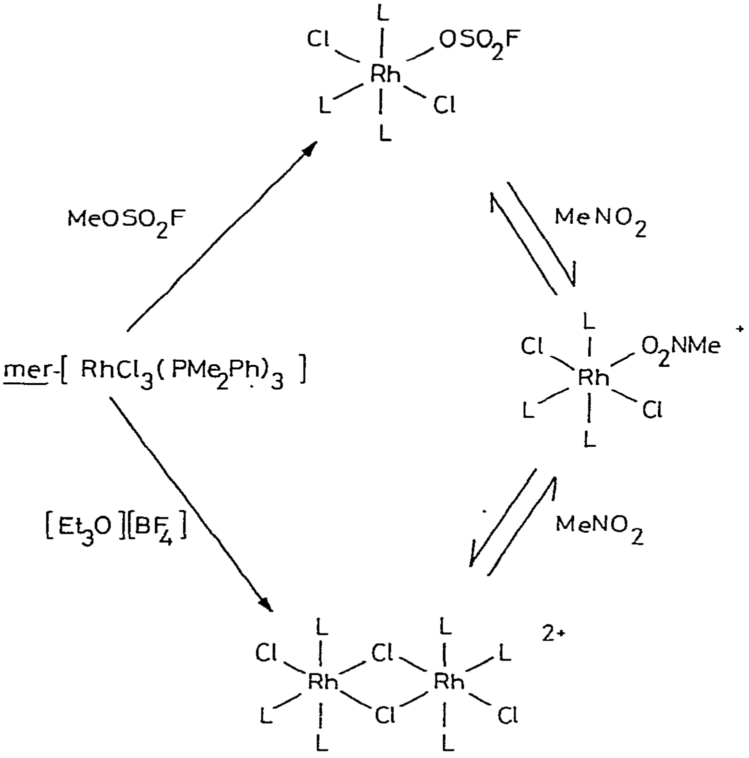
It is known that bulky tertiary phosphine ligands kinetically stabilise transition-metal hydrides of unusual types. The action of the even more bulky phosphines P-t-Bu_3, P-t-Bu_2Ph, or P-t-$Bu_2(C_6H_4Me$-*p*) on iridium(III) chlorides has now been investigated, (Scheme 34). Hydrides of the type$[IrCl_{3-x}H_x(PR\text{-t-}Bu_2)_2]$ ($x = 1$, R = Me; $x = 2$, R = t-Bu) react with $NaBH_4$ to give the complexes 218, which are non-fluxional. Complex 218 (L = PMe-t-Bu_2) decomposes slowly in deuteriotoluene to $[IrH_5(PMe\text{-t-}Bu_2)_2]$ but $[Ir(BH_4)H_2(P\text{-t-}Bu_3)_2]$ seems to be indefinitely stable [188]. A single crystal X-ray study of $[IrH(NO_3)_2(PPh_3)_2]$



(217)

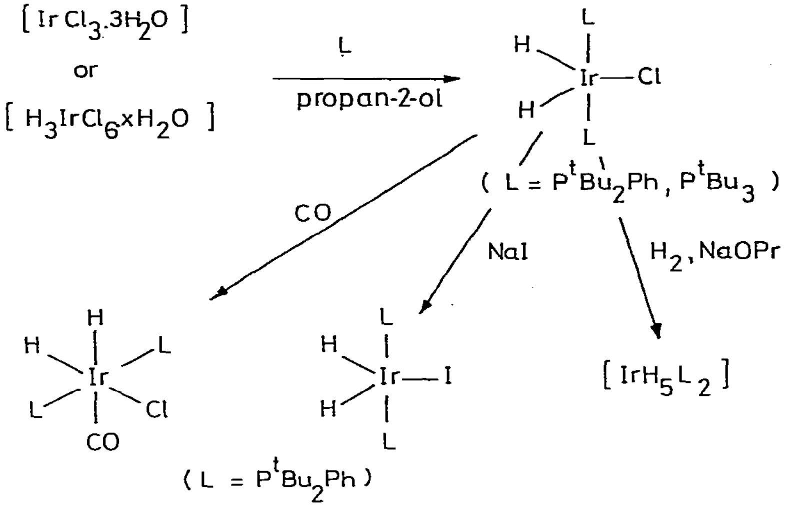
(L = PMe$_2$Ph, PEt$_2$Ph, P^{n}Bu$_2$Ph, P^{n}Bu$_3$ or PPh$_3$)

has been reported. There are two types of molecule present, both being trigonal bipyramidal with axial phosphines. However, both forms have disordered nitrate groups [189]. The complexes 219 are formed on treating [RhCl(1,5-cod)]$_2$ with carboxylic acids in the presence of an equivalent amount of Et$_3$N in benzene/

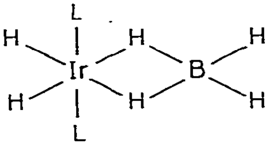


(L = PMe$_2$Ph)

SCHEME 33

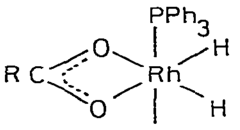


SCHEME 34



(218)

(L = PR^{t}Bu$_2$; R = Me, ^{t}Bu)

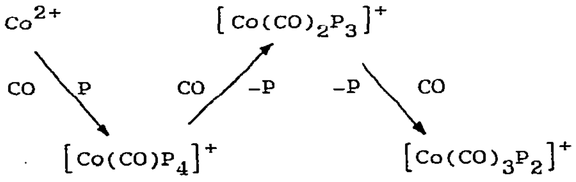


(219)

(R = n-C_5H_{11}, Ph, PhCH=CH, $PhCH_2CH_2$)

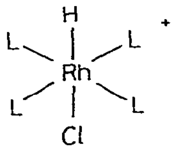
methanol solution. These complexes are active catalysts for hydrogenation of alkenes [190].

A full report has now appeared on the reaction of isopropanol solutions of $[Co(ClO_4)_2] \cdot 6\ H_2O$ with phosphines and carbon monoxide (Scheme 35). With smaller secondary phosphines ($PHPh_2$, $PHEt_2$, PHEtPh, PHMePh) the reaction stops at the first step, with formation of monocarbonyl complexes. With PHPhCy and the tertiary phosphines PMe_2Ph, $PMePh_2$ and PEt_2Ph bis-carbonyls



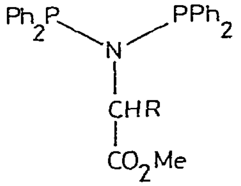
SCHEME 35

are readily formed. Under the same experimental conditions, the trialkylphosphines PEt_3, PPr_3 and PBu_3 yield tris-carbonyl products. Larger phosphines such as PPh_3, $PHCy_2$ and PCy_3 appear not to react. The first step in the reactions probably involves formation of $[CoP_4]^{2+}$ and in an inert atmosphere $[Co(ClO_4)_2] \cdot 6\ H_2O$ reacts with PMe_2Ph in isopropanol to give the tetrahedral paramagnetic complex, $[Co(PMe_2Ph)_4][ClO_4]_2$ [191]. The reactions of $[RhCl(1,5\text{-}cod)]_2$ and $[IrCl(cyclooctene)_2]_2$ with a variety of secondary phosphines lead to the formation of four-coordinate cationic complexes $[M(PHR_2)_4]^+$, (M = Rh or Ir, $PHR_2 = PH(C_6H_{11})_2$, $PHPh(C_6H_{11})$, $PHPh_2$; M = Rh, $PHR_2 = PHEt_2$, PHEtPh). The rhodium(I) complexes, with the exception of the dicyclohexylphosphine derivative, react reversibly with dihydrogen but no pure hydrido derivatives could be isolated. Solution IR spectra are consistent with the formation of *cis*-$[RhH_2(PHR_2)_4]^+$ cations. Hydrochloric acid oxidatively adds to give **220** and reactions of the cations with carbon monoxide give carbonyl compounds of the type $[Rh(CO)(PHR_2)_4]^+$. However, only in the case of the dicyclohexylphosphine derivative could a pure complex, $[Rh(CO)(PHCy_2)_3]^+$ be isolated. Similar results are obtained with the iridium complexes and all the complexes react with dioxygen but no pure dioxygen complexes could be isolated [192]. A cationic rhodium(I) complex 221 results from the action of the chelating phosphine 222 on [RhCl(1,5-cod)]. The addition of 222 to $[RhCl(CO)_2]_2$ affords 223 and these complexes are optically active for R = i-Pr in 222 [193]. The cationic complexes

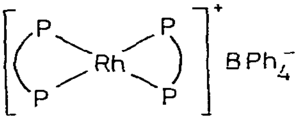


(L = PHR_2)

(220)

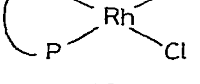


(222) (R = H or ${}^iPr$)



(221)

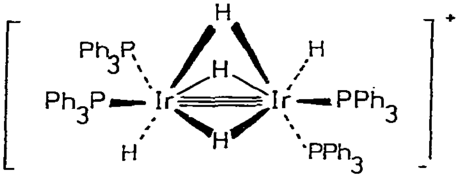
(P-P = 222)



(223)

of rhodium(I), $[Rh(CO)_2L_3][ClO_4]$ ($L = PPh_3$, $AsPh_2$, $AsMePh_2$ or $AsPrPh_2$) react with halogens to give *trans*$[RhX(CO)L_2]$ and $[RhX_3(CO)L_2]$. With halogen acids, however, only *trans*-$[RhX(CO)L_2]$ complexes are obtained [194]. The crystal structure of $[Rh(CO)_2(AsMePh_2)_3][ClO_4]$ has been reported [195]. The mechanism of ligand dissociation in cationic phosphite complexes of the type $[M\{P(OR)_3\}_5]^+$ (M = Co, Rh or Ir) has been studied in detail and evidence is presented to suggest a similarity between the reaction coordinates for intramolecular rearrangement and ligand dissociation [196].

The complex $[Ir(cod)(PPh_3)_2]^+ PF_6^-$ reacts with dihydrogen to give **224** which contains a metal—metal triple bond: The Ir—Ir bond distance of 2.518 Å is remarkably short [197]. The crystal structure of **225** has also been determined [198]. This and other triply-bridged dimeric complexes result from the action of chlorinated solvents on **226**. A convenient route to the complexes **226** involves the addition of a triarylphosphine to $[IrCl(cyclooctene)_2]_2$ followed by further reaction with the appropriate arenethiol [199]. The complex $[IrI_4(PMePh_2)_2]$, formed by the reaction of iodine on $[Ir(PMePh_2)_4]^+$, has also been characterised as a triply-bridged halo salt **227**. Complexes similar to **227** result from the action of iodine upon $[Ir\{P(OMe)Ph_2\}_4]^+$ and $[RhL_4]^+$, ($L = PMePh_2$ or $P(OMe)Ph_2$) [200].



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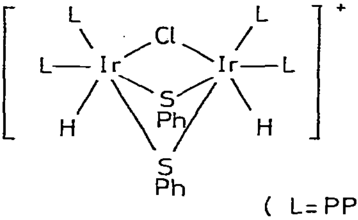
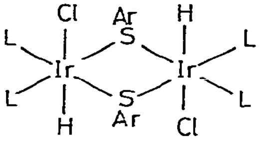


($L=PPh_3$)

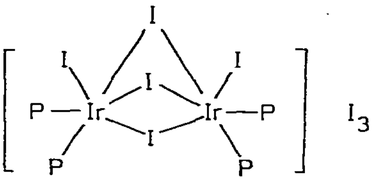
(225)



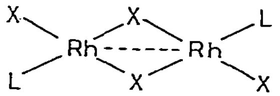
(226)

($L = PPh_3$; Ar = Ph , $4\text{-}MeC_6H_4$, $4\text{-}OMeC_6H_4$, $4\text{-}FC_6H_4$)

Tri-*o*-tolylstibine reacts with hydrated rhodium(III) chloride to give a rhodium(II) complex formulated as **228** (X = Cl). The corresponding bromide complex can also be prepared and it is suggested that the diamagnetism of the com-

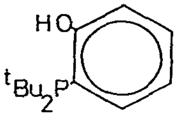


(227)



(228)

plex is the result of a strong rhodium—rhodium interaction [201]. Treatment of cobalt(II) chloride in boiling propan-2-ol with **229** gives the paramagnetic complex



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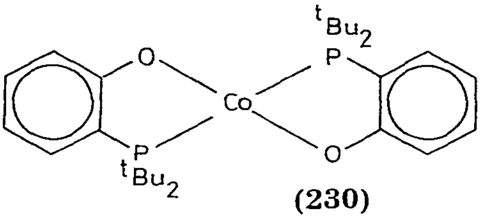


(230)

230 which probably has a *trans*-configuration and is square planar [202]. The cobalt hexaquo cation $[Co(H_2O)_6][BF_4]_2$ reacts with the poly(tertiaryphosphines) **231—233** according to the nature of the solvent, to afford two types of

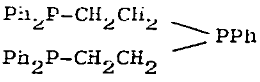
$N(CH_2CH_2PPh_2)_3$
np$_3$
(231)

$P(CH_2CH_2PPh_2)_3$
pp$_3$
(232)

$P(C_6H_4PPh_2)_3$
qp
(233)

according to the nature of the solvent, to afford two types of complexes, $[Co(OH)L_4]Y$ ($Y = BF_4$, BPh_4) and a series of aquo complexes $[Co(H_2O)L_4][BF_4]_2$. The cobalt complexes with np$_3$ are high spin and are assigned a tetrahedrally distorted trigonal bipyramidal geometry. The other cobalt complexes are low spin with distorted square-pyramidal geometry. These structural assignments come from single crystal X-ray studies on the complexes $[Co(OH)(pp_3)]BF_4 \cdot EtOH$ and $[Co(H_2O)(pp_3)][BF_4]_2 \cdot Me_2CO$ [203].

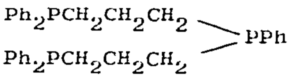
The stereochemistry and intramolecular exchange processes of a number of five-coordinate cobalt(I) complexes have been investigated. The preferred geometry in most cases appears to be based on a trigonal bipyramid although square pyramidal complexes can also be obtained. Six series of the complexes of the types $[Co(triphos)(CO)_2]X$ and $[Co(triphos)L(CO)]X$, where triphos is bis(2-diphenylphosphinoethyl)phenylphosphine (**234**), bis(3-diphenylphosphinopropyl)phenylphosphine (**235**) and 1,1,1-tris(diphenylphosphinomethyl)ethane (**236**) have been studied [204]. The complexes $[Co(etp)(CO)_2]^+$ (**237**) $[Co(etp)L(CO)]^+$ (**238**) and $[Co(etp)\{P(OMe)_2\}_2]^+$ (**239**) are assigned the structures illustrated. The structure **240** is assigned to an isomer of $[Co(etp)(PPh_3)(CO)]BF_4$. An X-ray structure determination of $[Co(ttp)\{P(OMe)_3\}CO]BF_4$ (**241**) reveals that this complex has a square pyramidal coordination around the cobalt [205].



$Ph_2P\text{-}CH_2CH_2$, $Ph_2P\text{-}CH_2CH_2$ > PPh

(etp)

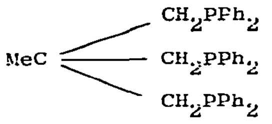
(234)



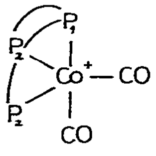
$Ph_2PCH_2CH_2CH_2$, $Ph_2PCH_2CH_2CH_2$ > PPh

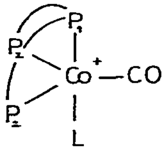
(ttp)

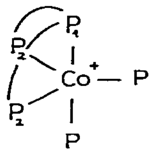
(235)


(tripod-P$_3$)

(236)


(237)


(238)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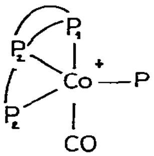
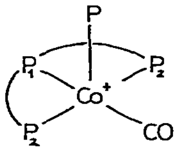

(240)

(L = $P(OMe)_3$, $PHPh_2$, PPh_3, $PMePh_2$, PEt_3)

The chemical shifts of ttp and the P—P coupling constants of [Co(ttp)-($PHPh_2$)CO]BF_4 indicate that this complex also has a square pyramidal structure with $PHPh_2$ occupying the apical position. The complexes [Co(tripod-P_3)-$(CO)_2$]X are fluxional at room temperature but the spectroscopic evidence suggests that this complex and [Co(tripod-P_3)L(CO)]X have distorted trigonal-bipyramidal structures **237** and **238**. The change from square-pyramidal geometry in **241** to trigonal-bipyramidal geometry in **239** has been rationalised in terms of a decreased "chelate bite angle" for the $PhP(CH_2CH_2PPh_2)_2$ ligand. The ^{31}P NMR studies on these complexes have provided a large number of P—P coupling constants which provide a correlation between coupling constants and structure [204,205]. Occupation of the apical site in the [Co(tpp){$P(OMe)_3$}-(CO)]$^+$ cation by the trimethyl phosphite ligand is surprising since calculations by Rossi and Hoffmann have shown that a strong π-acceptor ligand should prefer the apical site. It may be that the usually accepted π-acceptor nature of CO and $P(OMe)_3$ is reversed in this complex or that steric effects dictate that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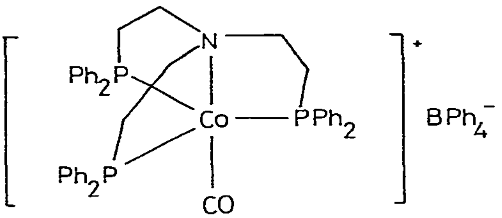
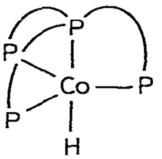
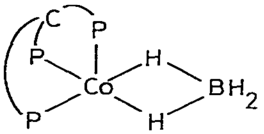
P = $P(OMe)_3$


(242)

the larger ligand occupy the apical site [205]. An X-ray study of [Co(np$_3$)(CO)]-BPh$_4$ · Me$_2$CO (**242**) reveals a trigonal bipyramidal geometry for this complex [206] and this geometry has also been found in the complex [CoH(QP)] (**243**) where QP is the tripod ligand P(o-C$_6$H$_5$PPh$_2$)$_3$ [207]. The tripod ligand **236** reacts with [Co(H$_2$O)$_6$]BF$_4$ in the presence of NO to give the pseudotetrahedral complex [Co(NO)(tripod-P$_3$)]. Addition of sodium borohydride to a solution of [Co(H$_2$O)$_6$]BF$_4$ containing **236** gives **244** which contains a very distorted square-pyramidal geometry about the cobalt [208].



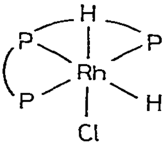
(**243**)



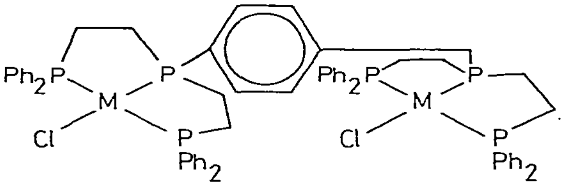
(**244**)

Treatment of [RhCl(ttp)] with [Et$_3$O][PF$_6$] gives the cationic alkyl [RhClEt-(ttp)]PF$_6$ and a similar reaction with MeOSO$_2$F gives [RhClMe(ttp)]SO$_3$F. These five-coordinate alkyl complexes show essentially no tendency to associate with solvents such as EtOH, SO$_2$ or DMSO. However, the related hydride-rhodium cation formed via protonation of [RhCl(ttp)] is stable only as six-coordinate complexes of the type [RhHCl(ttp)L]$^+$, (L = EtOH, MeCN, THF, CO). The hydride cation [RhHCl(ttp)]$^+$ also shows a much stronger tendency to add MeCN and CO than [RhClMe(ttp)]$^+$ [209]. Hydrido-cobalt and -rhodium complexes of chelating triphosphines can act as catalysts for rapid homogeneous hydrogenation of alkenes. Thus [RhH(ttp)] and [CoH$_3$(ttp)], which gives [CoH-(ttp)] in solution, act as hydrogenation catalysts. None of the coordinately-saturated complexes [CoH(triphosphine)CO] hydrogenate oct-1-ene under mild conditions and [RhCl(ttp)] adds H$_2$ irreversibly to give **245** which is also not a catalyst under mild conditions. Different chelate chain lengths affect the rates of hydrogenation, rates being faster with [CoH(etp)] than [CoH(ttp)] [210]. The structure and reactivity patterns of polyphosphine ligands and their complexes with cobalt(I) and rhodium(I) have been reviewed [211].

Reactions of the sexadentate ligand TDDX with the complexes *trans*-[MCl-(CO)(PPh$_3$)$_2$] give the dinuclear complexes **246**. A simple 1/1 mononuclear derivative of rhodium(I) or iridium(I) could not be obtained when the reaction was carried out with a 1/1 molar ratio of metal complex to TDDX indicating a preference for TDDX to form polynuclear complexes. The reaction of TDDX with



(**245**)

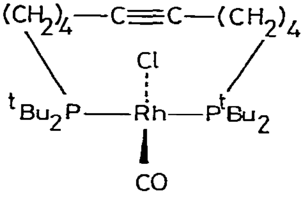


(M = Rh , Ir)

(**246**)

hydrated rhodium trichloride gives the salt $[Rh_2Cl_4(TDDX)]Cl_2$ whilst TDDX and hydrated iridium(III) chloride give $[Ir_3Cl_9(TDDX)]$. Addition of NH_4PF_6 to the iridium complex gives $[Ir_2Cl_4(TDDX)][PF_6]_2$ [212]:

Long flexible chains carrying donor atoms in α- and ω-positions prefer to bridge metal atoms in open chain structures rather than to form chelate complexes. However, long chain α,ω-diphosphines of the type t-Bu_2 $P(CH_2)_n$ P-t-Bu_2 ($n = 9$, 10 or 12) form mono-di- and tri-nuclear macrocyclic complexes with metal atoms in which the phosphorus donor atoms are *trans*-bonded. This unusual behaviour of diphosphines has been attributed to favourable internal entropy and conformational effects. Such effects also operate in the formation of macrocycles containing acetylenes and the reaction of t-$Bu_2P(CH_2)_4C{\equiv}C(CH_2)_4P$-t-$Bu_2$ with $[RhCl(CO)_2]_2$ gives **247** characterised by NMR and X-ray studies. There are no bonding interactions between the metal atom and the acetylenic function. A simple structural model shows that a shorter chain diphosphine such as t-$Bu_2P(CH_2)_6P$-t-Bu_2 cannot span *trans*-coordination positions. When this diphosphine is refluxed with a solution of rhodium trichloride in ethanol or propan-2-ol the phosphine loses dihydrogen to give **248** also characterised by an



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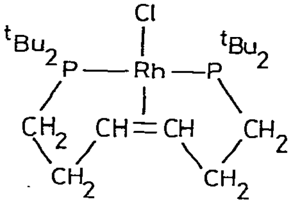
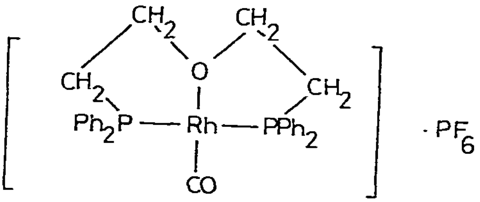


(248)

X-ray study. The structure corresponds to a *transoid* arrangement around the coordinated alkene fragment but NMR studies indicate that a minor component is present which may be the *cisoid* arrangement. The plane containing the olefin fragment is orthogonal to that containing the rhodium, phosphorus and chlorine atoms. The alkyne fragment in **247** has its C≡C vector-oriented within one degree of that of the P—P vector [213]. The crystal and molecular structures of **249** and **250**, which are formed from reactions with $Ph_2P(CH_2)_2O(CH_2)_2PPh_2$ and $Ph_2P(CH_2(OCH_2CH_2)_2PPh_2$ respectively have been reported [214].

The reaction of anhydrous rhodium trichloride with excess **251** at 200—270°C in an inert atmosphere gives **252** [215]. The crystal structure of an iridium(III) complex **253** of **251** has also been reported [216].



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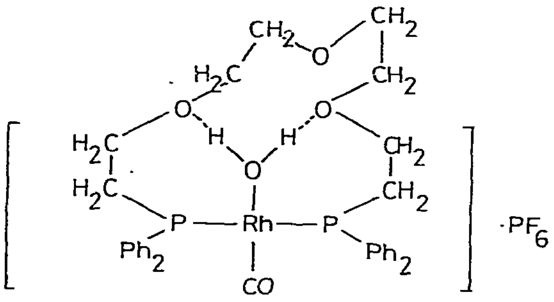

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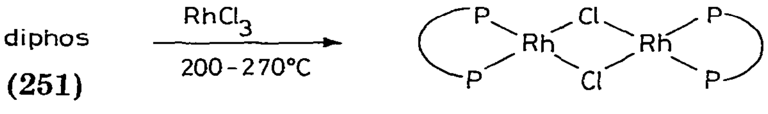
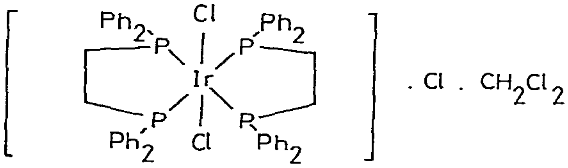
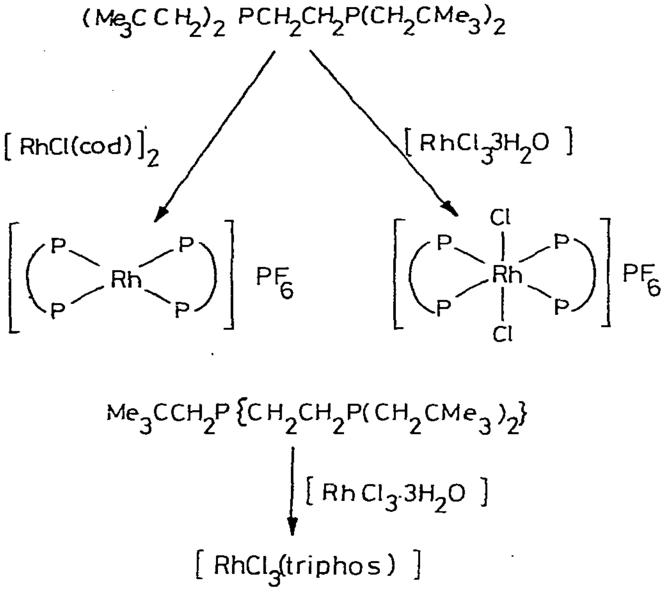


(251) **(252)**



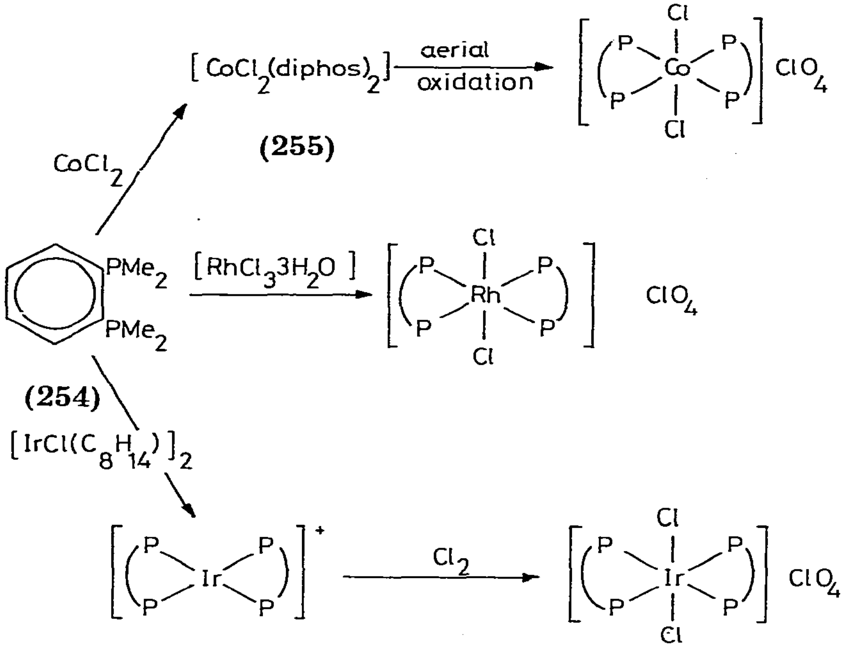
(253)

Rhodium complexes of neopentylpoly(tertiaryphosphines) have also been described (Scheme 36) [217].



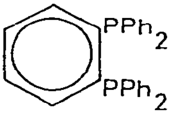
SCHEME 36

The ditertiary phosphine **254** stabilises high oxidation states of the first-row transition elements even more readily than the corresponding diarsine ligand. Reactions of this ligand are illustrated in Scheme 37. The magnetic moment of



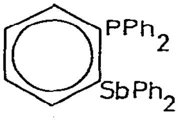
SCHEME 37

255 is in the range expected for a low-spin d^7 electron configuration and the failure to observe bands due to ν(Co—Cl) down to 200 cm^{-1} suggests that the complex may be best viewed as tetragonally distorted octahedral. The rhodium(III) and iridium(III) complexes do not undergo electrochemical oxidation but they do undergo an irreversible two-electron reduction to metal(I) species [218]. Rhodium(III) complexes of **256** and **257** [$RhX_2(pp)_2$]X (X = Cl, Br or I) and $RhX_2(sbp)_2$ (X = Cl or Br) have also been reported and some [$RhX_2(sbp)$]$_2$ and [$RhX_3(sba)$]$_2$ (sba = **258**) complexes are also formed [219]. Cobalt hydrido



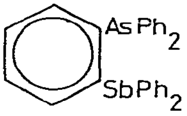
(pp)

(256)



(sbp)

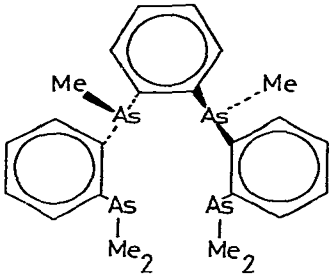
(257)



(sba)

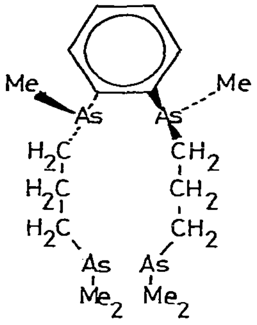
(258)

and "sideways" bonded dioxygen cobalt complexes containing quadridentate arsine ligands **259** and **260** have been prepared. The racemic fars ligand can adopt any of the *cis-α*, *cis-β*, and *trans* topologies about an octahedral metal centre as indicated for the dioxygen complexes in **261** and **262**. By contrast, the racemic quars ligand is inflexible and only adopts the symmetrical *cis-α*



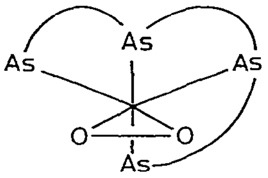
racemic Quars

(259)



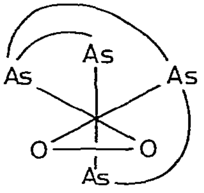
racemic Fars

(260)



cis-β

(261)



cis-α

(262)

geometry. The "sideways" bonded dioxygen complexes, *cis*-β-[Co(R,R:S,S-fars)O_2]ClO_4 and *cis*-α-[Co(R,R:S,S-quars)O_2]ClO_4 are best described as cobalt(III) peroxide species. The *cis*-[Co(R,R:S,S;quars)H_2]$^+$ ion reacts differently from the *cis*-[Co(diars)$_2H_2$]$^+$ analogue with O_2. In neutral protic or aprotic solvents, the latter spontaneously releases one equivalent of H_2 and absorbs one equivalent of O_2 to form [Co(diars)$_2O_2$]$^+$. The quars analogue does not spontaneously absorb O_2 to any extent presumably because the hydrido ligands are not as acidic. Thus the reaction requires base to initiate the removal of a single proton before rapid O_2 uptake occurs. Protic and hydridic character of the hydrido ligands is modified by the imposition of a *cis*-α topology [220].

Metal—nitrosyl and aryldiazo complexes

Treatment of [$Co_2(CO)_8$] with NO_2^- in acid solution is reported to produce [$Co(CO)_3(NO)$] in 63% yield [221]. The stoichiometry of the reaction is given in Scheme 38.

$$Co_2(CO)_8 + 3\ NO_2^- + 2\ H^+ \rightarrow 2\ Co(CO)_3NO + H_2O + NO_3^- + 2\ CO$$

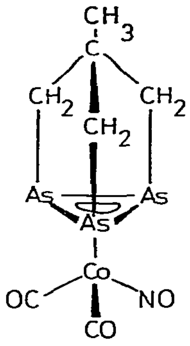
SCHEME 38

The acid used was ethanoic acid at a concentration of 1.7 *M*. Attempts to repeat the synthesis at higher acid concentrations (6—8 *M*) produced reaction between the starting material and the ethanoic acid. Although the reaction may be described in terms of the equation in Scheme 38, it is likely that the [$Co_2(CO)_8$] may first undergo a water-assisted disproportionation (Scheme 39).

$3\ Co_2(CO)_8 + 12\ H_2O \rightarrow 2[Co(H_2O)_6][Co(CO)_4]_2 + 8\ CO$

SCHEME 39

The $[Co(CO)_4]^-$ thus formed might be susceptible to attack by NO_2^- giving the product. Treatment of the complex $[Co(CO)_3(NO)]$ with 4-methyl-1,1,2,6-triarsinetricyclo[2.2.1.0]heptane, $CH_3C(CH_2As)_3$ in THF results in the evolution of carbon monoxide and formation of the complex $[Co(CO)_2(NO)(CH_3C(CH_2As)_3)]$ (263) [222].



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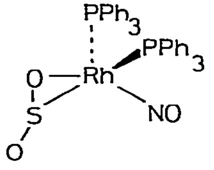


(264)

Reaction of $[Co(CO)_3NO]$ with trifluoromethylphosphines (L) leads to the production of $[Co(CO)_2(NO)L]$ in all cases except $L = P(CF_3)I_2$ [223]. Prolonged contact between reactants does eventually lead to more highly-substituted products and under forcing conditions the phosphine may substitute all carbonyl ligands. If the monosubstituted complex is treated with another related ligand (L′) no mixed complex is reported, but ligand exchange occurs according to Scheme 40, indicating that the incoming phosphine expels a coordinated phosphine in preference to CO and it is found that the displacement abilities of ligands adopt the order $P(CF_3)F_2 \simeq P(CF_3)_2F > P(CF_3)Cl_2 \simeq P(CF_3)_2Cl > PBr(CF_3)_2 > P(CF_3)H_2 > P(CF_3)_2I > PBr(CF_3)$. A reported complication to Scheme 40 is the redistribution reactions of the displaced ligand (L) with excess of ligand (L′) as in Scheme 41. In the initial displacement a trigonal bipyramidal intermediate is suggested to explain the observation that the rate of exchange depends on the bulk of the attacking species. By using the rigid-rotor harmonic oscillator approximation and by assuming the ideal gas behaviour some thermodynamic functions have been calculated for the complex $[Co(CO)_3NO]$ between 298 and 1000 K [224]. The dissociation of $[Rh(NO)(PPh_3)_3]$ according to the

$[Co(CO)_2(NO)L] + L' \rightleftharpoons [Co(CO)_2(NO)L'] + L$

SCHEME 40

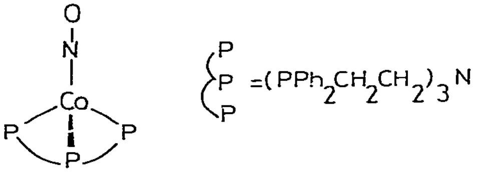
$[Co(CO)_2(NO)\{P(CF_3)Cl_2\}] + PBr_2(CF_3) \rightleftharpoons$

$[Co(CO)_2(NO)\{PBr_2(CF_3)\}] + P(CF_3)Cl_2$

$PBr_2(CF_3) + P(CF_3)Cl_2 \rightleftharpoons 2\ PBr(CF_3)Cl$

SCHEME 41

equation $Rh(NO)(PPh_3)_3 \rightleftharpoons Rh(NO)(PPh_3)_2 + PPh_3$ has been the subject of a spectrophotometric study in order to clarify the mechanism by which the complex $[Rh(NO)(PPh_3)_3]$ catalyses the hydrogenation of unsaturated organic compounds at 298 K [225]. The data presented are consistent with the postulate that phosphine dissociation is a prior step in the catalytic activity of the triphenylphosphine complex. A crystal structure determination on the novel sulphur dioxide complex $[Rh(NO((SO_2)(PPh_3)_2]$ has revealed that the SO_2 unit bonds to the rhodium through both the sulphur atom and one oxygen atom 264 [226] and that the rhodium atom exists in a tetrahedral environment, with no marked distortion towards a square planar structure. Equimolar quantities of NO and $[Co(NO)(PPh_3)_3]$ on reaction in benzene or methylbenzene solution are reported to produce $[Co(NO)_2(ONO)(PPh_3)]$, Ph_3PO, N_2 and N_2O [227]. The same reaction carried out in the proportions of cobalt complex to NO of 1/2 yields a trimeric complex $[Co_3(NO)_7(PPh_3)_3]$ which is capable of catalysing the disproportionation of nitric oxide. The trimer is reported to have both terminal and bridging NO ligands. Treatment of $[Rh(NO)(PPh_3)_3]$ and $[Ir(NO)(CO)(PPh_3)_2]$ with dilute aqueous nitric acid in methanol under reflux gives the complexes $[Rh(NO_3)_2(NO)(PPh_3)_2]$ and $[Ir(NO_3)_2(NO)(PPh_3)_2]$ respectively [228]. A spectroscopic study of the complex $[Rh(NO_3)(NO)_2(OPPh_3)_2]$ has led to the reformulation of the complex as $[Rh(NO_3)_2(NO)(PPh_3)_2]$ and it is suggested that the presence of triphenylphosphine oxide fragmentation in the mass spectrum of the complex is due to this species being present as a volatile trace impurity and not as a ligand. Reaction of $[Rh(NO)(NO_2)(PPh_3)_2]_2$, $[Rh(NO)_2(NO_2)(PPh_3)_2]$ or $[Rh(CO)(NO_2)(PPh_3)_2]$ in trichloromethane with an alcoholic solution of $HClO_4$ leads to the production of the single complex $[Rh(NO)_2(PPh_3)_2]ClO_4$. Treatment of this compound with SCN^- or PPh_3 gives $[Rh(NO)(NCS)_2(PPh_3)_2]$ and $[Rh(NO)(PPh_3)_3]$ respectively. If the latter complex or $[Rh(NO)_2(PPh_3)_2]^+$ is treated with a solution of concentrated HCl in ethanol the complex $[Rh(NO)Cl_2(PPh_3)_2]$ is produced [229]. Crystal structure data have appeared on the complex $[Co(NO)(np_3)]BPh_4$ (np_3 = tris(2-diphenylphosphinoethyl)amine) indicating that the cobalt atom is in a tetrahedral environment and that the central nitrogen atom of the ligand is not coordinated 265 [230].



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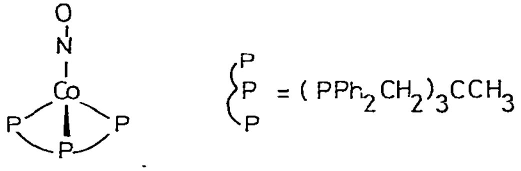
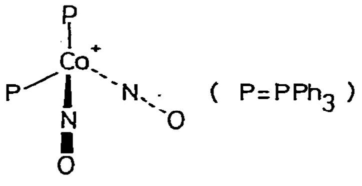


(266)

A pseudotetrahedral structure is also indicated by crystal structure data for the complex $[Co(p_3)(NO)]$ formed by the action of 1,1,1-tris(diphenylphosphinomethyl)ethane, p_3, on a solution of $[Co(H_2O)_6](BF_4)_2$ in ethanol through which nitric oxide gas is bubbled 266 [231].

Crystal structure data have also been reported for the dinitrosylbis(triphenylphosphine) cobalt cation $[Co(NO)_2(PPh_3)_2]^+$. The cobalt is shown to be in a tetrahedral environment (267) [232]. Interest in this complex was generated when it was found that both the rhodium and iridium analogues undergo a nitrogen coupling reaction on treatment with carbon monoxide (Scheme 42), whereas



(267)

$$[M(NO)_2P_2]^+ + 4CO \rightarrow [M(CO)_3P_2]^+ + N_2O + CO_2$$
$$(M = Rh,\ Ir;\ P = PPh_3)$$

SCHEME 42

the cobalt complex does not. The distortion of the tetrahedral structure towards that of a square plane in the case of the rhodium and iridium complexes contrasts with the closely tetrahedral cobalt complex reflecting the different electronic structure which is postulated as the reason for the lack of reactivity of the cobalt complex towards carbon monoxide. A study of the role of rhodium(I) complexes such as $[RhCl_2(CO)_2]^-$ in the catalysis of the reduction of nitric acid by carbon monoxide (Scheme 43) has shown that the oxygen in the CO_2 pro-

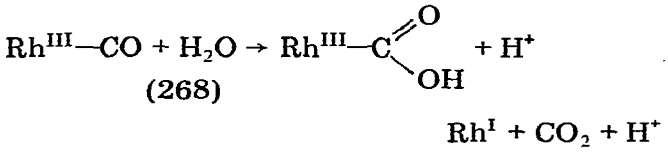
$$2\ NO + CO \rightarrow N_2O + CO_2$$

SCHEME 43

duct comes from water in the reaction mixture and not from the nitric oxide reactant directly [233]. The reaction mechanism is very complex, and the active catalyst has not yet been fully characterised. It appears that reaction proceeds as in Scheme 44, the incorporation of water oxygen following steps as indicated in Scheme 45. The complex in Scheme 45 is unstable and decarboxylation proceeds very quickly to CO_2. The role of water in the reaction is proved by ^{18}O

$$[RhCl_2(CO)_2]^- + 6\ NO \rightarrow [RhCl_2(NO)_2]^- + 2\ CO_2 + 2\ N_2O$$

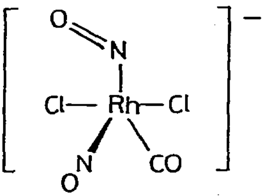
SCHEME 44



$$\underset{(268)}{Rh^{III}{-}CO} + H_2O \rightarrow Rh^{III}{-}C(=O)OH + H^+$$
$$Rh^{I} + CO_2 + H^+$$

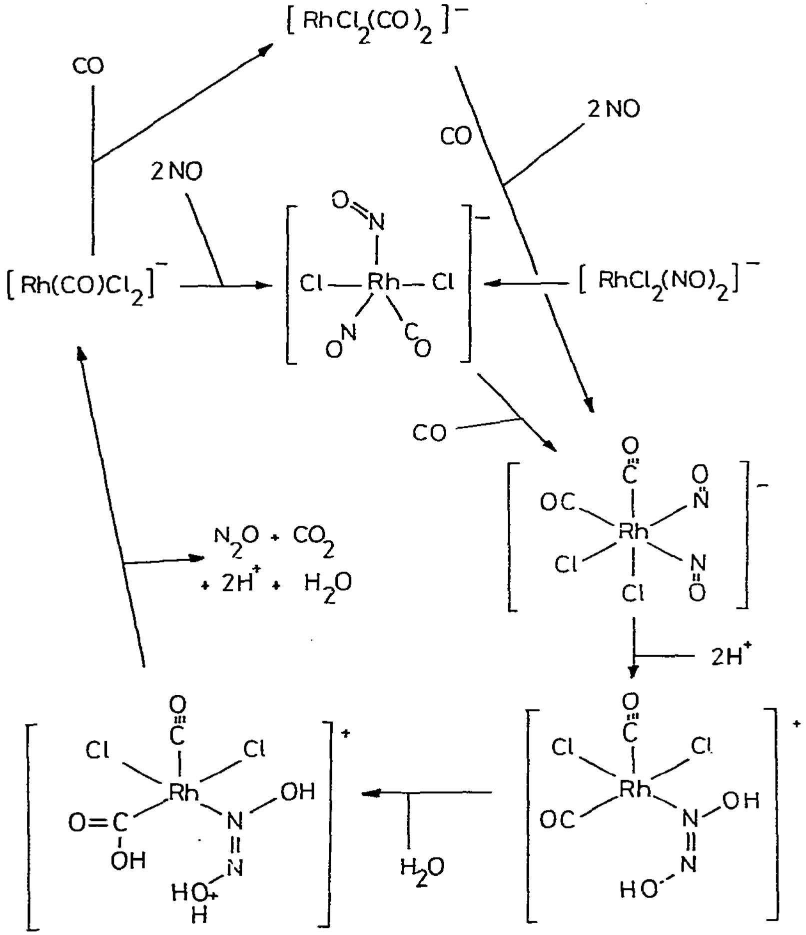
SCHEME 45

tracer experiments. A fuller study of this catalytic action has now appeared [234] which indicates that reduction of rhodium(III) to $[RhCl_2(CO)_2]^-$ is a prerequisite to the onset of catalytic activity, but the green catalytic intermediates has so far eluded characterisation. The green catalyst appears to develop under atmospheres of NO/CO mixtures (ideally in the ratio 4/3) and it is suggested that one possibility for its structure is as shown in **269** having at least one bent nitrosyl group. Two possible catalytic schemes are suggested and these are given in Schemes 46 and 47.

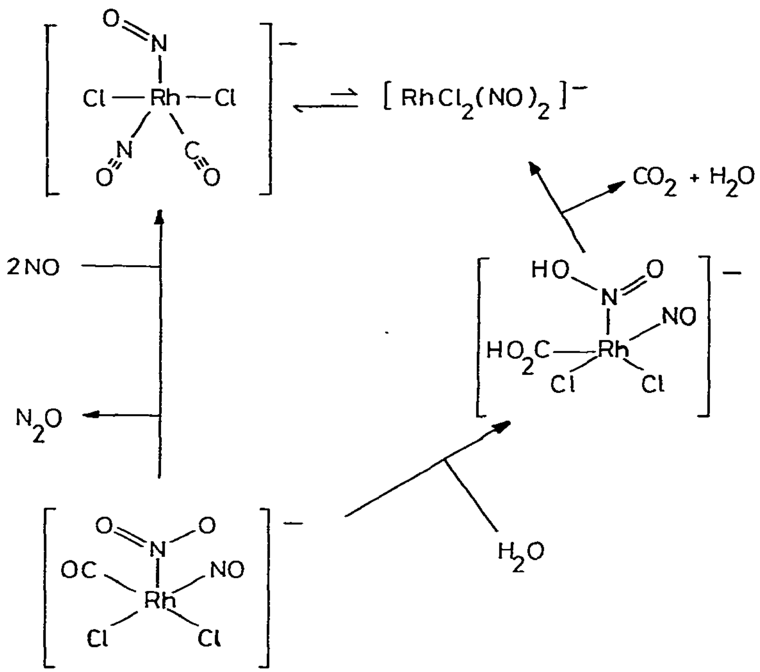


(269)

Scheme 47 also accounts for the observation that under higher NO/CO ratios a different and more reactive catalytic species appears, which is orange and is accompanied by accelerated product formation. Photo-induced ligand exchange occurs between $[Co(NO)_2X]_2$ (X = Cl, Br, I) and $[Cr(CO)_6]$ dissolved in THF forming a complex which is indicated as being $Cr(NO)X_2(THF)_n$ from a study of ESR parameters [235]. A crystal structure determination of the complex dinitrosyldithioacetylacetonatocobalt(—I) $[Co(NO)_2(SacSac)]$ reveals that the



SCHEME 46



SCHEME 47

cobalt atom is basically tetrahedral although slightly distorted and the nitrosyl group is bent with a Co—N—O angle of 168.9°(270) [236].

(270)

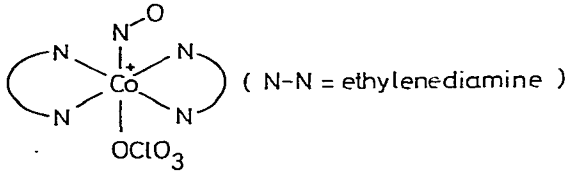
The bending of so called "linear" nitrosyls is discussed in terms of the two possibilities *attracto* and *repulso* shown in 271.

attracto-

repulso

(271)

The *attracto* conformer is characteristic of first-row transition metal complexes whereas *repulso* conformers are found in second and third row transition metal dinitrosyls. Geniculation (bending) of the coordinated nitrosyl appears to be determined primarily by the nature of the metal centre and the charge on the complex rather than σ- or π-donating capabilities of supporting ligands. When the diamagnetic mononitric oxide complex [Co(TPP)NO] (TPP = tetraphenylporphyrin) is exposed to nitric oxide in toluene solution a paramagnetic complex results. The ESR spectrum is consistent with the formulation [Co(TPP)-$(NO)_2$] [237]. The complex may be isolated but only as a metastable solid which quickly loses NO to reform the mononitrosyl complex. The odd electron is in an MO consisting of equal contributions from the two nitric oxide π^* orbitals. As the NO equilibrium pressure above the toluene solution of both complexes is increased a third (dimagnetic) complex is formed tentatively suggested to result from addition of a third NO molecule with spin-pairing involved. The dinitrosyl complex may react as if it contained coordinated NO^{2-}, i.e. [Co(TPP)-$(NO^+)(NO^{2-})$] and thus the third molecule could bind at the coordinated NO centre resulting in formation of coordinated $N_2O_2^{2-}$. The crystal structure of the complex $[Co(NO)(en)_2(ClO_4)]ClO_4$ has been reported [238]. The nitric oxide molecule is strongly bent with the oxygen atom disordered between two positions above the ethylenediamine rings. The perchlorate ligand is weakly bound into the sixth position in what is essentially an octahedral complex (272).



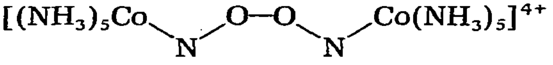
(272)

The weakly bound ClO_4^- ligand is stabilized in the solid state by hydrogen bonding with the (en) ligands coordinated to cobalt. Nitrosyl transfer implying the migration of coordinated NO from one metal to another may be categorised according to one of two mechanisms:

$$MNO + M' \rightarrow M'NO + M \qquad (A)$$

$$MNO + M'X \rightarrow MX + M'NO \text{ (X is a one-electron ligand)} \qquad (B)$$

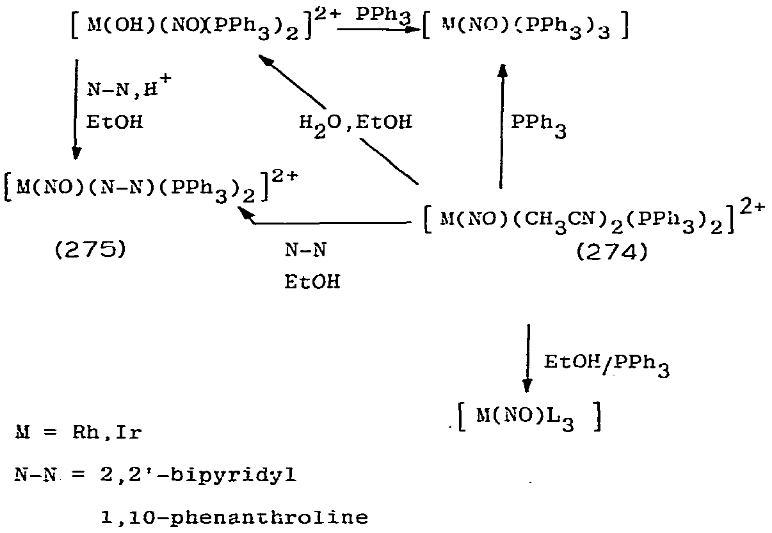
Intermolecular transfer of the nitrosyl ligand in the complex $[Co(NO)D_2]$ (D = monoanion of dimethylglyoxime) is reported to occur when this complex is treated with $[CoCl_2(PPh_3)_2]$; $[Co(NO)Cl_2(PPh_3)_2]$, $[RhH(CO)(PPh_3)_3]$ or [RhCl-$(PPh_3)_3$] in ethanol or benzene [239]. These transfer reactions are considered in terms of mechanisms A and B. Redox reactions are characterised as complementary or noncomplementary according to whether the oxidant and reductant do or do not transfer the same number of electrons. If $[Co(NO)D_2]$ formally transfers neutral NO, it can provide a ligand which donates one or three electrons. Thus $[Co(NO)D_2]$ can be said to undergo complementary simple NO transfer to 15- or 17-electron complexes such as $[CoCl_2(PPh_3)_2]$ and $[NiCl(PPh_3)_3$, Mechanism A. The more complex mechanism B is suggested for the reaction between $[Co(NO)D_2]$ and the other complex, unless the complex is coordinately unsaturated as in $[RhCl(PPh_3)_3]$. Nitric oxide as a ligand may be considered in three ways, i.e. acting as NO^+, NO or NO^- and this has led to a study of the relative electrophilicities of the atoms in the coordinated NO group [240]. The complex $[Co(en)_2(NO)(ClO_4)_2]$ on treatment with "super acid", $SbF_5 \cdot HSO_3F$, gives ^1H NMR data consistent with protonation on the oxygen atom. A study of nucleophilic attack is also reported using as the nucleophile the reduced form of bis(dimethylglyoximato) cobaltate(I). On reaction with *N*-nitrosodiethylamine nucleophilic attack proceeds at the NO nitrogen atom. Thus in this complex the most probable site for electrophilic attack is the nitric oxide oxygen atom. New red pentaamminenitrosylcobalt(III) complexes formulated as $[Co_2(N_2O_2)(NH_3)_{10}]Cl_4 \cdot 4\ H_2O$ or $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4 \cdot 2\ H_2O$ depending on the counterion is reported to result from the reaction between NO gas and an ammoniacal cobalt(II) solution. Molar conductivity measurements, UV spectra and ^{15}N-isotopic effects on IR spectra on ^{15}NO substitution and ^{15}N NMR are detailed [241]. The new salt is considered to be a new type of compound containing a dimer of nitrosyl, $N{-}O{-}O{-}N^{2-}$ ion (**273**) which bridges the two $Co(NH_3)_5$ groups.



$[(NH_3)_5Co{-}N{-}O{-}O{-}N{-}Co(NH_3)_5]^{4+}$

(273)

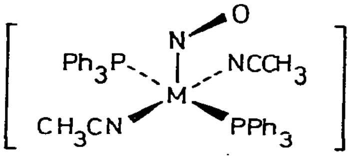
A new series of cationic penta-coordinate nitrosyl complexes of iridium and rhodium has been prepared and their physical and spectroscopic data are reported [242]. Cyanomethane suspensions of $[MI_2(NO)(PPh_3)_2]$ (M = Rh, Ir) react almost instantaneously with AgX (X = PF_6^-, ClO_4^-) to give green cationic crystalline compounds $[M(NO(CH_3CN)_2(PPh_3)_2]X_2$ in high yield. A series of reactions for these complexes is given in Scheme 48.

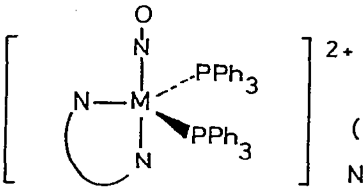


SCHEME 48

The spectroscopic data has led to the postulation that complex **274** in Scheme 48 is as shown having square pyramidal geometry and a strongly bent axial nitrosyl with basal *trans*-phosphines and nitrile ligands. Complexes **275** in Scheme 48 are thought to be trigonal bipyramidal with a linear nitrosyl group.

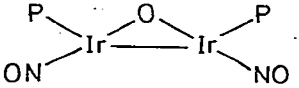
Treatment of **276** with aryldiazonium ions results in a complex **277** in which


(274)

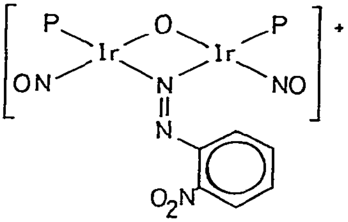

(275)

(M = Rh, Ir
N-N = 2,2'-bipyridyl,
1,10-phenanthroline)

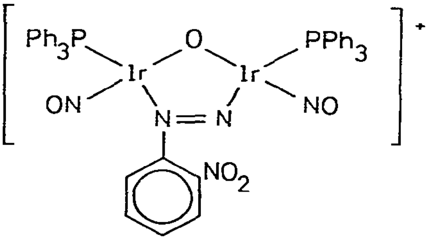
insertion into the metal—metal bond occurs. The crystal structure data of **277** are reported [243].


(276)

(P=PPh$_3$)


(277)

The other structural possibility **278** is not observed.


(278)

The five-coordinate aryldiazenatoiridium(III) complex [IrCl(CO)(PPh$_3$)$_2$-(N$_2$C$_6$H$_4$R)]BF$_4$ reacts readily with phenylacetylene according to Scheme 49 [244].

$$[\mathrm{Cl(PPh_3)_2(CO)Ir(N_2C_6H_4R}\text{-}p)]\mathrm{BF_4} + \mathrm{HC{\equiv}CPh} \xrightarrow[\mathrm{C_6H_6/acetone}]{\mathrm{EtOH\ or}}$$

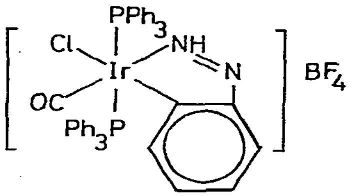
$$[\mathrm{(PPh_3)_2(CO)Ir(Cl)(HN{=}NC_6H_4R}\text{-}p)(\mathrm{C{\equiv}CPh})]\mathrm{BF_4} \underset{\mathrm{HBF_4}}{\overset{\mathrm{NEt_3}}{\rightleftharpoons}}$$

$$[\mathrm{(PPh_3)_2(CO)IrCl(N_2C_6H_4R}\text{-}p)(\mathrm{C{\equiv}CPh})]$$

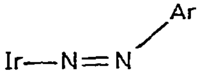
(R = NO$_2$, CN, COCH$_3$)

SCHEME 49

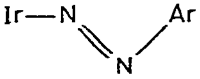
The ^{1}H NMR of **279** suggests a nitrogen-bonded proton and that this nitrogen atom is that coordinated to the metal. The crystal structure data on the complex [IrCl(N$_2$C$_6$H$_5$)(PMePh$_2$)$_3$]PF$_6$ reveals that this molecule contains a half-doubly-bent aryldiazo ligand and an intermediate geometry [245]. The possibilities for the bent nature of the ligand are as in **280**. The complex has a largely distorted square pyramidal structure **281**.



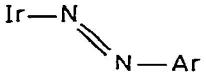
(279)



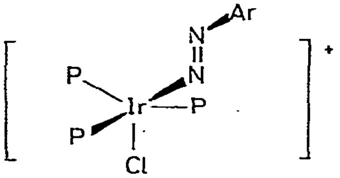
(280a)



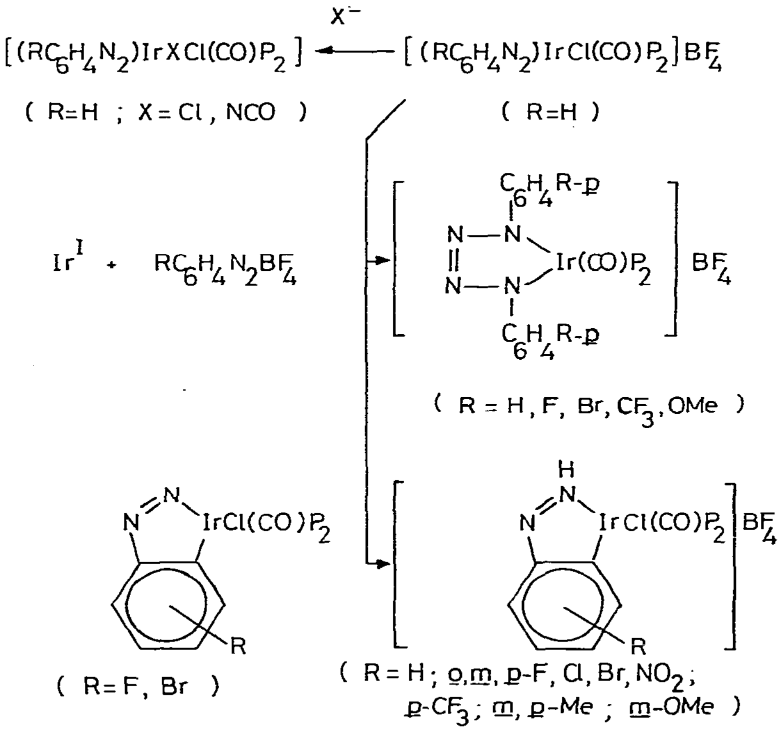
(280b)



(280c)



(281)

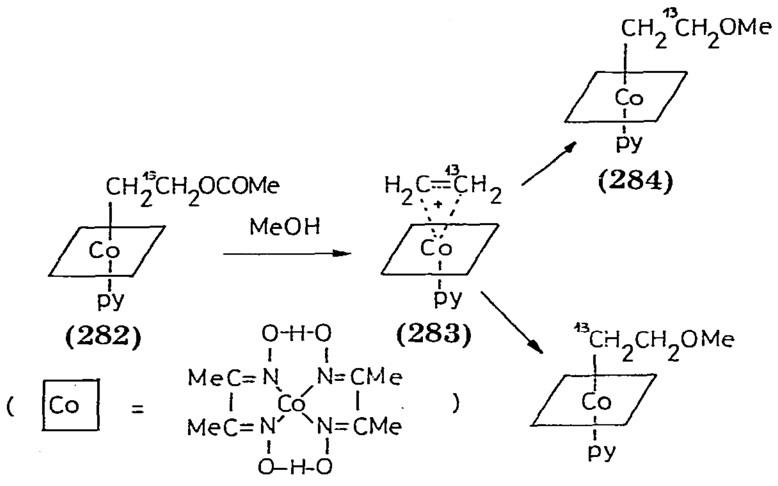


SCHEME 50

A photoelectron study on bent aryldiazonium complexes $[Ir(N_2\text{-}p\text{-}C_6H_4F)Cl_2(CO)(PPh_3)_2]$ and $[Rh(NHN\text{-}p\text{-}C_6H_4CH_3)Cl_3(PPh_3)_2]$ reveals that a marked increase of electron density occurs on coordination and that the bulk of this excess electron density resides on the nitrogen atom not directly attached to the metal when the complex is singly bent [246]. The reactions of *trans*-$[IrCl(CO)(PPh_3)_2]$ with aryldiazonium cations are given in Scheme 50 [247]. These complexes are useful as models in nitrogen fixation reactions producing ammonia and aniline simultaneously.

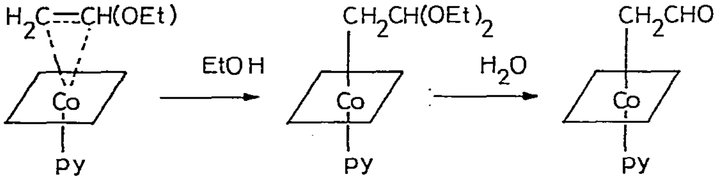
Metal—alkene and —alkyne complexes

Although the isolation and characterisation of a π-olefin-cobalt(III) complex has never been reported, it has been suggested as an intermediate in a number of reactions involving cobalt—carbon bonds. Evidence for the intermediacy of cobalt(III)-π-complexes has now been obtained in the chemistry of both cobalamins and cobaloximes. Thus methanolysis of 282, labelled with ^{13}C, gives equal



(282) (283) (284) (285)

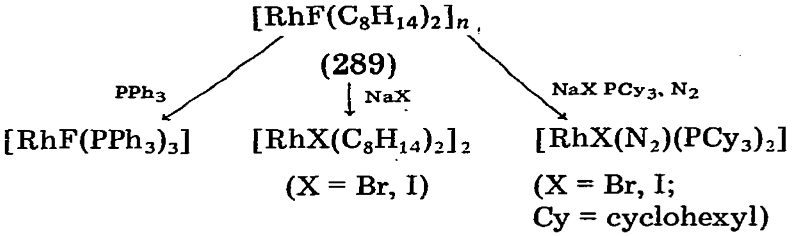
amounts of 284 and 285 and during solvolysis both carbon atoms of the ligand bonded to cobalt, become equivalent, via an olefin π-complex of cobalt(III) (283). Treatment of bromo(pyridine)cobaloxime and the electron rich olefin, ethyl vinyl ether, in the presence of silver trifluoromethanesulphonate and ethanol gives a mixture of 287 and 288, a reaction which can also be rationalised in



(286) (287) (288)

terms of an intermediate π-complex. However, no evidence for alkylated cobaloximes was found using ethylene, 2-methylbut-1-ene, 3,3-dimethylbut-1-ene or 2-ethylbut-1-ene [248].

An olefin-metal fluoride complex, $[RhF(cyclooctene)_2]_n$, (289) has been obtained from the reaction of silver(I) fluoride with $[RhCl(cyclooctene_2)]_2$.

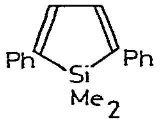


SCHEME 51

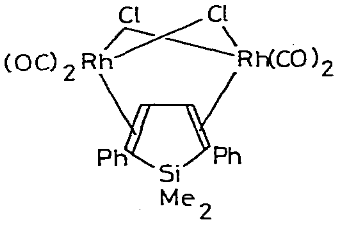
The fluoride and olefin ligands in **289** can be readily replaced and some reactions of the complex are illustrated in Scheme 51.

The chlorine metathesis of $[RhCl(cyclooctene)_2]_2$ with $AgNO_3$ and $AgOCOCH_3$ leads to complete displacement of chlorine but the cyclooctene complexes obtained are less stable than **290** [249].

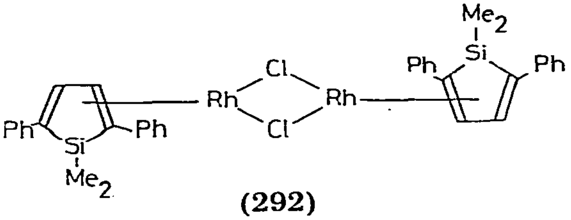
The silacyclopentadiene **290** reacts with $[RhCl(CO)_2]_2$ to give **291** and a small amount of **292**.



(290)



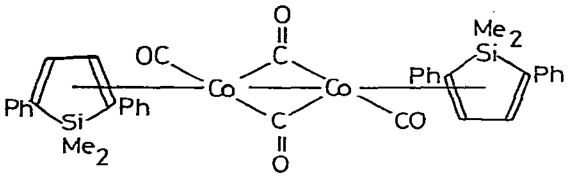
(291)



(292)

Dicobalt octacarbonyl reacts with **290** to give a mixture of $[Co_2(C_4Ph_2H_2SiMe_2)(CO)_6]$ and $[Co_2(C_4Ph_2H_2SiMe_2)_2(CO)_4]$ (**293**) but only the latter complex could be isolated [250].

Reaction of metallocene complexes, $[M(C_5H_5)_2]$ with an alkali metal results in the formation of alkalimetal C_5H_5 and elemental transition metal. However, deposition of the transition metal is suppressed on addition of cycloocta-1,5



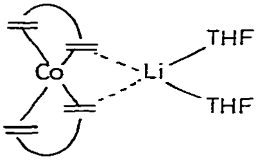
(293)

diene and using cobaltocene the new cycloocta-1,5-diene cobalt complex (294) can be isolated (Scheme 52).

$$\begin{tikzcd}[Co(\eta^5\text{-}C_5H_5)_2] \arrow[r, "\text{Li, cod}", "\text{THF, }0^\circ\text{C}"'] & CoCp(cod) + LiCp \arrow[d, "\text{THF, }0^\circ\text{C}"', "\text{2 Li, cod}"] \\ & [Co(cod)_2Li(THF)_2] \\ & (294)\end{tikzcd}$$

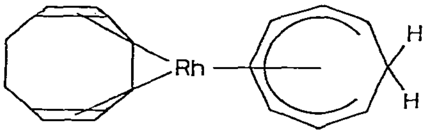
SCHEME 52

The crystal structure of 294 has been reported [251]. The reaction of [RhCl(diene)]$_2$ (diene = 1,5-cod, norbornadiene) with $Na_2C_8H_8$ in THF and successive



(294)

hydrolysis leads to the formation of the fluxional complexes 295 and 296. Protonation of 295 with HPF_6 in diethyl ether gives the dinuclear complex 296



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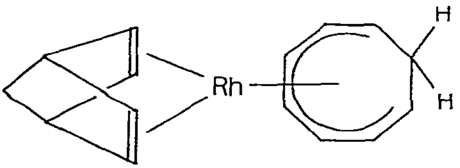
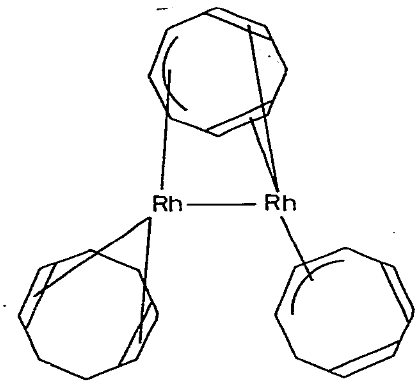


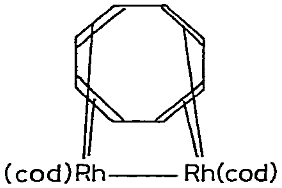
(296)

which has been the subject of an X-ray study or 298, depending on the reaction conditions. The complex 296 yields 299 as well as a complex $Rh_2C_{23}H_{26}$ which apparently has a structure analogous to 297 [252].

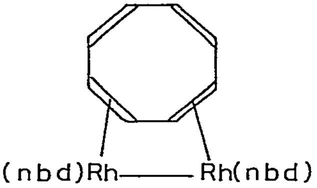
Olefin exchange reactions on [Rh(acac)(C_2H_4)$_2$] have been used to prepare complexes containing methoxy-substituted ethylenes. The complexes isolated are of the type [Rh(acac)L(C_2H_4)] (L = MeOCH=CH$_2$ *cis* and *trans*-MeOCH=CHOMe, (MeO)$_2$C=C(OMe)$_2$) and [Rh(acac)L$_2$] (L = MeOCH=CH$_2$ or *cis*- and *trans*-



(297)

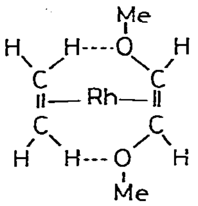


(298)



(299)

MeOCH=CHOMe). The barriers of olefin rotation in these complexes increase with an increasing number of methoxy substituents and when the olefin rotation is frozen out, the methoxy substituents of the olefins tend to be turned away from the acetylacetonate ligand if steric interactions between the two coordinated olefins are not too great. The low temperature arrangement of the *cis*-dimethoxyethylene compounds (**300** and **301**) has been deduced from low temperature NMR studies. A hindered movement of the acetylacetonate ligand has been observed in [Rh(acac)(C_2H_4){(MeO)C=C(OMe)$_2$}] and [Rh(acac)(*cis*-MeOCH=CHOMe)$_2$]. This movement, which is independent of olefin rotation, is considered to be a degenerate rearrangement of the tetragonal planar complexes via a tetrahedral transition state [253,254]. Treatment of [Rh(acac)-(C_2H_4)$_2$] with CH_2=CHOSiMe$_3$ at −80°C gives **302** but attempts to hydrolyse this complex to a hydroxy-ethylene complex were unsuccessful [255]. The crystal structures of the cycloocta-1,5-diene complexes **303** have been reported [256] and ^{13}C NMR studies of iridium(I)-cycloocta-1,5-diene complexes have been reported [257].



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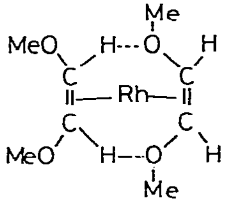
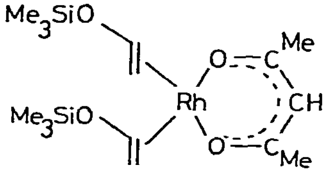


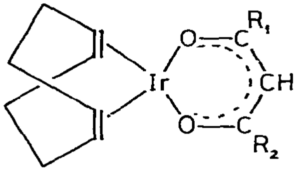
(301)

The reaction of allene with [Ir(acac)(cyclooctene)$_2$] at −78°C gives a pale-



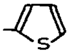
(302)

yellow crystalline precipitate which is considered to have the structure **304**. This complex decomposes at temperatures above —20°C and reacts with pyridine to give **305** [258].

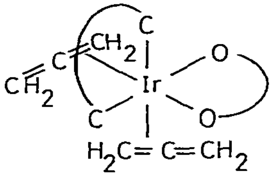


$R_1 = R_2 = CMe_3$

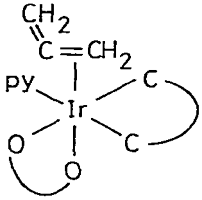
$R_1 = R_2 = Ph$

$R_1 = CF_3$ $R_2 =$ 

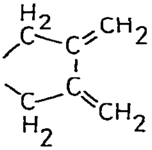
(303)

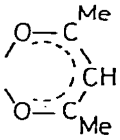


(304)

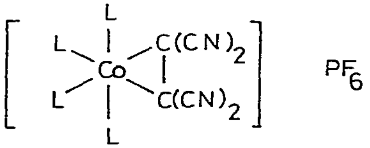


(305)

C - C = 

O-O = 

Protonation of $[CoMe\{P(OMe)_3\}_4]$ with a non-mineral acid in the presences of olefins and acetylenes gives high yields of the complexes $[CoL\{P(OMe)_3\}_4]^+$ (L = ethylene, propylene, hex-1-ene, diphenylacetylene) [259]. The reaction of tetracyanoethylene with $[Co(CNMe)_5]PF_6$ also gives a cationic olefin complex



(306)

(L = MeNC)

306. Radical intermediates are invovled in this reaction, the process occurring via an outer sphere electron-transfer step, Scheme 53 [260].

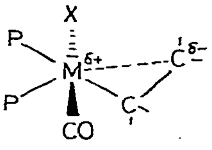
$CoL_5^+ + TCNE \rightarrow CoL_5^{2+} + TCNE^-$

$CoL_5^{2+} + TCNE^- \rightarrow$ **306** + L

(L = MeNC)

SCHEME 53

The kinetics of the addition reactions of tetracyanoethylene to the complexes *trans*-[RhX(CO)L$_2$] (X = Cl, L = P(*p*-MeOC$_6$H$_4$)$_3$, P(*p*-MeC$_6$H$_4$)$_3$, PPh$_3$, P(*p*-ClC$_6$H$_4$)$_3$, PMePh$_2$, AsPh$_3$, P(O-*o*-MeC$_6$H$_4$)$_3$, P(OPh)$_3$; X = Br, I, NCO, NCS, L = PPh$_3$), [RhCl(CS)(PPh$_3$)$_2$] and *trans*-[IrCl(CO)(PPh$_3$)$_2$] in acetone, tetrahydrofuran or benzonitrile have been investigated using stopped-flow techniques. The forward second-order rate constant k_2 increases in the following order of the anionic ligands X for *trans*-[RhX(CO)(PPh$_3$)$_2$] and of the neutral ligand L for *trans*-[RhCl(CO)L$_2$] respectively: X = NCS $\simeq$ Br < Cl $\simeq$ NCO and L = P(O-*o*-MeC$_6$H$_4$)$_3$ < P(*p*-ClC$_6$H$_4$)$_3$ < PPh$_3$ < P(OPh)$_3$ < P(*p*-MeC$_6$H$_4$)$_3$ < P(*p*-MeOC$_6$H$_4$)$_3$ < AsPh$_3$ << PMePh$_2$. *trans*-[IrCl(CO)(PPh$_3$)$_2$] reacts with TCNE about nine times faster than *trans*-[RhCl(CO)(PPh$_3$)$_2$] in acetone at 25°C. The k_2 value also increases with increasing solvent polarity. The nucleophilic attack of the metal complexes at the TCNE is considered to involve either an asymmetric interaction in a non-concerted fashion **307** or a symmetric coordination in a concerted manner **308**. Both of these transition states are considered to be dipolar, consistent with the observed large solvent effect on the reaction rate or activation parameters. In some of the reactions the formation of the TCNE anion radical is observed. The appearance of the TCNE anion radical (which might be the result of a side reaction) is dependent on the nature of the halide ligand. Thus with *trans*-[RhCl(CO)(PPh$_3$)$_2$] the radical is only formed in benzonitrile, while the bromo and iodo analogues produce the radical even in acetone. The nucleophilicity of the metal substrate increases in the order [RhCl(CO)(PPh$_3$)$_2$] < [Rh(*p*-MeOC$_6$H$_4$NC)$_2$(PPh$_3$)$_2$]$^+$ < [IrCl(CO)(PPh$_3$)$_2$] [261]. The dithiocarbamate complexes **309** also react smoothly with tetracyanoethylene, fumaroni-



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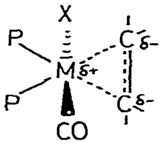

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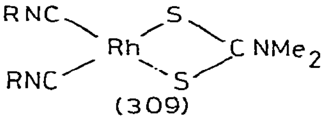
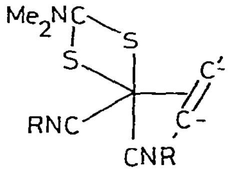


(309)

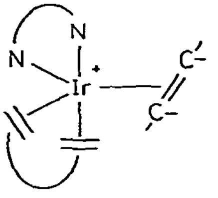
(R = p-MeC$_6$H$_4$, 2,4,6-Me$_3$C$_6$H$_2$)

(309)



(310)

trile, maleonitrile and maleic anhydride to give 1/1 adducts of the type **310**. Variable temperature ^{1}H NMR studies suggest that the olefin rotates around the metal—olefin bond accompanying Berry pseudorotation in a trigonal bipyramid, the barrier to rotation increasing in the order of π-acceptor capacity of the olefin, MA < MN ≃ FN < TCNE. It is also apparent from these studies that the metal basicity of [Rh(dtc)(CNR)$_2$] is greater than that of [Rh(acac)(CNR)$_2$] [262]. Tetracyanoethylene, acetylene, fumaronitrile, acrylonitrile, ethylene and dioxygen give stable pentacoordinate adducts **311** with the cationic complexes, [Ir(diene)(chel)]$^+$, (diene = cycloocta-1,5-diene, norbornadiene; chel = bipyridyl, *ortho*-phenanthroline, substituted *ortho*-phenanthroline). With acetylenes, hydrogen abstraction occurs in methanol or ethanol to give the acetylides [Ir(C≡CR)(cod)(*o*-phen)] (R = H or Ph). Treatment of these acetylides with dilute perchloric acid in methanol regenerates the starting adducts together with a hydridic complex **312** (Scheme 54). However, coordination of fumaronitrile to the cationic iridium complex enhances nucleophilic attack at the coordinated diene. Thus treatment of the white product formed on addition of fumaronitrile to [Ir(1,5-cod)(phen)]$^+$ in methanol with sodium hydroxide gives **313** characterised by an X-ray study [263,264].



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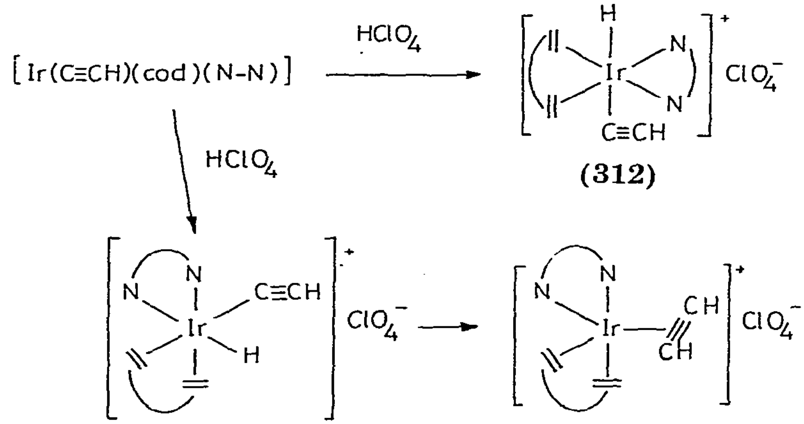
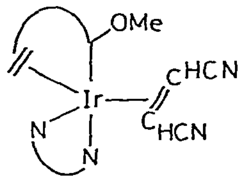


(312)

SCHEME 54

Complexes of the type [RhCp(C$_2$H$_4$)(C$_2$H$_3$X)] (X = Co$_2$Me, CN, F) react rapidly with HCl at −80°C, protonation occurring preferentially on the α carbon of the substituted olefin to form linear alkylrhodium complexes. The relative ease of reaction of [RhCp(C$_2$H$_3$X)$_2$] with HCl increases with the electron-



(N-N = o-phen)

(313)

releasing ability of X in the order X = CN < $CO_2Me \simeq F \simeq Me$. There is evidence for interaction between HCl and [$RhCp(C_2H_3CN)_2$], [RhCp(*trans*-$MeO_2CCHCHCO_2Me)_2$] and [$RhCp(C_2H_3CO_2Me)_2$] even at temperatures where alkylrhodium complexes cannot be detected and it is considered that an equilibrium may exist between the rhodium complex and HCl which does not involve H—Cl bond cleavage (Scheme 55) [265]. An X-ray study on the complex [RhCp-$(C_2H_4)(SO_2)$] reveals a planar Rh—SO_2 species. This is the first structure determination for a d^8 metal complex containing a planar M—SO_2 species, a result which has been interpreted in terms of a general MO model for metal—SO_2 complexes [266].

$$RhCp(olefin)_2 + HCl \rightleftharpoons RhCp(olefin)_2(HCl)_x$$

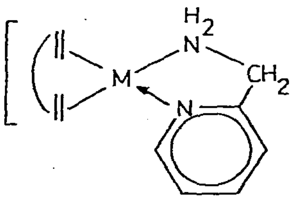
SCHEME 55

Various rhodium(I) complexes with nitrogen donor ligands [Rh-$(diene)L_2]^+$ (diene = cycloocta-1,5-diene, norbornadiene; L = quinoline, isoquinoline, pyridine, 2-ethylpyridine; L_2 = *N*,*N*,*N*′,*N*′,-tetramethylethylenediamine, 1,2-dipyridyl, 1,10-phenanthroline) have been isolated by addition of the N-donor ligands to [$Rh(diene_2]ClO_4$. Carbonylation of the complexes [Rh-$(diene)L_2[ClO_4$ leads to the dicarbonyl complexes $[Rh(CO)_2L_2]^+ClO_4^-$ in which one of the CO groups can be replaced by PPh_3 [267,268].

The halide bridged dimer, $[RhCl(1,5\text{-cod})]_2$ reacts with a variety of donor ligands to give adducts of general formula [RhCl(1,5-cod)L]. Solvation-minimized enthalpies and equilibrium constants have now been obtained calorimetrically for this reaction:

$$[RhCl(1,5\text{-cod})]_2 + 2B \rightarrow 2[RhCl(1,5\text{-cod})B]$$

where B = pyridine, tetrahydrothiophene, piperidine, 1-methylimidazole, 4-picoline, dimethylformamide, morpholine, 1-azabicyclo[2.2.2]octane, dimethylacetamide, 7-oxabicyclo[2.2.1]heptane, triethylamine, hexamethylphosphoramide, acetonitrile, dimethyl sulphoxide, triethyl phosphate, tetrahydrofuran and pyridine *N*-oxide [269]. The reactions of aminopyridines and aminoethylpyridines with $[MCl(1,5\text{-cod})]_2$ give the complexes **314**, **315**, **316** and **317** [270]. The cationic complexes **318** react with dihydrogen at −80°C to give **319**. Reactions of this type have been invoked in some olefin hydrogenation catalyst systems but this is the first time such a process has been directly observed. The complex **318** (L = $PMePh_2$) is a highly active hydrogenation catalyst [271]. Related cationic diene complexes of rhodium(I) also act as hydrogenation catalysts converting alkynes to *cis*-alkenes and dienes to monoenes [272—274]. The complex [Rh(cod)(+)(diop)]ClO_4 is a very active stereoselective catalyst in hydrogenation



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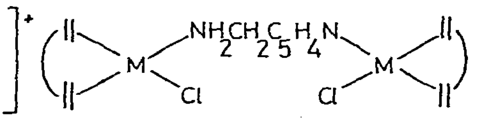

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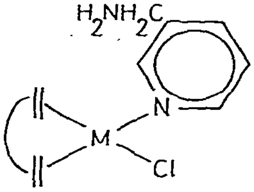

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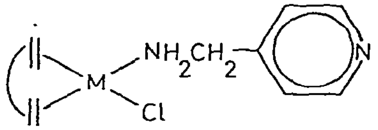

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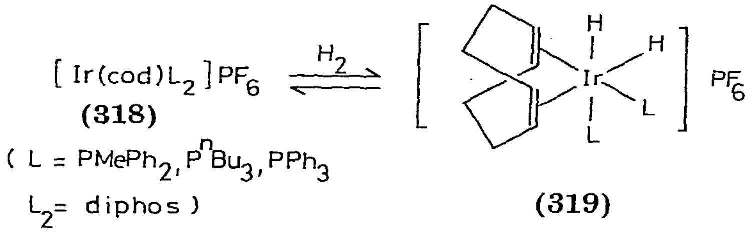


$[Ir(cod)L_2]PF_6$

(318)

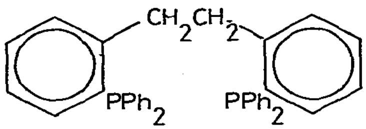
(L = $PMePh_2$, P^nBu_3, PPh_3

L_2= diphos)

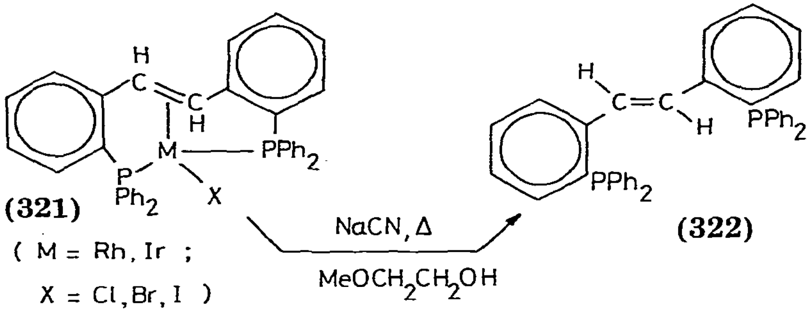
(319)

[275], this cationic complex of diop being a more active catalyst than the neutral complex [RhCl(cod)(diop)] [276]. The iridium complex [IrCl(cod)(+)-(diop)] has been the subject of an X-ray study [277]. The kinetics of the stoichiometric $[CoH(CO)_4]$ hydrogenation of diethyl fumarate, (DEF) to yield diethyl succinate (DES) in heptane has been reported [278].

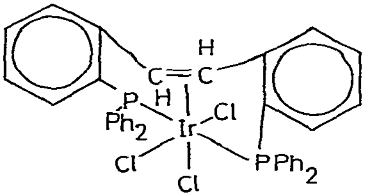
2,2′-Bis(*o*-diphenylphosphino)bibenzyl (**320**) is dehydrogenated by various rhodium complexes to give the planar rhodium(I) complex **321** from which the ligand **322** can be displaced. The C=C bond length of 1.436(6) Å found for **321** (M = Rh, X = Cl) is significantly longer than that observed in Zeise's salt (1.37(3) Å) indicating that there is more back-bonding to the double bond from rhodium(I) than from platinum(II). The reaction of **320** with iridium trichloride gives **323** which appears to be the first example of a monoolefin complex of iridium(III) [279]. The silbene complexes **321** react with carbon monoxide and ethylene to give five-coordinate, presumably trigonal bipyramidal complexes **324**. If the reactions are repeated in the presence of silver tetrafluoroborate cationic bis-carbonyl or bis-ethylene complexes can be isolated. The order of stability of the adducts **324** is Ir > Rh and CO > C_2H_4. In addition to the five-coordinate cations there is also spectroscopic evidence for four-coordinate cations formed by the reaction of silver tetrafluoroborate with **321**. These four-coordinate cationic complexes are unstable in solution and readily deposit a metal mirror on attempted isolation or on standing at room temperature. The coordinated ethylene in $[IrCl(C_2H_4)(bdpps)]$, (bdpps = **322**) undergoes intermolecular



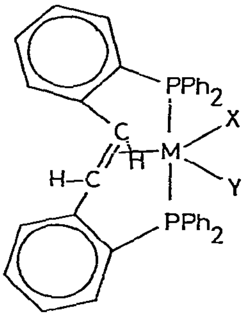
(320)



(321) (M = Rh, Ir ; X = Cl, Br, I) **(322)**



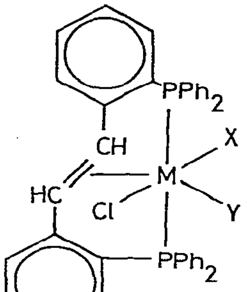
(323)



(324)

$X = CO$, $Y = Cl$, $M = Rh$;
$X = CO$, $Y = Cl$, $M = Ir$;
$X = C_2H_4$, $Y = Cl$, $M = Rh$;
$X = C_2H_4$, $Y = Cl$, $M = Ir$;
$X = Y = CO$, $M = Rh^+$;
$X = Y = CO$, $M = Ir^+$;
$X = Y = C_2H_4$, $M = Rh^+$;
$X = Y = C_2H_4$, $M = Ir^+$.

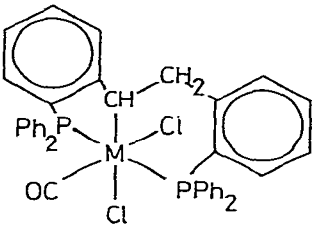
exchange and intramolecular rotation. [IrCl(bdpps)] oxidatively adds chlorine, hydrogen chloride and dihydrogen to give the octahedral chelate olefin complexes, [$IrCl_3$(bdpps)] (**323**), [$IrHCl_2$(bdpps)] and [IrH_2Cl(bdpps)] respectively. The addition of dihydrogen is reversible. However, dihydrogen does not react with [RhCl(bdpps)] and with either hydrogen chloride or chlorine [$RhCl_3$(bdpps)] is formed. These octahedral complexes **325** which contain an Ir—H bond have hydride *cis* to a coordinated olefin. However, they show no tendency to undergo the expected rearrangement to a chelate alkyliridium(III). This may be a consequence of the rigidity of the chelate olefin group and of the reluctance



(325)

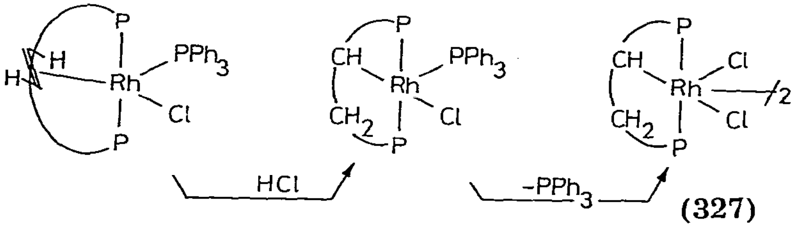
X = H, Y = Cl, M = Ir;
X = Y = Cl, M = Rh;
X = Y = Cl, M = Ir;
X = Y = H; M = Ir.

of iridium(III) to lose its six-coordinate geometry. However, in the presence of carbon monoxide the complexes **321** react with hydrogen chloride to give the chelate σ-alkyl complexes **326** and other ligands, e.g. triphenylphosphine produce a similar result to give **327** (Scheme 56) [280].



(M = Rh, Ir)

(326)



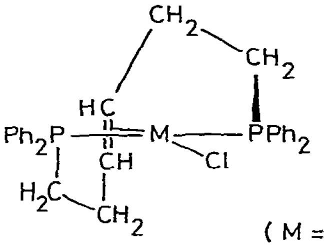
SCHEME 56

The reactions leading to the complexes **321** involve dehydrogenation of relatively active benzyl protons, however, the rhodium(I) and iridium(I) complexes, [MCl(1,5-cod)] dehydrogenate the alkane chain of **328** to give the olefin complexes **329**. The iridium complex activates dihydrogen reversibly at room temperature [281].

The structures of the five-coordinate compounds [$RhX(Ph_2PCH_2CH_2CH{=}CH_2)_2$] and [$RhCl\{P(CH_2CH_2CH{=}CH_2)_3\}$] have been investigated in solution by IR and ^{31}P NMR spectroscopy. Several isomers are observed which undergo exchange. Four-coordinate isomers of [$RhX(Ph_2PCH_2CH_2CH{=}CH_2)_2$] are present at 32°C. In these phosphine—olefin complexes the olefin can undergo a restricted

$Ph_2PCH_2CH_2CH_2CH_2CH_2CH_2PPh_2$

(328)



(M = Rh, Ir)

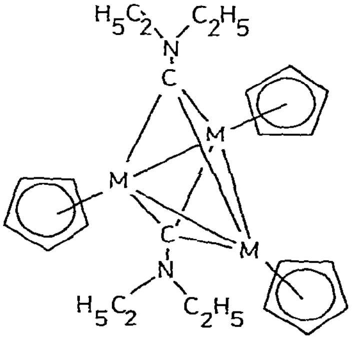
(329)

rotation of about 90° from a configuration with the olefin perpendicular to one with the olefin parallel to the metal—phosphorus bond but further rotation without bond breakage is not possible [282]. ^{13}C NMR studies of the five-coordinate complexes, $[RhX\{P(CH_2CH_2CH{=}CH_2)_3\}]$ and $[RhX\{P(CH_2CH_2CH_2CH{=}CH_2)_3\}]$ ($X = Cl$ or Br) also reveal a fluxional character in the olefinic carbons of $[RhX\{P(CH_2CH_2CH{=}CH_2)_3\}]$ which can be related to the partial rotation of the olefin about the rhodium—olefin bond [283].

The dihaloacetylene complexes $[Co_2(CO)_6(X_2C_2)]$ ($X = Cl$, Br or I) have been isolated from the reactions of the acetylenes C_2X_2 with dicobalt octacarbonyl. In these reactions $[Co_3(CO)_9C]_2$ is formed via a reaction of $[Co_2(CO)_6(X_2C_2)]$ with excess $[Co_2(CO)_8]$. Monosubstituted complexes $[Co_2(CO)_5L(C_2I_2)]$, ($L =$ B-n-Pu_3, PPh_3, $AsEt_3$, $SbEt_3$) can also be obtained [284]. The kinetics of substitution of one carbonyl ligand in the complex $[Co_2(CO)_6(C_2Ph_2)]$ by several phosphorus-donor ligands has been studied [285]. The crystal structure of $[Co_2(CO)_5(t\text{-}BuC{\equiv}CBu\text{-}t)]$ [286], infrared studies of the complexes $[Co_2(CO)_6(RC_2R')]$ [287,288] and a theoretical study on these complexes [289] have been reported.

Variable temperature ^{13}C NMR spectra have been reported for $[Co_4(CO)_{10}(C_2Ph_2)]$ suggesting the presence of a two-step exchange process. However, a further step in the intramolecular exchange has now been detected [290].

The cobalt and rhodium complexes $[MCp(CO)_2]$ cause complete cleavage of the carbon—carbon triple bond in $Et_2NC{\equiv}CNEt_2$ to give the complex **330**. This type of reaction is unprecedented in alkynemetal carbon chemistry but is reminis-



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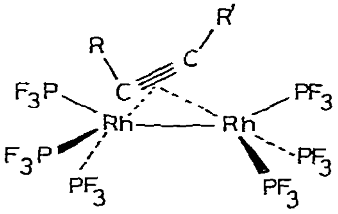
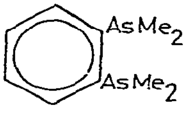


$R = R' = H$, Me, Ph, CF_3
$R = H$; $R' = Ph$, Bu-n, Bu-t
$R = Me$; $R' = Bu^n$, Ph, CO_2Me
$R = Ph$; $R' = Et$, CO_2Me
$R = p\text{-}NO_2C_6H_4$; $R' = CO_2Et$

(331)

cent of the cleavage by transition metals of the carbon—carbon double in certain electron-rich alkenes [291].

Acetylenes react with $[Rh_2(PF_3)_8]$ to give a series of binuclear complexes $[Rh_2(PF_3)_6(RC_2R')]$. Like the complexes $[Co_2(CO)_6(RC_2R')]$, the rhodium compounds **331** contain a bridging acetylene lying over and perpendicular to a metal—metal bond. The phenyl acetylene complex catalyses the linear polymerisation of phenylacetylene, unlike the corresponding cobalt complex, which catalyses cyclotrimerisation. The PF_3 groups in **331** undergo intramolecular exchange [292]. Treatment of complexes **331** with tertiary phosphines and arsines L give disubstituted complexes $[Rh_2(PF_3)_4L_2(ac)]$ (ac = Ph_2C_2, PhC_2Me, p-$NO_2C_6H_4C_2CO_2Et$). The diarsine ligand **332** gives $[Rh_2(PF_3)_2(diars)_2(ac)]$. A single crystal X-ray study of $[Rh_2(PF_3)_4(PPh_3)_2(Ph_2C_2)]$ has been carried out. The triphenylphosphine groups are on the same side of the molecule as the bridging acetylene. Around room temperature PF_3 exchange occurs in these disubstituted complexes, the process being initiated apparently by dissociation of the ligand L. A Newman projection along the Rh—Rh bond illustrating the proposed time-average structure is given in **333**.



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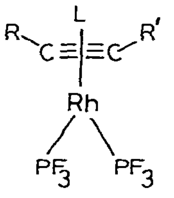

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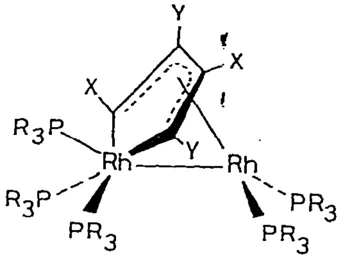
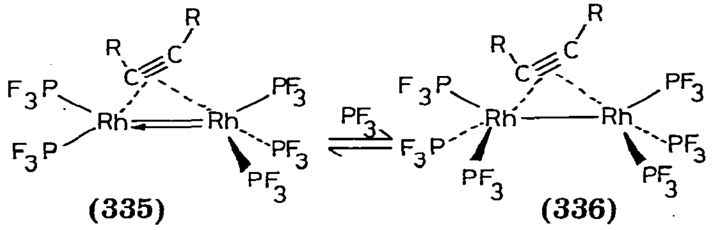


R = F, X = Y = CO_2CH_3
R = F, X = H, Y = CO_2CH_3
R = C_6H_5, X = H, Y = CO_2CH_3

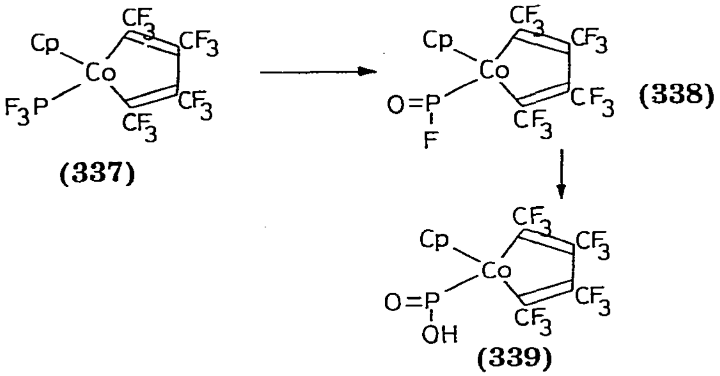
(334)

A 1/1 mixture of $[Rh_2(PF_3)_4(AsMePh_2)_2(Ph_2C_2)]$ and $[Rh_2(PF_3)_6(Ph_2C_2)]$ undergoes intermolecular PF_3 exchange in the temperature range 50—52°C, possibly via a pentakis intermediate $[Rh_2(PF_3)_5(AsMePh_2)(Ph_2C_2)]$ [293]. The acetylenes $MeO_2CC{\equiv}CCO_2Me$, $MeO_2CC{\equiv}CH$ and t-BuC≡CBu-t behave differently with $[Rh_2(PF_3)_8]$. The first two give rhodiacyclopentadiene complexes **334** and above room-temperature the reactions with these acetylenes lead to explosive polymerisation of the acetylene [294]. t-BuC≡CBu-t reacts with $[Rh_2(PF_3)_8]$ to give **335** which contains a rhodium—rhodium double bond. Steric hindrance by the bulky t-butyl groups is probably responsible for the stability of **335** and for the relative ease of intermolecular exchange in **336** [295]. The reaction of hexafluorobut-2-yne with $[CoCp(PF_3)_2]$ gives the metallacyclopentadiene complex **337** which can be successively hydrolysed to **338** and **339**. However, although hexafluorobut-2-yne does not react with $[RhCp(PF_3)_2]$ [296], $C_6F_5C{\equiv}CC_6F_5$ reacts with $[MCp(CO)(PPh_3)]$ to give **340**, **341** and **342**. The complexes **341** and **342** have been the subjects of X-ray studies [297,298]. The reaction of diphenylacetylene with $[RhCl(PF_3)_2]_2$ gives the cyclobutadiene complex **343** which undergoes halide bridge cleavage reactions to give **344** and **345** [299]. Some cyclobutadiene iron-

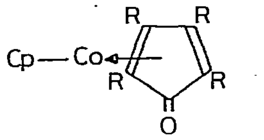


(335) **(336)**

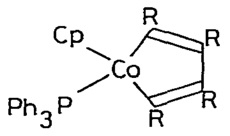
(R = ^{t}Bu)



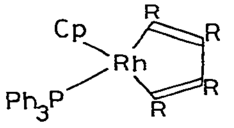
(337) **(338)** **(339)**



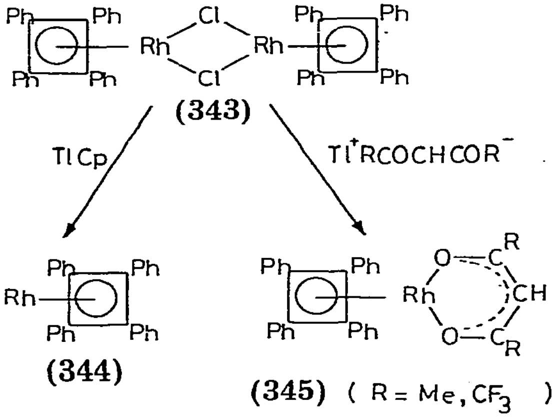
(R = C_6F_5)
(340)



(341) (R = C_6F_5)



(342) (R = C_6F_5)



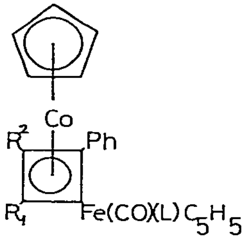
(343) **(344)** **(345)** (R = Me, CF_3)

$\pi\text{-}C_5H_5Co(PPh_3)(R^1C{\equiv}CR^2)$ + $\pi\text{-}C_5H_5Fe(CO)(L)C{\equiv}CPh$

(346)

$R^1, R^2 = Ph$
$R^1 = Ph, R^2 = CO_2CH_3$
$R^1, R^2 = CO_2CH_3$

$L = CO$
$L = PPh_3$



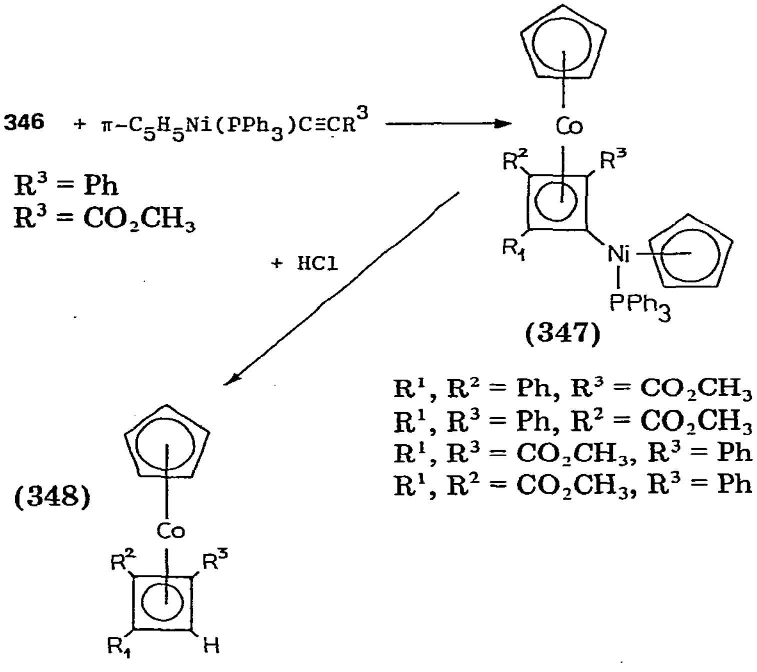
$R^1, R^2 = Ph, L = CO$
$R^1 = Ph, R^2 = CO_2CH_3, L = CO$
$R^1, R^2 = CO_2CH_3, L = CO$
$R^1 = Ph, R^2 = CO_2CH_3, L = PPh_3$

SCHEME 57

and nickel-substituted complexes also result from the reaction of acetylene complexes of the type [CoCp(RC≡CR)(PPh$_3$)] (**346**) with ethynyl complexes of iron (Scheme 57) and nickel (Scheme 58).

The nickel—carbon bonds in the complex **347** are readily cleaved by HCl (generated by addition of methanol and acetyl chloride to the complex) to give new cyclobutadiene complexes [300]. Cyclobutadiene complexes may arise via intermediate metallacyclopentadiene complexes. However, these types of intermediates have not been detected in the formation of **348** [300]. Metallacyclopentadienes are generally thought to be involved in the metal cyclotrimerisation of acetylenes. Further evidence for this mechanism is provided by the reaction of **349** with diphenylacetylene which gives the arene complex **350**. Heating **350** with sodium cyanide in aqueous ethanol affords the free ligand **351**.

Hexafluorobut-2-yne is known to add 1,4 to coordinated cycloocta-1,5-diene in the complex [RhCl(1,5-cod)]$_2$ and the full paper on the single crystal X-ray structure of the acetylacetonate derivative **352** has appeared [302]. Hexafluorobut-2-yne is also known to add 1,4 across β-diketonato systems coordinated to rhodium(I). The macrocyclic cobalt complex **353** has now been shown to undergo similar additions with acetylenes and nitriles, (Scheme 59). Propyne adds to give **354** and **355** but more bulky acetylenes add to give only **354** [303].



$R^3 = Ph$
$R^3 = CO_2CH_3$

(347)

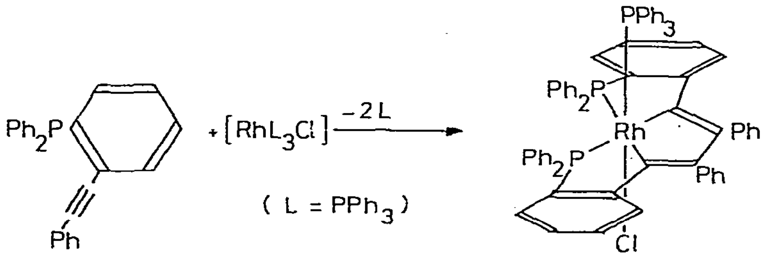
$R^1, R^2 = Ph, R^3 = CO_2CH_3$
$R^1, R^3 = Ph, R^2 = CO_2CH_3$
$R^1, R^3 = CO_2CH_3, R^3 = Ph$
$R^1, R^2 = CO_2CH_3, R^3 = Ph$

(348)

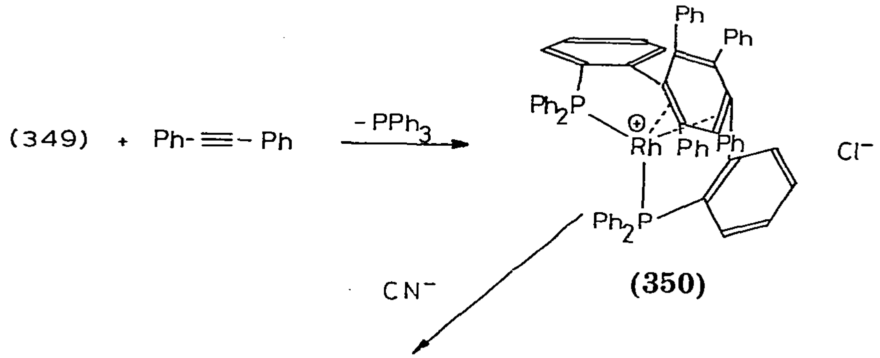
$R^1, R^2 = Ph, R^3 = CO_2CH_3$
$R^1, R^3 = Ph, R^2 = CO_2CH_3$
$R^1, R^3 = CO_2CH_3, R^2 = Ph$
$R^1, R^2 = CO_2CH_3, R^3 = Ph$

SCHEME 58

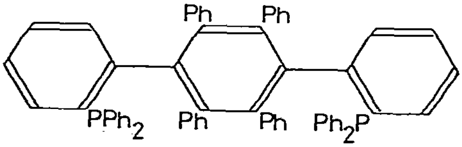
The butenolide complexes **356** are intermediates in the generation of bifurandiones which arise from them by reaction with acetylene and carbon monoxide. Reactions of acetylenes with **356** (R = H, Me or Ph) give products in which two acetylenes have been inserted. Purification of these products has given rise to two series of isomeric products. X-ray analysis shows that one series has the structure type depicted in **357** while the other series probably has the structure **358** [304].



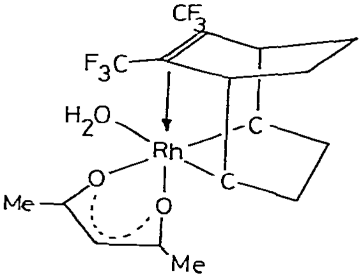
(349)



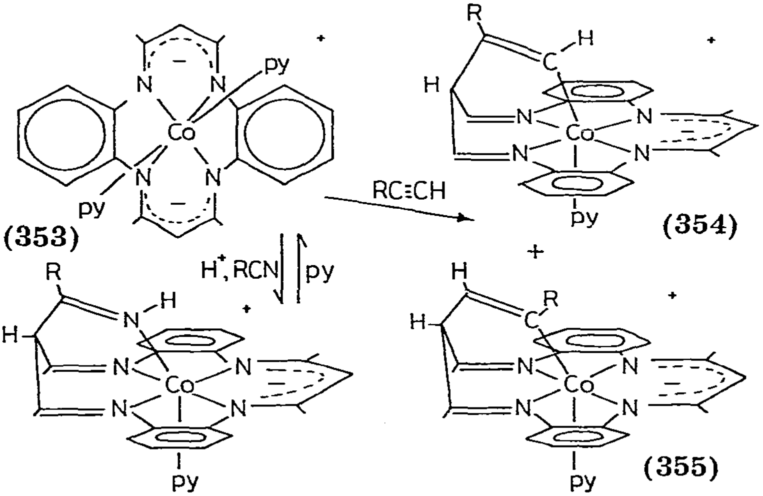
(350)



(351)



(352)

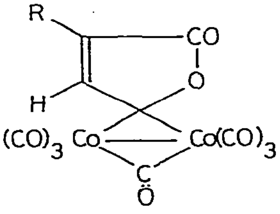


(353)

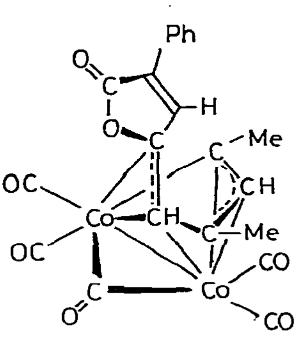
(354)

(355)

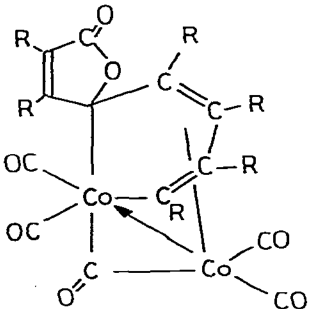
SCHEME 59



(356)



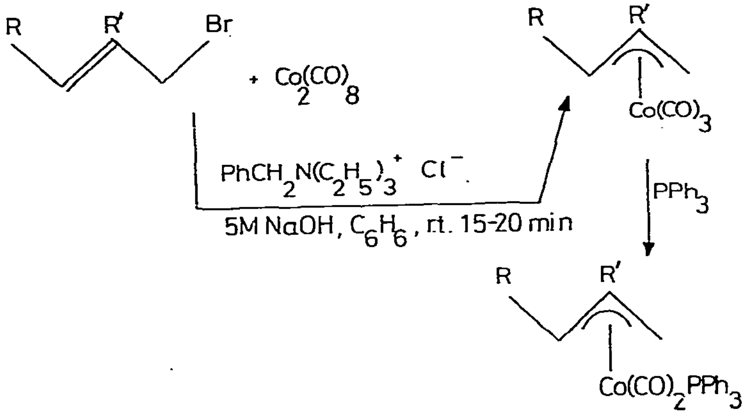
(357)



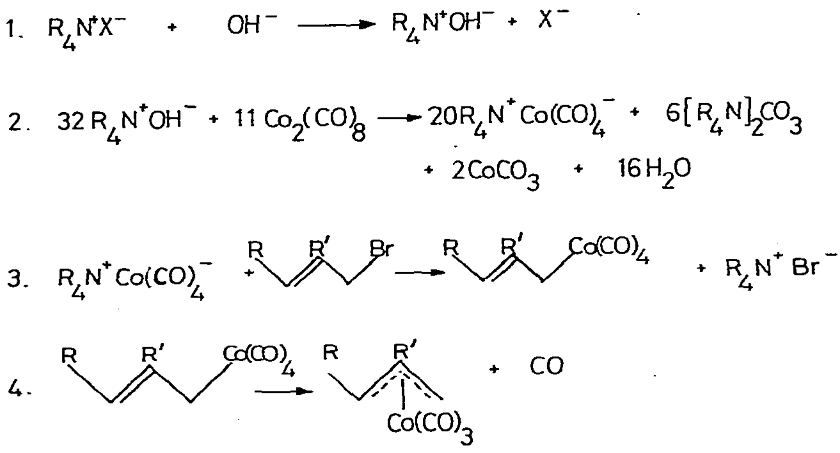
(358)

Metal—π-allyl complexes

Reaction of $[Co_2(CO)_8]$ with allyl bromide using a phase transfer reaction and benzyltriethylammonium chloride as catalyst results in 70—80% yields of π-allylcobalt tricarbonyl complexes. Triphenylphosphine substituted derivatives may



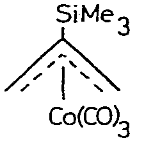
SCHEME 60



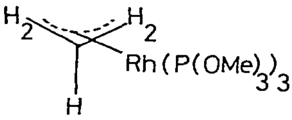
SCHEME 61

also be prepared (Scheme 60) [305]. The reaction probably proceeds by the transfer of the initially formed ammonium hydroxide into the organic phase as an ion pair, where it readily attacks the $[Co_2(CO)_8]$ to give $[Co(CO)_4]^-$. After reaction, the ammonium halide generated migrates back into the aqueous phase (Scheme 61).

When treated with sodium hydroxide under the same conditions but in the absence of the catalyst the metal carbonyl $[Co_2(CO)_8]$ was recovered in 85% yield and no evidence of the formation of the $[Co(CO)_4]^-$ ion was observed. The reaction of 2-trimethylsilyl-3-chloroprop-1-ene and $Na[Co(CO)_4]$ in THF results in the formation of the π-allyl complex 359 in 55% yield [306].



(359)



(360)

A study on the thermally induced rearrangements of polyfluoroallylmetal carbonyls indicates that the process in Scheme 62 does not occur when the metal is iridium [307], whereas manganese and rhenium undergo facile rearrangement.

$CF_2{=}CClCF_2{-}ML \rightarrow CF_3CCl{=}CF{-}ML$

$M = Mn, Re; L = (CO)_5$
$M = Ir; L = Cl_2(CO)(PPh_3)_2$: no reaction

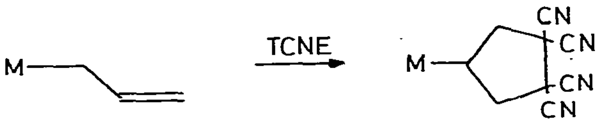
SCHEME 62

This is probably due to steric effects in the suggested intermolecular process in which a fluorine from the CF_2 group α to the metal acts as a nucleophile towards a terminal $CF_2 =$ group in a second molecule. Treatment of $[Rh(\eta^3\text{-}C_3H_5)(CO)_2]$ with trimethylphosphite results in replacement of both carbonyls and addition of one phosphite to give an air-sensitive complex $[Rh(\eta^3\text{-}C_3H_5)(P(OMe)_3)_3]$ (360) [308].

Reaction of **360** with carbon monoxide gives a σ-allyl complex which gives ^{31}P NMR data consistent with an interconverting (Berry pseudorotation process) trigonal bipyramidal species. A benzene solution of **360** absorbs two molar equivalents of molecular hydrogen to produce a red solution which is an active hydrogenation catalyst for alkenes. The active species in this solution has not been isolated. A (3 + 2)-cycloaddition reaction between TCNE and an η^1-allylcobaloxime complex is reported to give a solid product (Scheme 63) [309].

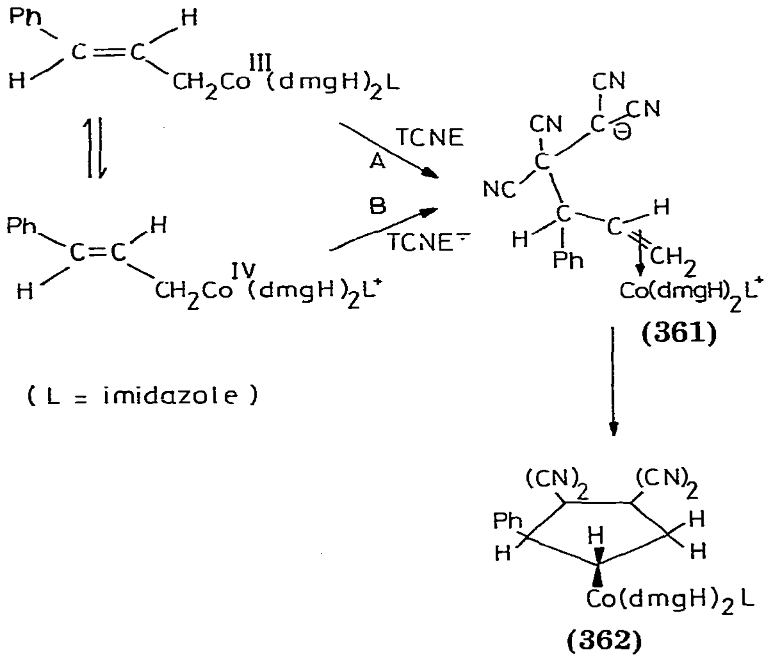
Further examples of cyclisation between allylcobaloxime complexes and TCNE are reported, and the product **362** in Scheme 64 has been the subject of a crystal structure determination [310].

The data indicate that the cobalt and phenyl group are mutually *trans* with respect to the cyclopentane ring suggesting that the reaction must proceed via a (3 + 2)-cycloaddition with a 1,2-migration of the cobalt, or attack of the TCNE or its radical ion on the γ-carbon of the cinnamyl complex (path A) or its oxida-



M = (pyridine)bis(dimethylglyoximato)cobalt

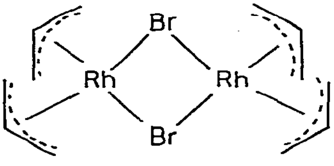
SCHEME 63



SCHEME 64

tion product (path B) respectively, to give the intermediate **361**. This step determines the stereochemistry and subsequent ring closure accompanied by a further metal shift from the α,β-double bond to a σ-bond at the β-position gives the product **362**. A crystal structure determination has been carried out on the complex [$Rh_2Br_2(allyl)_4$] (**363**) [311].

On treatment of [$Rh_2Br_2(allyl)_4$] or [$RhBr_2(allyl)]_n$ with amines, phosphines

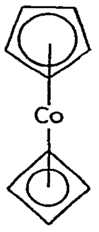


(363)

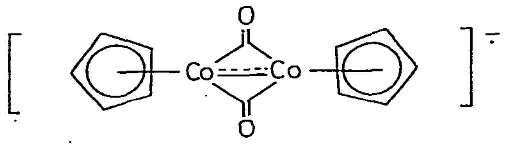
and sulphides in ethanolic solution, saturated with hydrogen, complexes are formed which have catalytic activity in the hydrogenation of cyclohexene to cyclohexane. The activities are in the order amines $\simeq$ phosphines $>>$ sulphides. A series of allylcobalt complexes $[Co(\eta^3\text{-}C_3H_5)L_3]$ with L representing a phosphine or phosphite ligand has been prepared and their activity as arene hydrogenation catalysts is reported [312]. The activity order in the complex $[Co(\eta^3\text{-}C_3H_5)L_3]$ is $L = P(OCH_3)_3 < P(OC_2H_5)_3 < P(CH_3)_3 < P(O\text{-}i\text{-}Pr)_3$. $[Co(\eta^3\text{-}C_3H_5)(CO)_3]$ is reported to be inactive as an arene hydrogenation catalyst at 298 K, probably due to the relatively higher activation energy for CO dissociation and the lower electron density on the cobalt atom in this complex with respect to the corresponding situation in the phosphine and phosphite analogues.

Metal carbocyclic complexes

Mono-π-cyclopentadienyl complexes and bis-π-cyclopentadienyl complexes of transition metals including cobalt, rhodium and iridium have been the subject of two reviews [313,314]. The structure of $[Co(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4H_4)]$ has been determined by single crystal X-ray diffraction methods and is given in 364 [315].

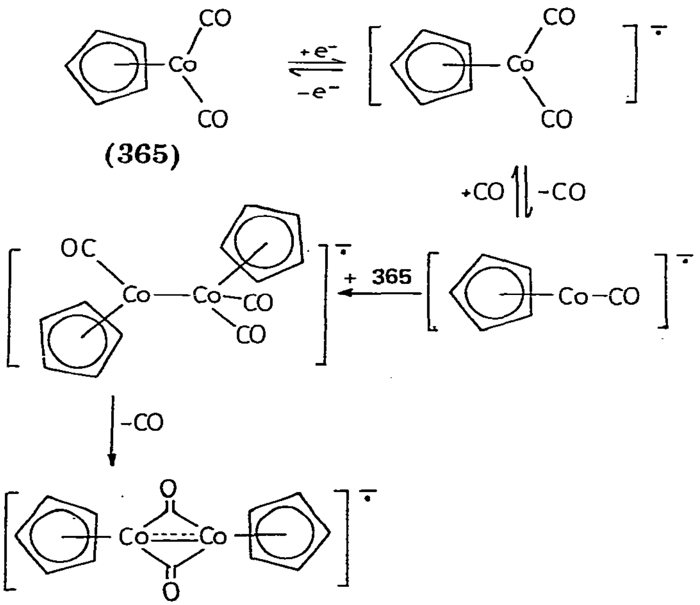


(364)



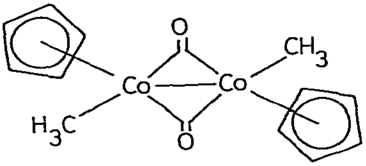
(366)

Reduction of η^5-cyclopentadienyldicarbonylcobalt (365, $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$) using sodium amalgam in THF was found to produce a binuclear cobalt radical anion 366 by a complex reaction course (Scheme 65) [316].



SCHEME 65

The crystal structure of **366** has been the subject of a study involving ESR electronic spectra and X-ray crystal structure determination [317]. The study was undertaken on the bis(triphenylphosphine)iminium salt and reveals the information that the Co—Co bond is perpendicular to the plane of the two cyclopentadienyl groups, the cobalt atoms and bridging carbonyls are essentially coplanar and the Co—Co bond order is 1.5. The complex may be considered as a mixed-valence complex on the basis of its electronic transitions in the near-infrared, the low extinction coefficient in this region indicating a high degree of mixing between the +1 and 0 valence states. On reduction of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ with sodium in hexamethylphosphoramide a redistribution of ligands results in the formation of $[Co(CO)_4]^-$ and the novel binuclear radical anion $[Co(\eta^5\text{-}C_5H_5)CO]_2^-$ (**366**) neither of which reduce further when excess of sodium is present [318]. Using the Chatt—Dewar—Duncanson model for bonding the stability of these highly reduced transition metal species is thought to be a sensitive function of the number of π-acceptor ligands attached to the metal centre, the more coordinated π-acceptor ligands there are the more stable the highly reduced species should be. Reaction of the bis(triphenylphosphine)iminium salt of **366** with two equivalents of iodomethane in THF at room temperature produces a neutral complex which is assigned the structure **367** on the basis of spectral data [319].



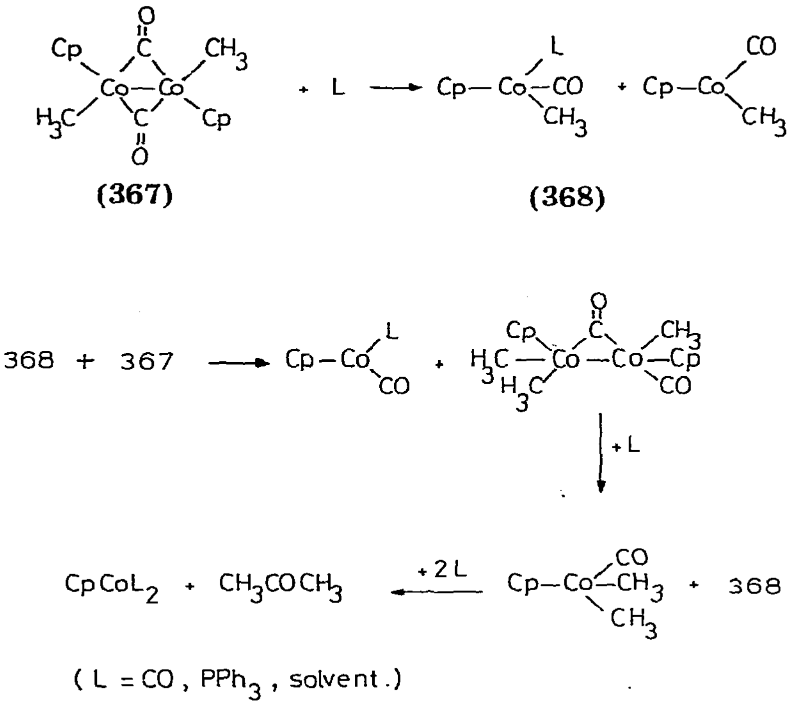
(367)

In THF or benzene, complex **367** decomposes thermally at room temperature to give propanone and a mixture of cobalt cluster complexes (Scheme 66), but in the presence of CO reaction occurs more rapidly and propanone and $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ (**365**) are the only products. The NMR monitoring of this reaction indicates that propanone formation is not the first observable step in this reaction, and the effect on rate and composition of products of added ligands (e.g. CO, PPh_3) suggest a complex mechanism tentatively suggested as Scheme 67, which involves initial metal—metal bond cleavage to give the 19-electron complex **368**.

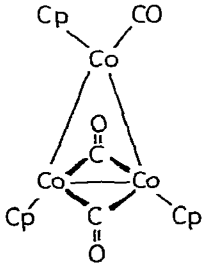
$$\mathbf{367} \rightarrow CH_3COCH_3 + [Co(\eta^5\text{-}C_5H_5)(CO)]_3 + [\{Co(\eta^5\text{-}C_5H_5)\}_4(CO)_2]$$

SCHEME 66

The crystal structure of the complex tris(η^5-cyclopentadienyl)tricobalt tricarbonyl is reported [320]. The molecule is found to consist of an isosceles triangle of cobalt atoms, each bonded to one cyclopentadienyl molecule. The structure contains a triply-bridging carbonyl group **369**. Interestingly the IR spectrum of **369** varies markedly depending on the solvent used, and in benzene for example the data indicate a structure **370** for the complex. It thus appears that the geometry of the three CO ligands is very sensitive to subtle changes in the molecule's



SCHEME 67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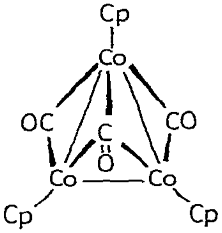
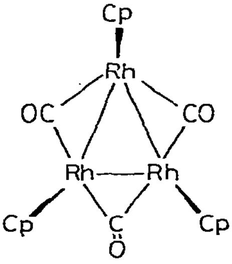
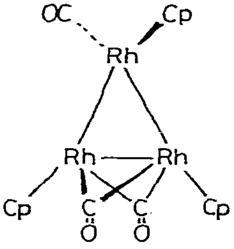
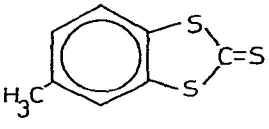

(369)

environment. To describe molecules of such extraordinary deformability or plasticity the term *fictile* is proposed. Two isomers of a related complex [$Rh_3(CO)_3Cp_3$] (**371** and **372**) have already been the subject of single-crystal X-ray


(371)


(372)

diffraction studies, but a new larger scale method of preparing isomer **371** has led to an examination of its solution structure and dynamics [321]. On the basis of spectral data it is reported that the solution structure of **371** is identical to that in the solid state and that complete scrambling of the CO ligands over the Rh_3 framework occurs. Reaction of $[RhCl(COD)]_2$ with trithione **373** results in halogen-bridge cleavage but not alkene displacement, and isolation of a 1/1 adduct $[Rh(Cl)(C_8H_{12})(C_8H_6S_3)]$ (**374**) [322]. On treatment of **373** with cyclopentadienylcobaltcyclooctadiene [Co(COD)(Cp)] elimination of a thiocarbonyl group occurs and complex **375** is formed.



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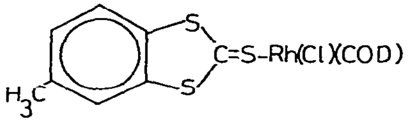
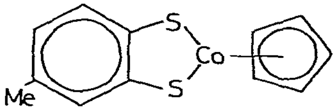
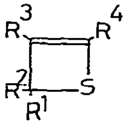


(374)

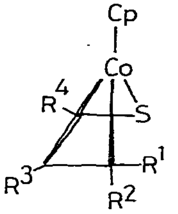


(375)

Reaction of thiacyclobutenes (thietes) (**376**) with $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ in hexane solution under UV irradiation leads to the dark green or green-brown complexes **377** [323].



(376)

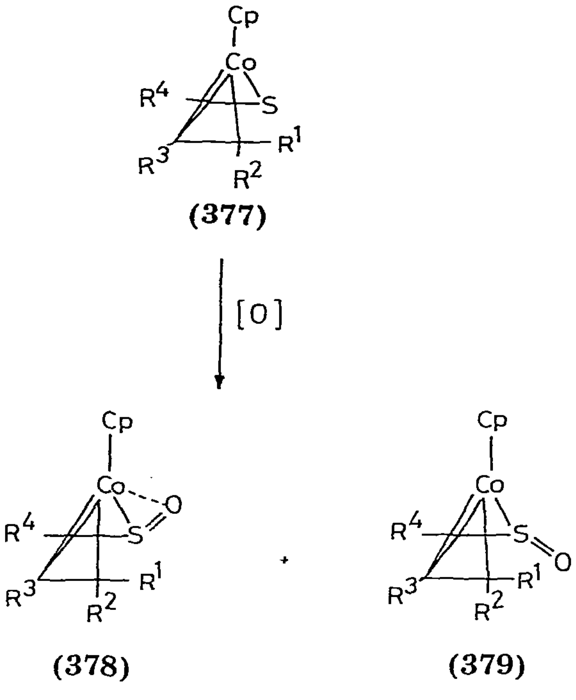


(377)

(a) $R^1 = R^2 = R^3 = R^4 = H$

(b) $R^1 = R^4 = H$; $R^2 = CH_3$ $R^3 = C_2H_5$

These complexes are studied on the basis of their NMR and mass spectra. On treatment of **377** with *m*-chloro perbenzoic acid oxidation of the sulphur atom occurs (Scheme 68) leading to complexes **378** or **379**. The IR data indicate the possibility of a metal—sulphur—oxygen bond, strongly suggesting isomer **378** as the more likely. In acetone solution complex **377** ($R^1 = R^4 = H$; $R^2 = CH_3$, $R^3 = C_2H_5$) undergoes autooxidation to give a mixture of the corresponding isomers **378** and **379**. Treatment of **377** with triphenylmethyl or tropylium fluoroborate or tropylium hexafluorophosphate gives dark brown salts $[Co_2(\eta^5\text{-}C_5H_5)_2(C_3H_3S)]BF_4$ (if $R^1 = R^2 = R^3 = R^4 = H$) and $[Co_2(\eta^5\text{-}C_5H_5)_2(C_6H_9S)]X^-$ (if $R^1 = R^4 = H$ and $R^2 = CH_3$, $R^3 = C_2H_5$, $X = BF_4^-$ or PF_6^-), postulated as **380** although alternative structures such as **381** are regarded as possible.

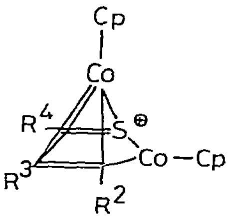


(377)

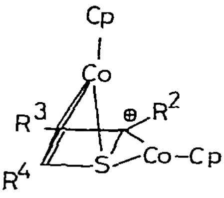
(378) (379)

(R^1, R^2, R^3, R^4 as in 13a & b)

SCHEME 68



(380)

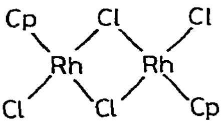


(381)

Treatment of $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ (382) with NaS_2PR_2 (R = Me, Ph) in 1/1 mole ratio gives complex 383.

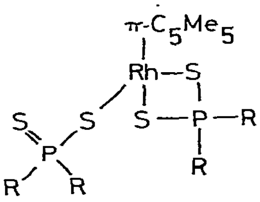
The stronger nucleophiles $^-S_2CNR_2$ and ^-S_2COR react with 382 to give 384, the inequivalent dithioacid ligands being confirmed by NMR studies.

Reaction of 382 with NaS_2CNMe_2 and then NaS_2PMe_2 results in the mixed dithioacid complex $[Rh(\eta^5\text{-}C_5Me_5)(S_2CNMe_2)(S_2PMe_2)]$ isostructural with 384 having bidentate $^-S_2CNMe_2$ and unidentate $^-S_2PMe_2$. The crystal structure and NMR spectra of the complex formed when $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ is treated with $AgPF_6$ in solvents such as cyanomethane, pyridine and dimethylsulphoxide have been investigated [325]. The structure is given in 385. The dicationic pentamethylcyclopentadienyl-rhodium and -iridium acetone solvate complexes (386) react with indene in acetone to give initially the η^6-indene complexes 387 in which the metal is complexed to the 6-membered ring [326]. These complexes deprotonate and quantitatively rearrange in solution to the η^5-indenyl com-

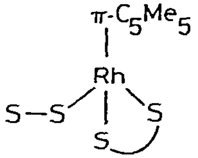


(382)

($Cp = C_5Me_5$)



(383)

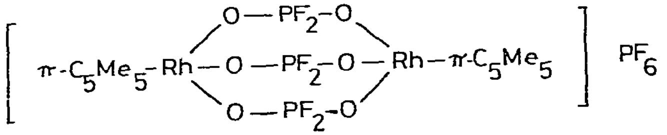


(384)

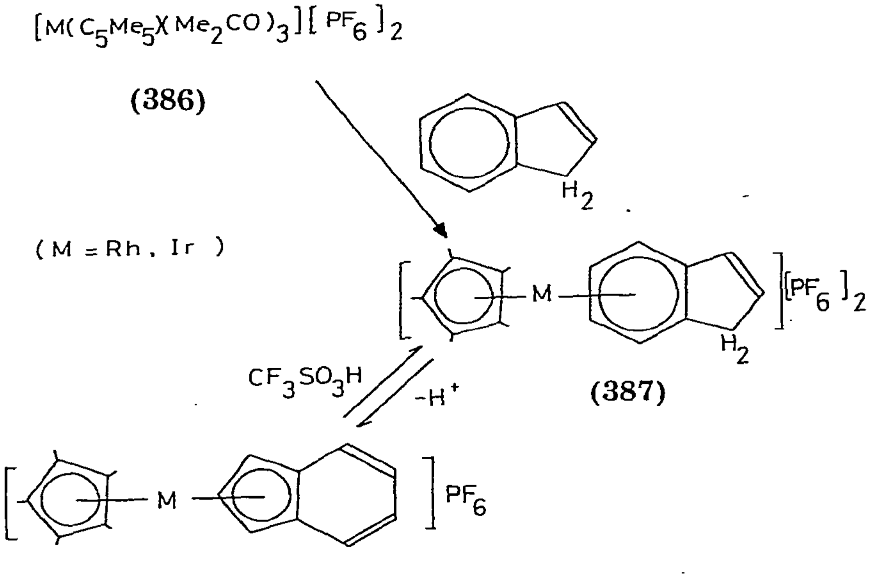
S-S = unidentate $^-S_2CNR_2$ or ^-S_2COR

S͡S = bidentate $^-S_2CNR_2$ or ^-S_2COR

plexes 388 in which the metal is bound to the 5-membered ring (Scheme 69).



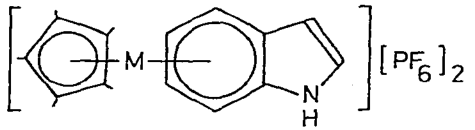
(385)



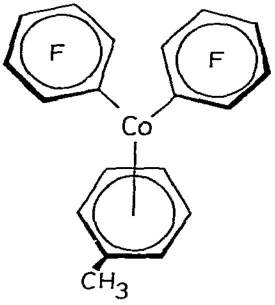
SCHEME 69

Closely related reactions occur using **386** and indole giving complexes **389**, which in the case of M = Ir undergoes a similar reversible rearrangement as for

387 ⇌ **388**, but the rhodium complex decomposed in the presence of base. In these rearrangements H—D exchange studies indicate that the rate-determining step is the movement of the metal from the 5- to the 6-membered ring or vice-versa. The co-condensation of cobalt vapour and *F*-bromobenzene at —196°C yields a complex which when crystallised from toluene contains a π-bonded toluene molecule **390** [327]. This complex is a paramagnetic, 17-electron, 5-coordinate system as revealed by X-ray diffraction studies and is the first example of an η^6-arene complex of an R_2M system.



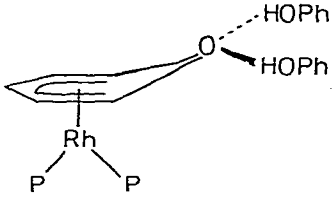
(389) (M = Rh,Ir)



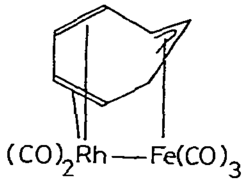
(390)

Re-investigation of the reaction between [RhMe(PPh$_3$)$_3$] or [RhPh(PPh$_3$)$_3$] and phenol in methylbenzene confirms the formation, in both cases, of the solvate [Rh(OPh)(PPh$_3$)$_2$ · 3 PhOH · PhCH$_3$]. This complex when stirred in petroleum gives a pink solid [Rh(OPh)(PPh$_3$)$_2$ · 2 PhOH] (391). The bonding in this complex is more realistically formulated as a η^5-oxocyclohexadienyl complex [328].

The reaction of [Fe(C$_7$H$_7$)(CO)$_3$]$^-$ with [RhCl(CO)$_2$]$_2$ in THF leads to a heterodimetallic cycloheptatrienyl complex [Fe(C$_7$H$_7$)(CO)$_3$Rh(CO)$_2$] (392) whose crystal structure has been determined [329]. Furthermore, the ^{1}H NMR data indicate very rapid ring "whizzing" for this molecule consistent with both metal centres being *cis* with respect to the 7-membered ring, but ^{13}C NMR data prove that no carbonyl exchange occurs between metals. Three *tetrahapto* modes of coordination of cyclooctatetraene are known: 1,4-η; 1,2:5,6-η and 1,3:6-η shown as A, B and C respectively in 393.



(391)

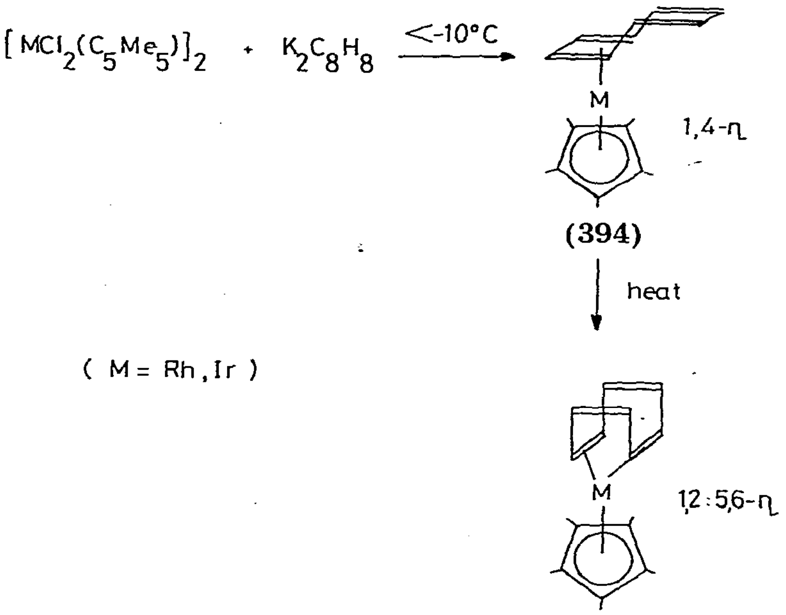


(392)

(A) (B) (C)

(393)

When complexes $[MCl_2(C_5Me_5)]_2$ (M = Rh, Ir) are treated with $K_2C_8H_8$ in THF two isomeric complexes **394** and **395** are produced in low yield, the ratio of the isomers being dependent on the reaction temperature or the temperature of any subsequent product isolation (Scheme 70) [330]. When the temperature

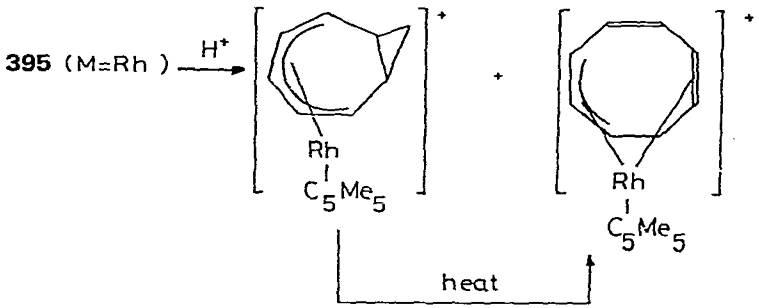


(394)

(395)

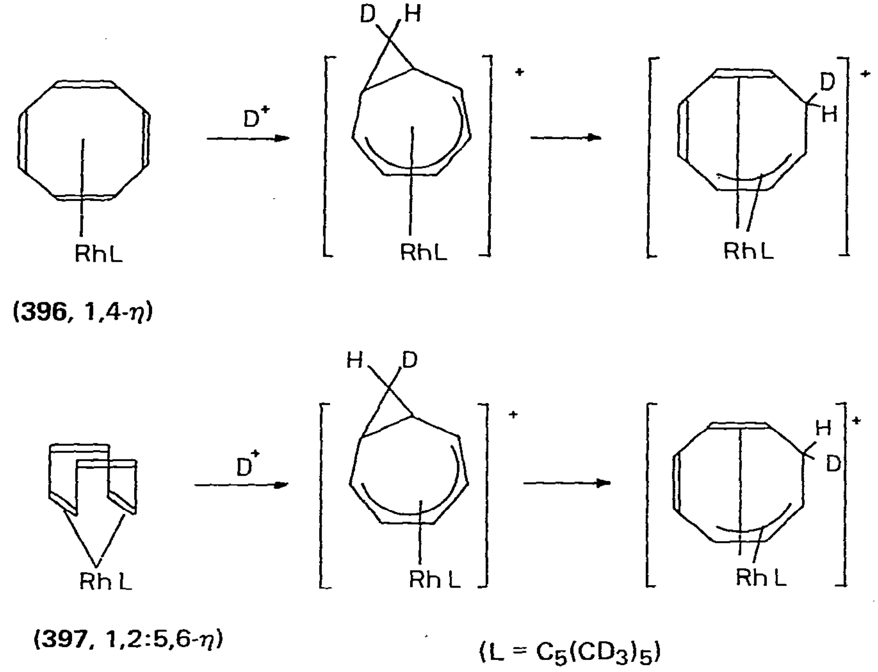
SCHEME 70

of the reaction and isolation of product was kept below −10°C, more than 90% of the product was **394**, whereas higher temperatures of reaction and isolation, or maintaining the reaction at 20°C in solution gave isomers **395** in higher yield. The complexes are studied on the basis of their NMR spectra. Protonation of $[Rh(C_5Me_5)(1,2{:}5,6\text{-}\eta\text{-}C_8H_8)]$ (**395**, M = Rh) by CF_3CO_2H produces a mixture of isomers as shown in Scheme 71 the reaction again being sensitive to temperature.



SCHEME 71

The lack of workable amounts of the iridium complex **395** (M = Ir) made the analogous iridium reactions difficult to study but preliminary results indicate a similar reaction course to that shown in Scheme 71. As an extension to these protonation reactions and to attempt to clarify the stereochemistry of the mechanisms the reactions were studied by ^1H NMR but using deuterated complexes **396** and **397**. The results indicate that the 1,4-η- and the 1,2:5,6-η-rhodium complexes are both protonated stereospecifically but in different ways. It appears that the 1,4-η-C_8H_8 complex is protonated stereospecifically *exo* by direct attack at the cyclooctatetraene, while protonation of the 1,2:5,6-η-C_8H_8 complex occurs stereospecifically *endo* via an M—H$^+$ intermediate (Scheme 72).



(396, 1,4-η)

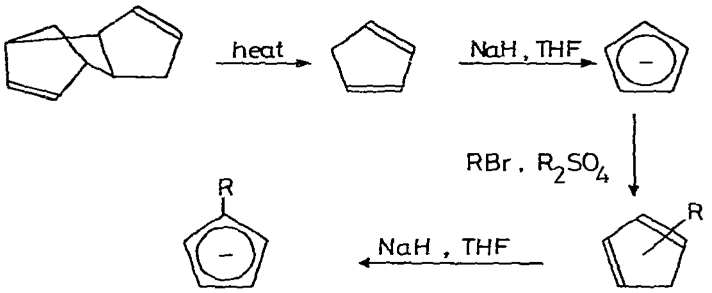
(397, 1,2:5,6-η)

($L = C_5(CD_3)_5$)

SCHEME 72

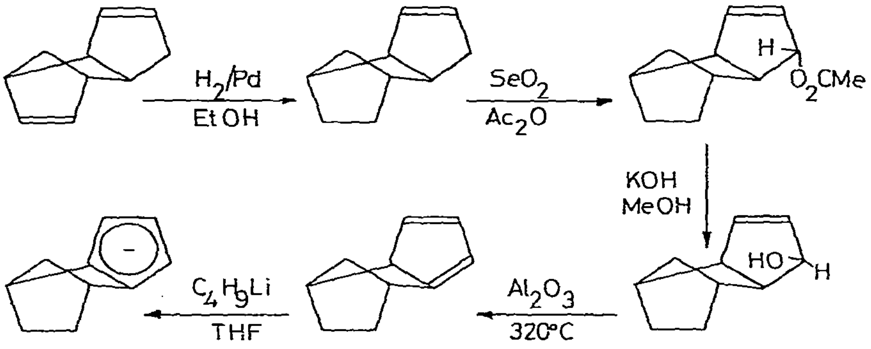
The industrial uses of many transition metal-dicyclopentadienyl complexes including cobaltocene have been reviewed [331]. Papers concerning heat capacities and transitions in solid state dicyclopentadienyl complexes given at the 1975 International Conference of Thermodyanmic Chemistry have appeared in an edited form [332]. In order to elucidate the nature of the change of metal—cyclopentadienyl bond dissociation energies in dicyclopentadienyl complexes of *3d* transition elements, the combustion enthalpies have been calculated for various metallocenes including cobaltocene [333]. These dissociation energies change with atomic number symbatically to the metal atomisation enthalpy. An NMR study on a substituted cobaltocene $[Co(\eta^5\text{-}C_5H_4{}^iPr)_2]$ at various temperatures has revealed an interesting anomaly. It appears that two forms of the molecule exist in which certain carbon atoms of the cyclopentadienyl rings may be close together or wider apart. The transition between the two is fast on the NMR time-scale at normal temperatures but can be deduced on the basis of ^1H NMR and ^{13}C NMR data at various lower temperatures [334]. This behaviour applies to other substituted cobaltocene complexes and more work on these systems is in progress. Magnetic susceptibility measurements on cobaltocene between 83 and 293 K suggest an appreciable orthorhombic splitting of the

$^2\Pi(\sigma^2\pi\delta^4)$ ground state [335]. A series of new mono- and di-alkylated metallocenes have been prepared by generally applicable synthetic routes as shown in Schemes 73 and 74 [336].



Synthesis of monoalkylcyclopentadiene

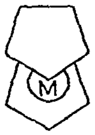
SCHEME 73



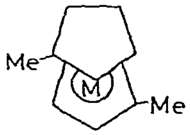
Synthesis of isodicyclopentadiene

SCHEME 74

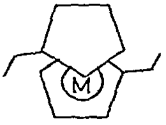
The complexes ML_2 thus formed are studied by ^1H and ^{13}C NMR leading to full assignment of the NMR parameters and hence a determination of their structures 398—402



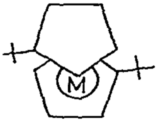
(398)



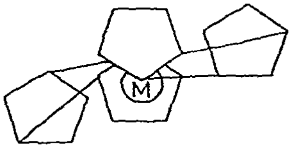
(399)



(400)

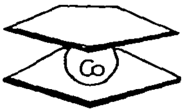


(401)
(M=Co)

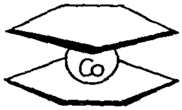


(402)

The molecular structure of cobaltocene $[Co(\eta^5\text{-}C_5H_5)_2]$ has been determined by gas phase electron diffraction. The best agreement between calculated and observed intensity curves is obtained with a model having eclipsed C_5H_5 rings (**403**), although the possibility of the staggered form **404** is not entirely rejected [337].

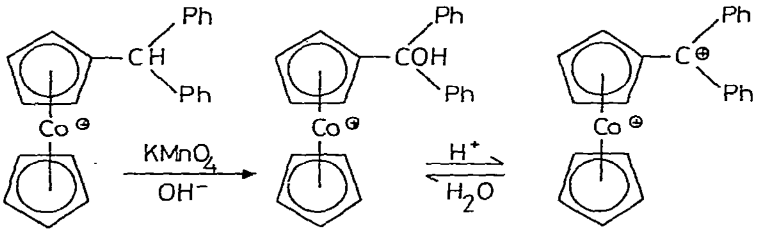


(403)



(404)

The high value obtained for the C—C vibrational amplitude confirms the presence of a dynamic Jahn—Teller effect of the magnitude calculated from ESR data. As an extension to the studies on ground and excited state properties of ferrocene a more general theoretical interpretation of these properties based on molecular orbital models has appeared, dealing with metallocenes of the other first-row transition elements [338]. The electronic properties and the variations in the bonding schemes within the series are rationalised. Because of the strongly electron-withdrawing inductive, field and resonance effects the cobalticinium group $[Co(\eta^5\text{-}C_5H_5)_2]^+$ greatly decreases the stability of carbonium ion in the α-position of a side-chain. The stability constant of $[(C_5H_5)Co^+C_5H_4\text{—}Ph_2C^+]$ has been determined spectrophotometrically in 80—96% sulphuric acid [339]. The carbonium ion **406** is produced by oxidation of benzhydrylcobalticinum hexafluorophosphate (**405**) followed by dissolution in sulphuric acid (Scheme 75).



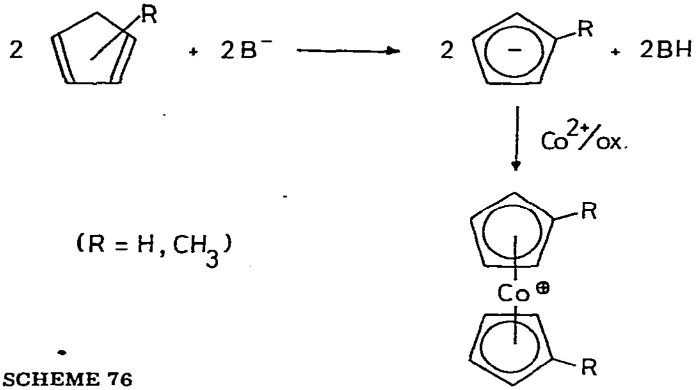
(405) **(406)**

SCHEME 75

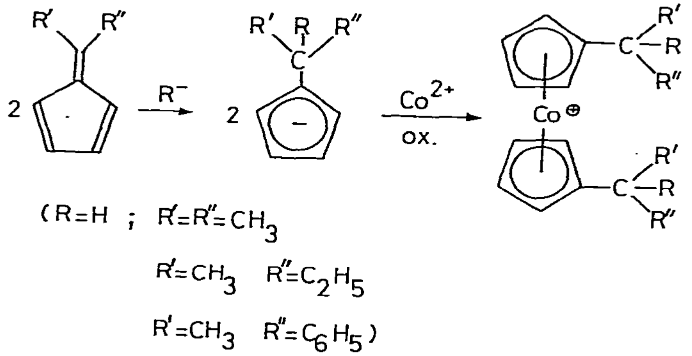
The relative stabilities for $R(C_6H_5)_2C^+$ are: cobalticinium, 1; H, 10^2; phenyl, 5×10^8; ferrocenyl, 10^{16}. NMR studies carried out on **406** in $ClSO_3H/D_2SO_4$ in which the ion is stable indefinitely indicate greater delocalisation of the positive charge onto the phenyl groups compared to that of $(C_6H_5)_2CH^+$ and $(C_6H_5)_3C^+$ and delocalisation to a much lesser extent onto the cobalticinium group. Unlike ferrocene, the cobalticinium cation $[Co(\eta^5\text{-}C_5H_5)_2]^+$ is chemically inactive towards electrophilic attack. Substituted cobalticinium salts are usually prepared indirectly from substituted cyclopentadienyl derivatives, which can be obtained by treating substituted cyclopentadienes with strong bases or by reducing fulvenes (Schemes 76 and 77).

Utilising the stability of these cobalticinium cations to electrophilic and oxidising agents a new series of reactions has been developed which uses known

reactions to produce new derivatives by transforming ring-substituted cobalticinium salts [340] (Schemes 78, 79 and 80).



SCHEME 76

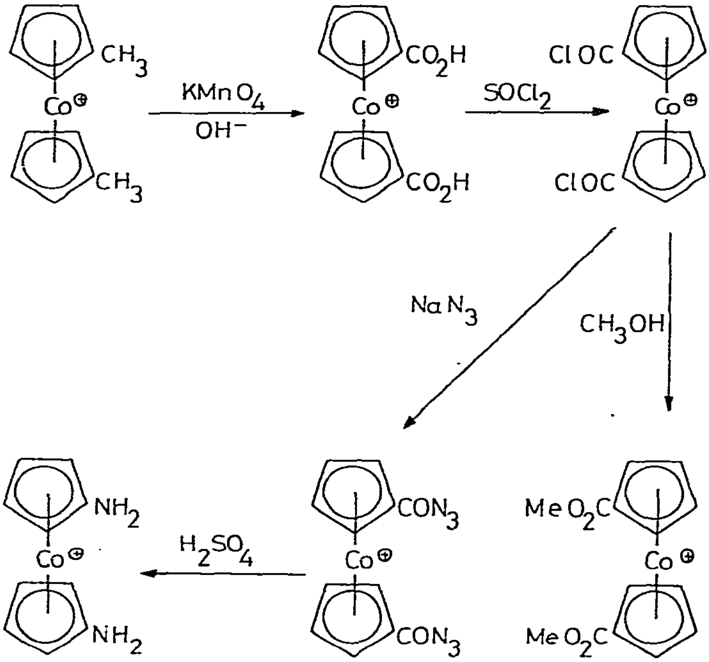


(R=H ; $R'=R''=CH_3$

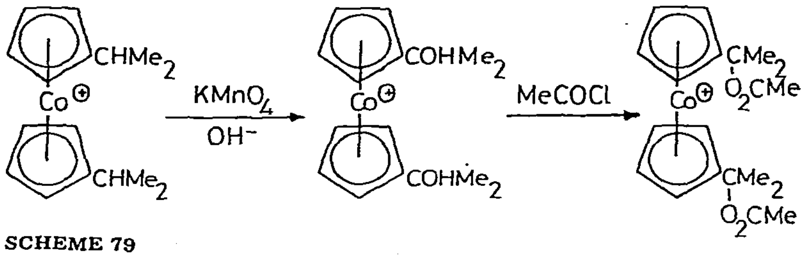
$R'=CH_3$ $R''=C_2H_5$

$R'=CH_3$ $R''=C_6H_5$)

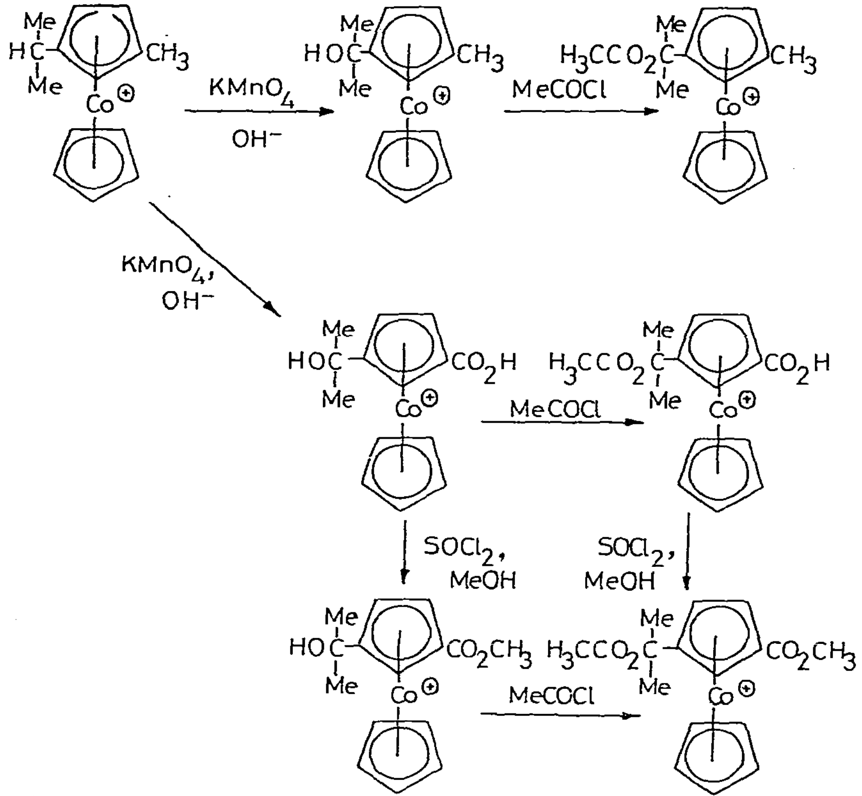
SCHEME 77



SCHEME 78

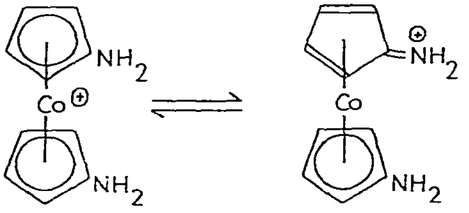


SCHEME 79



SCHEME 80

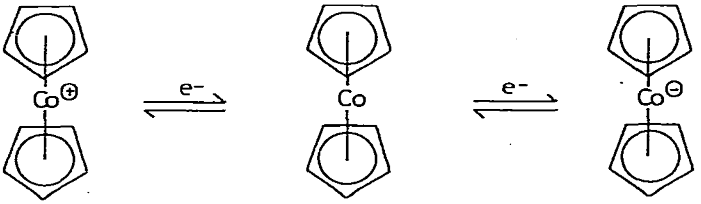
The UV, IR and NMR spectra and polarographic properties of these derivatives of cobalticinium have been studied and reveal some interesting results [341]. There is evidence that the higher p*K*a value for the diamino-derivative 407 is due to delocalisation onto one nitrogen atom (Scheme 81).



(407)

SCHEME 81

Using a dropping mercury electrode, a polarographic study on the unsubstituted salt shows two successive cathodic waves corresponding to formation firstly of cobaltocene and then reduction of cobaltocene to give a cobaltocene anion (Scheme 82).

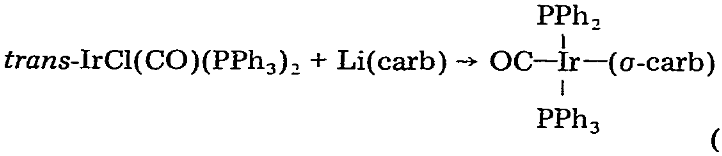


SCHEME 82

A study of the thermal stability of the cobalticinium ion in aqueous solution at pH values between 3 and 12.5 shows that the rate of decomposition increases with increasing concentration of undissociated $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2](\text{OH})$. The reaction order varies with pH, temperature and heating time [342]. At higher pH the temperature dependence of the first order dissociation constant conforms to the Arrhenius equation and gives a value of the activation energy of around 100 kJ mol^{-1}. In an attempt to study the tumour imaging properties of some new organometallic compounds as compared to the ones in present use, (notably ^{67}Ga citrate), various ^{57}Co labelled organometallic compounds were injected intravenously into mice which had previously been implanted with tumour tissue [343]. The retention characteristics of these ^{57}Co labelled complexes, including cobalticinium chloride, $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]\text{Cl}$, bis(indenyl)cobalt(III) chloride, $[\text{Co}(\pi\text{-C}_9\text{H}_7)_2]\text{Cl}$ and bis(fulvalene)dicobalt(III,III) chloride, $[\text{Co}_2(\pi\text{-C}_{10}\text{H}_8)_2]\text{Cl}_2$ were compared with those of ^{67}Ga citrate in various organs and tissue material at various times up to 48 hours after treatment. The results indicate that the agents in present use are equal to or better than the cobalt sandwich complexes, some of which have unexpectedly high toxicities, but that these cobalt metallocenes are in general rapidly cleared from most organs in the body. A complex having high tumour retention and low body retention together with low general toxicity is still being sought.

Metal—carbaborane and —borane complexes

A series of stable iridium(I) complexes of type 409 have been prepared by treating *trans*-$[\text{IrCl(CO)(PPh}_3)_2]$ with the appropriate lithium derivative of $\text{B}_{10}\text{C}_2\text{H}_{10}\text{R}^-$.



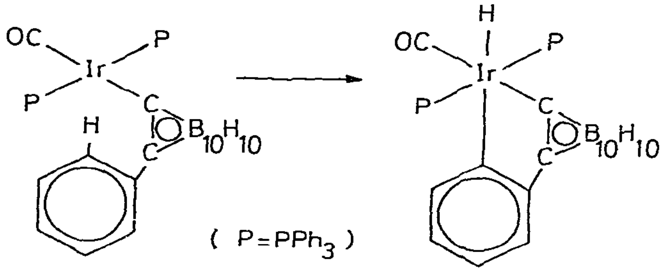
$$\textit{trans}\text{-IrCl(CO)(PPh}_3)_2 + \text{Li(carb)} \rightarrow \text{OC}-\overset{\text{PPh}_2}{\underset{\text{PPh}_3}{\text{Ir}}}-(\sigma\text{-carb})$$

(408)

Li(carb) = 1-Li-2-R-1,2-$\text{B}_{10}\text{C}_2\text{H}_{10}$ (R = H, Me)
= 1-Li-7-R-1,7-$\text{B}_{10}\text{C}_2\text{H}_{10}$ (R′ = H, Me, Ph)

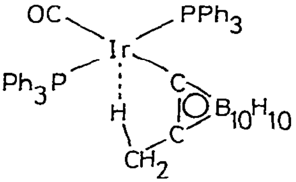
Complex 409 analogous to 408 can also be obtained by the reaction of *trans*-

[IrCl(CO)(PPh$_3$)$_2$] with 1-Li-2-Ph-1,2-B$_{10}$C$_2$H$_{10}$. However, in the course of purification or on standing **409** yields the iridium(III) hydride **410** formed via an



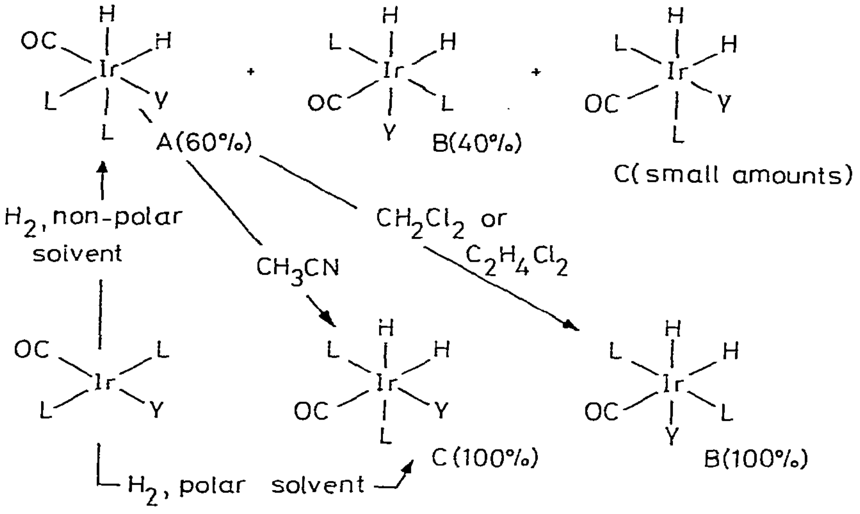
(409) **(410)**

intramolecular oxidative addition. Although no intramolecular oxidative addition reaction is observed to take place with the methyl derivative **411** the low ν(CO)



(411)

value (1950 cm^{-1}) found for this complex has been explained in terms of an interaction between the methyl group and the iridium atom. The complexes **408** (R = Ph; R′ = Ph, Me) react rapidly with dihydrogen to give dihydrides of general formula [IrH$_2$(σ-carb)(CO)(PR′R$_2$)$_2$]. The stereochemical course of these oxidative addition reactions appears to be solvent dependent and three different isomeric adducts have been identified, (Scheme 83). The addition of dihydrogen

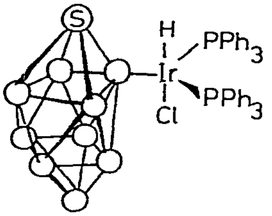


L = PPh$_3$, PMePh$_2$; Y = 2-H-1,2-B$_{10}$C$_2$H$_{10}^-$,
7-R-1,7-B$_{10}$C$_2$H$_{10}^-$ (R=H, Me, Ph)

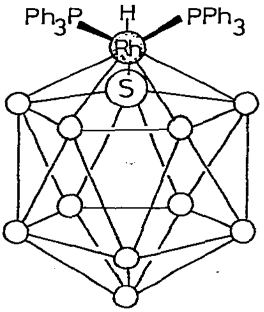
SCHEME 83

to complexes of the type *trans*-[IrCl(CO)$(PPh_3)_2$] is always stereospecifically *cis* and is unaffected by the nature of the solvent, a single isomer of configuration B being formed. Steric crowding effects resulting from the presence of the large carborane ligands are considered to be responsible for the formation of more than one isomer [344].

The oxidative addition of exopolyhedral B—H and B—Br bonds in carbaboranes and boranes to low-valent metal complexes are known to form carbaborane and borane complexes containing a metal—boron, two-centre, two-electron bond. Some *closo*-thiaboranes also oxidatively add to transition metal complexes and the reaction of [$IrClL_2$] (L = PPh_3, $AsPh_3$) with *closo*-1-SB_nH_n (n = 9 or 11) give high yields of the metallothiaboranes, [2-(L_2IrHCl)-1-SB_9H_8] and [2-{$(PPh_3)_2IrHCl$}-1-$SB_{11}H_{10}$]. The metallothiaboranes are considered to contain an exodeltahedral metal bonded to a single boron atom of the *closo* framework (412). Similar reactions of 6-Br-1-SB_9H_8 and the linked thiaborane 2,2′-$(SB_9H_8)_2$ appear to result in addition to the B—H bond but the products are less stable than 412 and they readily regenerate 6-Br-1-SB_9H_8 or 2,2′-$(SB_9H_8)_2$ respectively. The rhodium thiaborane complex 413 can be obtained from the reaction of [$RhCl(PPh_3)_3$] and $SB_{10}H_{11}^-$ and has been shown to function as a homogeneous alkene isomerisation and hydrogenation catalyst [345]. Some *nido*- or *arachno*-carbaborane anions containing bridging hydrides also oxidatively add to rhodium(I) or iridium(I) complexes to give ten- and eleven-vertex hydridometallocarbaboranes. Thus [$RhCl(PPh_3)_3$] and $NaC_2B_7H_{12}$ give the compound 414 (L = PPh_3). Due to extensive dissociation of triphenylphosphine no rhodium hydride resonance can be observed in the ^1H NMR spectrum. However, the less labile compound (414, L = (p-$MeC_6H_4)_3P$) does show the expected hydride resonance. The triphenylphosphine derivative again catalyses alkene isomerisation and hydrogenation. Similar treatment of [$IrCl(PPh_3)_3$] with $NaC_2B_8H_{11}$ gives the *closo*-complex 415 [346].

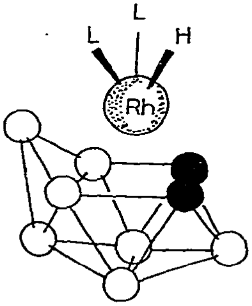


(412)

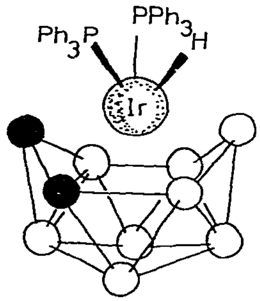


(413)

Investigations of thermal rearrangements in small polyhedral metallocarbaboranes have shown that reversible thermal migration of metal atoms can occur on the polyhedral surface. The two isomers, red 1,8,5,6- and green 1,7,5,6-$(\eta^5$-$C_5H_5)_2Co_2C_2B_5H_7$ are known to undergo reversible thermal interconversion in the vapour phase at elevated temperatures and their crystal and molecular structures 416 and 417 have been determined. The structures give some support to the hypothesis that the thermal equilibrium between the two isomers at elevated temperature reflects opposing tendencies toward metal—metal bond formation and

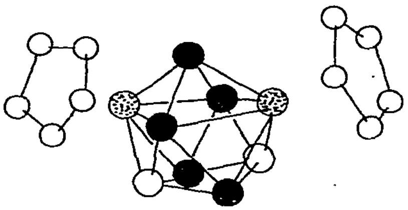


(414)



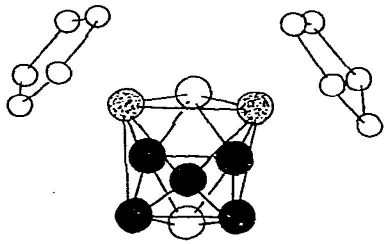
(415)

○ = BH
● = CH



(416)

▨ = Co
● = BH
○ = CH

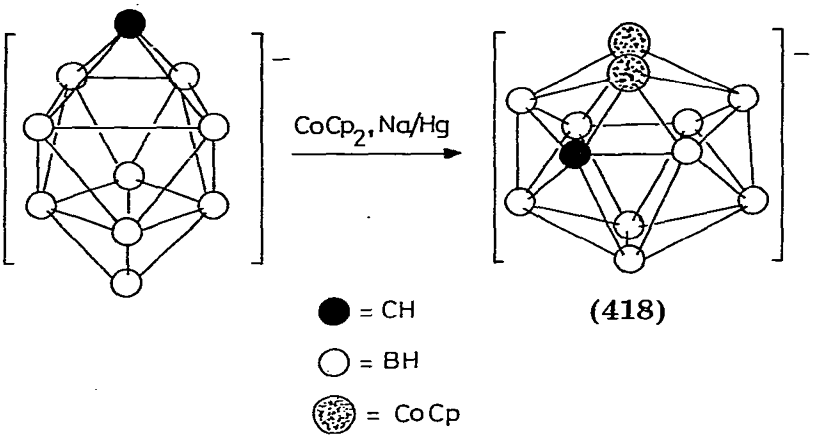


(417)

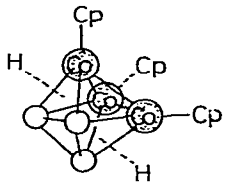
steric repulsion of the C_5H_5 rings in the 1,7,5,6 system [347].

The carborane, *closo*-1-$CB_9H_{10}^-$ does not react with cobaltocene in refluxing tetrahedrofuran. However, on addition of sodium amalgam a reaction occurs and the *closo* icosahedral bimetallic species **418** can be isolated.

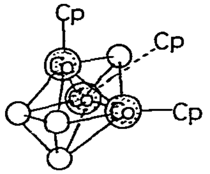
Since only one isomer of **418** is obtained a mechanism involving the opening of 1-$CB_9H_{10}^-$ to a decaborane(14)-like intermediate is probably involved [348]. The reaction of Na^+ $B_5H_8^-$ with excess cobalt(II) chloride and NaCp in tetrahydrofuran below −20°C is an exceedingly complex system yielding a large number of products. Two of the three compounds which can be isolated from this reaction (**419, 420** and **421**) are examples of the first types of cluster compounds to be isolated which contain as many metal as boron atoms. The isolation of these compounds provides evidence that the borane and the non-boron clusters are



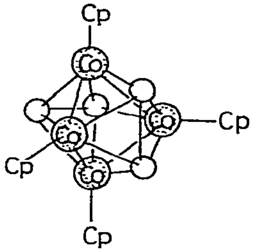
(418)



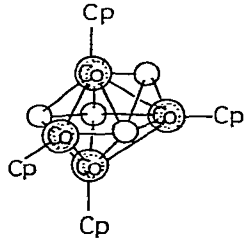
(419)



(420)



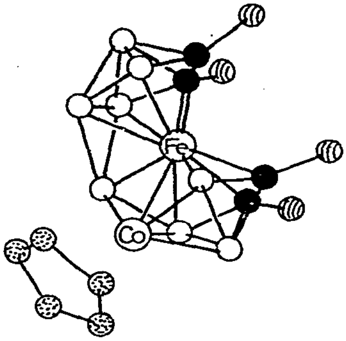
(421)



(422)

members of a single broad family. The structure **422** is a possible alternative structure for **421** [349].

The reaction of $[2,3\text{-Me}_2C_2B_4H_4]_2FeH_2$ with $[CoCp(CO)_2]$ gives an iron—cobalt metallocarborane $[Me_4C_4B_8FeCoCp]$ (**423**) the crystal structure of which has been determined by an X-ray study [350,351]. Some η-cyclopentadienylcobalt(III) complexes of 7-phosphaundecaboranes (**424**) have been obtained by the reaction of $7\text{-}B_{10}H_{11}PR^-$ with cobalt(II) chloride and cyclopentadiene in the presence of excess potassium hydroxide in anhydrous ethanol. The unsubstituted complex anion $[CpCo(\eta\text{-}7\text{-}B_{10}H_{10}P)]^-$ can also be obtained and alkylation of this anion gives the *P*-methyl, -ethyl and -propyl complexes [352]. The reaction of Na-$(Me_2C_2B_4H_5)$ with cobalt(II) chloride gives the cobalt(III) hydride [(C,C′-



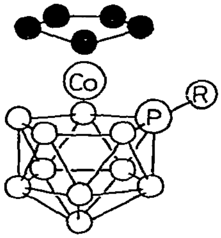
(423)

◍ = CH_3

○ = BH

▨ = CH

● = C



● = CH

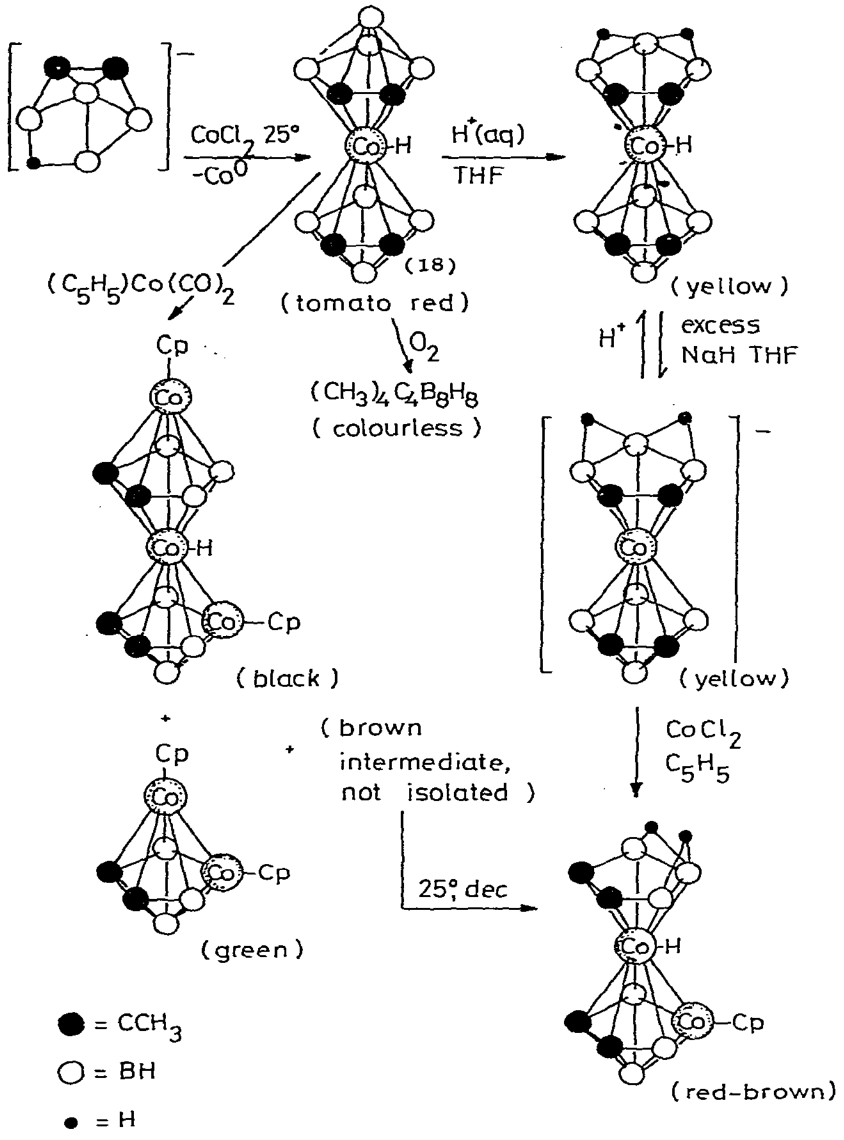
○ = BH

R = Me, Et, ^{n}Pr, Ph

(424)

$Me_2C_2B_4H_4)_2CoH]$ (425). Some reactions of this complex are illustrated in Scheme 84 [353].

Substitution of a hydrogen atom in a cyclopentadienyl ring of $[(\eta\text{-}CpCo)_2\text{-}\eta\text{-}(3,6)1,2\text{-}B_8C_2H_{10}]$ occurs on the reaction of this complex with butyllithium and phenyllithium. The products are $[3\text{-}(\eta\text{-}CpCo)\text{-}6\text{-}(\eta\text{-}RC_5H_4Co)\text{-}\eta\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10}]$ (R = Bu or Ph) [354]. Nitration of $[CpCoB_9H_9C_2HPh]$ gives $[CpCoB_9H_9C_2HC_6H_4NO_2\text{-}p]$ and $[CpCoB_9H_8(ONO_2)C_2HC_6H_4NO_2\text{-}p]$, no *ortho-* or *meta*-isomers being obtained. These nitro derivatives can be reduced to the corresponding amine compounds. Nitration of $[PhC_5H_4CoB_9H_9C_2H_2]$ gives $[p\text{-}NO_2C_6H_4C_5H_4CoB_9H_9C_2H_2]$ and $[p\text{-}NO_2C_6H_4CoB_9H_8(ONO_2)C_2H_2]$. Reduction of the compound $[CpCoB_9H_8(ONO_2)C_2H_2]$, obtained by nitration of $[CpCoB_9H_9C_2H_2]$, gives $[CpCoB_9H_8(OH)C_2H_2]$ [355]. Examination of the electronic structure of the triple-decked metallocarborane complexes 1,7,2,3- and 1,7,2,4-$Cp_2Co_2C_2B_3H_5$ by ^{11}B and ^1H pulse Fourier transform nuclear magnetic resonance spectroscopy of a series of derivatives containing substituents on the central $C_2B_3H_5^{4-}$ or Cp rings suggest that the 1,7,2,4-complex contains a highly electron-delocalised, metallocene-like central ring, while the 1,7,2,3-system is dominated by strong local π-interactions between the metals and an ethylenic C—C bond in the central ring [356].



SCHEME 84

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