COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1975

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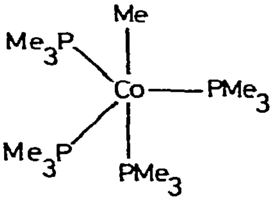
CONTENTS

Metal-carbon σ-bonded complexes and metal carbene complexes.

Treatment of chlorotris(trimethylphosphine)cobalt(I) with methyllithium in the presence of trimethylphosphine produces the strong reducing agent $[CoMe(PMe_3)_4]$, (1). The cobalt-carbon bond of this complex is cleaved by protic acids, e.g.

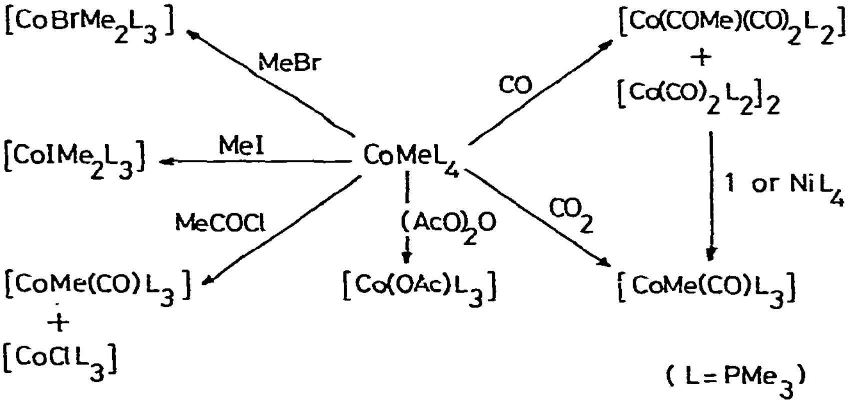
Cobalt, rhodium and iridium, Annual Survey covering the year 1974 see J. Organometal. Chem., Vol. 115(1976)326-415.

phenylacetylene or alcohols, ROH, with liberation of methane. The cobalt complexes produced are an acetylide, $[Co(C{\equiv}CPh)(PMe_3)_4]$ or polymers of the formula $[Co(OR)_2]$, (R = Me,Et,SiMe$_3$,Ph). The temperature dependence of the ^1H n.m.r. spectrum of (1) reveals a fluxional behaviour similar to that of the isosteric



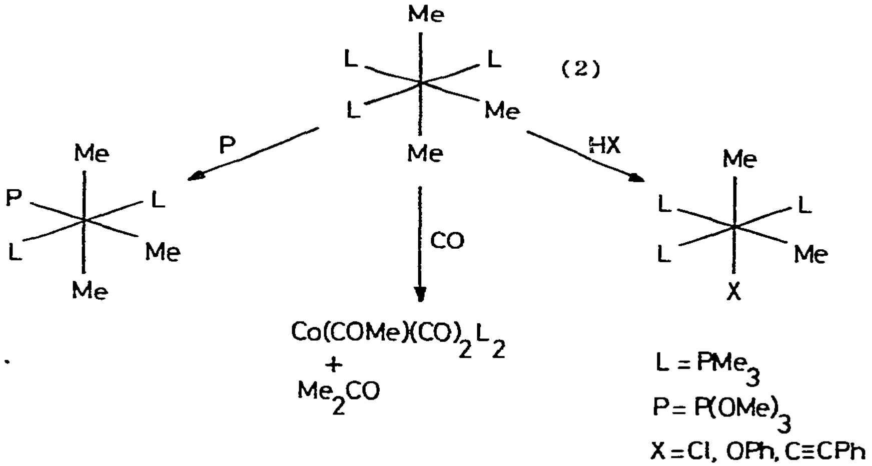
(1)

species $[NiMeL_4]^+$. The complex (1) undergoes a variety of reactions with carbon monoxide, carbon dioxide, acetyl chloride, acetic anhydride and MeX. (X = Br,I), which are summarised in Scheme (1)^1.



Scheme (1)

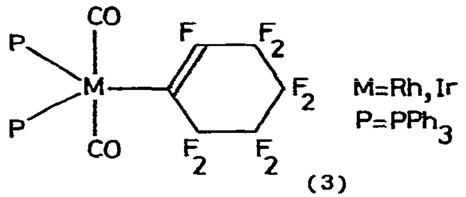
Treatment of tris(acetylacetonato)cobalt(III) with methyllithium in the presence of trimethylphosphine gives the octahedral cobalt(III) complex mer-[$CoMe_3(PMe_3)_3$], (2). Reactions of (2) with protonic acids result in the elimination of the methyl ligand trans- to methyl and trimethylphosphite selectively displaces the trimethylphosphine ligand opposite to the Co-Me group. The reactions of the complex are summarised in Scheme (2)[2].



Scheme (2)

Alkylation of [$Co(acac)_3$] with either trimethylaluminium or dimethylaluminium ethoxide in the presence of triphenylphosphine gives the cobalt(I) alkyls, [$CoMe(PPh_3)_2$] and [$CoMe(PPh_3)_3$]. However, with diethylaluminium ethoxide an intermediate acetylacetonato complex is formed which appears to be the ethylene complex, [$Co(acac)(C_2H_4)(PPh_3)_2$] rather than an ethyl(acetylacetonato)cobalt complex.[3] Although mer-[$RhCl_3(PMe_2Ph)_3$] is not alkylated by $2\text{-}MeOC_6H_4SnMe_3$, a reaction does occur with mer-[$RhCl_2(OSO_2F)(PMe_2Ph)_3$] to give mer-[$RhCl_2(C_6H_4OMe\text{-}o)(PMe_2Ph)_3$], the reaction presumably being facilitated by the presence of the good leaving group, SO_3F. Interestingly it has been reported that Grignard or organolithium reagents do not give identifiable products with rhodium(III) complexes.[4]

Perfluorocyclohexene and perfluorocyclobutene react with the anions $[M(CO)_2(PPh_3)_2]^-$, (M = Rh or Ir) at room temperature under an atmosphere of carbon monoxide to give the complexes (3) and (4) respectively. The yields of the rhodium complexes are considerably higher than those for the corresponding iridium complexes, in agreement with the higher nucleophilicity of the rhodium anion. The rhodium anion also reacts with chlorotrifluoroethylene to give (5) but under similar conditions the iridium anion gives no fluoro-organometallic compound and only $[IrH(CO)_2(PPh_3)_2]$ is isolated



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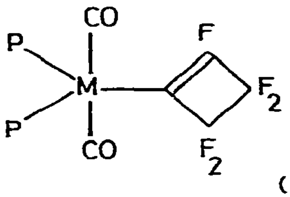

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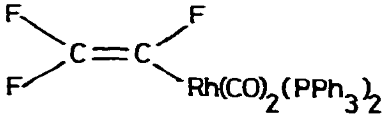
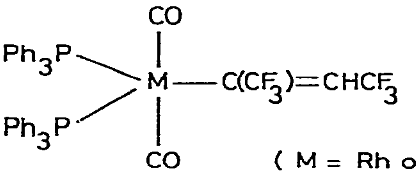


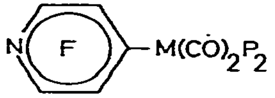
(5)

No perfluoroallenyl complexes containing the ligand system, $CF_2=C=C(CF_3)M$, are formed upon treating the anions with hexafluorobut-2-yne. Instead the alkenyl complexes (6) are formed in yields which range from 51% for the rhodium complex to 8% for the iridium complex. Although hexafluorobut-2-yne undergoes insertion reactions with the hydrides $[MH(CO)(PPh_3)_3]$, (M = Rh,Ir), no such insertion is observed with $[RhH(CO)_2(PPh_3)_2]$.[5] Reactions of the anions $[M(CO)_2(PPh_3)_2]^-$, (M = Co,Rh or Ir) with various perfluoroaromatic compounds have yielded the complexes (7) - (11). Attempts to obtain disubstituted metal species indicate that replacement of fluorine by a transition metal-containing group greatly deactivates an aromatic ring to nucleophilic attack.[6]



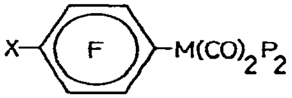
(6)

(M = Rh or Ir)



(7)

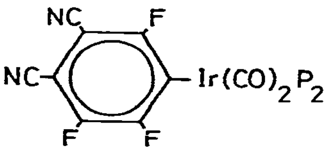
M = Co.Ir



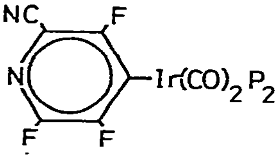
(8)

M = Co.Ir X = CN

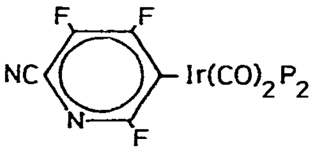
M = Ir X = COCEt



(9) (P = PPh$_3$)



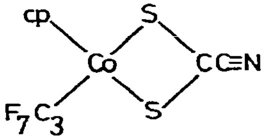
(10) (P = PPh$_3$)



(11) (P = PPh$_3$)

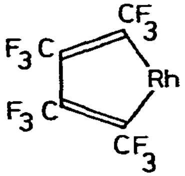
The pentafluorophenyl group reduces the ability of the four co-ordinate-complex, trans-$[Ir(C_6F_5)(CO)(PPh_3)_2]$ to undergo oxidative addition reactions. However, a crystal structure study reveals that π-overlap between the iridium and pentafluorophenyl group does not occur and overlap of this type cannot reduce electron density of the metal.[7] The reduced reactivity of the complex may be a consequence of steric effects.

Treatment of $[CocpI(C_3F_7)(CO)]$ with sodium cyanodithioformate results in displacement of carbon monoxide and iodide to give (12).[8]



(12)

Derivatives of the rhodacyclopentadiene system (13) catalyse the cyclotrimerisation of hexafluorobut-2-yne.

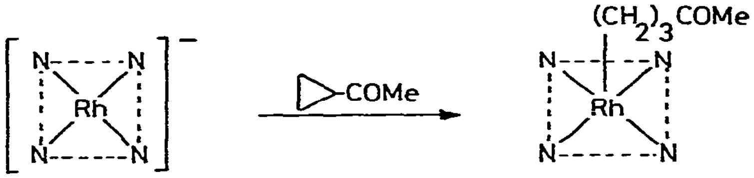


(13)

A step in the cyclotrimerisation process may involve the rhodacycle and a third molecule of the acetylene. However, definite evidence that $[RhCl(AsMe_3)_2C_4(CF_3)_4]$ can bind a molecule of hexafluorobut-2-yne is lacking.

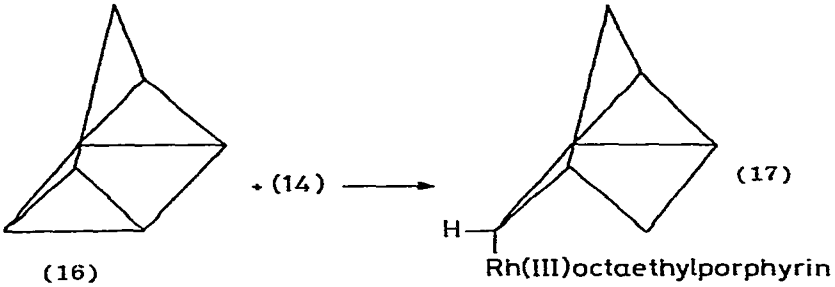
Nevertheless the five co-ordinate complexes $[RhClL_2C_4(CF_3)_4]$, (L = $AsMe_3$, $AsMe_2Ph$, $AsMe_2$p-$MeOC_6H_4$) readily react with neutral ligands to give six-co-ordinate complexes $[RhClL'L_2C_4(CF_3)_4]$, (L' = py, NH_3, MeCN, $PHPh_2$, $P(OMe)_3$, $AsMe_3$ or $P(OCH_2)_3(C_2H_5)$. The L' ligands in the complexes $[RhClL'L_2C_4(CF_3)_4]$, (L' = py, MeCN, $AsMe_3$ or H_2O) undergo exchange reactions in solution but static octahedral structures result at low temperature. The carbonyl complexes $[RhCl(CO)L_2C_4(CF_3)_4]$ react with silver salts to produce $[RhX(CO)L_2C_4(CF_3)_4]$, (X = $CF_3CO_2^-$, ClO_4^-) or $[RhXL_2C_4(CF_3)_4]$, (X = bidentate $CH_3CO_2^-$, p-$MeC_6H_4SO_3^-$). Reaction with [Tl(dike)] gives $[Rh(dike)L_2C_4(CF_3)_4]$, (dike = acetylacetonate or hexafluoroacetylacetonate). The ionic complexes $[RhL_2'L_2C_4(CF_3)_4]ClO_4$, (L' = MeCN, $P(OMe)_3$, L_2' = diars) can be prepared by addition of $AgClO_4$ to $[RhCl(CO)L_2C_4(CF_3)_4]$ followed by the ligand L'.[9]

Cyclopropane rings are usually cleaved by an acid-catalysed process or oxidative addition to transition metal complexes. It has now been found that nucleophilic attack of rhodium(I) octaethylporphyrin anion on some cyclopropyl derivatives leads to the cleavage of the cyclopropyl ring under mild conditions. Thus reaction of cyclopropyl-methyl ketone with (14) gives (15) in high yield. In contrast, cyclopropane and phenylcyclopropane are not cleaved under the same conditions suggesting that transformation through the π-complex to the σ-complex intermediate requires the presence of an electron-withdrawing group to stabilise the negatively charged site. The reaction of (14) with quadricyclane (16) results in cleavage of one cyclopropane ring to give the

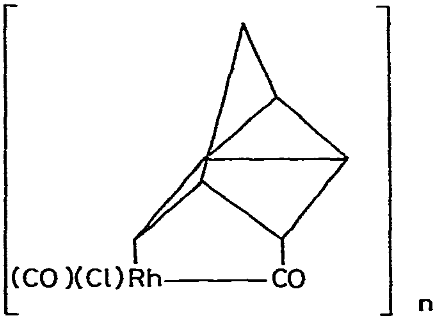


(14) (15)

nortricyclylrhodium complex (17).[10] $[RhCl(CO)_2]_2$ is also known to cleave only one cyclopropane ring of (16) to give (18) and the structure of (18) has now been confirmed.[11] However, some rhodium(I) complexes can catalyse the valence isomerization of (16) to norbornadiene.

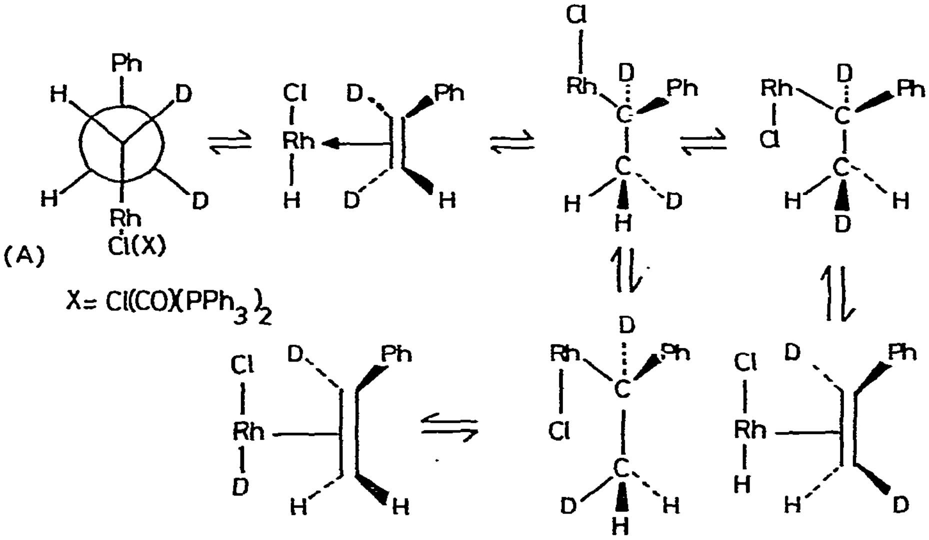


(16) (17)



(18)

Treatment of $[RhCl(PPh_3)_3]$ with threo-PhCHDCHDCOCl gives the acyl complex $[RhCl_2($threo$-COCHDCHDPh)(PPh_3)_2]$, which on heating in the presence of hexamethyldisiloxane to remove the liberated HCl(DCl) gives a mixture of deuterated styrenes. The styrene elimination is either non-stereospecific or it may involve a series of stereospecific reversible steps as outlined in Scheme (3). The postulated intermediate (A) was not detected but reaction of threo-PhCHDCHDCOCl with trans-$[IrClN_2(PPh_3)_2]$ gives an unstable threo-acyl complex which readily isomerises to $[IrCl_2(CHDCHDPh)(CO)PPh_3)_2]$. The alkyl-migration thus proceeds with retention of configuration of the alkyl group. Although these results do not unambiguously demonstrate that the decarbonylation and dehydrohalogenation of the phenylpropionyl rhodium complexes involve a cis-ß-elimination step the results are consistent with this process.[12]

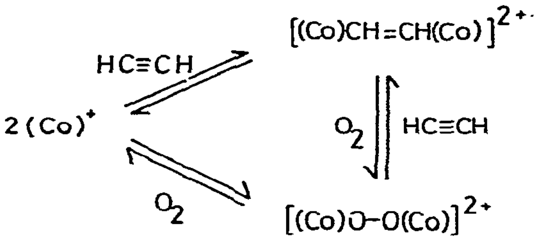


Scheme (3)

However, although the decarbonylation of erythro- and threo-2,3-diphenylbutyryl chloride with $[RhCl(PPh_3)_3]$

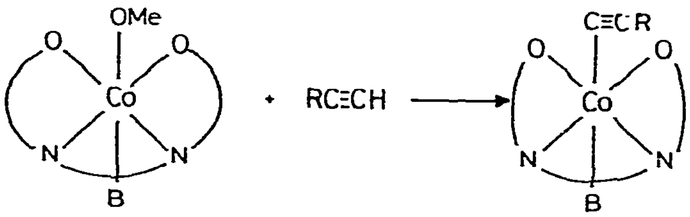
gave trans- and cis-β-methylstilbene, respectively, the β-elimination mechanism was rejected because an alkylrhodium intermediate (A), could not be detected.[13] However, on heating a toluene solution of $[RhCl_2(COCH_2CH_2Ph)(PPh_3)_2]$ a rhodium(III) carbonyl species can be observed in the i.r. spectrum consistent with the mechanism in Scheme (3).[12]

The strong nucleophiles $[Co^{I}(Chel)]^-$, (Chel = N,N'-ethylenebis(acetylacetoneiminato); N,N'-ethylenebis-(salicylideneiminato), (bae); N,N'-ethylenebis(7,7'-dimethylsalicylideneiminato), (salen) are known to readily react with acetylene in the presence of water to give vinylaquo derivatives. It has now been found that the complexes, $[Co^{III}(Chel)(OH)(H_2O)]$ react with acetylene and phenylacetylene in anhydrous ethanol to give the acetylides, $[Co(C{\equiv}CR)(Chel)(H_2O)]$ (R = H,Ph). These acetylides, unlike alkyl and aryl derivatives do not form five-co-ordinate complexes. The water ligand, however, is readily displaced by N-donor ligands, the stability of the six-co-ordinate adducts being associated with the lower trans-influence of the acetylide group.[14] Acetylene reacts with $[Co^{II}\{(DO)(DOH)pn\}(H_2O)]PF_6$, ({(DO)(DOH)pn} = diacetylmonoximeiminodiacetylmonoximatoiminopropane), to give a binuclear complex analogous to that obtained with $[Co(CN)_5]^{3-}$ This reaction is reversible, Scheme (4). The salen and bae adducts, however, only give binuclear derivatives with oxygen gas.[14] Phenylacetylene and 4-methylphenylacetylene also react with [Co(salen)] and [Co(salpn)] derivatives (19)



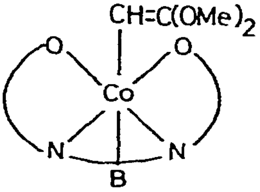
Scheme (4)

to give the acetylides, (20). With 3-butyn-2-one the expected alkynyl species was not obtained and the reactions gave the alkenyl complex, (21).[15]



(19)

(20)



(21)

Studies on the homolytic substitution reaction in Scheme (5) indicate that it involves effectively complete

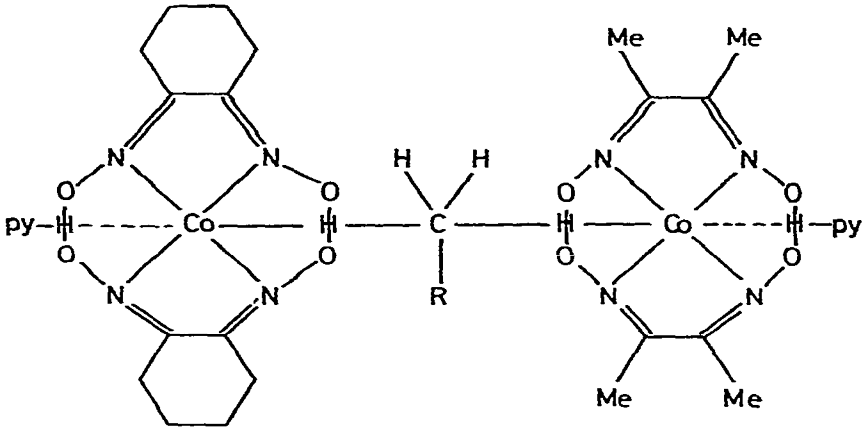
$$[Co(dmgH)_2py]+[RCo(chgH)_2py] \rightarrow [CoR(dmgH)_2py]+[Co(chgH)_2py]$$

(dmgH)= dimethylglyoximato

(chgH)= cyclohexanedionedioximato

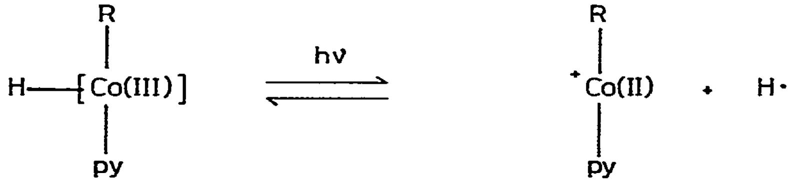
Scheme (5)

inversion of configuration of the saturated carbon centre through a highly restricted transition state, (22).[16]



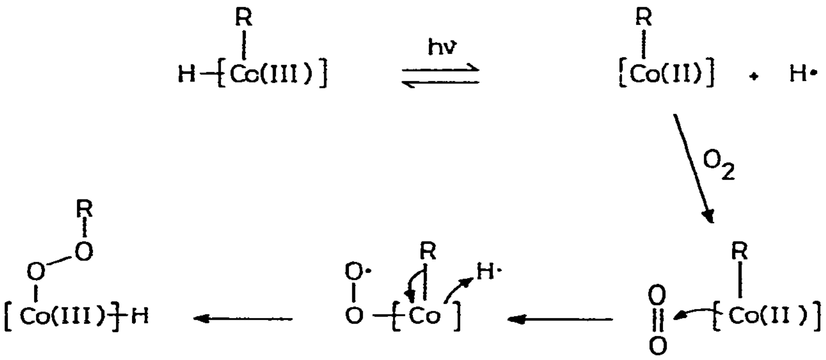
(22)

The anaerobic photolysis of methyl- and benzylpyridinecobaloximes and some analogous compounds proceeds via an electron transfer reaction to form a cobalt(II) complex containing both of the original axial ligands, and it has been suggested that the electron for this reduction comes either from the solvent or the equatorial ligands. Further studies have now shown that in chloroform or benzene hydrogen atoms are produced as intermediates and that they originate from the equatorial ligands of the complex, Scheme (6).[17] In studies of the photolysis of alkyl



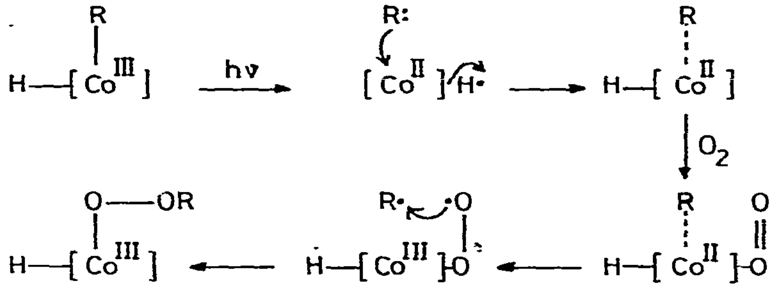
Scheme (6)

cobaloximes it has been noted that the presence of oxygen greatly increases the rate of cleavage of the Co–C bond and mechanisms for photo-induced insertion of oxygen in the Co–C bond have been proposed. In aprotic solvents and for the cobaloximes $[CoR(dmgH)_2py]$, (R = Me, benzyl, $-CH_2C_6H_4CN$-*p*) the mechanism in Scheme (7) operates.



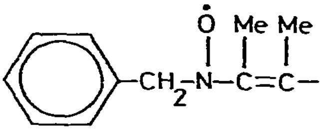
Scheme (7)

Whereas for the compounds R = Et, i-Pr, i-Bu, n-pentyl, cyclohexyl and some other derivatives in chloroform, benzene, isopropanol or water it is proposed that the first steps of the photo-induced insertion of oxygen is a homolytic cleavage of the Co-C bond, Scheme (8).



Scheme (8)

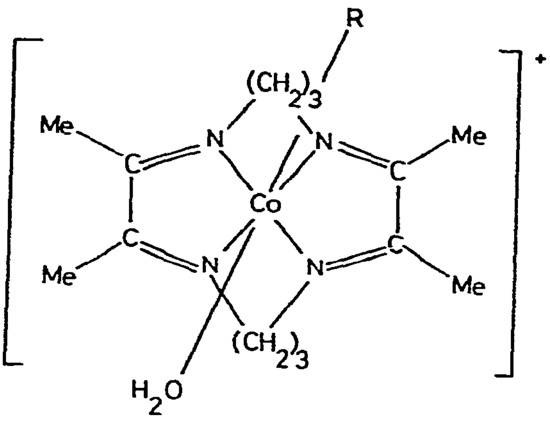
This mechanism also operates for the complexes in Scheme (7) when the reactions are carried out in isopropanol or water. Interestingly if after the anaerobic photolysis of the benzyl(pyridine)cobaloxime oxygen is introduced a nitroxide radical of the type (23) is produced via attack of a benzyl radical on the equatorial dimethyglyoxime ligand.[18]



(23)

Some studies on the cleavage of the organic group from the complexes (24) have also been reported. Anaerobic pyrolysis and photolysis of the alkyl complexes result in the formation of a cobalt(II) complex along with alkenes and alkanes.

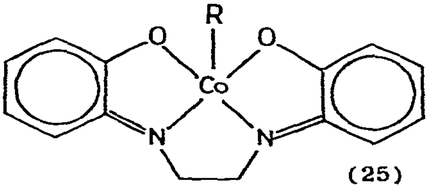
The complexes are stable for the several days in 6M HCl or $HClO_4$ but Co-C bond cleavage results in 3M HNO_3 at 25°C. Electrophiles such as iodine also cause Co-C bond cleavage,[19]



(24)

R=Me, Et, nPr, nBu or $PhCH_2$

as does the action of both iodine and iodine monochloride on the complexes (25) - (28).[20] In the mono-alkyl complexes



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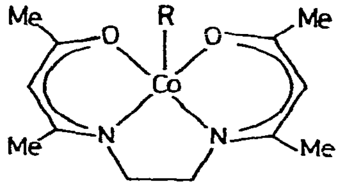

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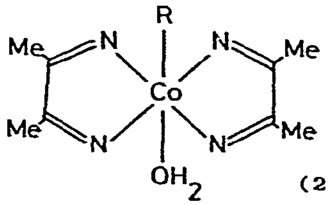

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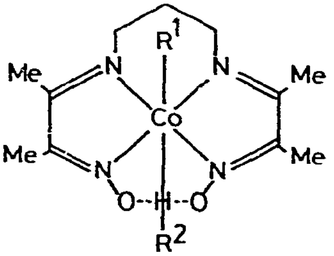
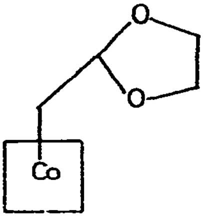


(28)

cleavage of the Co-C bond can occur either by an electrophilic or radical cleavage. However, in the bis-organo complexes (28) electrophilic cleavage always occurs. Interestingly, in the unsymmetrical phenylmethyl derivative of (28) cleavage occurs more readily at the alkyl carbon than at the aryl carbon although in the alkylarylmercury(II) compounds the reverse sequence is usually found.

It is known that 1,3-dioxa-2-cyclopentylmethyl- and 2,2-diethoxyethyl-cobalamins, (29) and (30) are hydrolysed by two different routes, direct cobalt-carbon bond fission, and decomposition to the aldehyde, (31), followed by cobalt-carbon bond fission. The corresponding cobaloxime acetals



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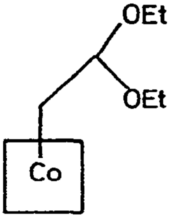

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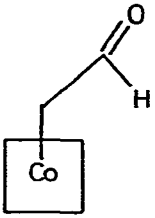


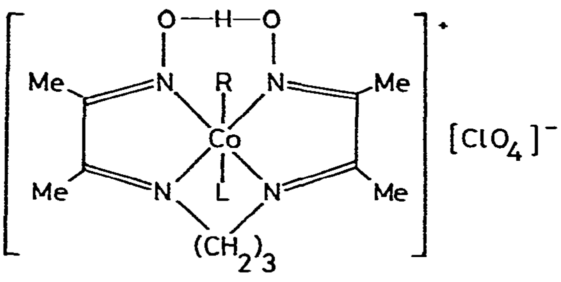
(31)

undergo analogous decomposition.[21] Studies on the oxidative cleavage of benzylaquobis(dimethylglyoximato)cobalt(III) have provided indirect evidence for transient organocobalt(IV) species. Such species have now been detected and characterised. Spectral titrations at -78^{o} have demonstrated the occurrence of the stoichiometric reaction:

$$[CoR(dmgH)_2H_2O] + Ce(IV) \rightarrow [CoR(dmgH)_2(H_2O)]^+ + Ce(III)$$

Solutions of the organocobalt(IV) species are stable for many hours. From cyclic voltammograms it can be deduced that the lifetimes of the $[CoR]^+$ radical cations decrease in the order $R = Me,Et > i\text{-}Pr$ and $p\text{-}NO_2C_6H_4CH_2 > PhCH_2 >> p\text{-}MeOC_6H_4CH_2$. This order is consistent with a decomposition mode involving nucleophilic attack on R.[22] Electro-oxidation of the organocobalt(III) and rhodium(III) chelates, $[CoR(dmgH)_2py]$, $(R = Me,Et,PhCH_2)$, $[CoR(salen)]$, $(R = Me,Et,n\text{-}Bu,i\text{-}Pr)$, $[CoPr^n(salen)py]$, and $[RhR(salen)py]$, $(R = Me,n\text{-}Pr,i\text{-}Pr)$ also show that fairly stable formally tetravalent species can be formed. Reactions with nucleophiles such as Cl^- or pyridine result in the heterolysis of the M^{IV}-C bond.[23]

Studies on Co^{III}-alkyl complexes have shown that these complexes are diamagnetic. Indeed ^{31}P n.m.r. spectra of the adducts $[CoR(dmgH)_2(PR'_3)]$ and (32) have been reported.[24] However, some six-co-ordinate Co^{III}-alkyl complexes, (33),

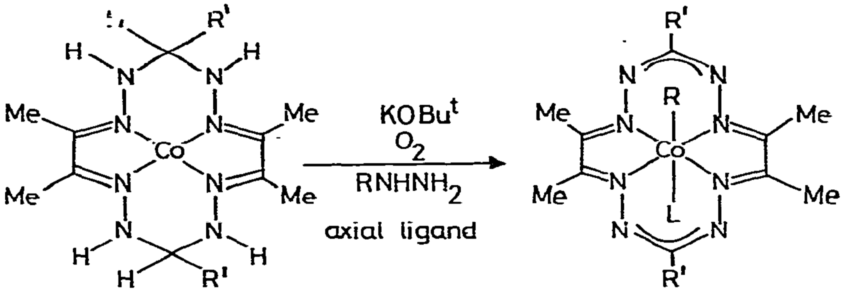


(32)

(R = Me L = PEt_3 PBu^n_3
R = Ph L = PBu^n_3)

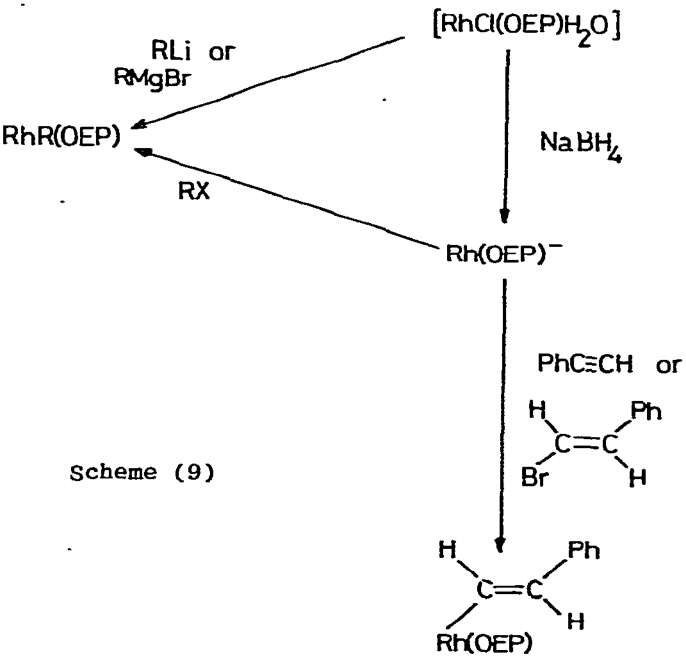
have been prepared which, although virtually diamagnetic, exhibit anomalous n.m.r. behaviour which can be attributed to paramagnetic shifts arising from a thermally populated state. The crystal structure of the complex, (R = Me, L = NH_2NHMe) has been determined.[25]

New rhodium(I) porphyrins, [porphyrin $Rh_2(CO)_4$] and [N-alkylporphyrin $Rh_2Cl_2(CO)_4$] have been isolated from the reaction of $[RhCl(CO)_2]_2$ with octaethylporphyrin and N-alkyloctaethylporphyrin. The reaction with octaethylporphyrin also yields $[RhCl(OEP)(H_2O)]H_2O$ which can be used as a precursor to organorhodium(III)-porphyrin complexes Scheme (9).[26]



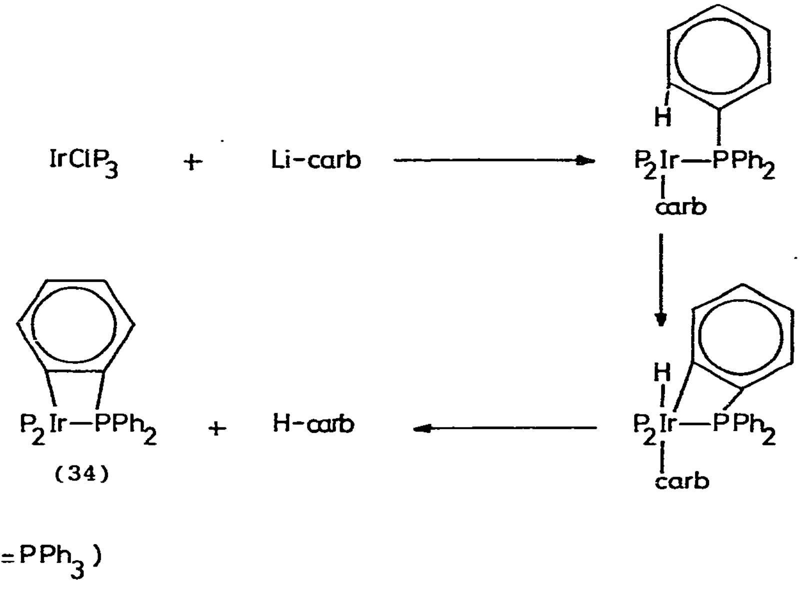
(33)

R = Me, Et, Ph
R = H, Me, Ph
L = py, CN$^-$, MeCN, MeNHNH$_2$



Scheme (9)

Although the reaction of lithium carborane with $[RhCl(PPh_3)_3]$ and trans-$[IrCl(CO)(PPh_3)_2]$ give metal-carbon σ-bonded complexes of the type $[Rh(\sigma\text{-carb})(PPh_3)_2]$ and $[Ir(\sigma\text{-carb})(CO)(PPh_3)_2]$ incorporating 1,2- and 1,7-diacarba-closo-dodecarborane ligands the reaction between $[IrCl(PPh_3)_3]$ and 1-Li-2-R-1,2-$B_{10}C_2H_{10}$, (R = Me,Ph) does not give iridium-carborane complexes. Instead the internally metallated complex (34) is formed probably via the mechanism outlined in Scheme (10).



(34)

(P=PPh$_3$)

Scheme (10)

The bulky carborane ligand probably forces the phenyl groups of the phosphine closer to the metal atom thus promoting the ortho-metallation reaction.[27] In contrast reactions with the corresponding rhodium complex produce three co-ordinate rhodium carbon bonded complexes, Scheme (11).

$$[\mathrm{RhClP_3}] \quad + \quad \text{Li-carb} \longrightarrow [\mathrm{Rh(\sigma\text{-}carb)P_2}] \quad (35)$$

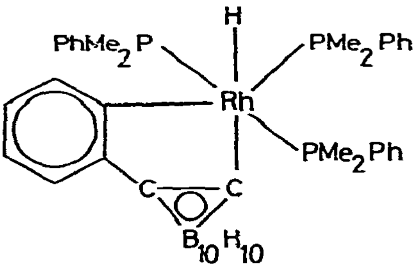
$$\text{Li-carb} = \text{1-Li-2-R-1,2-}\mathrm{B_{10}C_2H_{10}},$$

$$\text{1-Li-7-R-1,7-}\mathrm{B_{10}C_2H_{10}}$$

$$\mathrm{R = H, Me, Ph} \;;\; \mathrm{P = PPh_3}$$

Scheme (11)

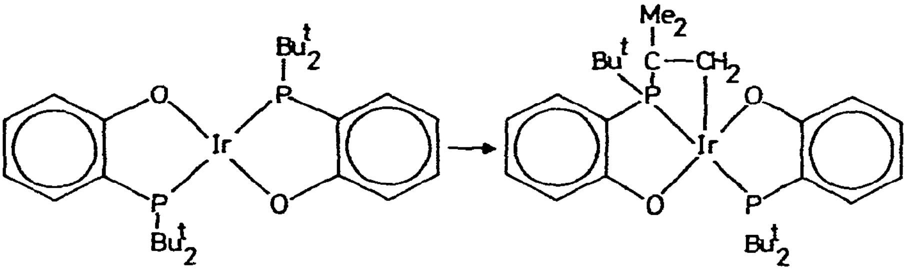
Treatment of the complexes (35) with dimethylphenylphosphine results in displacement of triphenylphosphine and now three molecules of the smaller phosphine co-ordinate to the rhodium to produce four co-ordinate complexes $[\mathrm{Rh(\sigma\text{-}carb)(PMe_2Ph)_3}]$ (σ-carb = 1,2-$\mathrm{B_{10}C_2H_{11}}$, 7-Ph-1,7-$\mathrm{B_{10}C_2H_{10}}$). The less sterically demanding triphenylphosphite similarly produces $[\mathrm{Rh(\sigma\text{-}carb)\{P(OPh)_3\}}]$, ($\sigma$-carb = 2-Me-1,2-$\mathrm{B_{10}C_2H_{10}}$). However, the reaction of $\mathrm{PMe_2Ph}$ with $[\mathrm{Rh(\sigma\text{-}carb)(PPh_3)_2}]$, ($\sigma$-carb = 2-Ph-1,2-$\mathrm{B_{10}C_2H_{10}}$) gives the phenyl metallated complex (36).



(36)

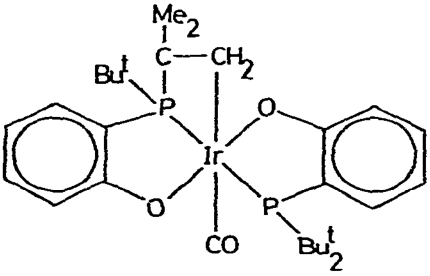
the bulky carborane ligand again promoting the metallation reaction.[23]

Metallation of a tertiary butyl group occurs when a solution of (37) in benzene is allowed to stand, and it is



(37) (38)

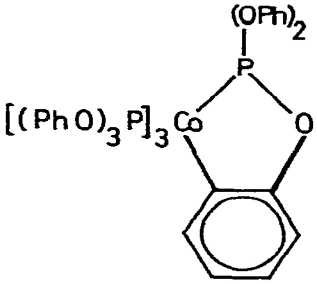
possible that this reaction proceeds via an oxygen complex of (37) before C-metallation of the Bu^t group occurs. The hydrogen is probably lost as H_2O or H_2O_2. Passage of carbon monoxide through a benzene solution of (37) produces (39).



(39)

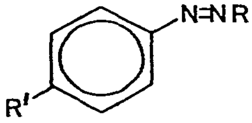
These complexes are the first examples where a Bu^t group has been internally metallated.[29]

Heating solutions of $[CoH\{P(OPh)_3\}_4]$ or reaction of triphenylphosphite with $[Co(C_8H_{13})(C_8H_{12})]$ produces the ortho-metallated compound (40). This compound catalyses the hydrogenation of but-1-ene and undergoes ligand hydrogen exchange with D_2.[30]



(40)

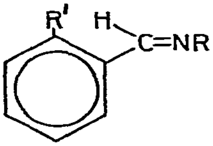
The reaction of the aromatic azo or imine compounds, (41) - (43) with trans-$[IrCl(CO)(PPh_3)_2]$ yields the ortho-metallated complexes, (44).



(41)

R' = H ; R = Ph
R' = Me ; R = p-MeC_6H_4

2-(Methylazo)propene, (45), gives (46).[31]

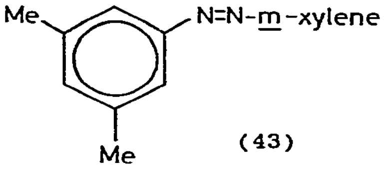


(42)

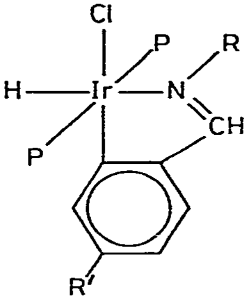
R' = H ; R = Me
R' = R = Me
R' = H ; R = Ph
R = Me ; R = p-MeC_6H_4

The crystal structure of the complex (44), (R = Ph, R' = H) has been determined,[32] and the proposed mechanism for this metallation is given in Scheme (12). Co-ordination of the

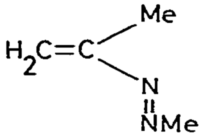
N-donor ligand to the iridium should increase the electron



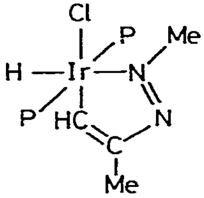
(43)



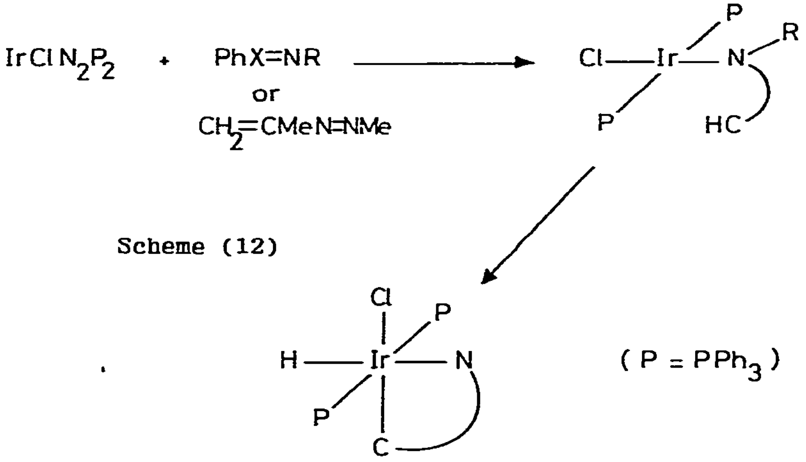
(44)



(45)

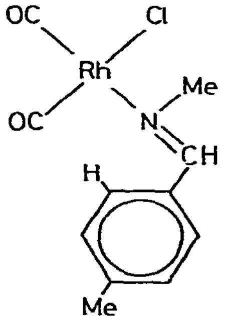


(46)



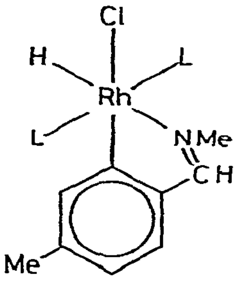
Scheme (12)

density at the metal and hence enhance the oxidative addition of the ortho or olefinic CH group to the metal atom. No observable C-H bond cleavage takes place with the aliphatic azo compounds and azomesitylene, the activation energy for cleavage of the aliphatic C-H bond probably being too high for metal insertion to occur.[31] That metal basicity is important in the C-H bond breaking reactions of Rh(I) and Ir(I) is provided by further studies on the reactions of azo and imine compounds. Thus treatment of p-tolylCH=NMe with $[RhCl(C_8H_{14})_2]_2$ in the presence of carbon monoxide gives (47), and the imino compound $PhCH=CH-CHNC_3H_7$ gives an



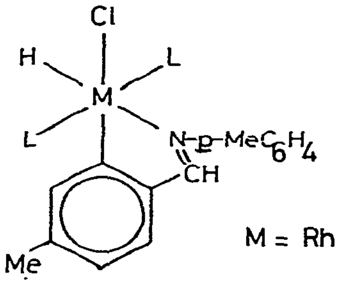
(47)

analogous compound. These compounds do not undergo cyclometallation reactions in refluxing benzene or petroleum spirit (b.p. 120°C) and no metallated products could be isolated from the reaction of olefinic azo or imino compounds with Rh(I) in the presence of PPh_3 or PCy_3. The low field n.m.r. shifts of the ortho CH groups in (47) indicate that they are situated above the bonding plane of the square planar molecule, but the metal atom is presumably not sufficiently nucleophilic to cause C-H bond cleavage. However, addition of the azo or imine compounds to $[MCl(C_8H_{14})_2]_2$, (M = Rh,Ir), followed by addition of tricyclohexylphosphine affords the cyclometallated complexes (48) and (49). Similarly



(48)

L = Pcy_3

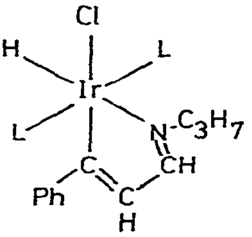


(49)

M = Rh, Ir

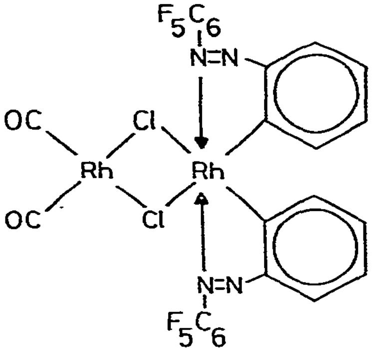
$PhCH=CH-CHNC_3H_7$ gives the iridium complex (50). From these

(50)



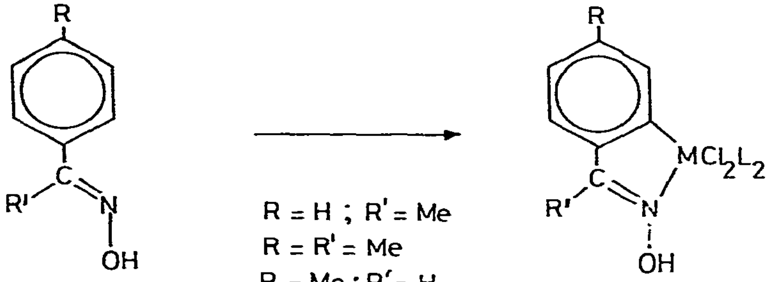
(L = Pcy_3 , PPh_3)

studies it emerges that the ease of C–H bond cleavage decreases in the order aromatic CH > olefinic CH > aliphatic CH and that the cleavage is dependent upon the basicity of the metal complex.[33] Treatment of pentafluoroazobenzene with $[RhCl(CO)_2]_2$ affords the complex (51), displacement of hydrogen taking precedence over displacement of fluorine.[34]

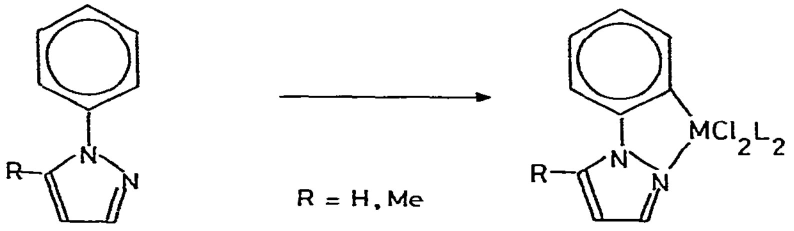


(51)

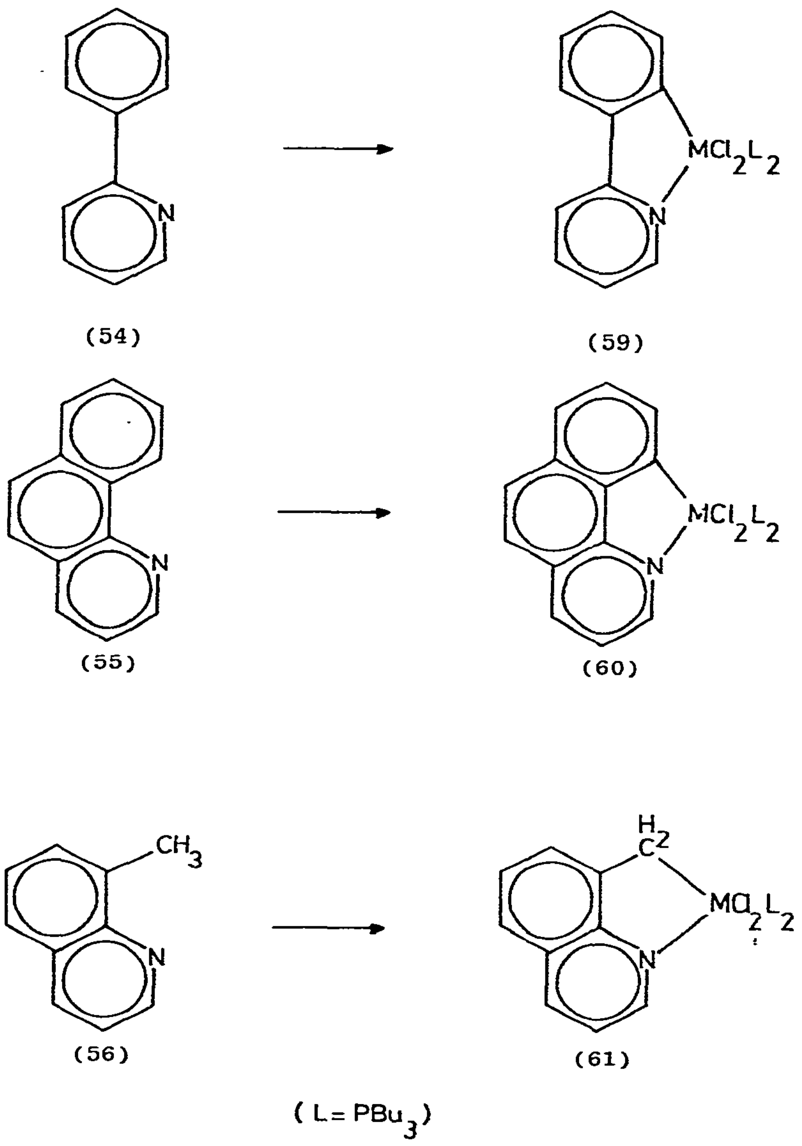
C-metallation with rhodium(III) complexes other than halides has received little attention. However, it has now been found that $[Rh_2X_6(PBu_3)_4]$, (X = Cl,Br) in refluxing xylene metallates a variety of organic nitrogen compounds (52) - (56) to afford the cyclometallated complexes (57) - (61)



(52) (57)



(53) (58)



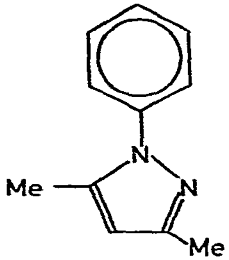
(54) → (59)

(55) → (60)

(56) → (61)

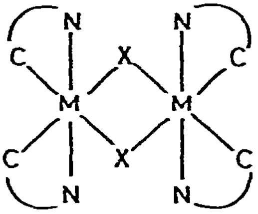
(L = PBu_3)

Metallation with rhodium(III) halides usually give bis-chelate type complexes, $[RhX(C\text{-}N)_2]_2$ and it is apparent that co-ordination of PBu_3 to rhodium(III) decreases the ability of rhodium(III) to metallate organic nitrogen compounds. Treatment of N,N-dimethylbenzylamine, N,N-dimethylallylamine and azobenzene with $[Rh_2X_6(PBu_3)_4]$ has only given impure products.[35,36] As expected N-phenylpyrazole, (53), (R = H) and (62) react with rhodium(III)



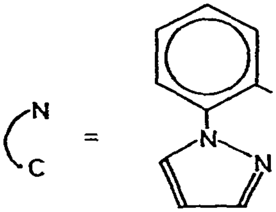
(62)

halides and $[Na_3IrCl_6]$ to give the complexes (63) and (64) which undergo typical halide bridge splitting reactions with PBu_3 and ethylenediamine.[37]

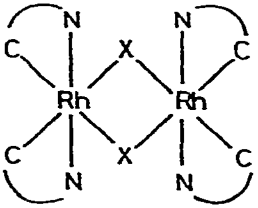


(63)

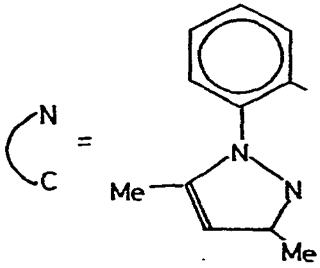
M=Rh,Ir



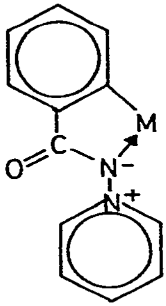
X=Cl,Br



(64)

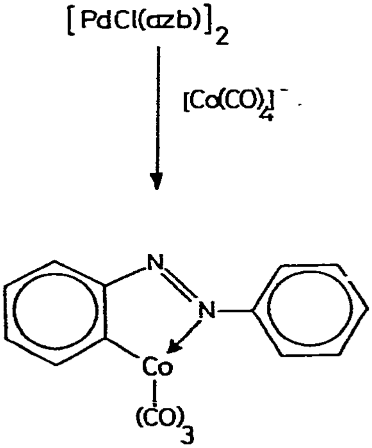


Full details have now appeared on the reactions of the resonance stabilised ylide $PhCO\overset{+}{N}\overset{-}{N}C_5H_5$ with rhodium(III) and iridium(III) salts.[38] These reactions yield cyclometallated products containing the formula unit (65) and were reported in the last Annual Survey.



(65)

Treatment of the ortho metallated azobenzene complex (66) with hexafluorobut-2-yne results in the insertion of a formally three-carbon unit [CO + C_4F_6] into the Co-C bond of (66) together with the quinoline-1-one (68).



(66)

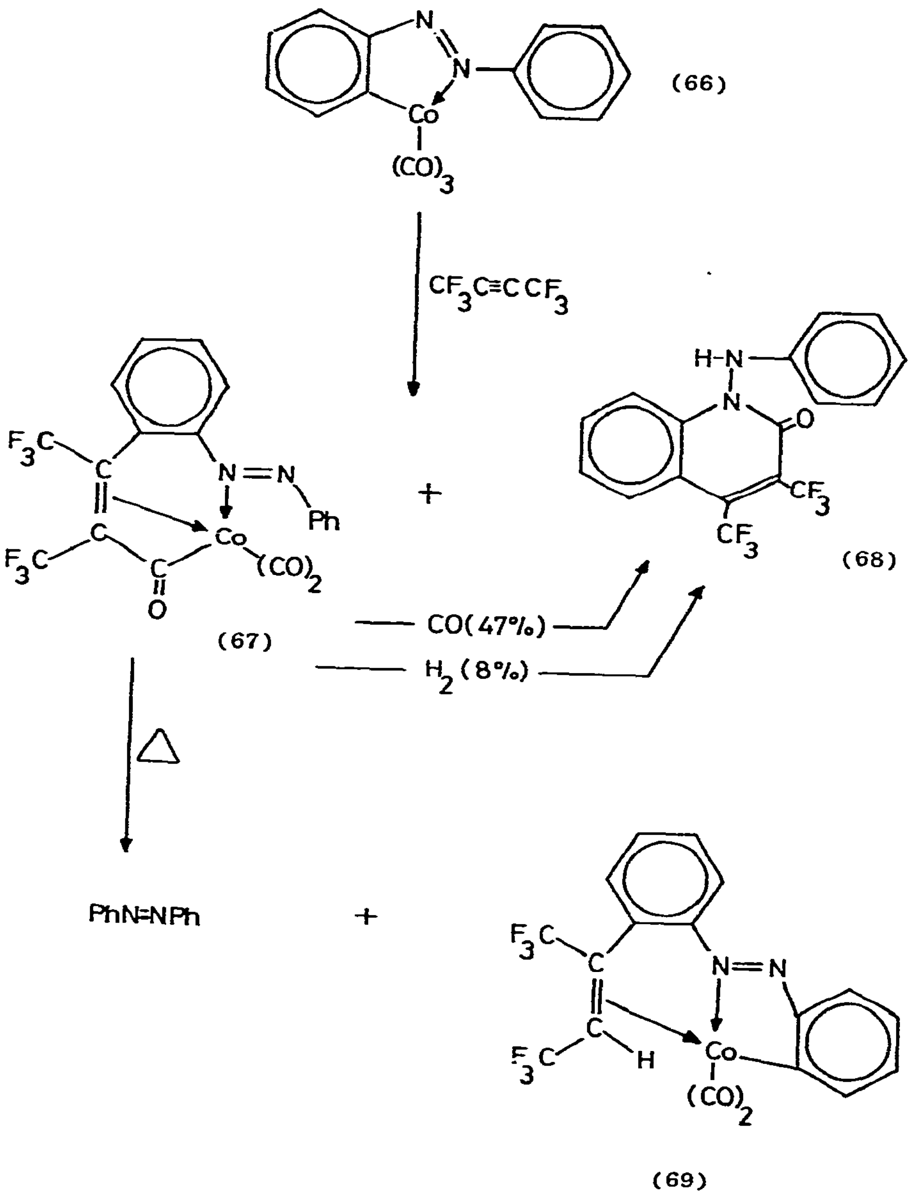
The complex (67) is an intermediate in the formation of

(68) and various substituted quinoline-2-ones have been prepared using this method. Other reactions of (67) have been studied and some of these are outlined in Scheme (13). A common feature of the reactions of (67) is the ready formation of azobenzene. Pyrolysis of (67) results in the formation of (69) which contains a novel type of tridentate chelating organometallic ligand, formed by ortho-metallation of the second, unsubstituted, ring of the azobenzene part of the ligand.[39]

The crystal structure of bis(ortho-metallated)tris-(triphenylphosphine)iridium(III) hydride has been determined[40] and the ^{13}C n.m.r. spectra of several ortho metallated complexes have been measured.[41] From an ion cyclotron resonance study on the reactions of methyl iodide with $[Co(NO)(CO)_3]$, limits on the gas phase cobalt-carbon bond strength have been inferred.[42]

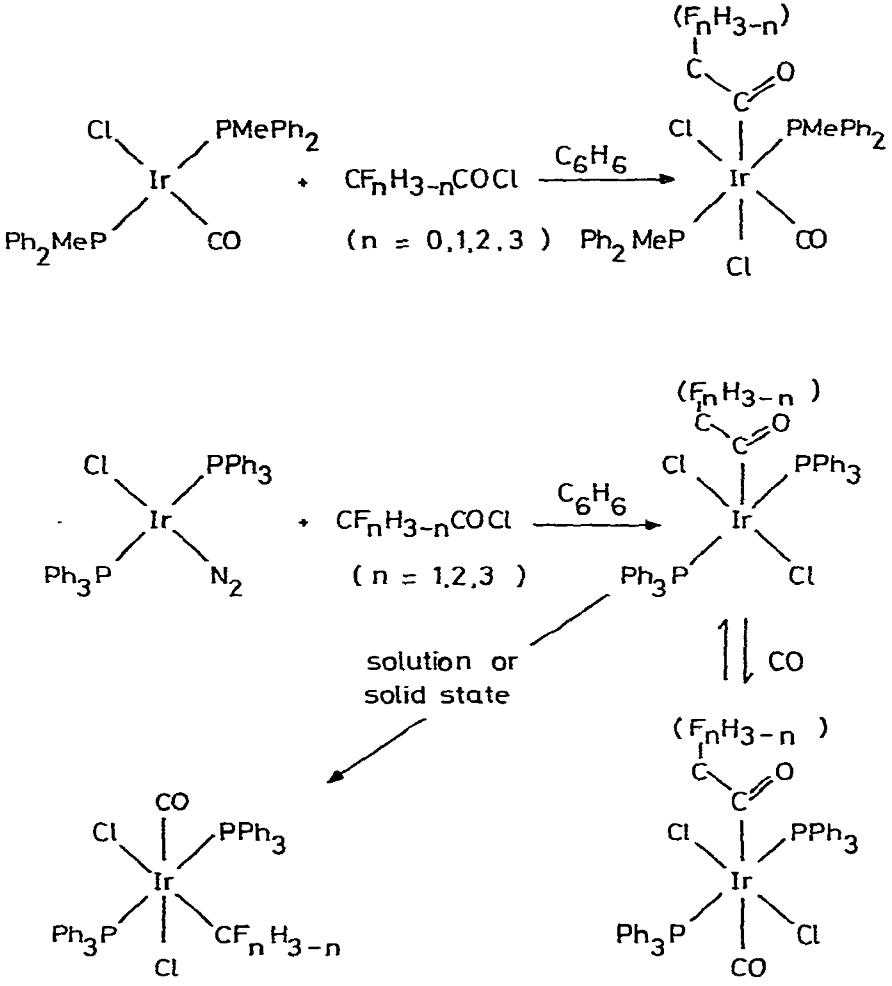
Oxidative addition of methyl iodide to $[Rh(CN)_4]^{3-}$ is known to yield $[RhIMe(CN)_4]^{3-}$ and a similar reaction has been observed with $PhCH_2Cl$. Other alkyl halides also oxidatively add and the rate of addition decreases in the order MeI >> EtI > PrI, a trend reflecting the effect of increasing steric influence. However, the reactions with EtI and ^{n}PrI give $[RhI(OH)(CN)_4]^{3-}$ and not the expected alkyls.[43]

Some five and six-co-ordinate acyl complexes $[IrCl_2(COCF_nH_{3-n})(PPh_3)_2]$, (n = 1,2) and $[IrCl_2(COCF_nH_{3-n})(CO)(PMePh_2)_2]$, (n = 1,2,3) have been obtained


N
N
Co
(CO)3
(66)
CF3C≡CCF3
F3C
C
C
F3C
C
O
N=N
Ph
Co
(CO)2
(67)
+
H-N
N
O
CF3
CF3
(68)
CO(47%)
H2(8%)
△
PhN=NPh
+
F3C
C
C
F3C
H
N=N
Co
(CO)2
(69)

Scheme (13)

by oxidative addition of acyl halides to iridium(I) complexes Scheme (14).



Scheme (14)

The trans-influence of the acetyl groups decreases with increasing fluorine substitution and the trans-influence of the substituted methyl groups decreases in the order Me > CHF_2 = CH_2F > CF_3. The five co-ordinate acyl complexes undergo an alkyl group migration when refluxed in benzene or when heated in the solid state. Interestingly the temperature at which the migration occurs in the solid state is sensitive to the presence of solvent in the lattice. The rate of migration decreases in the order CFH_2 > CF_3 > CF_2H and the enthalpy change for the migration becomes less exothermic in the order CF_3 > CF_2H > CFH_2. The insertion of carbon monoxide into a metal fluorocarbon bond has never been achieved and the present data indicate that the reaction would be very slow.[44]

Under high pressure, ethylene reacts with $[IrH(CO)_3(PPr^i_3)]$ to give $[Ir(C_2H_5)(CO)_3(PPr^i_3)]$ which on subsequent reaction with carbon monoxide gives the acyl $[Ir(COC_2H_5)(CO)_3(PPr^i_3)]$. Treatment of the acyl with a pressure of hydrogen gas regenerates the hydride, $[IrH(CO)_3(PPr^i_3)]$ and propionaldehyde is formed. These reactions are key steps in the hydroformylation reaction and only mononuclear species are observed throughout these reactions. During this spectroscopic study two additional carbonyl frequencies were observed after the initial formation of the alkyliridium tricarbonyl. These appear to be due to a dicarbonyl species. Possible reactions explaining this behaviour are indicated in Scheme (15)[45].

$$Ir(C_2H_5)(CO)_3L + C_2H_4 \rightleftharpoons Ir(C_2H_5)(C_2H_4)(CO)_2L + CO$$

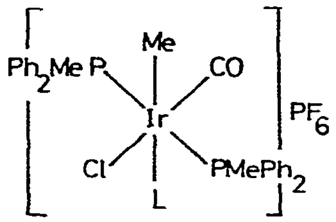
$$Ir(C_2H_5)(CO)_3L \rightleftharpoons IrH(C_2H_4)(CO)_2L + CO$$

Scheme (15)

The formation of isomeric aldehydes in the hydroformylation reaction has been suggested to occur via the disproportionation of the acylcobalt carbonyl species into alkene and aldehyde, a reaction known to occur at room temperature. However, under hydroformylation conditions acylcobalt carbonyls do not isomerize and this reaction cannot be responsible for the formation of isomeric aldehydes in the hydroformylation of alkenes.[46]

Some acylrhodium(III) complexes $[Rh(COMe)Br(PMe_2Ph)_2]_2[PF_6]_2$ result on treatment of $[RhBr_2Me(CO)(PMe_2Ph)_2]$ with $AgPF_6$. Reactions of the cationic complex with bipyridyl and $Ph_2PCH_2CH_2PPh_2$ (diphos) give $[Rh(COMe)Br(bipy)(PMe_2Ph)_2]PF_6$ and $[Rh(COMe)Br(diphos)(PMe_2Ph)]_2[PF_6]_2$ respectively, the bulky diphos ligand probably causing the loss of a PMe_2Ph ligand.[47]

In contrast to $[RhBr_2Me(CO)(PMe_2Ph)_2]$, treatment of $[IrClIMe(CO)(PMePh_2)_2]$ with $AgPF_6$ in a polar solvent such as acetone or methanol followed by addition of a neutral ligand L affords a variety of cationic iridium(III) methyl complexes, (70).



(70)

$L = CO.\ NCC_6F_5.\ \underline{p}\text{-}NCC_6H_4NO_2$

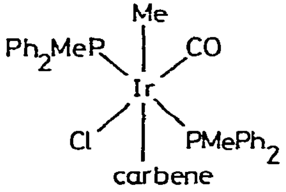
$\underline{p}\text{-}NCC_6H_4CH_3.\ \underline{p}\text{-}NCC_6H_4OMe.$

$NCC_6H_4CN\text{-}M,$

$NCC_6F_4CN\text{-}M.$

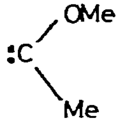
$M = (70)\text{-}L$

If the neutral ligands are certain acetylenes then carbene complexes, (71) are formed.

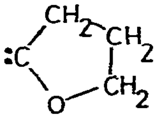


(71)

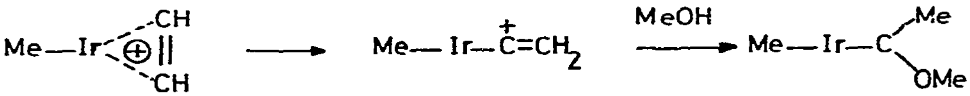
(a) carbene =



(b) carbene =

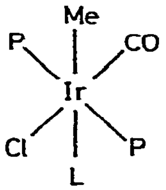


The carbene complex (71a) is obtained with acetylene gas while but-3-yne-1-ol ($HC{\equiv}CCH_2CH_2OH$) gives (71b). These carbene complexes result via a metal-induced carbonium ion, Scheme (16), as has been proposed for methyl platinum(II) compounds.



Scheme (16)

In methanol or ethanol as solvent imino ether complexes (72) are formed with certain nitriles. Treatment of the complexes $[MCl_3(PMe_2Ph)_3]$, (M = Rh,Ir) in acetone or methanol with $AgPF_6$ generates cationic complexes $[MCl_2(solvent)(PMe_2Ph)_3]^+PF_6^-$ which react with but-3-yne-1-ol to give the cyclic carbene complexes (73).[47]



(72)

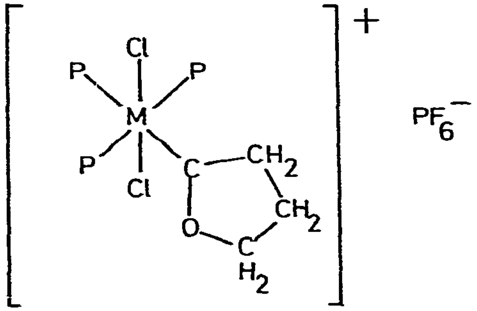
L = $-NH{=}C(OMe)C_6F_5$,

$-NH{=}C(OEt)C_6F_5$,

$-NH{=}C(OMe)C_6F_4(OMe)C{=}NH-$,

$-NH{=}C(OEt)C_6F_4(OMe)C{=}NH-$.

P = $PMePh_2$

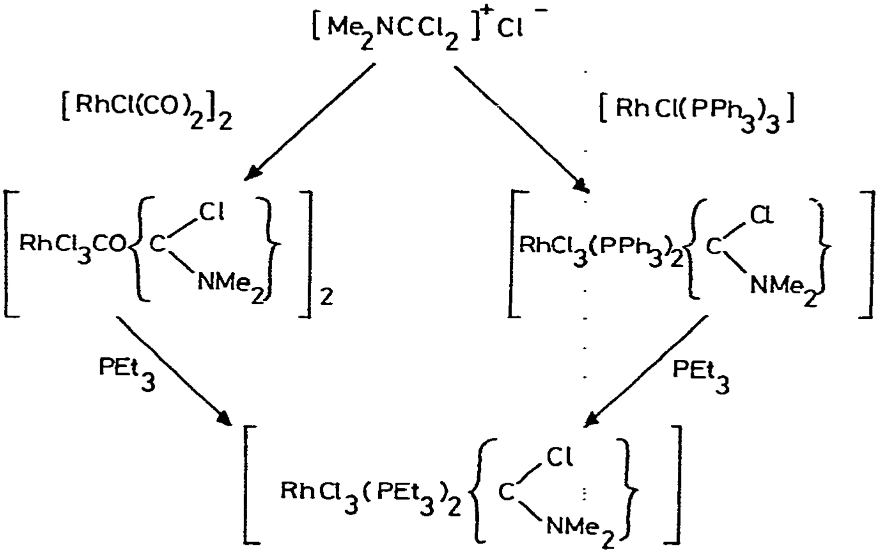


(73)

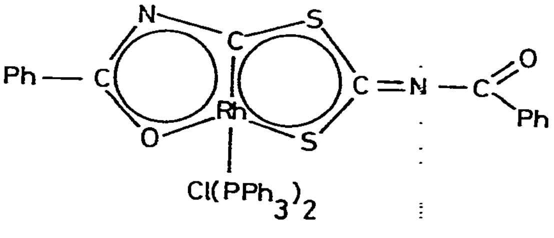
M = Rh, Ir

P = PMe_2Ph

C-Chlorocarbene complexes of rhodium(III) have been obtained from $[Me_2NCCl_2]^+Cl^-$ and rhodium(I) complexes as illustrated in Scheme (17).[48] A novel carbene complex, (74), also results upon addition of benzoyl isothiocyanate to $[RhCl(PPh_3)_3]$. The complex has been characterised crystallographically.[49]



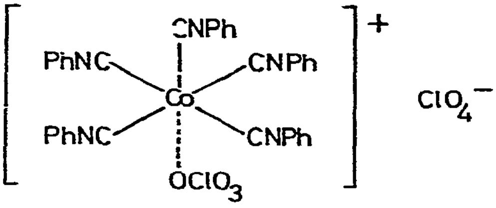
Scheme (17)



(74)

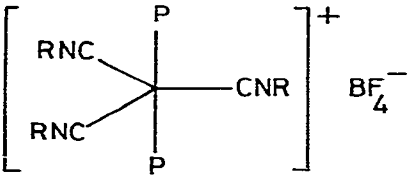
Metal isocyanide complexes.

The complex $[Co(CNPh)_5]^{2+}$ as the perchlorate salt forms three species of different colours: light blue, dark green and bright yellow. The geometry of the green form, isolated as the solvate $[Co(CNPh)_5][ClO_4]_2.\frac{1}{2}ClCH_2CH_2Cl$, can be described as square pyramidal in which the average C_{apical}-Co-C_{basal} angle has decreased to 95.0° as a result of weak co-ordination by a perchlorate anion below the basal plane of the complex, (75). The axial Co-C bond length in (75) is longer than that found in the cobalt(I) cation $[Co(CNPh)_5]^+$ and this is probably a consequence of decreased back-bonding in the cobalt(II) complex.[50] Recrystallisation of the cobalt(I) complex, $[Co(CNPh)_5][ClO_4]$ from various solvents also results in the formation of various structure types. The prototype type (I) complex, $[Co(CNPh)_5][ClO_4].CHCl_3$ has been shown to be square pyramidal and representative types $[Co(CNC_6H_4Cl\text{-}p)_5][BF_4]$ and $[Co(CNPh)_5][ClO_4]$ are somewhat differently distorted trigonal bipyramids. Further studies reveal that the same three isomeric structures are evident for $[Co(CNPh)_5][BF_4]$ but only one structure (typeII) is observed for para-substituted phenylisocyanide complexes.[51] A fourth distinct structural type has also been observed



(75)

with the ligand 2,4,6-trimethylphenylisocyanide.[52] The complex $[Co(CNC_6H_4Cl\text{-}\underline{p})_5][BF_4]$ reacts with $P(OMe)_3$ to give (76) and



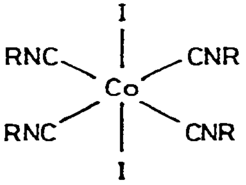
R= $\underline{p}$-ClC_6H_4-

P= $P(OMe)_3$

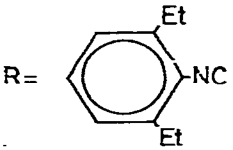
(76)

the same complex can also be isolated via addition of the isocyanide to $[Co\{P(OMe)_3\}_5][BF_4]$.[53] The complexes $[Co(\underline{p}\text{-}NO_2C_6H_4NC)_2\{PPh(OEt)_2\}_3]ClO_4$, $[Co(CNR)_3L_3]ClO_4$, R = Ph, $\underline{p}$-MeC_6H_4, $\underline{p}$-$MeOC_6H_4$, $\underline{o}$-MeC_6H_4, 2,6-$Me_2C_6H_3$, C_6H_{11}; L = $PPh(OEt)_2$, $P(OMe)_3$ have also been prepared and these complexes again appear to have isocyanide ligands in equatorial positions.[54]

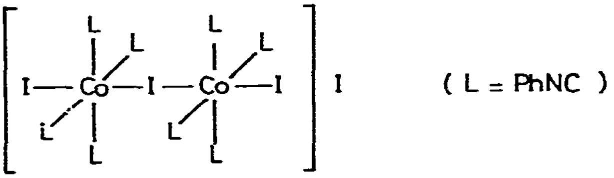
X-ray crystallographic studies have shown that while the paramagnetic complex (77) has a monomeric structure, the complex $[CoI_2(CNPh)_4]$ should be formulated as the



(77)

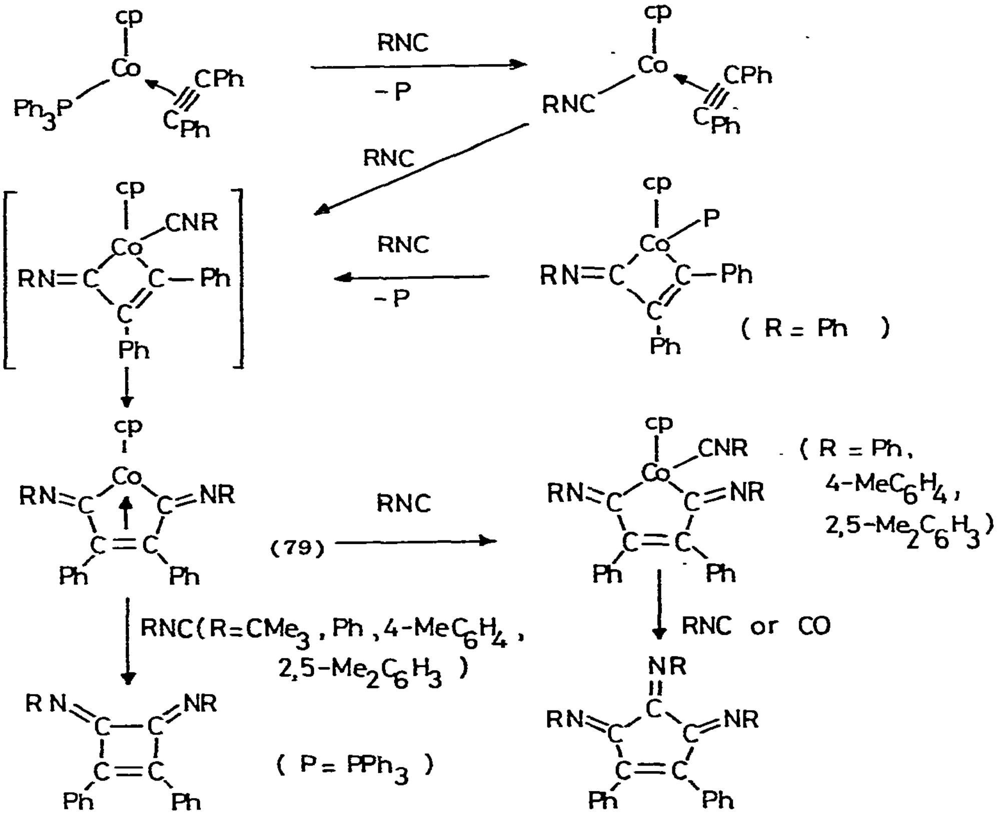


binuclear complex, (78), the diamagnetism of the complex being a result of spin-exchange in the central Co–I–Co unit.[55]



(78)

Some interesting metallocyclic complexes result on reacting $[\mathrm{CoCp(PhC{\equiv}CPh)(PPh_3)}]$ with isocyanides, Scheme (18).



Scheme (18)

The structure of complex (79), R = Ph has been substantiated by an X-ray structural study.[56]

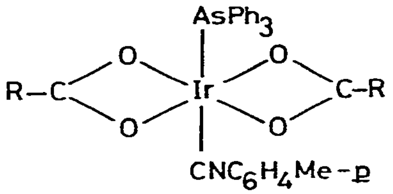
Dilute solutions of the salts, $[Rh(CNPh)_4]^+ X^-$, $(X = BF_4^-, BPh_4^-, PF_6^-)$ in acetonitrile solution are yellow but on concentration they become blue. Spectroscopic studies on these solutions indicate that oligomerisation of the cations occurs in concentrated solution as indicated in Scheme (19). Infrared evidence rules out the possibility

$$2\,[Rh(CNPh)_4]^+ \rightleftharpoons [Rh(CNPh)_4]_2^{2+}$$

$$[Rh(CNPh)_4]_2^{2+} + [Rh(CNPh)_4]^+ \rightleftharpoons [Rh(CNPh)_4]_3^{3+}$$

Scheme (19)

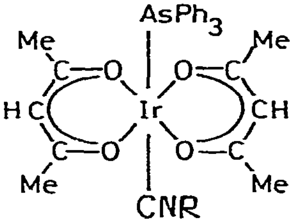
of bridging isocyanides and the dimer is probably bound through direct Rh---Rh interactions.[57] Electronic absorption and magnetic circular dichroism spectral measurements in acetonitrile have been reported for $[M(CNEt)_4]^+$, (M = Rh,Ir).[58]



(R = Me p-ClC_6H_4
p-$MeOC_6H_4$
2,4,6-$Me_3C_6H_3$)

(80)

Some iridium(II) isocyanide complexes (80) result on reacting $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ with carboxylic acids and an acetylacetonate complex (81) can also be prepared.[59]



(81)

^{13}C N.m.r. studies on some isocyanide complexes have been investigated.[60]

Metal carbonyls and related compounds.

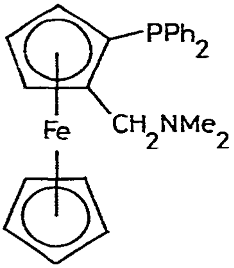
(a) Zero oxidation state compounds.

Co-condensation reactions of cobalt atoms with carbon monoxide have given the binary carbonyls of cobalt, $Co(CO)_n$, (n = 1-4).[61] The reduction of $Co_2(CO)_8$ by sodium-potassium alloy provides a rapid and clean method for the production of the anion $[Co(CO)_4]^-$,[62] and treatment of $Co_2(CO)_8$ with potassium graphite, C_8K, gives $K[Co(CO)_4]$.[63] A comparison of the relative reactivities of the anions $[M(CO)_2(PPh_3)_2]^-$, (M = Co,Rh,Ir), towards pentafluoropyridine has established the order Rh > Ir > Co. However, studies with d^8 complexes of these metals have shown that the nucleophilicities of the metal ions decrease in the order Co > Ir > Rh.

A review on cyclic phosphine complexes of transition metals contains examples of complexes in the cobalt, rhodium, iridium triad[64] and cobalt carbonyl complexes of polytertiary phosphines have been considered in a symposium[65] as has the effect of bridging ligands on the C-O stretching force constants of the compounds $[Co_2(CO)_6(\mu\text{-}Y)_2]$, (Y = CO, P,As,CR).[66]

Treatment of $Co_2(CO)_8$ with fluorocarbon-bridged di(tertiary arsines and phosphines) results in carbonyl-bridged or ligand- and carbonyl-bridged chelate complexes depending on the ligand, and in one case a mixture of isomers is reported.[67]

The reaction of $Co_2(CO)_8$ with the chelating ligand (82), (P–N), gives the ionic product $[Co(CO)_3(P\text{-}N)_2][Co(CO)_4]$ in which the chelating ligand is monodentate, the phosphorus acting as the donor atom.[68]



(82)

An ionic product, $[\{CoL_5\}\{Co(CO)_4\}_2]_n$, also results from the action of poly-1-vinyl-2-pyrrolidinone, (L) upon $Co_2(CO)_8$.[69]

Addition of tri-n-butylphosphine to $Co_2(CO)_8$ is known to produce an improved catalyst for hydroformylation reactions. Examination of this system, in the absence of alkene has been investigated under varying conditions of temperature, partial pressure of hydrogen and of carbon monoxide and the phosphorus-cobalt ratio. Infrared spectral studies indicate that the reactions illustrated in Scheme (20) occur.[70]

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

$$PBu_3 + Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7PBu_3 + CO$$

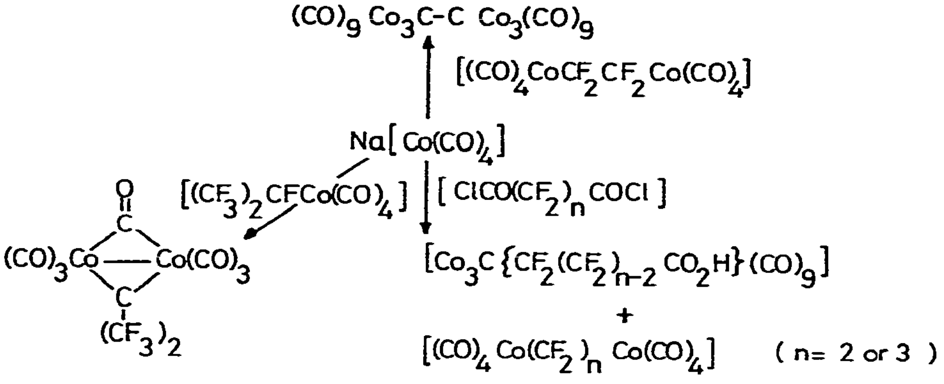
$$H_2 + Co_2(CO)_7PBu_3 \rightleftharpoons HCo(CO)_4 + HCo(CO)_3PBu_3$$

$$PBu_3 + HCo(CO)_4 \rightleftharpoons HCo(CO)_3PBu_3 + CO$$

Scheme (20)

The standard enthalpies of formation of crystalline $Co_2(CO)_8$, $[Co_3(CCl)(CO)_9]$ and $[Co_3(CBr)(CO)_9]$ have been determined as -298.9 ± 1.2, -283.5 ± 2.4, and -284.3 ± 2.2 kcal mol^{-1} respectively.[71] The thermal decomposition of $Co_2(CO)_8$ is inhibited by carbon monoxide and catalysed by powdered cobalt. The energy of activation for the thermal decomposition of $Co_2(CO)_8$ has been determined as 3.7 kcal mol^{-1}.[72]

A wide variety of methods have been reported for the preparation of the cluster compounds, $[Co_3(CR)(CO)_9]$. A method which is frequently used involves the reaction of 1,1,1-trihalogenoalkanes with $Na[Co(CO)_4]$ or $Co_2(CO)_8$ in donor solvents under conditions where disproportionation occurs to give $[Co(donor)_6][Co(CO)_4]_2$. The first step in this reaction may be the formation of an intermediate, $[Co(CX_2R)(CO)_4]$, which can undergo further attack by the anion to give the cluster compounds. In agreement with this scheme it has been found that treatment of the fluoroalkyl derivatives, $[Co(CF_2R)(CO)_4]$, (R = F, CF_3, C_2F_5, CHF_2) with either $Na[Co(CO)_4]$ or $Co_2(CO)_8$ in donor solvents such as tetrahydrofuran or diethyl ether gives the clusters $[Co_3(CR)(CO)_9]$. Other reactions are illustrated in Scheme (21). However, treatment of $[Co(C_3F_7)(CO)_4]$ with either $[Co(CO)_3PPh_3]^-$,

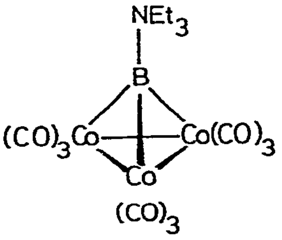


Scheme (21)

$[Co(CO)_3\{P(OPh)_3\}]^-$, $[Mn(CO)_5]^-$, $[Mn(CO)_4PPh_3]^-$ or $[FeCp(CO)_2]^-$ failed to give cluster compounds. Similarly no mixed cluster could be obtained on treating $[Co(CF_3)(CO)_4]$ with $Na[Rh(CO)_4]$.[73] Polar solvents are not essential for the cluster formation and reactions of halogenoalkanes with $Co_2(CO)_8$ in hexane have shown that both radical and carbene intermediates are formed under these conditions. An attempt to prepare one of the proposed intermediates, $[Co(CCl_3)(CO)_4]$, by the reaction of $[TlCo(CO)_4]$ with CCl_4 gives $[Co_3(CCl)(CO)_9]$. in varying yields depending on whether the thallium compound or CCl_4 are in excess. These results can be readily explained if the initially formed $[Co(CCl_3)(CO)_4]$ reacts rapidly with $[TlCo(CO)_4]$ to form $[Co_3(CCl)(CO)_9]$. In the absence of excess $[TlCo(CO)_4]$ or $Co_2(CO)_8$ the $[Co(CCl_3)(CO)_4]$ can undergo decomposition to C_2Cl_4 and C_2Cl_6.[74a]

Treatment of $Co_2(CO)_8$ with trans-$[CrBr(CR)(CO)_4]$, (R = Me,Ph) results in the transfer of the carbyne ligand from chromium to cobalt and formation of the clusters, $[Co_3(CR)(CO)_9]$.[74b]

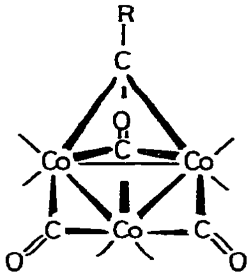
The electron rich cluster compound, $[Co_3(CNMe_2)(CO)_9]$, has been prepared by the reaction of $Na[Co(CO)_4]$ with $[Me_2NCCl_2]Cl$,[48] and the series of methylidyne-cluster compounds of the type $[Co_3(COMX_2NEt_3)(CO)_9]$, (M = B, X = Cl,Br; M = Al, X = Br) have been extended to include the compounds M = B, X = F,I and M = Al, X = Cl. The compounds can be prepared by the reaction of $Co_2(CO)_8$ with the adducts $[MX_3.NEt_3]$. Fluorination of $[Co_3(COBBr_2.NEt_3)(CO)_9]$ with $AgBF_4$ gives $[Co_3(COBF_2.NEt_3)(CO)_9]$. Treatment of $Co_2(CO)_8$ with BBr_3 at 60°C gives $[Co_6B(CO)_{18}]$ and the same cobalt-boron cluster results from the action of B_2H_6 upon $Co_2(CO)_8$. However, BBr_3 reacts with $[TlCo(CO)_4]$ in tne presence of stoichiometric amounts of NEt_3 to give (83).[75]



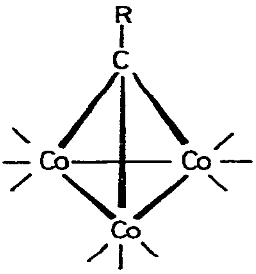
(83)

The crystal structure of $[Co_3(COBCl_2NEt_3)(CO)_9]$ has been determined.[76] Paramagnetic phosphido cobalt carbonyl clusters, $[Co_3(PR)(CO)_9]$, (R = Ph,Bu^t,Et_2N) are present in the reaction products of the phosphines $RPCl_2$ with $Co_2(CO)_8$. The black air-sensitive crystals have magnetic moments around 1.7 BM.[77]

Phosphine and arsine derivatives of the type $[Co_3(CY)(CO)_8L]$ are known to form two structural types, distinguished by the presence or absence of bridging carbonyls, (84) and (85). Variable temperature n.m.r. and i.r. studies on the complexes



(84)



(85)

$[Co_3(CMe)(CO)_8L]$, {L = PBu_3^n, $P(cyclohexyl)_3$}, indicate that both structural forms can exist in equilibrium in non-polar solvents. The isomerism and non-rigid behaviour of these phosphine complexes has been interpreted in terms of isomer distribution and intramolecular scrambling. Only in the case of the tricyclohexylphosphine derivative was it possible to obtain the "instantaneous" solution structure, characterised as the bridged form (84).[78]

The reactions of phosphines with the complexes $[Co_3(CY)(CO)_9]$ is rapid and reversible and kinetic studies reveal that the formation of $[Co_3(CY)(CO)_8L]$ Scheme (22), involves a simple dissociative mechanism.

$$Co_3(CY)(CO)_9 \rightleftharpoons Co_3(CY)(CO)_8 + CO$$

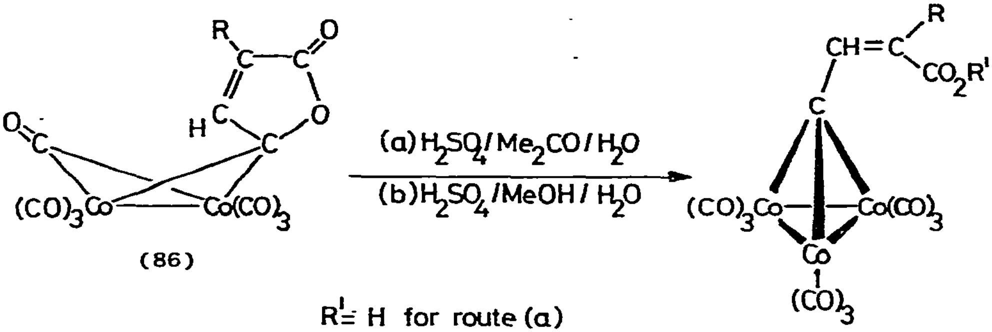
$$Co_3(CY)(CO)_8 + PPh_3 \rightleftharpoons Co_3(CY)(CO)_8PPh_3$$

$$(Y = Ph, Me, H, Cl, F)$$

Scheme (22)

The kinetic parameters are also found to vary with the nature of the apical substituent Y.[79] Treatment of the complexes (86) with acid gives further examples of the

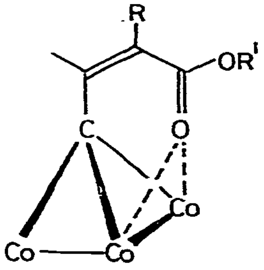
$[Co_3(CCH{=}CRCO_2R')(CO)_9]$, (87) derivatives. Infrared studies on the complexes (87) suggest that there is interaction between the carboxylic group and two or one cobalt atoms of the cluster as indicated in (88) or (89).[80]



(86)

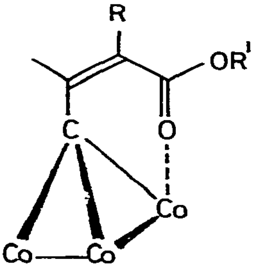
(87)

R' = H for route (a)
R' = Me for route (b)



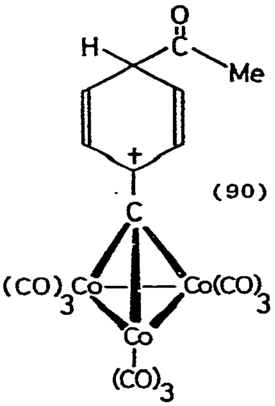
(88)

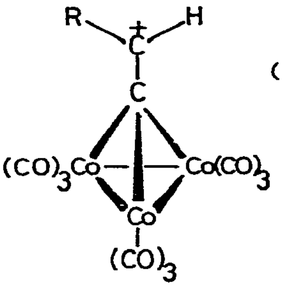
R = R' = H
R = H, R' = Me
R = Me, R' = H
R = R' = Me
R = Pr^n, R' = H
R = Pr^n, R' = Me
R = Ph, R' = H
R = Ph, R' = Me



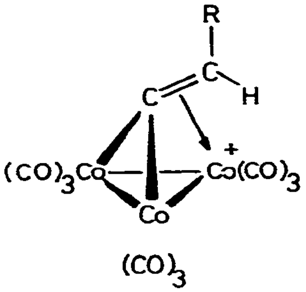
(89)

Friedel-Crafts acylation of the aryl groups in $[Co_3(CAryl)(CO)_9]$ has been studied. The reaction proceeds easily to give the para-substituted derivatives and it is apparent that the carbonium ion centre (90) is stabilised by the $[Co_3C(CO)_9]$ moiety.[81a] Previous studies on carbonium ions of this type (91) have shown that such species are


(90)

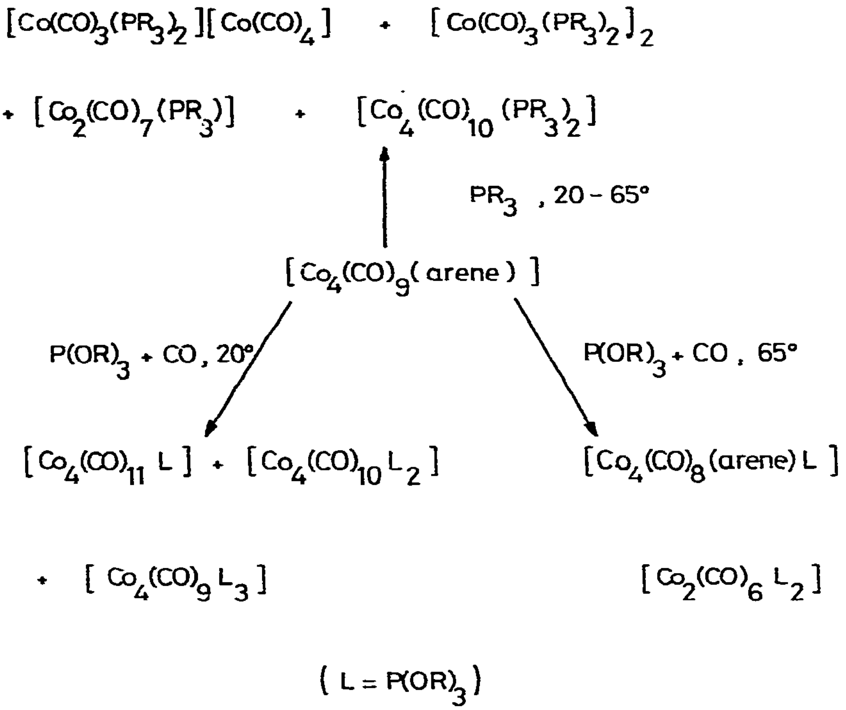

(91)

exceptionally stable and this appears to result from substantial delocalisation of charge into the cluster. ^{13}C n.m.r. studies on carbonium ions of this type have been undertaken but the structure and bonding of these highly stabilised ions remains to be elucidated. Crystallographic studies on a suitable salt would be extremely interesting and would indicate whether there is any contribution from a structure of type (92).[81b]


(92)

Treatment of $[Co_4(CO)_9(arene)]$ with carbon monoxide above 70°C gives $Co_4(CO)_{12}$, the rate of reaction increasing in the order iso-durene ∿ mesitylene < m-xylene < p-xylene ∿

o-xylene < toluene < anisole < biphenyl < fluorene < phenanthrene < benzene. This order is also the same as the decreasing thermal stability of the arene complexes. The reactions of the arene complexes with alkyl- and arylphosphines also result in displacement of the arene to give mono- and di-substituted cobalt carbonyl complexes. However with phosphites, arene complexes, $[Co_4(CO)_8(arene)P(OR)_3]$ can be isolated, Scheme (23).



Scheme (23)

These arene-phosphite complexes can also be obtained from the action of arenes on $[Co_4(CO)_{11}P(OR)_3]$.[82]

There is some controversy in the literature as to whether $[Co_4(CO)_{12}]$ has C_{3v} or D_{2d} molecular symmetry in solution. In the solid state the structure possesses C_{3v} molecular symmetry but the low temperature ^{13}C n.m.r. spectrum has been interpreted in terms of a structure possessing D_{2d} symmetry.[83] However, there are intensity anomalies in the ^{13}C n.m.r. spectrum and the results of the ^{59}Co n.m.r. spectrum strongly suggest that the C_{3v} form is predominant at room temperature.[82] $[Co_4(CO)_{11}P(OMe)_3]$ in solution is also derived from the C_{3v} structure of $[Co_4(CO)_{12}]$ with a terminal CO group of one of the basal Co atoms replaced by the phosphite.[84] It is further apparent from the variable temperature ^{13}C n.m.r. studies that CO scrambling occurs in solutions of $[Co_4(CO)_{12}]$, $[Co_4(PhMe)(CO)_9]$ and $[Co_4(RCCR)(CO)_{10}]$, (R = Ph,CO_2Me).[83]

Infrared spectroscopic studies on ^{13}C enriched samples of $[Co_4(CO)_{12}]$ and $[Rh_4(CO)_{12}]$ have been reported[85] and the electronic structure of $[Ir_4(CO)_{12}]$ has been calculated by the extended Hueckel M.O. theory.[86] Crystallographic studies indicate that $[S_2Co_4(CO)_{10}]$ is a dimer, $[SCo_2(CO)_5]_2$.[87]

The reductive carbonylation of $[RhCl(CO)_2]_2$ with $NaHCO_3$ and CO in n-hexane to give $[Rh_4(CO)_{12}]$ has been studied and the effect of water on this reaction has been discussed. $[RhCl(CO)_2]_2$ reacts with sodium methoxide to give $[Rh(OMe)(CO)_2]_2$ which on treatment with water and carbon monoxide gives $[Rh_4(CO)_{12}]$.[88] Treatment of $[Rh_6(CO)_{16}]$ with $[Et_4N]I$ at 50°C initially gives the salt $[Et_4N][Rh_6I(CO)_{15}]$. However, after longer reaction times a solution containing $[RhI_2(CO)_2]^-$ and a dark brown crystalline precipitate of $[Et_4N]_2[Rh_7I(CO)_{16}]$, are formed.[89] This metal atom cluster consists of a monocapped octahedron similar to that found in $[Rh_7(CO)_{16}]^{3-}$. Ten of the carbonyl ligands are terminally co-ordinated, two are edge-bridging and four are face-bridging, the iodine is in an edge-bridging position.[90] The anions $[Rh_7X(CO)_{16}]^{2-}$, (X = Br,I) can also be obtained by condensation of $[RhX(CO)_2]_2$ with the hexanuclear anion $[Rh_6(CO)_{15}]^{2-}$. Treatment of $[Rh_7(CO)_{16}]^{3-}$ with iodine also gives $[Rh_7I(CO)_{16}]^{2-}$.[89] ^{13}C n.m.r. studies on the three structurally related carbonyl clusters, $[Rh_6(CO)_{16}]$, $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$ have been reported. $[Rh_6(CO)_{16}]$ is not fluxional at 70°, $[Rh_7(CO)_{16}]^{3-}$ undergoes partial intra-carbonyl exchange at 25° but $[Rh_6(CO)_{15}]^{2-}$ readily undergoes intra-carbonyl exchange at -70°.[91] The carbonyliridate anions $[Ir_4H(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$, $[Ir_8(CO)_{20}]^{2-}$, $[Ir_6(CO)_{15}]^{2-}$ and $[Ir(CO)_4]^-$ can be obtained by the reaction of $Ir_4(CO)_{12}$ with potassium hydroxide in methanol and/or sodium in tetrahydrofuran. The compounds $[Ir_4H_2(CO)_{11}]$ and $[Ir_6(CO)_{16}]$ can also be obtained. The anion, $[Ir(CO)_4]^-$ is a very strong base. It is protonated by ethanol to give $Ir_4(CO)_{12}$ and reacts with $[Ph_3PCH_2CH_2PPh_3]Cl_2$ to give $[Ir(CO)_3PPh_3]_2$.[92] Reaction of the $[Rh_{12}(CO)_{30}]^{2-}$ dianion with hydrogen in Pr^iOH is known to take place initially with cleavage of the bond between the two octahedra to give the $[Rh_6H(CO)_{15}]^-$ mono-anion. With prolonged reaction times a further transformation into a mixture of brown anions is observed. The anion $[Rh_{13}H_3(CO)_{24}]^{2-}$ has been isolated from this mixture and it reacts with base to give $[Rh_{13}H_2(CO)_{24}]^{3-}$, Scheme (24). The 13 rhodium atoms of $[Rh_{13}H_3(CO)_{24}]^{2-}$ are located in three nearly

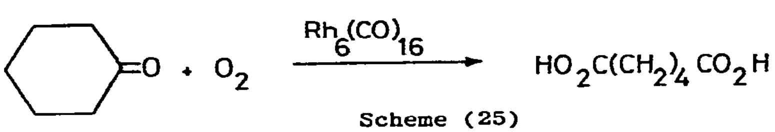
$$[\mathrm{Rh_{13}H_3(CO)_{24}}]^{2-} \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftharpoons}} [\mathrm{Rh_{13}H_2(CO)_{24}}]^{3-}$$

Scheme (24)

parallel layers giving a cluster of D_{3h} idealised symmetry and representing a fragment of hexagonal close packing. The central atom is 12-connected, while all the surface atoms are 4-connected with the other metal atoms and 3-connected with the carbonyl ligands. Each of the 12 surface metal atoms has one linearly bonded carbonyl and there are 12 carbonyls bridging one half of the polyhedron edges. The presence of a central metal atom is similar to that observed in $[Rh_{15}C_2(CO)_{28}]^-$.[93] The neutral carbide, $[Rh_8C(CO)_{19}]$ possesses a Rh_8 metal atom cluster which can be described as a monocapped prism plus one edge-bridging atom. The carbide atom occupies the centre of the prism. It can be envisaged as resulting from the insertion of two $[Rh(CO)_2]^+$ groups on one rectangular face of the $[Rh_6C(CO)_{15}]^{2-}$ anion.[94]

$[Rh_6(CO)_{16}]$ has been shown to catalyse the oxidation of CO to CO_2 and the oxidation of ketones to carboxylic acids by molecular oxygen, Scheme (25).[95] The standard enthalpy of formation of $[Rh_6(CO)_{16}]$ has been determined as -557.9 ± 4 kcal mol^{-1}.

$$\mathrm{CH_3COCH_3 + O_2 \xrightarrow{Rh_6(CO)_{16}} CH_3CO_2H + HCO_2H}$$



Scheme (25)

The bond enthalpy contributions (Rh-CO) and (Rh-Rh) have been estimated at 39.6 and 27.3 kcal mol^{-1}.[96]

(b) Heteronuclear metal-metal bonded carbonyl compounds.

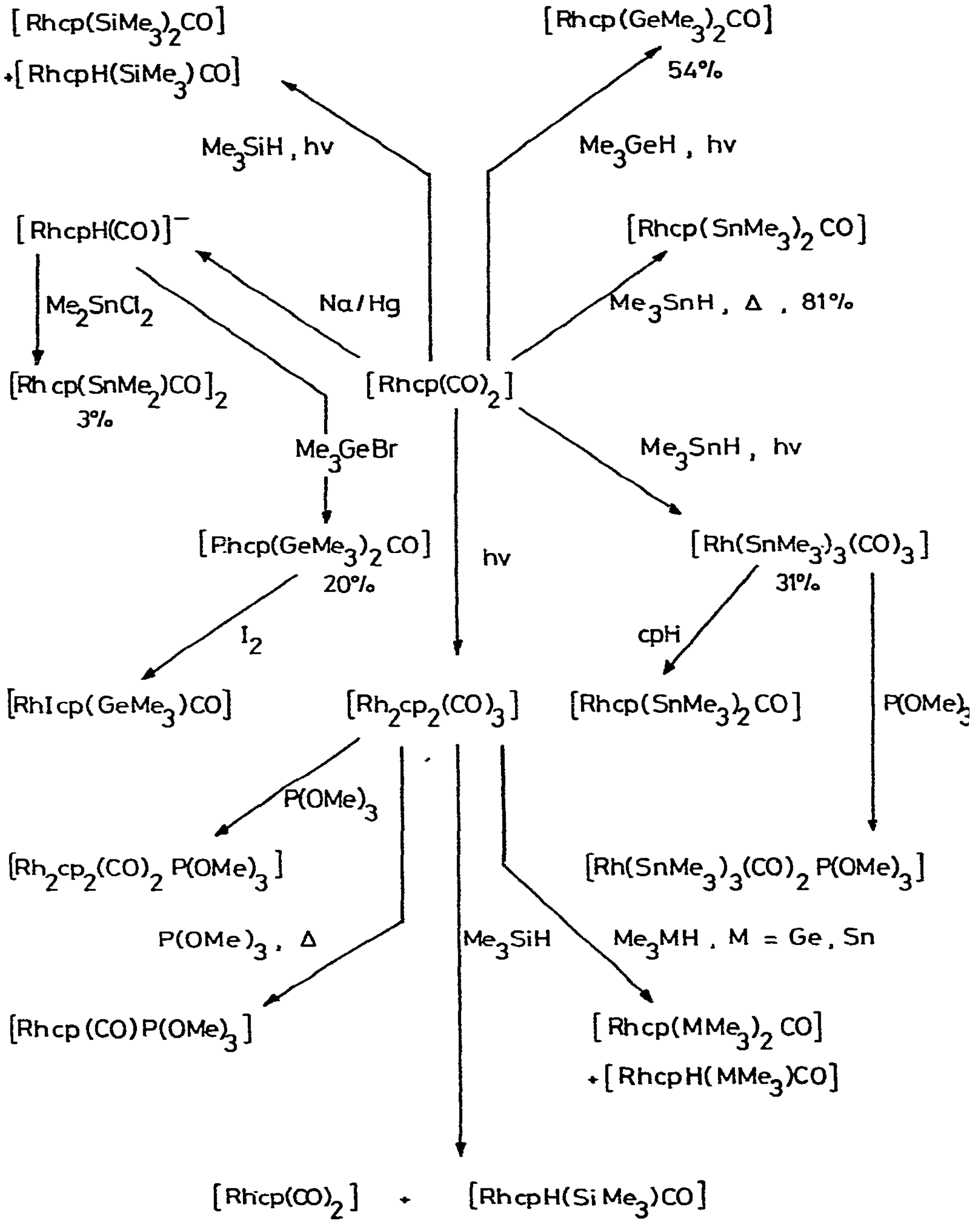
Treatment of $[TlCo(CO)_4]$ with a variety of Lewis bases in non-co-ordinating solvents leads to either $[TlCo(CO)_3L]$ or $[Tl\{Co(CO)_3L\}_3]$ and thallium metal. It now appears that stable thallium(I) compounds are formed in solution at room temperature with Lewis bases which give substituted cobalt carbonyl anions of relatively low basicity. Thus the reaction of $[TlCo(CO)_4]$ with either $P(OPh)_3$ or $P(OC_6H_4Cl\text{-}\underline{p})_3$, (L) gives $[TlCo(CO)_3L]$. Lewis bases such as $P(OMe)_3$, $P(OEt)_3$, PPh_3, $AsPh_3$, $SbPh_3$, or $PBu_3{}^n$ which give substituted hydridocobaltcarbonyl derivatives with $p\underline{K}_a>5$ yield $[Tl\{Co(CO)_3L\}_3]$ derivatives and thallium metal.[97]

Calculation of bond dissociation energies from appearance potential measurements on the complexes $[Me_3MCo(CO)_4]$, (M = Ge,Sn) have given the following values, D(Ge-Co), 3.2eV; D(Sn-Co), 2.8eV. These values indicate strong intermetallic bonding in these compounds. Accurate data for $[Me_3SiCo(CO)_4]$ could not be obtained due to its low thermal stability.[98] Molecular electric dipole moments measurements on a series of Sn-Co bonded compounds, $[R_nY_{m-n}Sn\{Co(CO)_4\}_{4-m}]$, ($m = 1\text{-}3$; $n \leqslant m$; R = alkyl,phenyl; Y = halogen) reveal that there is a linear correlation between the $\mu\overleftarrow{(CO)_4Co\text{-}Sn}$ group moment and the Taft induction constants of the substituents at the tin atom. It is apparent from this relationship that the polarity of Co-Sn bond is principally determined by the inductive properties of the substituents on tin.[99] Complete vibrational assignments have been made on the complexes

$X_3SiCo(CO)_4$, (X = H,F,Cl) and evidence for π-interaction in the Si-Co bond has been considered.[100] In a variety of Sn-Co bonded complexes of this type tin-119 magnetic double resonance data indicate that the tin magnetic shielding is dominated by the extent of the π-overlap in the Sn-Co bond.[101] A variety of rhodium complexes of Group 4B ligands have been obtained by the action of the hydrides Me_3MH, (M = Si,Ge,Sn) on $[RhCp(CO)_2]$ and some of the results of this study are summarised in Scheme (26).[102] The anions $[Rh(GeMe_3)(CO)Cp]^-$ and $[RhH(CO)Cp]^-$ provide useful routes into Group IVB-rhodium chemistry.[102]

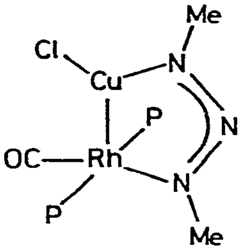
Electrochemical reduction of $[Co(CO)(diphos)_2]^+$ in methylcyanide at -30° followed by controlled addition of carbon monoxide generates the anion, $[Co(CO)_2(diphos)]^-$. Addition of $Hg(CN)_2$ or Ph_3SnCl gives the metal-metal bonded complexes $[Hg\{Co(CO)_2(diphos)\}_2]$ and $[Ph_3SnCo(CO)_2(diphos)]$ respectively. Electrochemical reduction of $[Rh(diphos)_2]^+$ under an atmosphere of CO similarly generates $[Rh(CO)_2(diphos)]^-$ from which $[Ph_3SnRh(CO)_2(diphos)]$ can be obtained. The corresponding iridium compound, $[Ph_3SnIr(CO)_2(diphos)]$ can be obtained via electrochemical reduction of $[Ir(CO)(diphos)_2]^+$ in the presence of CO.[103]

Some novel rhodium- and iridium-copper bonded complexes, $L_2(CO)MCu(RN\text{-}N\text{-}NR')X$, (L = PPh_3,PMe_2Ph, $AsPh_3$; M = Rh,Ir; X = Cl,Br,I result from the reactions of trans-$[MX(CO)L_2]$ with $[Cu(RN\text{-}N\text{-}NR')]_n$, (n = 4, R = R' = Me; n = 2, R = R' = p-tolyl; R = Me,R' = p-tolyl). The crystal structure of (93) has been determined and an analogous



Scheme (26)

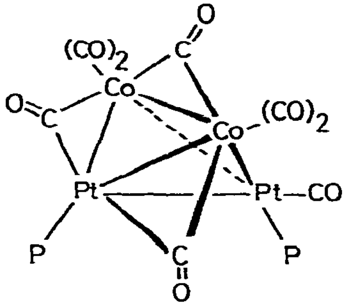
(M= Ge, Sn)



(P = PPh_3) (93)

trifluoroacetate complex, $[(Ph_3P)_2(CO)IrCu(OCOCF_3)_2]$ can be obtained.[104]

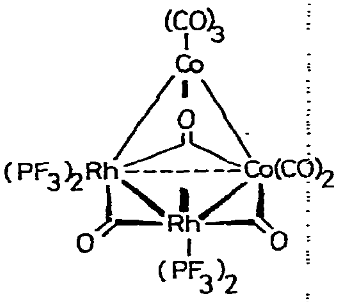
The reactions of $Na[Co(CO)_4]$ with either $AgNO_3$ in water or CuCl in aqueous ammonia give respectively the air and light sensitive yellow crystalline compounds $[AgCo(CO)_4]_n$ and $[Cu(L_y)Co(CO)_4]$, (L_y = indeterminate number of H_2O and NH_3 ligands). The compounds $[AgCo(CO)_3PBu_3{}^n]_n$ and $[CuCo(CO)_3PBu_3{}^n]_n$ can be similarly prepared from $Na[Co(CO)_3PBu_3{}^n]$. Treatment of these complexes with 1,10-phenanthroline, 2,2'-bipyridyl or $Ph_2PCH_2CH_2PPh_2$ gives the 1:1 adducts, $[Co(CO)_4Cu(bipy)]_n$, $[Co(CO)_4Cu(phen)]_n$, $[Co(CO)_4Ag(phen)]_n$,$[Co(CO)_3(PBu_3{}^n)Cu(phen)]_n$, $[Co(CO)_3(PBu_3{}^n)Ag(phen)]_n$,$[Co(CO)_3(PBu_3{}^n)Ag(diphos)]_n$. In carbon disulphide or chloroform the complexes are non-conducting but in donor solvents the complexes ionise. Thus in tetrahydrofuran both $[AgCo(CO)_4]_n$ and $[Cu(L_y)Co(CO)_4]_n$ give carbonyl species considered to be $[Ag\{Co(CO)_4\}_2]^-$ and $[Cu\{Co(CO)_4\}_2]^-$ respectively and the i.r. spectra are similar to the neutral isostructural complex $[Hg\{Co(CO)_4\}_2]$.[105] Indeed the salts $[Et_4N][M\{Co(CO)_4\}_2]$, (M = Cu,Ag) have been isolated,[106] and treatment of $[Et_4N][AuBr_2]$ with $[Co(CO)_4]^-$ gives the corresponding gold compound $[Et_4N][Au\{Co(CO)_4\}_2]$.[107] The copper salt dissociates reversibly to $[Co(CO)_4]^-$ in methyl cyanide solution.[106] The reactions of $[NiCl_2(PPh_3)_2]$ with $Na[Co(CO)_4]$, $Na[Co(CO)_3PPh_3]$, $Na[Rh(CO)_2(PPh_3)_2]$ or $Na[Ir(CO)_3PPh_3]$ do not yield heteronuclear metal-metal bonded complexes and $[Ni(CO)_2(PPh_3)_2]$ can be isolated. Similar reactions occur between $[MCl_2(PPh_3)_2]$, (M = Ni,Pd,Pt), and $Na[Co(CO)_3PPh_3]$ but with the rhodium and iridium anions cluster complexes appear to be formed. trans-$[PtCl_2py_2]$ reacts with the appropriate cobalt anion to give trans-$[Pt\{Co(CO)_3L\}_2py_2]$, ($L = PPh_3, PMePh_2, PMe_2Ph, PBu_3^n$) and the palladium complex $[Pd\{Co(CO)_3PPh_3\}_2py_2]$ can similarly be obtained.[108] In contrast to these results treatment of either cis- or trans-$[PtCl_2(PPh_3)_2]$ gives, amongst other products, (94), the structure of which has been confirmed by an X-ray structure determination.[109]



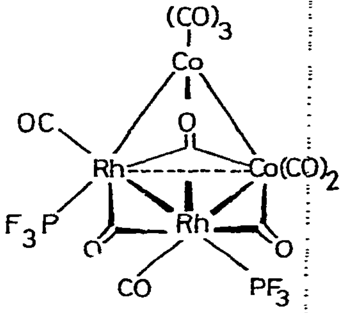
(P = PPh_3)

(94)

Treatment of $[RhCl(PF_3)_2]_2$ with either $[TlCo(CO)_4]$ or $[Co_2(CO)_8]$ gives the new cluster (95) which undergoes a ready intramolecular exchange process with $[Rh_2Co_2(CO)_{12}]$ to give (96). This is the first example of an intramolecular ligand exchange between two compounds containing tetranuclear clusters of metal atoms.[110] Infrared studies on the cluster $[HFeCo_3(CO)_{12}]$ indicate a considerable polarisation of the



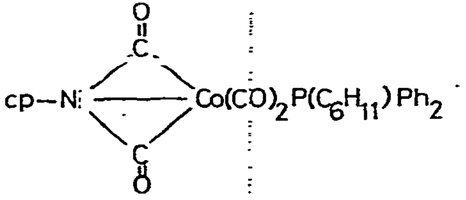
(95)



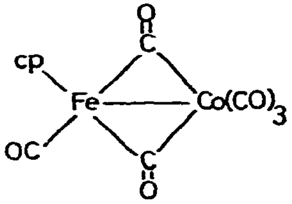
(96)

Fe-H bond in the sense Fe(δ^-)-H(δ^+). The position of the H atom is considered to be in the cage near or on the Co_3 plane.[85]

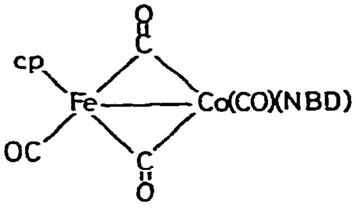
The compounds (97)[111], (98)[112] and (99)[113] have been the subjects of X-ray structure determinations. Each compound



(97)



(98)



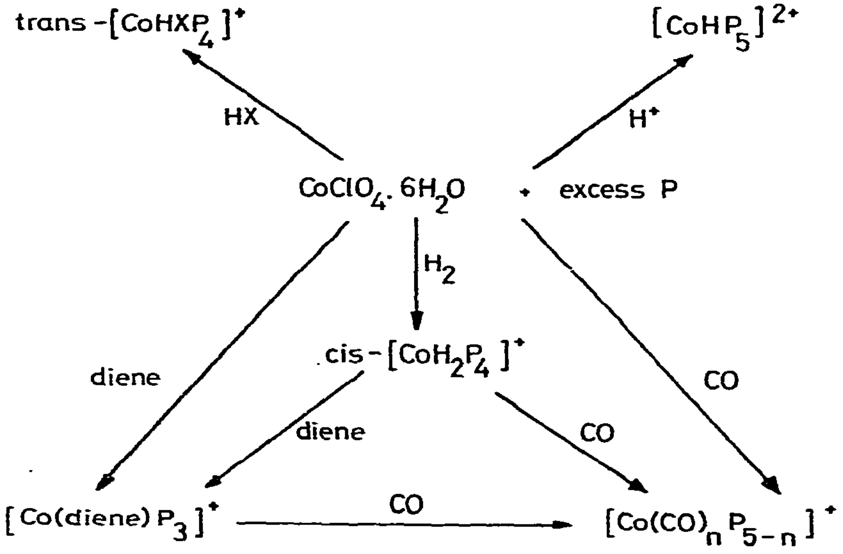
(99)

has a non-planar carbonyl bridge system and the cobalt atoms are in a square-based pyramidal environment.

The Raman spectrum of $[Hg\{Co(CO)_4\}_2]$ has been reported and the CO stretching force field has been calculated.[114] The Co-Au stretching frequency in $[Et_4N][Au\{Co(CO)_4\}_2]$ occurs at 189 cm^{-1}.[107]

(c) Metal -(I), -(II) and -(III) compounds.

A variety of cationic cobalt(I) and cobalt(III) complexes can be obtained via the reactions of phosphines with $Co(ClO_4)_2$ $6H_2O$ in isopropanol, Scheme (27).



(P = 2° to 3° phosphines)

Scheme (27)

The rate of formation of the carbonyl complexes, $[Co(CO)_nP_{5-n}]ClO_4$ is very high with small phosphines, e.g. $PHEt_2$,PHMePh, but decreases with increasing size of the ligands. No carbonyl complexes are formed with large phosphines such as PPh_3 and $P(C_6H_{11})_3$. In a number of the reactions acetone is present in the reaction mixtures suggesting that isopropanol is involved in the reduction processes.[115] Carbonylation of pentacyanocobaltate(II) leads to $[Co(CN)_3(CO)_2]^{2-}$ in all cases.[116]

Treatment of anhydrous cobalt(II) halides with carbon monoxide in the presence of diethyl phenylphosphonite leads to the cationic complex $[Co(CO)\{PhP(OEt)_2\}_4]^+X^-$ which on reaction with carbon monoxide and trace amounts of water yields both $[Co(CO)_2L_3]^+$ and $[CoX(CO)_2L_2]$. Reduction is thought to be due to carbon monoxide rather than the phosphine ligand.[117] Similar pentaco-ordinate and cationic species are reported as products in the addition of carbon monoxide to complexes of the type $CoXL_3$ (L = Me_3P; X = Cl,Br,I), followed by treatment with excess phosphine. In the absence of carbon monoxide a tetrahedral cobalt(I) cation is isolated, $[CoL_4]^+$ [118]

Electrochemical reduction of $[Co(CO)_2(PMe_3)_3]BPh_4$ proceeds via a two electron step to give $[Co(CO)_2(PMe_3)_2]^-$ which reacts with the starting material to produce $[Co(CO)_2(PMe_3)_2]_2$, Scheme (28).

$$[Co(CO)_2(PMe_3)_3]^+ + 2e^- \longrightarrow [Co(CO)_2(PMe_3)_2]^- + PMe_3$$

$$[Co(CO)_2(PMe_3)_2]^- + [Co(CO)_2(PMe_3)_3]^+ \longrightarrow [Co(CO)_2(PMe_3)_2]_2 + PMe_3$$

Scheme (28)

Electrochemical reduction of the complexes trans-$[RhCl(CO)L_2]$, (L = PPh_3, $P(NMe_2)_3$, PMe_2Ph, PMe_3, PEt_3) and trans-$[IrX(CO)(PPh_3)_2]$, (X = Cl,Br,I) also proceeds via a two electron step leading to zerovalent species, Scheme (29). It is apparent that the values are more negative when the basicity of the ligand L and electronegativity of X increase.[119]

$$[RhCl(CO)L_2] + 2e^- \longrightarrow [RhS(CO)L_2]^- + Cl^-$$

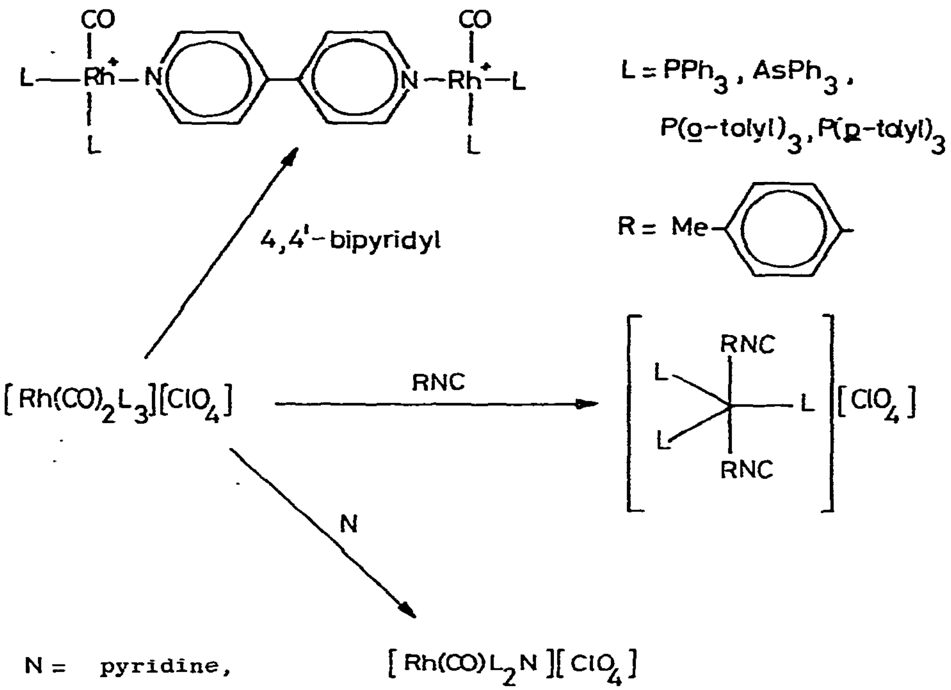
$$[RhS(CO)L_2]^- + [RhCl(CO)L_2] \longrightarrow [RhS(CO)L_2]_2 + Cl^-$$

$$(\ S = \text{solvent}\ )$$

Scheme (29)

Electrochemical reduction of the complexes, $[Co(CO)(diphos)_2]^+$, $[Rh(diphos)_2]^+$ and $[Ir(CO)(diphos)_2]^+$ in the presence of CO also proceed via a two electron step the anionic species $[M(CO)_2(diphos)]^-$ being formed.[103,120.] Solution and solid state electronic spectral measurements have been carried out on the low-spin five-co-ordinate complexes, $[Co(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ and $[CoI(CO)_2\{PPh(OEt)_2\}_2]$.[121]

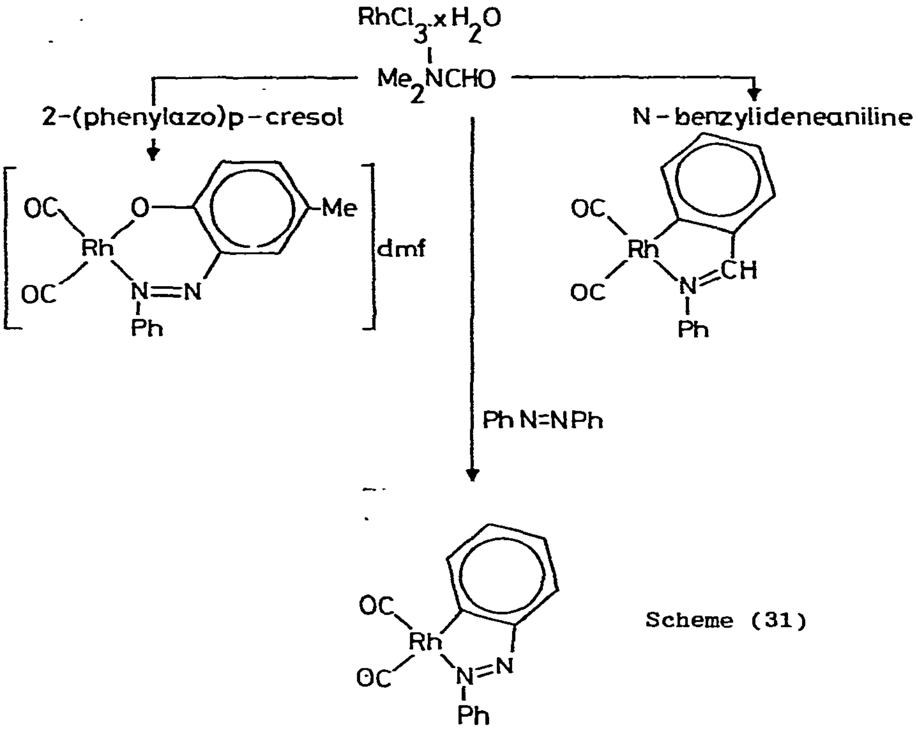
Some reactions of the cationic complexes of rhodium(I) $[Rh(CO)_2L_3]ClO_4$ with nitrogen donor ligands and p-tolylisocyanide have been reported and are illustrated in Scheme (30).[122] The reaction of 2,2'-bipyridyl with $[RhCl(CO)_2]_2$ has been reported to yield the bipyridyl bridged complex $[(OC)_2ClRh(\mu\text{-bipy})RhCl(CO)_2]$. However, it has now been shown that both 2,2'-bipyridyl and 1,10-phenanthroline react with $[RhCl(CO)_2]_2$ to give the salts $[Rh(N\text{-}N)(CO)_2][RhCl_2(CO)_2]$. Further the complexes previously formulated as $[Rh(acac)(phen)]$



N = pyridine,
α-, β-, γ-picoline,
quinoline,
isoquinoline,
benzo(f)quinoline

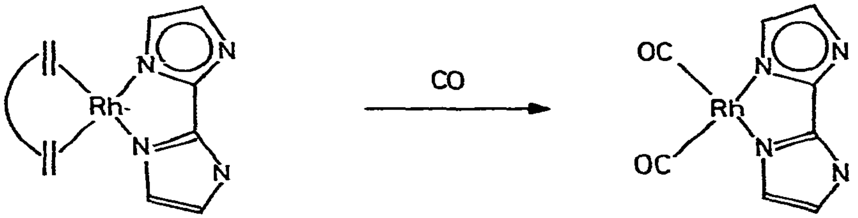
Scheme (30)

and Rh(quin)(phen), (acac = acetylacetonato, quin = quinolin-8-olato) have been shown to be $[\mathrm{RhCl(CO)_2(phen)}]$. Salts of $[\mathrm{Rh(CO)_2(phen)}]^+$ have also been obtained.[123] Addition of either 2-(phenylazo)-p-cresol, azobenzene, or N-benzylideneaniline to the rhodium dicarbonyl species produced by heating hydrated rhodium(III) chloride in dimethylformamide followed by u.v. irradiation produces some rhodium(I) dicarbonyl complexes, Scheme 31.[124]



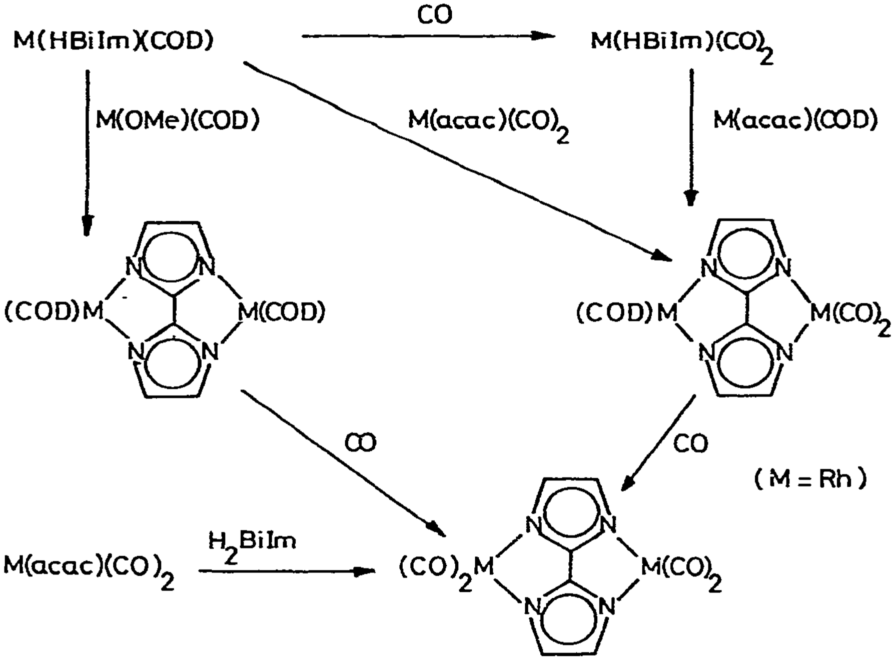
Scheme (31)

The reaction of the conjugated ligand 2,2'-biimidazole, (H_2BiIm) with $[Rh(OMe)(COD)]_2$ gives the air stable complex (100) which can be converted to the dicarbonyl complex (101)



(100) (101)

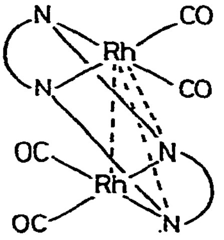
The corresponding iridium complexes can similarly be prepared and preparations of the complexes are summarised in Scheme (32)[126]



Scheme (32)

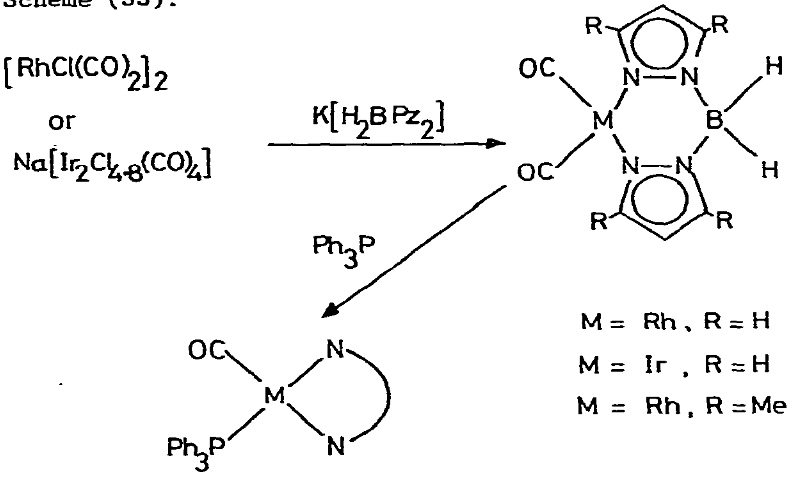
Octaethylporphyrin, $OEPH_2$, reacts with $[RhCl(CO)_2]_2$ to produce $[Rh_2(OEPH)Cl(CO)_4]$ which liberates HCl upon recrystallisation to give the more stable complex, $[(porphyrin)Rh_2(CO)_4]$,(102)[26] which has been the subject of an X-ray study. The structure of the inner core of the complex is illustrated, (102). The Rh·····Rh distance is shorter than that found in $[RhCl(CO)_2]_2$.[126]

Potassium bis(pyrazolyl)borate reacts with $[RhCl(CO)_2]_2$ to give the dicarbonyl complex, $[Rh(H_2BPz_2)(CO)_2]$ and related



(102)

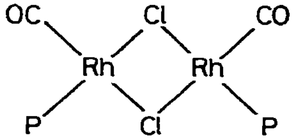
complexes of rhodium(I) and iridum(I) have been prepared Scheme (33).[127]



Scheme (33)

A study of the reaction of PMe_2Ph with $[RhCl(CO)_2]_2$ reveals that under an atmosphere of carbon monoxide the main course of the reaction is chloride bridge cleavage followed by carbon monoxide substitution. However, in refluxing cyclohexane substitution occurs initially. Electrolytes, e.g. $[Rh(CO)_2(PMe_2Ph)_3]Cl$ are also formed under an atmosphere of carbon monoxide and this type of behaviour is dependent upon solvent and the presence of carbon monoxide.[128] A crystal structure determination on the carbon monoxide substitution complex (103) reveals the presence

(103)



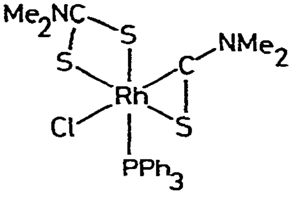
(P=PMe$_2$Ph)

of a cis-geometry and a bent rhodium-chlorine bridge system. However, in cyclohexane solution there is some isomerisation to the trans-isomer. Similarly cis-$[RhCl(CO)PMe_3]_2$ gives a mixture of cis- and trans-isomers in solution. However, the complex $[RhCl(CO)P(NMe_2)_3]_2$ appears to have a trans-geometry in the solid state and gives a small proportion of the cis-isomer in solution.[129]

$[RhCl(CO)(C_2H_4)]_2$ reacts with Et_2NH to give trans-$[RhCl(CO)C_2H_4)(Et_2NH)]$. In solution this complex exists as a dimer.[130] However, the reaction between $[Rh_2Cl_2(CO)_x(C_2H_4)_{4-x}]$ (x = 1-3) and triarylstibine ligands leads only to monomeric products in which the ethylene ligand always appears trans-to the chlorine.[131]

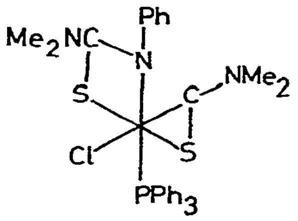
Addition of tertiary phosphines to $[Rh(SR)(CO)_2]_2$, (S = Ph,Bu^t) gives the penta-co-ordinated dinuclear rhodium complexes, $[Rh(SR)(CO)_2L]_2$. These complexes can lose carbon monoxide to give $[Rh(SR)(CO)L]_2$ which can also be obtained by treating $[RhCl(CO)L]_2$ with LiSR.[132] The structure and reactivity of halide bridged rhodium(I) complexes has been discussed in a review lecture.[133]

Treatment of $[RhCl(CO)_2]_2$ or $[RhCl(PPh_3)_3]$ with diphenyl dithiophosphate, $(PhO)_2PS_2^-$ and dicyclohexyldithiophosphinate $(H_{11}C_6)_2PS_2^-$ gives the neutral complexes, $[RhL_2(S\text{-}S)]$. The metal-sulphur bonds in these complexes are cleaved by the ligands $Ph_2PCH_2CH_2PPh_2$ and $Ph_2AsCH_2CH_2AsPh_2$ to give the salts $[Rh(L\text{-}L)_2(CO)]$ S-S which readily lose carbon monoxide. The complexes, $[Rh(CO)_2(S\text{-}S)]$ react with bromine or iodine to give $[RhX_2(S\text{-}S)(CO)]_2$ while methyl iodide gives $[Rh(COMe)I(S\text{-}S)(CO)]$.[134] In contrast to these reactions $[RhCl(PPh_3)_3]$,$[RhH(CO)(PPh_3)_3]$, $[RhNO(PPh_3)_3]$ and $[Rh(OCOCF_3)_2(NO)(PPh_3)_2]$ react with sodium dimethyldithiocarbamate or tetramethylthiuram disulphide under mild conditions to give $[Rh(S_2CNMe_2)_3]$. An expected product of these reactions $[Rh(S_2CNMe_2)(PPh_3)_2]$ is known[135] and tetramethylthiuram monosulphide, $Me_2NC(S)SC(S)NMe_2$, reacts with $[RhCl(PPh_3)_3]$ to give (104)[136] the crystal structure of which has been determined.[137]



(104)

An analogous C-N bond breaking occurs in the reaction of $Me_2NC(S)N(Ph)C(S)NMe_2$ with $[RhCl(PPh_3)_3]$ to give (105) which probably has a similar structure to (104).[136] The complex $[RhCl(SMe)(SCNMe_2)(PPh_3)_2]$ results on addition of $MeSC(S)NMe_2$ to $[RhCl(PPh_3)_3]$. This complex (106) is considered to be



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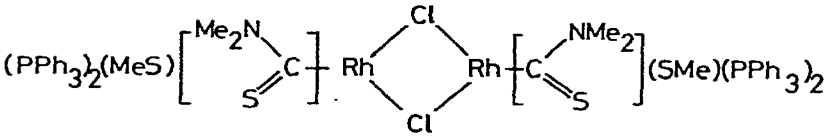
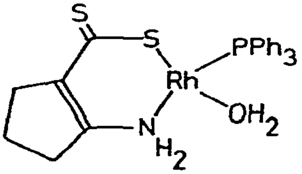


(106)

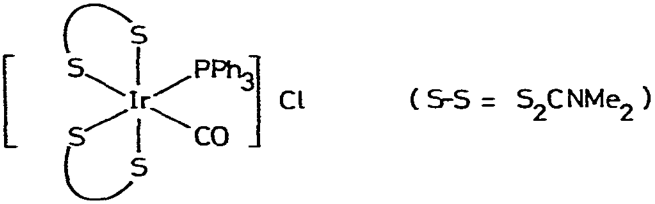
a dimer containing a carbon-bonded thiocarboxamido group. In $CHCl_3$ solution (106) decomposes to give $[RhCl_2(SCNMe_2)(PPh_3)_2]2CHCl_3$. The MeS group in (106) reacts with CS_2 to form $[RhCl(S_2CSMe)(SCNMe_2)(PPh_3)]$.[136] An unusual aquo complex, $[Rh(ACDA)(H_2O)(PPh_3)]$, (107), is reported to



(107)

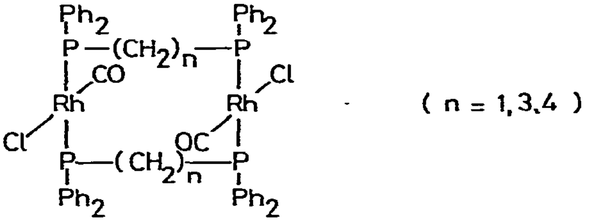
result from the action of 2-aminocyclopentene-1-dithiocarboxylic acid, (HACDA) with $[RhCl(PPh_3)_3]$ and HACDA appears to reduce Rh(III) to a univalent complex, $[Rh(ACDA)2H_2O]$.[138] Tetramethylthiuram disulphide reacts with trans-$[IrCl(CO)(PPh_3)_2]$

to give the salt (108). $[IrH_2(OCOMe)(PPh_3)_3]$ reacts with sodium



(108)

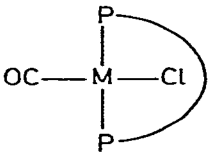
dithiocarbamates and O-alkyldithiocarbamates in boiling acetone to give $[IrH_2(S_2CNR_2)(PPh_3)_2]$ and $[IrH_2(S_2COR)(PPh_3)_2]$ respectively.[135] The reactions of equivalent amounts of $Ph_2P(CH_2)_nPPh_2$ and $[RhCl(CO)_2]_2$ give the complexes $[RhCl(CO)\{Ph_2P(CH_2)_nPPh_2\}]_m$. The ^{31}P n.m.r. and i.r. spectra of the series n=1-4 indicate that all the complexes are dimeric (m = 2), (109), except the complex, n = 2, which is monomeric



(109)

with a cis-configuration.[139] The crystal structures of $[IrCl(CO)\{Bu_2{}^tP(CH_2)_{10}PBu_2{}^t\}]$, and $[RhCl(CO)\{Bu_2{}^tP(CH_2)_{10}PBu_2{}^t\}]$

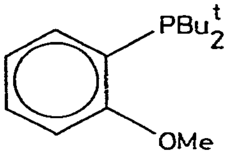
(110) have been reported. The effect of di-t-butyl substituents in promoting large chelate ring formation has been



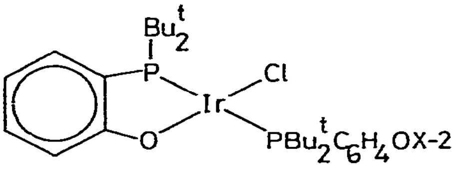
(M = Rh, Ir
$P\text{-}P = Bu^t_2P(CH_2)_{10}PBu^t_2$)

(110)

interpreted in terms of a favourable conformational effect and internal entropy changes.[140] On passing carbon monoxide through a boiling 2-methoxyethanol solution of Na_2IrBr_6 containing (111) the bright yellow O-metallated species (112), (X = Me), is produced.[29] The complex exists as rotational conformers and



(111)

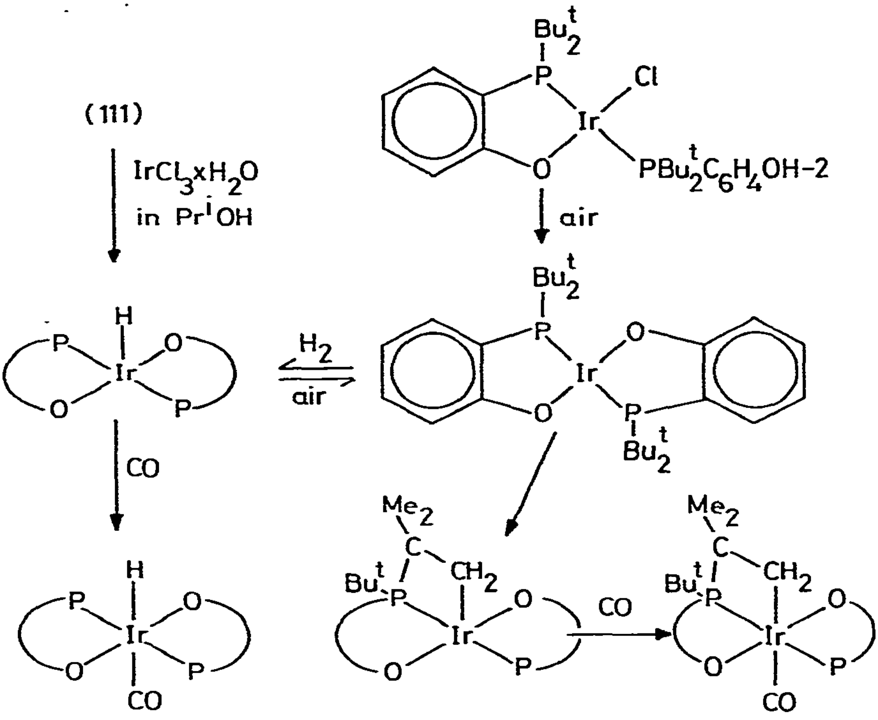


(X = H, D, Me)

(112)

is probably formed from $[IrCl(CO)\{PBu^t_2(C_6H_4OMe\text{-}2)\}_2]$ as an intermediate. On refluxing a solution of H_2IrCl_6 and (111) in the presence of carbon monoxide complete demethylation occurs to give (112), (X - H). Some reactions of (111) are illustrated in Scheme (34).[29]

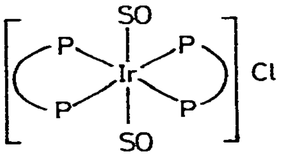
A convenient route to the iridium complexes, trans-$[IrCl(CO)L_2]$ involves addition of the phosphine ligand, L to $[IrCl(\text{cyclo-octene})_2]_2$ suspended in benzene followed by the



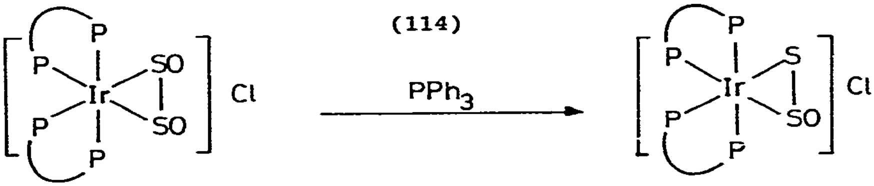
Scheme (34)

passage of carbon monoxide gas.[104] The carboxylate complexes, $[M(OCOCF_3)(CO)(PPh_3)_2]$ result on boiling a suspension of trans-$[MCl(CO)(PPh_3)_2]$, (M = Rh,Ir), in benzene with $[Cu(OCOCF_3)]_4$.[104] The reactions of perfluorocarboxylic acids with $[RhH(CO)(PPh_3)_3]$ in boiling ethanol also lead to the complexes, $[Rh(OCOR)(CO)(PPh_3)_2]$, $(R = CF_3, C_2F_5, C_6F_5)$. With $[RhH(PPh_3)_4]$ the complexes $[Rh(OCOR)(PPh_3)_3]$ can be isolated. The iridium hydride mer-$[IrH_3(PPh_3)_3]$ reacts with perfluorocarboxylic acids in boiling ethanol to give the complexes, $[IrH_2(OCOR)(PPh_3)_3]$, $(R = CF_3, C_2F_5, C_6F_5)$.

$[IrH(CO)(PPh_3)_3]$ gives the iridium(III) complexes $[IrH(OCOR)_2(CO)(PPh_3)_2]$, ($R = CF_3, C_2F_5$).[141] Carbon dioxide reacts with $[RhCl(PPh_3)_3]$ in the presence of Et_3SiH or $(EtO)_3SiH$ to give trans-$[RhCl(CO)(PPh_3)_2]$. The carbonyl compound also results from the action of HCO_2SiEt_3 upon $[RhCl(PPh_3)_3]$.[142] Phenazene (L) reacts with $[Ir(OClO_3)(CO)(PPh_3)_2]$ to give the salt $[IrL(CO)(PPh_3)_2]ClO_4$ which has been the subject of an X-ray study. The corresponding rhodium complex can also be isolated as can the complexes with dihydroxyphenazine.[143] A novel complex containing co-ordinated sulphur monoxide, SO, has been obtained by the action of sodium periodate on $[Ir(S_2)(diphos)_2]Cl$. Two isomeric iridium complexes can be obtained from this reaction and one isomer has been shown by an X-ray structure determination to contain co-ordinated S_2O_2, (113). The other isomer is considered to have the structure (114). Treatment of (113) with triphenylphosphine results in a deoxygenation reaction to give a complex of S_2O, (115), which may have a similar structure to the S_2O_2 complex. The disulphur monoxide complex can also be



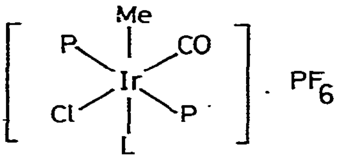
(114)



(113)

(115)

obtained by the action of an equimolar quantity of $NaIO_4$ upon $[Ir(S_2)(diphos)_2]Cl$.[144] Some cationic iridium(III) complexes, (116), result from the action of $AgPF_6$ and carbon monoxide or nitriles upon the complex $[IrClI(Me)(CO)(PMePh_2)_2]$.



(116)

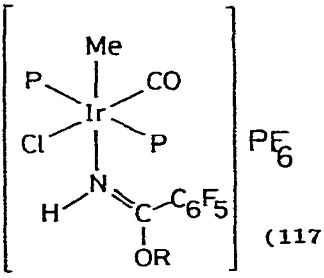
[P = $PMePh_2$

L = CO, C_6F_5CN,

p-NCC_6H_4X,

(X = NO_2,Me ,OMe)]

With methanol or ethanol as solvents, C_6F_5CN gives imino ether complexes (117).



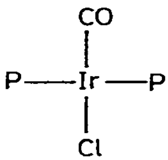
P = PMe_2Ph

R = Me, Et

(117)

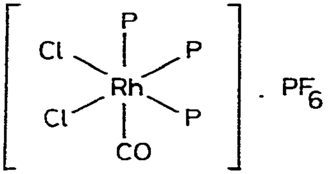
The chloride ligand trans- to phosphine in mer-$[RhCl_3(PMe_2Ph)_3]$ is labile and reaction with $AgPF_6$ and carbon monoxide leads to $[RhCl_2(CO)(PMe_2Ph)_3]PF_6$, (118). The corresponding iridium(III) complex can likewise be obtained.[47]

The complex (119) is unreactive toward H_2,O_2,SO_2 and cyano-alkenes but it does undergo slow oxidative addition reactions with hydrogen halides. A crystal structure determination reveals that a methyl group from each phosphine



(119)

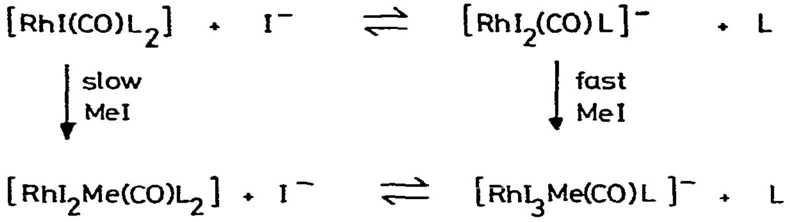
(P = P(o-$MeC_6H_4)_3$)



(118)

(P = PMe_2Ph)

is located near the apical positions of the square plane in (119) and the lack of reactivity can be explained by steric effects.[145] It is known that the oxidative addition of methyl iodide to trans-[$IrCl(CO)(PMe_2C_6H_4OMe$-2$)_2$] occurs 100 times faster than the addition to trans-[$IrCl(CO)(PMe_2Ph)_2$]. The large increase in rate is considered to be a consequence of direct interaction between the iridium and an ortho-methoxy-group in the polar transition state. Studies on the addition of H_2 reveal that the methoxy group does not have an accelerating effect and this is probably a consequence of the much lower polarity in the transition state involving addition of H_2.[146] In agreement with this mechanism only a weak solvent dependence is observed for the oxidative addition of H_2 to trans-[$IrCl(CO)(PPh_3)_2$] and trans-[$IrCl(CO)\{P(C_6H_4Me\text{-}4)_3\}_2$].[147] Studies on the rate of addition of methyl iodide to [$RhI(CO)L_2$], (L = PPh_3,$AsPh_3$,$SbPh_3$) in the presence of Bu_4NI reveal that added halide ions exert a powerful catalytic effect on the rate of oxidative addition in the case of the arsine and stibine complexes. The proposed mechanism is depicted in Scheme (35). The lack of halide catalysis with the phosphine complex may result from the position of



Scheme (35)

equilibrium between neutral and anionic complexes. No halide catalysis is observed with $[IrX(CO)L_2]$ complexes.[148]

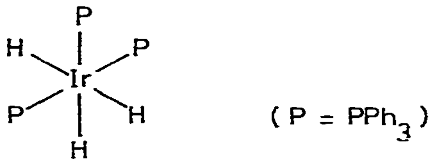
Oxidative addition of halogens to cis-$[RhX_2(CO)_2]^-$ is known to give the octahedral anions $[RhX_4(CO)_2]^-$. An X-ray analysis of the salt $[Pr^n_4N][RhI_4(CO)_2]$ establishes a trans-dicarbonyl structure for the anion. Preliminary results also indicate the existence of a trans- form of $[RhBr_4(CO)_2]^-$. These are unusual geometries since such species would normally be expected to adopt a cis-dicarbonyl arrangement. There appears to be no evidence for a trans- form of $[IrI_4(CO)_2]^-$.[149] Oxidative addition of halogens to $[RhCl(PPh_3)_3]$ is reported to give complexes of the type $[RhClX_2(PPh_3)_3]$, (X = Cl,Br,I), but whether these are true mixed halogeno complexes or merely mixtures of such complexes as $[RhCl_3(PPh_3)_3]$ or $[RhX_3(PPh_3)_3]$ is not clear. Halogens also oxidatively add to $[RhCl(\text{1-phenyl-tetrazoline-5-thione})_2(PPh_3)_2]$.[150]

A redetermination of the crystal structure of $[IrO_2(Ph_2PCH_2CH_2PPh_2)_2]PF_6$ reveals that the previous report of an O-O bond length of 1.625 (23) Å is incorrect, an error due to crystal decomposition. The O-O bond length is 1.52 (1) Å and this result provides further evidence that there is no correlation between O-O bond length and oxygen lability as had been previously supposed.[151,152] Ultraviolet irradiation of the O_2 and H_2 adducts of trans-$[IrX(CO)(PPh_3)_2]$, (X = Cl,I), $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ and $[Ir(Ph_2PCH{=}CHPPh_2)_2]^+$ induces reductive elimination of oxygen and hydrogen and regenerates the square planar complexes. Singlet oxygen is not formed in the photoinduced deoxygenation reactions.[153] The kinetics of decarbonylation of $[Ir(CO)(diphos)_2]Cl$ and $[IrCl(CO)_2(PPh_3)_2]$ have also been reported.[154]

The caged phosphite ester, $P(OCH_2)_3CMe$, (L), reacts with trans-$[IrCl(N_2)(PPh_3)_2]$ and trans-$[IrCl(CO)(PPh_3)_2]$ to give a variety of cationic complexes, $[IrL_5]^+$, $[IrL_4(PPh_3)]^+$, $[Ir(CO)L_3(PPh_3)]^+$, $[Ir(CO)L_4]^+$, $[IrL_3(PPh_3)_2]^+$, $[Ir(CO)L_2(PPh_3)_2]^+$ some of which are stereochemically non-rigid.[155] However, n.m.r. studies on the complexes $[Co\{P(OMe)_3\}_5]ClO_4$ and $[Rh\{P(OMe)_3\}_5]BPh_4$ reveal that in solution these five-co-ordinate complexes are in equilibrium with a four-co-ordinate complex and free ligand.[156]

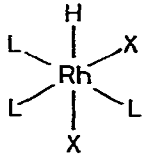
Treatment of $[Ir(CO)(PMePh_2)_3]^+$ with excess PPh_2Me gives $[Ir(PPh_2Me)_4]^+$ and the crystal structure of $[Ir(PPh_2Me)_4]BF_4 \cdot C_6H_{12}$ has been determined. The phosphine ligands around the iridium are in a very distorted square-planar arrangement. The inability of the cation to form adducts with O_2 or CO is considered to be a consequence of steric and electronic effects. It readily reacts with HCl, H_2 and Cl_2.[157]

The reaction of $[Co(acac)_3]$ with $AlBu^i_3$ in aromatic hydrocarbons in the presence of hydrogen gives a mixture which catalyses the hydrogenation of alkenes. The structures of the compounds formed in this type of reaction have been considered and the reactions of the mixture with benzyl bromide, diphenylmercury and styrene have been reported. From the results it is suggested that for molar ratios $[Co(acac)_3]/AlBu^i_3$ = 1:1 to 1:5 the formula of the cobalt compound present can be represented as $[Co_2H]_x$. For molar ratios 1:5 to 1:10 it is $[Co{-}H]_y$.[158] The hydride $[CoH_3(PPh_3)_3]$ has a dynamic structure on the n.m.r. time scale at room temperature and it is slightly dissociated into a bisphosphine complex and free PPh_3.[159] The hydride (120) has been characterised crystallographically



(120)

and the hydrogen atoms have been located. The Ir-H bond lengths vary from 1.58 - 1.62 Å.[160] The alpha (121) and beta (122) isomers of $[RhHX_2L_3]$, (X = Cl,Br; L = tertiary phosphine or arsine) have been shown to have the same structures as the



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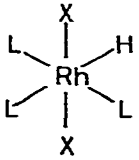
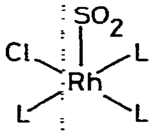


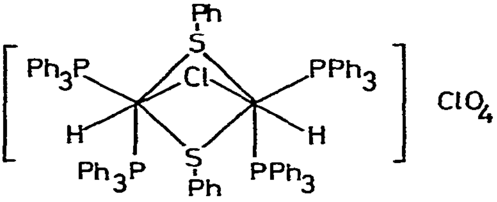
(122)

corresponding iridium structures. The beta isomers are formed by the action of cold ethanolic phosphinic acid on the complexes, $[RhX_3L_3]$. On warming isomerisation to the alpha form occurs. The complexes, $[RhX_3L_3]$, which contain the more basic ligands, appear to be resistant to reduction by an excess of the ligand and the best route to the alpha isomers involves the oxidative addition of HCl to $[RhClL_3]$, (L = $PMePh_2$, PMe_2Ph, $PEtPh_2$, PEt_2Ph, PBu_2Ph, PEt_3, PBu^n_3, $AsMePh_2$). The beta (122) to alpha (121) isomerisation occurs more readily than with the corresponding iridium complexes and the isomerisation is accelerated by light. Since the isomerisation is inhibited by free ligand the mechanism is probably dissociative. Loss of ligand trans- to hydride giving a five co-ordinate intermediate is probably involved. The least stable complexes are formed with the ligands $PPh_n(C_6H_{11})_{3-n}$, (n = 0-3) and $AsPh_3$ for which satisfactory analytical data could not be obtained.[161] The alpha isomers are generally inert to acids but both isomers react with nitric acid to give $[RhX_2(NO_3)L_2]$. The alpha isomers undergo dehydrohalogenation by bases and with weak bases equilibria can be established which reveal that the stability to dehydrohalogenation increases in the series $PRPh_2 < PR_2Ph < PR_3$, R = Et < Me. For the complexes $[RhX_2HL_2]$ stability to dehydrohalogenation increases in the order L = $PPh_3 < AsPh_3 < SbPh_3$. The beta isomers similarly react with bases and give trihalogeno complexes with hydrogen halides. Both isomers react with sulphur dioxide to give $[RhX(SO_2)L_3].HX$, (123), (X = Cl,Br). The mode of



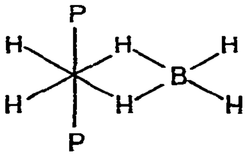
(123)

incorporation of HX is not known.[162] Treatment of $[IrHCl(SPh)(PPh_3)_2]_2$ with $AgClO_4$ gives the dimeric species (124) which has been characterised by X-ray crystallography.



(124)

The hydride $[IrHCl(SPh)(PPh_3)_2]_2$ dissolves in $CHCl_3$ or $ClCH_2CH_2Cl$ to give a clear yellow solution from which a complex, $[(Ph_3P)_2(H)Ir(SPh)_2ClIrH(PPh_3)_2]Cl.2H_2O$ similar to (124) precipitates.[163] Treatment of $[IrHCl_2(PMeBu_2{}^t)_2]$ with sodium borohydride in ethanol at 0°C gives (125), $(P = PMeBu_2{}^t)$. At 25°C some $[IrH_5(PMeBu_2{}^t)_2]$ is also formed and this hydride is

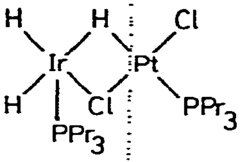


$(P = PMeBu^t_2,\ PBu^t_3,\ PBu^nBu^t_2,\ PPhBu^t_2)$

(125)

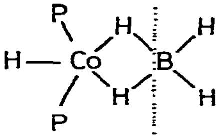
slowly formed during the decomposition of (125) in dry deuteriotoluene at 25°C. Analogous complexes with other bulky phosphines can also be obtained. However, sodium borohydride reduction of $[IrHCl_2(AsBu_2{}^tPr^n)_2]$ gives $[IrH_5(AsBu_2{}^tPr^n)_2]$. These complexes are the first examples of non-fluxional metal hydroborates. Sodium borohydride reduction of $[RhHCl_2(PMeBu_2{}^t)_2]$ gives $[RhH_2(BH_4)(PMeBu_2{}^t)_2]$ which exhibits some fluxional behaviour.[164]

The addition of $[PtCl_2(PPr_3)]_2$ to $[IrH_5(PPr_3)_2]$ in toluene at 20°C results in evolution of hydrogen and formation of (126).[165]



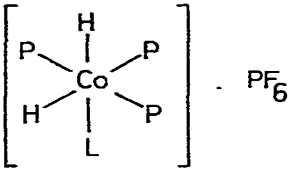
(126)

Treatment of $CoCl_2.6H_2O$ and $P(C_6H_{11})_3$ in toluene-ethanol with sodium borohydride gives (127) which has been characterised



(127)

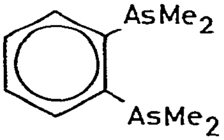
by X-ray studies. This paramagnetic complex is an active catalyst for the hydrogenation and isomerisation of alkenes.[166] Oxidation of the cobalt(II) hydride complex, $[CoH\{PPh(OEt)_2\}_4]PF_6$, with $[FeCp_2][PF_6]$ in the presence of the ligands L = MeCN, PhCN, $ClCH_2CN$, $PPh(OEt)_2$ gives the cobalt(III) complexes, $[CoHL\{PPh(OEt)_2\}_4]PF_6$, (128). Reaction of the cobalt(II) complex with carbon monoxide in the presence of $[FeCp_2]PF_6$ gives $[Co(CO)\{PPh(OEt)_2\}_4]PF_6$. An aquo complex which may be $[CoH(OH_2)\{PPh(OEt)_2\}_4]PF_6$ reacts with halide ions to give $[CoHX\{PPh(OEt)_2\}_4]PF_6$.[167] The aquo group of the



(128)

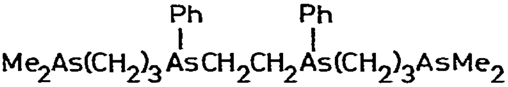
(P = PPh(OEt)$_2$)

cobalt(III) complex, trans-[$CoH(H_2O)(diars)_2$][ClO_4]$_2$, (diars = 129) is also labile and can be readily displaced by unidentate



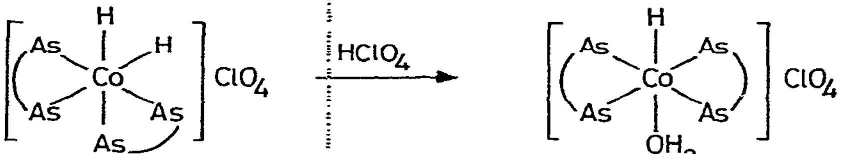
(129)

ligands to give a series of complexes [$CoHL(diars)_2$]$^{n+}$, (L = Cl^-,Br^-,I^-,NCS^-,NO_3^-,$OCOCF_3^-$,MeCN). Reduction of the cobalt(III) complexes trans-[$CoCl_2(diars)_2$]Cl, trans-[$CoCl_2$(R,S-tetars)]Cl, and cis-α-[$CoCl_2$(R,R:S,S-tetars)]Cl, (tetars = 130), with sodium borohydride is known to give extremely oxygen



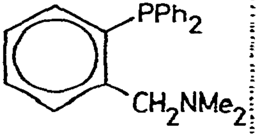
$$Me_2As(CH_2)_3\overset{Ph}{As}CH_2CH_2\overset{Ph}{As}(CH_2)_3AsMe_2$$

sensitive complexes which react with oxygen to form the complexes [$Co(O_2)As_4$]$^+$. If, however, the solutions are kept acid during the reduction the complexes [$CoHClAs_4$]ClO_4 can be isolated. These hydrido complexes are inert to oxygen in acidic or neutral media, but in the presence of base they all give dioxygen adducts. The base is considered to deprotonate the hydrido complexes and generate a cobalt(I) complex which can form the dioxygen adduct. However, treatment of $[CoCl_2(diars)_2]Cl$ with excess sodium borohydride in basic (pH∼8) solutions gives *cis*-$[CoH_2(diars)_2]^+$ which can be isolated as a perchlorate salt. The salt (131) readily reacts with oxygen to give $[CoO_2(diars)_2]ClO_4$. Treatment of (131) with perchloric acid gives (132). The dihydride (131) is stereochemically non-rigid.[168]

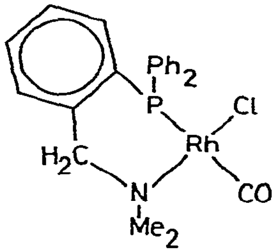


(131) (132)

The unsymmetrical chelate, (133), reacts with $[RhCl(CO)_2]_2$ to give (134). The complex (134) is less basic than the somewhat similar complex (135). Thus allyl chloride readily forms

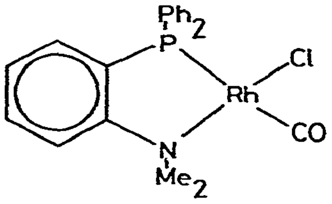


(133)



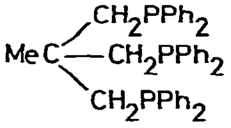
(134)

a σ-allyl complex with (135) but the corresponding reaction with (134) is reversible.[169]



(135)

Cobalt(II) chloride forms a tetrahedral complex with (133).[169] Treatment of cobalt(II) halides with the phosphine p3, (136) and sodium borohydride gives the monovalent complexes $[CoX(p3)]$.



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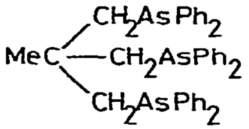
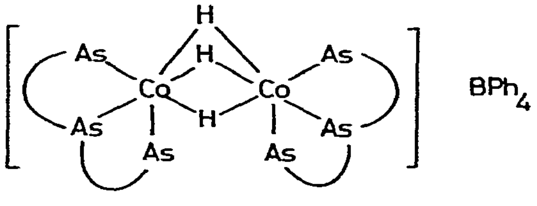


(137)

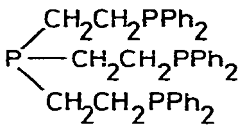
However, if cobalt(II) salts of poorly co-ordinating anions such as BF_4^- are used a cobalt(II) complex $[Co_2H_3(p3)_2]BPh_4$, can be isolated upon addition of $Na[BPh_4]$. The arsine ligand (137) forms an analogous complex (138), and this has been



(138)

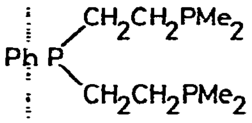
characterised by an X-ray study.[170] The tetradentate tripod ligand (139) reacts with cobalt(II) salts in the presence of

(139)



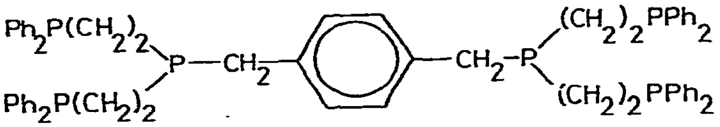
sodium borohydride to give the low spin five-co-ordinate complex [CoX(pp3)], {pp3 = (139); X = H,SCN,halide}. The hydride complex [CoH(pp3)] has a trigonal bypyramidal structure with the hydride ligand in an axial position.[171,172] The related cobalt(II) hydride complex, [CoH(pp3)]BF_4 has a similar geometry,[173] as does the complex hydridotris(2-diphenylphosphinophenyl)phosphinecobalt(I).[174] Photoelectron spectra of the hydrides [$MH(PF_3)_4$], (M = Co,Rh,Ir) have been presented.[175] Five-co-ordinate complexes of the general formula [$MX(L'L_3)$], (M = Co,Rh; $L'L_3$ = quadridentate tripod-like ligand containing P, As or Sb donor atom sets) have been prepared.[176] Treatment of $RhCl_3xH_2O$ with $Me_2PCH_2CH_2PPh_2$ gives [$RhCl_2(Me_2PCH_2CH_2PPh_2)_2$]$Cl2H_2O$ and the cobalt(II) complex [$CoCl_2(Me_2PCH_2CH_2PPh_2)$] has also been prepared. Hydrated iridium(III) chloride reacts with (140) to give [$Ir_3Cl_9(P_m$-P_f-$Pm)_2$].[177] The reaction of the sexadentate ligand, TDDX,

(140)



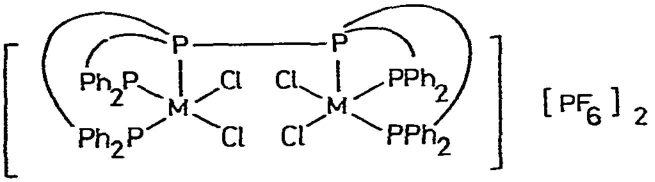
= P_m-P_f-P_m

(141) with hydrated iridium(III) chloride gives a precipitate



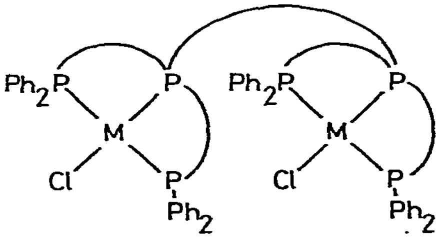
(141)

of composition [Ir_3Cl_9(TDDX)]. Addition of NH_4PF_6 to the filtrate gives the yellow complex [Ir_2Cl_4(TDDX)][PF_6]$_2$ which may have the structure (142), (M = Ir).



(142)

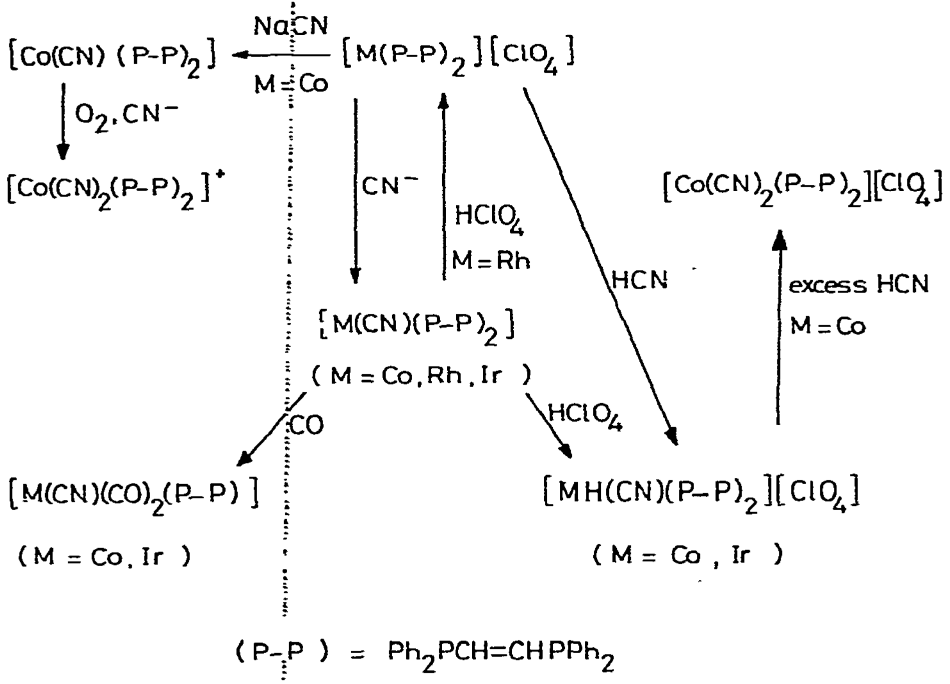
The reaction of TDDX with hydrated rhodium(III) chloride gives a similar complex [Rh_2Cl_4(TDDX)]Cl_2. Complexes of the type (143) can be obtained by the reactions of TDDX with



(143)

trans-$[MCl(CO)(PPh_3)_2]$, (M = Rh,Ir) and $[RhCl(PPh_3)_3]$.[178]

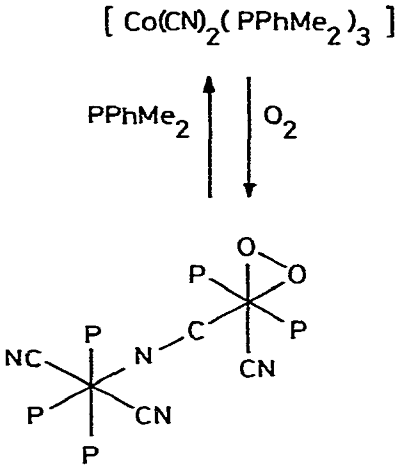
The five-co-ordinate complexes, $[M(CN)(Ph_2PCH{=}CHPPh_2)_2]$, (M = Co,Rh,Ir) have been prepared and some reactions of the complexes are illustrated in Scheme (36).



(P-P) = $Ph_2PCH{=}CHPPh_2$

Scheme (36)

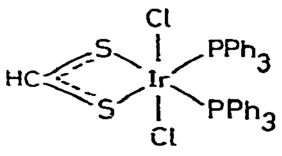
These studies indicate that the sequence of reactivity and adduct stability is qualitatively Co$\sim$Ir>Rh. The complexes $[M(CN)(Ph_2PCH{=}CHPPh_2)_2]$ do not react with dihydrogen at room temperature and decompose in the presence of dioxygen.[179] Oxidation of $[Co(CN)_2(PPhMe_2)_3]$ gives the cyanide bridged complex (144) which has been characterised crystallographically.



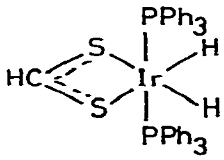
(144)

Kinetic studies are consistent with a mechanism of formation of (144) through a CN-bridged inner sphere electron transfer reaction between $[Co(CN)_2(PPhMe_2)_3]$ and $[Co(CN)_2(PPhMe_2)_2O_2)]$ Since treatment of (144) with $PPhMe_2$ regenerates $[Co(CN)_2(PPhMe_2)_3]$ a catalytic cycle for the oxidation of the phosphine to $PhMe_2PO$ can be devised.[180] EPR spectra of $[CoCl(diphos)_2]SnCl_3$, (tetragonal pyramidal) and $[CoCl(diphos)_2]SnCl_3 \cdot PhCl$, (trigonal bipyramidal) have been reported[181] and single-crystal polarised reflectance spectra of $[Rh(acac)(CO)_2]$ and $[Ir(acac)(CO)_2]$ have been obtained.[182]

The hydride $[IrHCl_2(PPh_3)_3]$ (<u>trans</u>-chlorides) and <u>mer</u>-$[IrH_3(PPh_3)_3]$ react with carbon disulphide to give (145) and (146) respectively. However, <u>fac</u>-$[IrH_3L_3]$ (L = PPh_3, $AsPh_3$) is inert to carbon disulphide.[183]



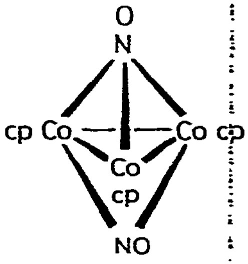
(145)



(146)

Metal nitrosyl and aryldiazo complexes.

Thermolysis of $[CoCpNO]_2$ gives the cluster (147) which on the basis of spectroscopic measurements is given the structure (147). However, treatment of $[CoCpNO]_2$ with $[Co_2(CO)_8]$ or $[CoCp(CO)_2]$ gives (148).[184]



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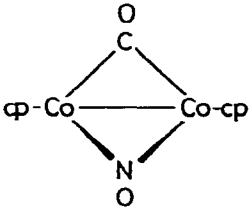


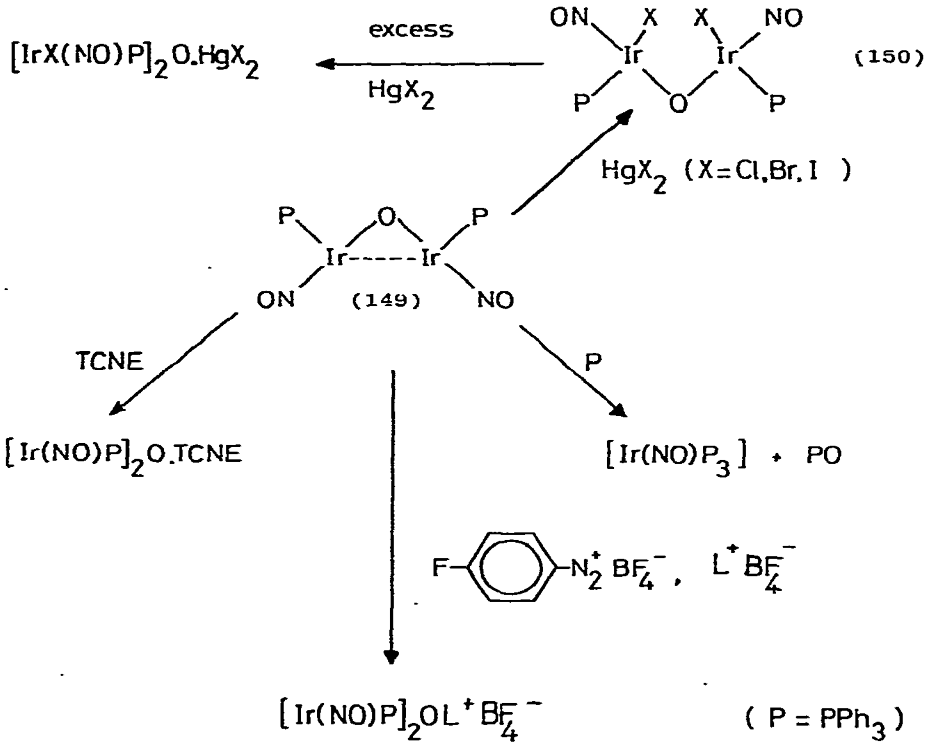
(148)

The reactions of nitric oxide with Co^{2+} ions and cobalt ammine complexes in cobalt exchanged zeolites have been studied. Infrared and adsorption data indicate the formation of $[Co(NO)_2]^{2+}$, $[Co^{II}(NH_3)(NO)_2]^{2+}$ and $[Co^{III}(NH_3)_nNO]^{2+}$ (n is probably equal to 5).

Intramolecular and intermolecular reaction of $[Co^{III}(NH_3)_nNO]^{2+}$ with NO gives N_2, N_2O and $[Co^{III}(NH_3)_nNO_2]^{2+}$. The N_2 results from the reaction of NO^- ligand with NH_3, a reaction which readily occurs on a supported platinum catalyst at elevated temperature. However, this reaction has not previously been observed for conventional nitrosyl complexes at room temperature. N_2O and NO_2 are produced by disproportionation of the NO^- ligand with two nitric oxide molecules.[185]

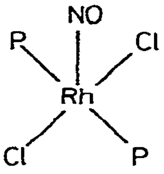
The novel complex (149) is obtained as a benzene solvate in low yield when trans-$[IrCl(CO)(PPh_3)_2]$ is treated with

$NaNO_2$ in the absence of oxygen in a mixture of aqueous ethanol and benzene. Some reactions of (149) are illustrated in Scheme (37). Tetrafluoroethylene also reacts with (149) but the product is a brown intractable solid.[186] The crystal structure of $[IrCl(NO)PPh_3]_2O$, (150) has been determined.[187]



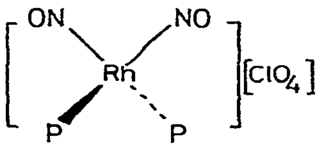
Scheme (37)

Perfluorocarboxylic acids, RCO_2H, ($R = CF_3$, C_2F_5 and C_6F_5) readily react with $[Ir(NO)(PPh_3)_3]$, to give the salts $[Ir(OCOR)(NO)(PPh_3)_2]OCOR$, ($\nu(NO)$ ca. 1800 cm^{-1}). However, with [$Rh(NO)(PPh_3)_3$] non-ionic species [$Rh(OCOR)_2NO(PPh_3)_2$], (ν(NO) ca. 1665 cm^{-1}) are obtained. Unlike the reactions with the iridium compound the reactions with [$Rh(NO)(PPh_3)_3$] only occur in the presence of dioxygen.[188] The crystal structures of [$RhCl_2(NO)(PPh_3)_2$] (151) and [$Rh(NO)_2(PPh_3)_2$]ClO_4 , (152), have been determined.[189,190] The co-ordination geometry about the rhodium in (152) is intermediate between tetrahedral and square planar. The trend in M-N-O angles for the ions $[M(NO)_2(PPh_3)]^+$, (M = Co,Rh,Ir) is approximately Rh<Ir<Co and the greater bending of the nitrosyl groups in the rhodium complex and longer M-N bonds indicate a greater amount of NO^- character. The relative activity of these complexes as catalysts for the reaction:



($P = PPh_3$)

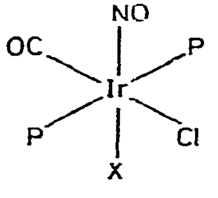
(151)



(152)

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

is Rh>Ir>Co.[190] Treatment of the salt [$IrCl(NO)(CO)(PPh_3)_2$] BF_4 with co-ordinating anions X^- gives the complexes (153).



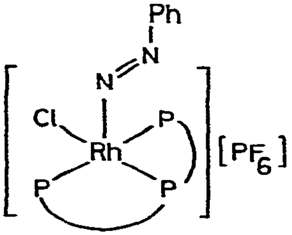
$P = PPh_3$

$X = N_3$, NCO , NCS, Cl, Br, I .

(153)

These complexes have NO stretching frequencies in the region 1520 - 1560 cm^{-1}, and these are among the lowest yet reported for metal nitrosyl complexes. The complexes are structurally analogous to the aryldiazo complexes, $[IrXCl(N_2R)CO(PPh_3)_2]$. The complexes (153) are exclusively oxygenated to nitrato complexes, $[IrClX(NO_3)(CO)(PPh_3)_2]$, the rate of oxygenation decreasing in the order $X = I > Br > Cl > NCS > NCO > N_3$. There is no noticeable reaction of $[IrCl(NO)(CO)(PPh_3)_2]BF_4$ with dioxygen, however, in the presence of pyridine or picoline reaction with dioxygen is rapid giving a mixture of nitrato, nitro and nitrito complexes. The complex $[IrCl(NO)(CO)(PPh_3)_2]BF_4$ reacts with CO to give $[IrCl(NO)(CO)_2(PPh_3)_2]BF_4$.[191] It is known that $[RhCl(PPh_3)_3]$ reacts with NO to give $[RhCl(NO_2)(NO)(PPh_3)_2]$ and it has now been found that this nitro-nitrosyl complex reacts further with NO to give $[RhCl(NO_2)_2(PPh_3)_2]$.[192] The ability of platinum group metal complexes to promote NO disproportionation and reduction has been discussed in a review.[193]

A crystal structure determination of the complex (154) reveals the presence of a doubly bent aryldiazo ligand. The complex has a very similar structure to the corresponding nitrosyl complex and this is the first example of the



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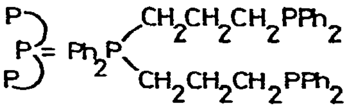


aryldiazo analogue of NO^-,N_2Ph^-.[194]

The cationic nitrosyl complex $[Rh(NO)(diphos)_2][PF_6]_2$ undergoes a reversible reaction with excess halide to give a complex which may be six-co-ordinate.[195] Proton n.m.r. studies on $[Ir(NO)(PPh_3)(N_4R_4)]$, (R = p-$MeC_6H_4SO_2$), at low temperature reveal a splitting of the methyl resonance of the tolyl residue which has been attributed to a conformational effect.[196]

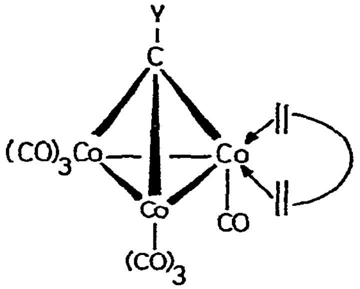
The relative shifts of O 1s and N 1s binding energies, obtained from Esca studies, have been shown to offer an additional technique to i.r. spectroscopy[193] for distinguishing between linear and bent nitrosyls.[197] From calculations of the Langevin diamagnetism for the complexes, $[RhX_2(NO)(PPh_3)_2]$ it appears that the polarity of Rh-X bond increases in the order X = $Cl<Br<NO_2<NO_3$.[198] Gamma irradiation of $[Co(NO)(CN)_5]^{2-}$ produces $[Co(CN)_5]^{3-}$ and $[Co(NO)(CN)_5]^{4-}$ which appears to contain a bent Co-N-O bond.[199] Crystal structure studies on complexes of the type $[Co(NO)(das)_2X_2]$ (X = monoanion; das = o-phenylenebis(dimethylarsine)) reveal differing co-ordination geometries and Co-N-O bond angles. When X = ClO_4^-, the cobalt complex is essentially 5-co-ordinate and has a Co-N-O bond angle of 179°, whereas when X = NCS^- the complex is 6-co-ordinate and has a Co-N-O bond angle of 132°. Treatment of the perchlorate complex with HBr in methanol yields a complex having similar structural properties to the thiocyanate complex.[200]

Metal alkene and alkyne complexes.

Oxidation of the dimers $[Co(CO)_2(diene)]_2$ in the presence of triphenylphosphine is known to yield the cationic species

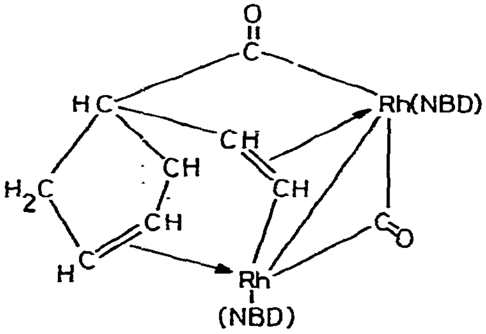
$[Co(CO)_n(diene)(PPh_3)_{3-n}]^+$, (n = 1,2). A simple procedure for preparing these cations has now been reported. Thus treatment of $Co(ClO_4)_2.6H_2O$ in isopropanol at room temperature with butadiene in the presence of excess PMe_2Ph gives $[Co(butadiene)(PMe_2Ph)_3]ClO_4$. The diene is readily displaced by carbon monoxide and an isoprene complex can similarly be obtained. Analogous complexes can be obtained with $PHPh_2$ but the larger phosphines, $PMePh_2$ and PPh_3 do not yield the diene complexes. The cationic diene complexes may also be obtained by the action of dienes on <u>cis</u>-$[CoH_2(PR_3)_4]^+$.[115,201] Treatment of anhydrous $CoCl_2$ with butadiene-d^6 and $NaBD_4$ gives the complexes $[Co(C_8D_{13})(butadiene)]$ and $[Co(C_8D_{12}H)(butadiene)]$ where C_8D_{13} is 3-methyl-d_3-heptadienyl-d_{10} and $C_8D_{12}H$ is 3-methyl-d_2-heptadienyl-d_{10}.[202]

Norbornadiene and cyclohexa-1,3-diene react with the cluster compounds $[Co_3(CY)(CO)_9]$, (Y = alkyl,aryl,F) to give the dark green complexes $[Co_3(CY)(CO)_7(diene)]$. The aryltricobalt carbon complexes form the most stable diene complexes but no similar complexes can be isolated with cyclooctadienes, cycloheptadiene or butadiene. The co-ordinated diene in these complexes is extremely labile and is readily displaced by carbon monoxide, phosphines and phosphites. However, a small yield of $[Co_3(CPh)(CO)_6(PPh_3)(NBD)]$ can be obtained. The norbornadiene complexes (155) are non-rigid in solution.[203] Treatment of $Rh_6(CO)_{16}$ with norbornadiene in refluxing methylcyclohexane gives the substituted derivatives $[Rh_6(CO)_{14}(NBD)]$, $[Rh_6(CO)_{12}(NBD)_2]$, and $[Rh_6(CO)_{10}(NBD)_3]$. If the red solution containing $[Rh_6(CO)_{10}(NBD)_3]$ is heated further yellow needles of a novel acyl-vinyl complex, (156)



(155)

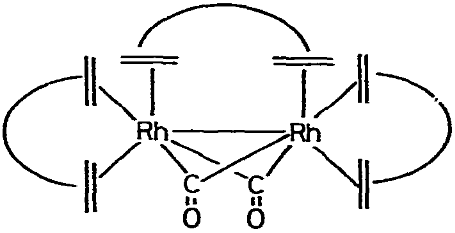
are deposited. A crystal structure determination of



(156)

$[Rh_6(CO)_{10}(NBD)_3]$, the apparent precursor to (156) reveals that the tris-norbornadiene complex is derived from $[Rh_6(CO)_{16}]$ by displacing two terminal carbonyl groups from three rhodium atoms each of which co-ordinates to the diene. There appears to be steric strain in the molecule and the molecule is probably unable to accommodate a fourth diene molecule.[204] The complex (156) may be identical to the product $[Rh_2(CO)_2(NBD)_3]$ which is formed on treating $[Rh_4(CO)_{12}]$ with norbornadiene for which the simple structure (157) was proposed as described in last year's Annual Survey.

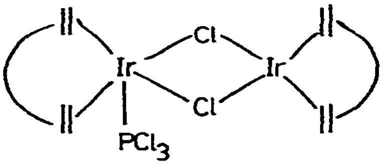
The photorearrangement of cyclo-octa-1,5-diene to cyclo-octa-1,4-diene in the presence of rhodium(I) chloride



(157)

occurs via an intramolecular [1,3] shift of hydrogen, cleavage of an allylic C-H bond being rate determining. The mechanism for the photorearrangement of dienes catalysed by rhodium(I) involves initial photodissociation of one of the two metal alkene bonds, oxidative addition of an allylic C-H bond and reductive elimination of the η^3-allylrhodium hydride intermediate.[205] The thermal isomerisation of penta-1,4- and cis-penta-1,3-dienes in complexes of the type [Rh(diene)(acac)], [Rh(diene)Cp] and [Rh Cl(diene)$]_2$ also occurs via a [1,3] hydrogen shift. Resulting from these studies it is apparent that conversion of an η-alkene to an η-allyl complex involves a σ-allyl complex.[206] Studies on the reactions of cis, cis-1,3-, and 1,4-cyclo-octadienes with Rh(I) and Ir(I) systems indicate that the co-ordinated dienes rearrange to the more stable cyclo-octa-1,5-diene. However, reaction of cis,trans-cyclo-octa-1,3-diene with $[RhX_2(CO)_2]^-$, (X = Cl,Br) gives unusual complexes of stoicheiometry, $[Rh_2X_2(CO)_4(c,t\text{-}1,3\text{-}COD)_5]$.[207] Cis-cis-1,3-cyclononadiene also gives a rhodium(I) complex of the 1,5-diene.[208]

Infrared and X-ray diffraction studies indicate that $[RhCl(NBD)]_2$ exists in two crystallographic forms.[209] Slow oxidation of $[IrCl(1,5\text{-}COD)]_2$ in methylene chloride or benzene gives crystalline complexes which are considered to be probably monomeric complexes $[IrCl(OH)(1,5COD)]$.[210] As such these are complexes of iridium(II). Treatment of $[MCl(1,5\text{-}COD)]_2$ (M = Rh,Ir) with either PCl_2Ph or $PClPh_2$ gives the complexes $[MCl(COD)(PCl_xPh_{3-x})]$ which on treatment with excess of the phosphine yield $[MCl(PCl_xPh_{3-x})_3]$, (x = 1,2). With iridium an intermediate in these reactions, $[IrCl(COD)(PCl_xPh_{3-x})_2]$ can be formed. Some interesting PCl_3 complexes, $[Ir_2Cl_2(COD)_2(PCl_3)]$ and $[Ir_2Cl_2(COD)_2(PCl_3)_3]$ can also be obtained. The structures (158) - (160) have been proposed for these complexes and they may contain novel bridging PCl_3 groups.[211]



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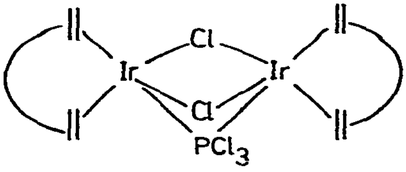

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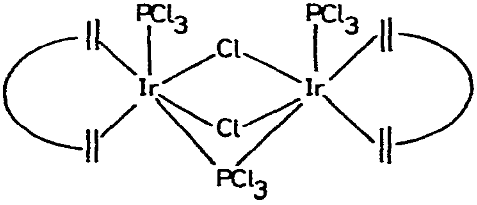
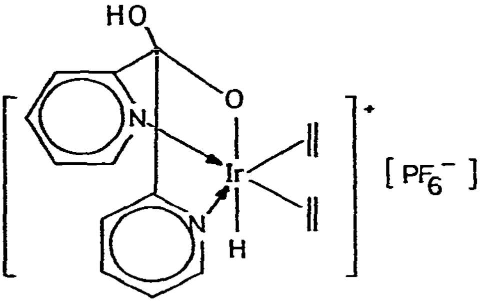


(160)

A variety of rhodium and iridium complexes of the type

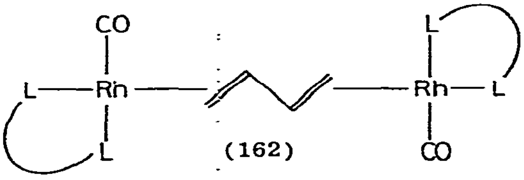
[MClL(diene)], [ML_2(diene)]X and [M(chel)(diene)]X, (L = NH_3, piperidine, $BuNH_2$, N-methylimidazole; diene = cyclo-octa-1,5-diene, cyclo-octa-1,3,5,7-tetraene, norbornadiene; chel = 8-aminoquinoline, phenylenediamine, dipyridylketone, bipyridyl, substituted phenanthrolines; X = Cl^-, PF_6^-, ClO_4^-) have been prepared. Some of the complexes have bacteriocidal, viricidal and anti-neoplastic activity. The reaction of dipyridylketone (DPK) with $[RhCl(COD)]_2$ in ethanol followed by addition of NH_4PF_6 gives the expected complex, [Rh(DPK)(COD)]PF_6. However, the corresponding reaction with $[IrCl(COD)]_2$ in methanol gave the hydride (161). The complexes



(161)

[ML_2(diene)]Cl and [M(chel)(diene)]Cl are easily oxidised in air. In general the bipyridyl complexes are oxidised more rapidly than those of ortho-phenanthroline and norbornadiene more rapidly than those of cyclo-octa-1,5-diene. Reactions with cyclo-octa 1,3,5,7-tetraene are very slow. Iridium complexes are also oxidised more rapidly than the rhodium complexes.[212] The neutral complexes [$Rh(S_2PR_2)$(1,5-COD)], (R = Ph,C_6H_{11}) have also been reported.[134]

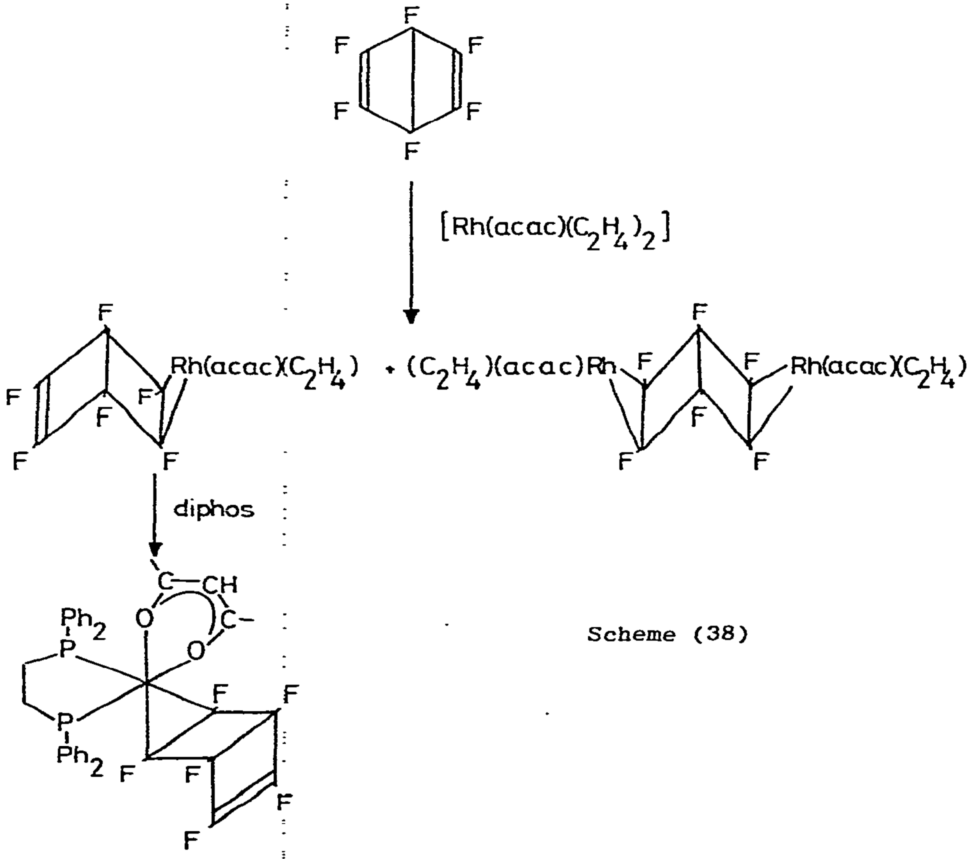
Treatment of either $[Rh(acac)(CO)C_8H_{14})]$ [213] or $[Rh(O\text{-}N)(CO)(C_8H_{14})]$, (O-N = 8,quinolinolato, C_8H_{14} = cyclo-octene) with butadiene gives the dinuclear complexes (162) and a similar type of substitution reaction gives



(162)

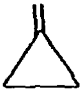
L-L = acac or 8-quinolinolato

alkene complexes of the para-bonded benzene, C_6F_6, Scheme (38).[214]

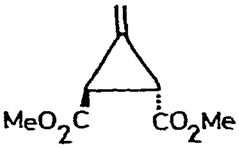


Scheme (38)

Treatment of the methylene cyclopropanes, (163) - (165)



(163)



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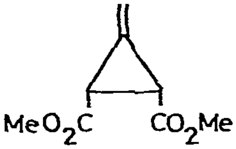
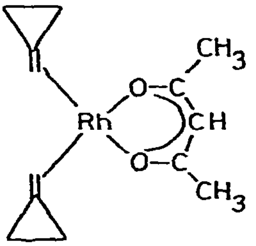


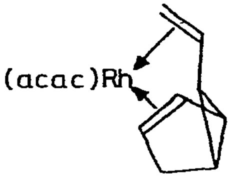
(165)

with ethylene rhodium(I) or iridium(I) complexes gives the η-bonded methylene cyclopropane complexes, $[Rh(acac)(alkene)_2]$, (alkene = 163 - 165), $[RhCl(alkene)_2]$, (alkene = 164, 165), $[RhCp(alkene)_2]$, (alkene = 164), and the complexes $[Rh(acac)(alkene)(CO)]$, and $[RhCp(alkene)(CO)]$, (alkene = 164) have also been prepared. Crystallographic studies on (166)



(166)

reveal considerable asymmetry in the bonding of methylenecyclopropane to rhodium(I) and it is apparent that there are similarities between the co-ordination geometries of methylenecyclopropanes and 1,2-dienes. The methylenecyclopropane complexes are stable towards heat and u.v. irradiation and no tendency for the rhodium or iridium to insert into the cyclopropane has been observed. Since on co-ordination the cyclopropane ring is bent away from the metal, intramolecular cleavage of the ring will be inhibited.[215] The *cis*-divinylcyclopropane complex (167) does, however, rearrange at 80°C to give the isomer (168) and it has been proposed



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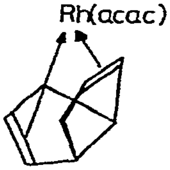
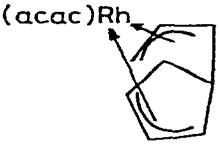
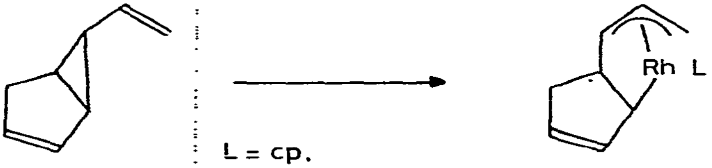


(168)



(169)

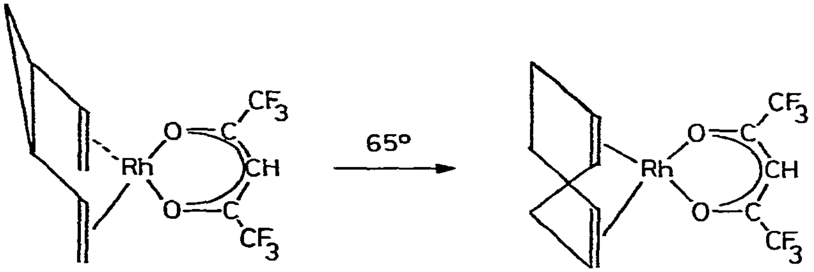
that the reaction proceeds via the *transoid* bis-π-allyl (169). The related hexafluoroacetylacetonate complex of (167) rearranges more rapidly than (167) but the corresponding iridium(I) complex shows no evidence of thermal rearrangement up to 145°C.[216] The *trans*-divinylcyclopropane (170) also forms rhodium(I) complexes (171), ring opening of the cyclopropane ring occurring.



(170) L = cp. $CF_3COCHCOCF_3$ (tetramer), (171)
acac (dimer).

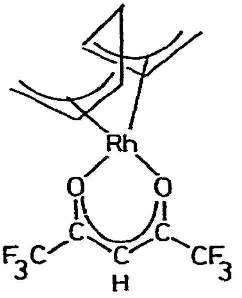
The acetylacetonate derivative of (171) rearranges readily to a mixture of (167) and (168) and it is proposed that these reactions also proceed via the intermediate (169). The cyclopentadienyl derivative of (171) cannot form a bis-π-allyl analogous to (169) and the complex is much more stable.

However, there is evidence for a similar transformation of this complex which occurs slowly at 120°C. The tetrameric hexafluoro-analogue of (171) rearranges to the hexafluoroacetylacetonate derivative of (168).[217] Both *cis*- and *trans*-divinylcyclopropane also readily form 1:1 hexafluoroacetylacetonatorhodium(I) complexes. In the former the cyclopropane ring is not cleaved and complex (172) is formed Conversion to a new complex, (173) does occur at 65°C.



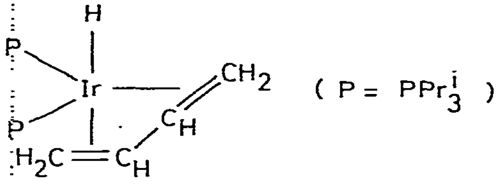
(172) (173)

However, *trans*-divinylcyclopropane reacts with ring-opening to give the bis-π-allyl complex (174) which has been characterised crystallographically.[218]



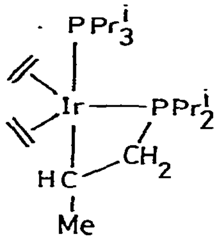
(174)

Butadiene, 2-methylbutadiene and penta-1,3-diene react with $[RhCl(PF_3)_2]_2$ to give yellow complexes of stoichiometry $[RhCl(PF_3)_2diene]_n$ which may be either monomeric or dimeric.[219] A single crystal X-ray structure determination[220] reveals that the complex (175) has a distorted trigonal bipyramidal structure and these trifluorophosphine complexes may have similar geometries. $[RhCl(PF_3)_2]_2$ does not form isolable complexes with simple alkenes but it forms an adduct, $[RhCl(PF_3)_2(CH_2{=}CHCN)]_n$ with acrylonitrile. It also catalyses the isomerisation of dec-1-ene to dec-2-ene.[219]



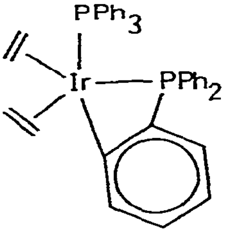
(175)

The unsolvated complex, trans-$[IrCl(C_2H_4)(PPh_3)_2]$, is significantly more stable in the solid state when exposed to air than the benzene solvate, trans-$[IrCl(C_2H_4)(PPh_3)_2]$.0.5 C_6H_6. The unsolvated complex exhibits a sharp band of moderate intensity at 1971 cm^{-1} in its i.r. spectrum. This peak is not present in the i.r. spectrum of the solvate and the origin of this peak is not clear. An X-ray structure[221] determination of trans-$[IrCl(C_2H_4)(PPh_3)_2]$ reveals that the co-ordinated ethylene exerts a negligible trans-influence, the C=C distance being significantly shorter than that observed in (176). The novel bis-ethylene complex (176) is formed



(176)

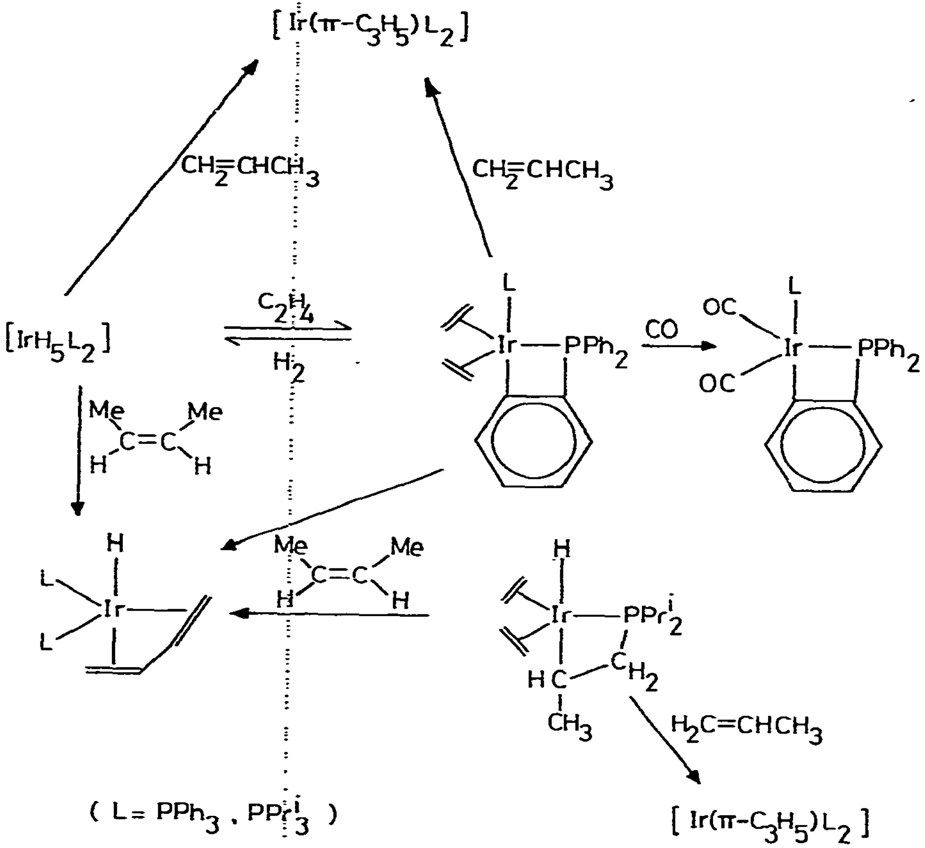
on the reaction of ethylene with $[IrH_5(PPr^i_3)_2]$ in benzene solution and a triphenylphosphine analogue (177) can similarly be obtained.



(177)

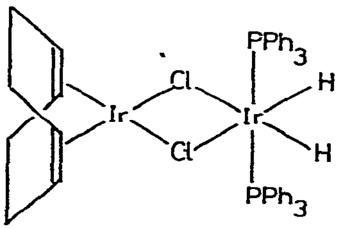
Further reactions of these complexes are illustrated in Scheme (39).

The complexes $[IrH_5L_2]$, ($L = PPh_3, PPr^i_3, PMe_3$) and *mer*-$[IrH_3(PPh_3)_3]$ catalyse hydrogen transfer between mono-alkenes in homogeneous solution giving equimolar amounts of dienes and alkanes.[222] The iridium complex (178) catalyses the isomerisation of cyclo-octa-1,5-diene, Scheme (40) and under



(L= PPh_3 , PPr^i_3)

Scheme (39)



(178)

dihydrogen a selective hydrogenation of the non-conjugated 1,5 and 1,4 isomers of cyclo-octadiene leads to cyclo-octene.[223]

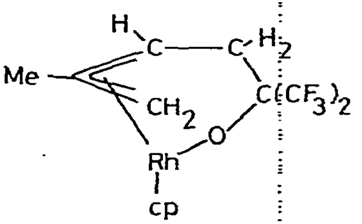
$$1,5\text{-}C_8H_{12} \rightleftharpoons 1,4\text{-}C_8H_{12} \rightarrow 1,3\text{-}C_8H_{12} \qquad \text{Scheme (40)}$$

Some cobalt ethylene complexes, [$Co(acac)(C_2H_4)(PPh_3)_2$] and [$Co(C_2H_4)(PPh_3)_3$] have been isolated from the reaction of [$Co(acac)_3$] with [$Al(OEt)Et_2$].[3]

The hydride, [$RhH(PPh_3)_4$] readily cleaves the carbon-oxygen bond in vinyl- and allyl acetate to give [$Rh(OAc)(PPh_3)_3$] releasing ethylene and propene respectively in the process. A similar reaction occurs with vinyl propionate to give [$Rh(OCOEt)(PPh_3)_3$]. Predissociation of a phosphine ligand appears to be a prerequisite for this reaction to occur and this is supported by the observation that [$CoH(diphos)_2$] does not react with vinyl acetate. However, vinyl acetate reacts with [$CoH(N_2)(PPh_3)_3$] to give ethylene and what appears to be a cobalt(I) compound, Co(OAc).[224] Treatment of $EtOCH{=}CH_2$ with [$CoH(CO)_4$],[$CoH(CO)_3(PR_3)$], (R = Ph,$\underline{p}$-MeC_6H_4,$\underline{p}$-ClC_6H_4, $\underline{p}$-$MeOC_6H_4$,Bu), [$CoH(CO)_3P(OR)_3$], (R = Et,Ph) and [$CoH(CO)_2\{P(OPh)_3\}_2$] gives the acyl derivatives [$Co\{COCH(OEt)Me\}(CO)_{4-n}L_n$], (L = CO,$PR_3$), the order of reactivities paralleling the electron-acceptor ability of the ligand.[225]

Nucleophilic substitution reactions on [$Rh(C_2H_4)_2Cp$] usually occur via initial dissociation of an ethylene. A group of nucleophiles, PF_3,PMe_3,$P(OMe)_3$,PEt_3,$P(OEt)_3$,$P(OPh)_3$,

$P(O\text{-}C_6H_4\text{-}\underline{o}\text{-}Me)_3$, $P(OCH_2)_3CEt$, $PBu_3{}^n$, have now been found which appear to displace ethylene via direct attack of the ligand at the metal complex without prior dissociation of ethylene. It is suggested that in order for the metal to retain a rare gas configuration in the transition state there is a reorganisation of the pentahapto cyclopentadienyl ligand to a trihapto allylic ligand. Consistent with this proposal ethylene is more readily displaced from $[Rh(h^5\text{-}C_5\text{-}H_4CN)(C_2H_4)_2]$ than $[RhCp(C_2H_4)_2]$ while displacement of ethylene from $[Rh(h^5\text{-}C_5Me_5)(C_2H_4)_2]$ is more difficult. Alkene displacements from $[RhCp(C_2H_4)(CH_2{=}CHF)]$, $[RhCp(CH_2{=}CHCN)_2]$, and $[RhCp(C_2H_4)(CH_2{=}CHOAc)]$ by PMe_3 are also consistent with an S_N2 mechanism.[226] Alkene complexes of this type are susceptible to electrophilic attack and a further indication of this behaviour is provided by some novel studies with hexafluoroacetone. This ketone reacts with [RhCp(isoprene)] to give a mixture of the two isomers (179) and (180).



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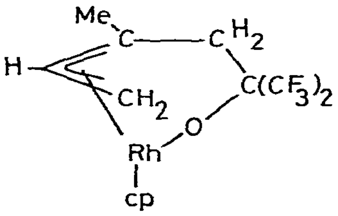
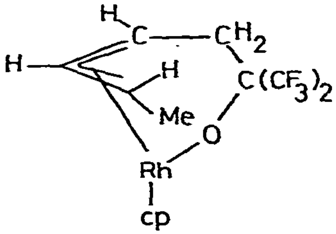


(180)

Similarly [RhCp(trans-pentadiene)] gives the $\underline{h}^3$-allyl complex (181). In contrast treatment of [RhCp(2,3-dimethylbuta-1,3-diene)] with hexafluoroacetone affords a 1:2 adduct (182)



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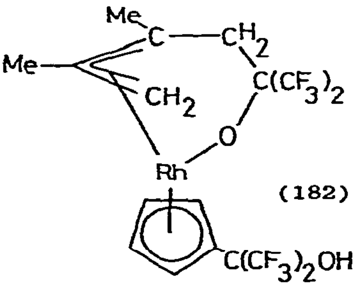

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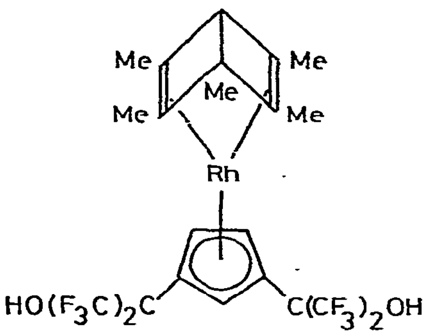
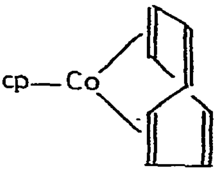


(183)

and attack at the cyclopentadienyl ring also occurs in the reaction of hexafluoroacetone with [RhCp(hexamethyl-Dewar-benzene)] to give (183).[227] A novel addition of methylene to the unco-ordinated double bonds of the cyclo-octatetraene complex (184) to give (185) has also been described.[228]



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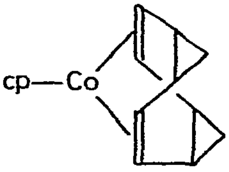
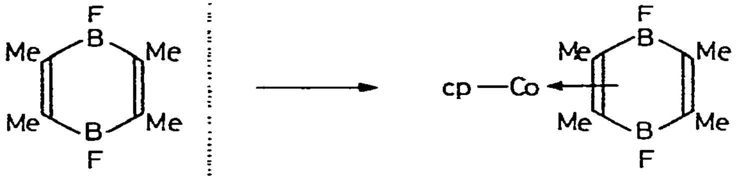


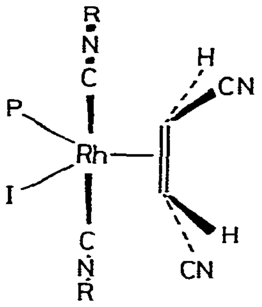
(185)

The diene (186) reacts with [CoCp(CO)$_2$] to give (187).[229]



(186) (187)

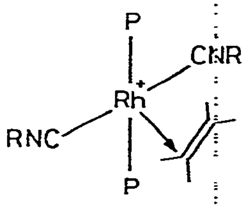
A variety of tetracyanoethylene and fumaronitrile complexes of rhodium(I) have been obtained via addition of the alkene to square planar rhodium(I) isocyanide complexes. The tetracyanoethylene in the complexes $[Rh(CNR)_2L_2(TCNE)]\ ClO_4$ $[R = p\text{-}MeC_6H_4, p\text{-}MeOC_6H_4;\ L = P(OPh)_3, PPh(OMe)_2, PPh_2(OMe)]$, is rigidly bound to the rhodium and this is considered to be related to steric hindrance inhibiting free rotation of the alkene. Treatment of the triphenylphosphite complexes with sodium iodide gives the neutral complexes, $[RhI(CNR)_2\{P(OPh)_3\}(TCNE)]$. The analogous fumaronitrile complexes, $[Rh(CNR)_2L_2(FN)]ClO_4$, $R = p\text{-}MeOC_6H_4$, $L = P(OPh)_3$, $PPh(OMe)_2$; $R = p\text{-}MeC_6H_4$, $L = PPh(OMe)_2$ and $[RhI(CNR)_2\{P(OPh)_3\}(TCNE)]$ tend to dissociate in solution. The neutral complex (188) exhibits dynamic solution behaviour below -15°C where the amount of free fumaronitrile is negligible on the n.m.r. time scale. The temperature dependent n.m.r. spectrum has been interpreted in terms of restricted rotation of an apical fumaronitrile in a tetragonal pyramidal configuration.[230] However, a single crystal X-ray structure determination of (188) reveals that the solid state configuration for the complex is trigonal bipyramidal with equatorial fumaronitrile. If this geometry is maintained



$P = P(OPh)_3$
$R = p\text{-}MeOC_6H_4$

(188)

in solution then the dynamic solution behaviour of (188) can be interpreted in terms of alkene rotation around the rhodium-FN bond accompanying an axial-equatorial interchange of the four remaining ligands of the trigonal-bipyramidal co-ordination sphere in the Berry pseudorotation mechanism.[231] A similar mechanism has been proposed to explain the dynamic solution behaviour of $[Rh(acac)(CNR)_2(TCNE)]$, (R = Bu^t,*p*-$MeOC_6H_4$, *p*-MeC_6H_4,*p*-ClC_6H_4,2,4,6-$Me_3C_6H_2$). However, substitution of an isocyanide ligand in these complexes by PPh_3 gives rigid TCNE complexes, $[Rh(acac)(CNR)(PPh_3)(TCNE)]$.[232] While tetracyanoethylene gives 1:1 adducts with $[Rh(CNR)_4]ClO_4$, (R = *o*-,*p*-tolyl,*p*-anisyl). The complexes $[Ir(CNR)_4]X$, (R = *p*-tolyl,*p*-anisyl; X = I,PF_6)appear not to react with π-acidic alkenes even at high temperatures.[233] Two different transition states can be considered for the addition of tetracyanoethylene to rhodium(I) complexes, an asymmetric one (189) with a dipole formed by nucleophilic attack of the metal at one end of the alkene, and a symmetric one (189a) with little charge separation. Kinetic studies on the addition of TCNE to *trans*-$[Rh(CNR)_2L_2]ClO_4$, (R = *p*-$MeOC_6H_4$,*p*-ClC_6H_4,



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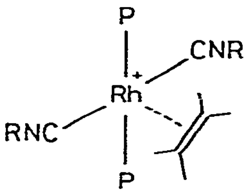
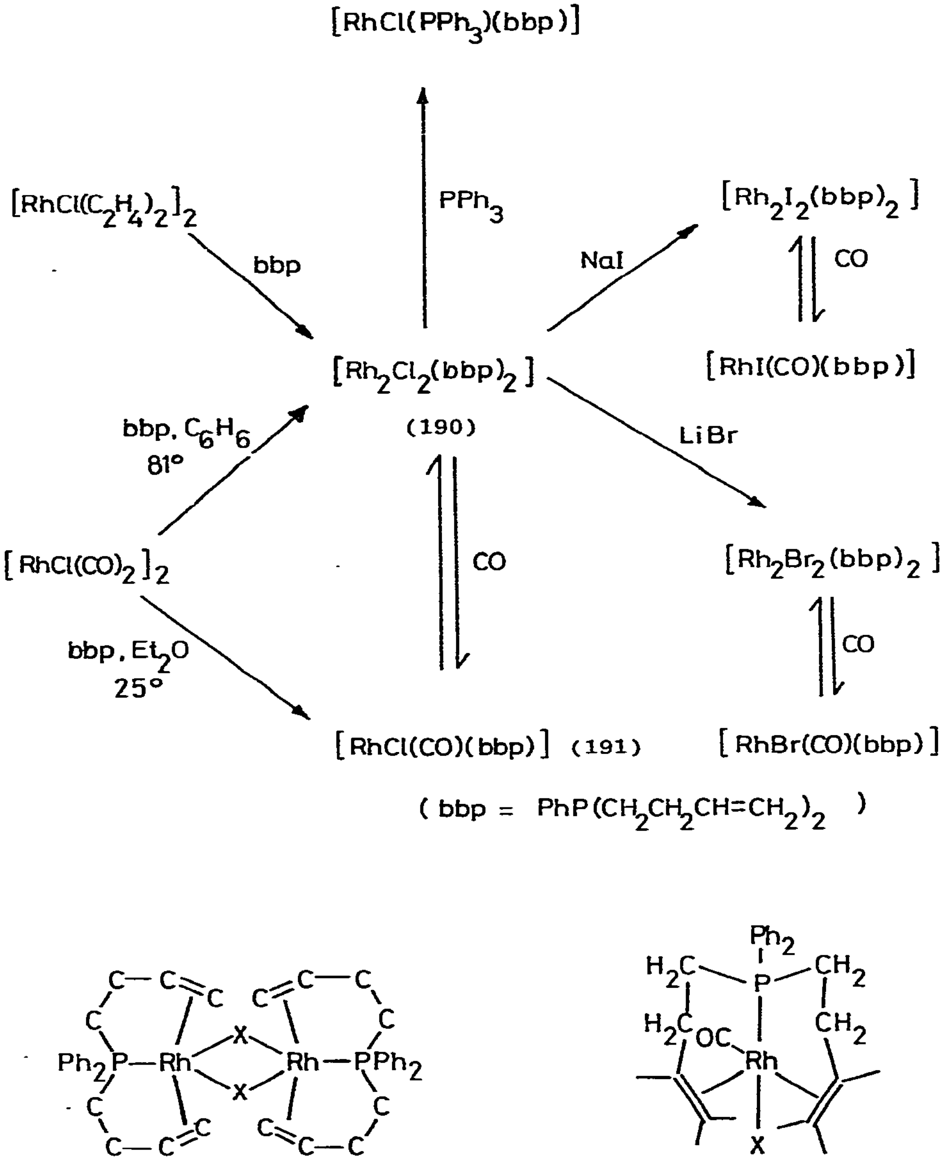


(189a)

C_6H_{11}; L = $P(OPh)_3$,PPh_3) in acetone, acetonitrile and tetrahydrofuran suggest that the reactions proceed via the transition state (189).[234]

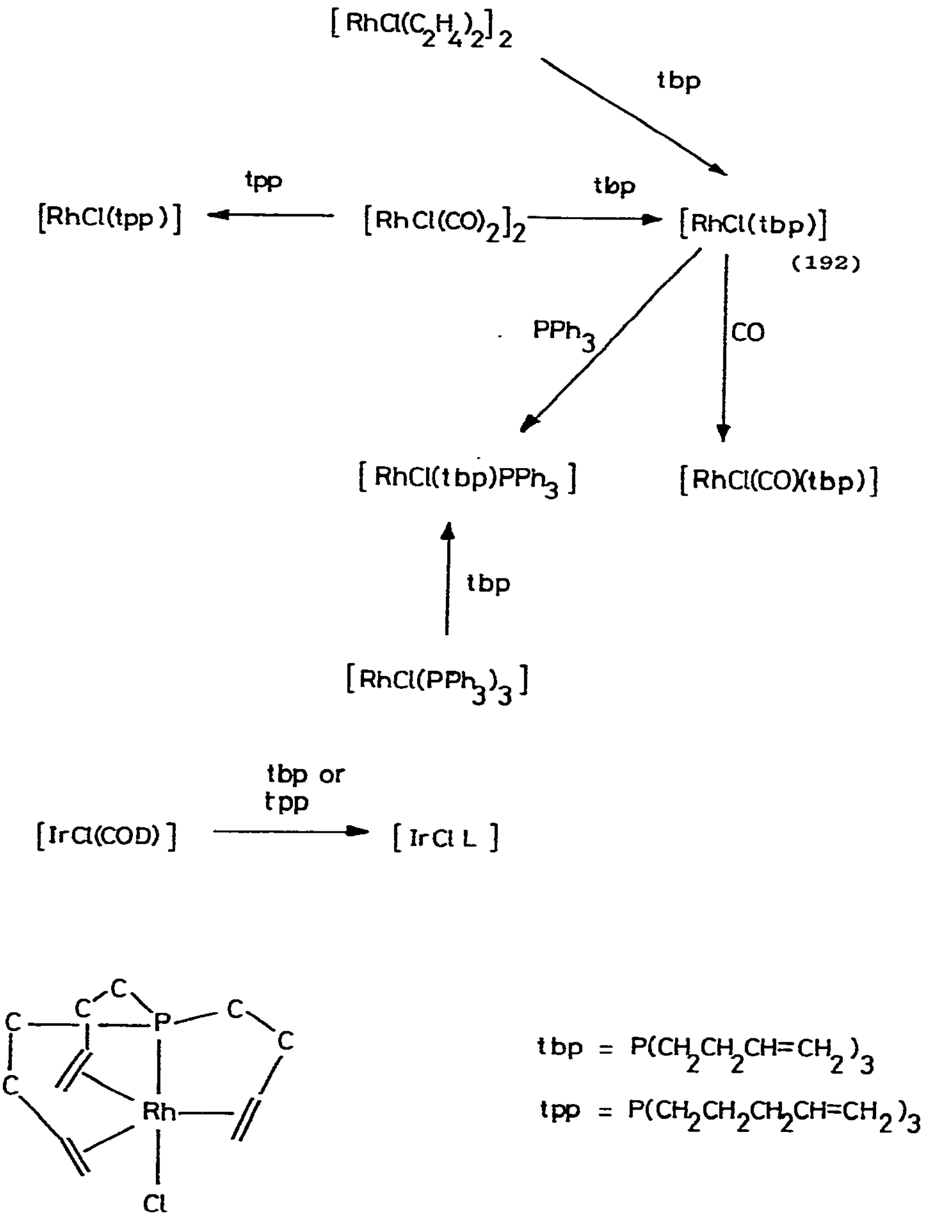
Various unsaturated phosphines react with rhodium(I) compounds to give complexes in which both the phosphorus atom and the double bonds are co-ordinated to the rnodium. The preparations and reactions of these complexes are summarised in Schemes (41), (42) and (43).[235-237] In contrast to the chloro complex [RhCl(tbp)], (192) the corresponding iodo complex, [RhI(tbp)] exhibits an infrared band typical of an unco-ordinated double bond and it is suggested that this complex may be dimeric and have a similar structure to that proposed for (190). However, in solution [RhI(tbp)] appears to have the same five-co-ordinate structure as (192). Spectroscopic studies on the corresponding iridium complexes of tbp and tpp (Scheme 41) reveal that iridium alkene bonding is stronger than rhodium alkene bonding in these complexes.[236] The structure of (193) has been confirmed by a single crystal X-ray study.[238] Treatment of rhodium(III) chloride with

(Continued on p. 343)



(190) (191)

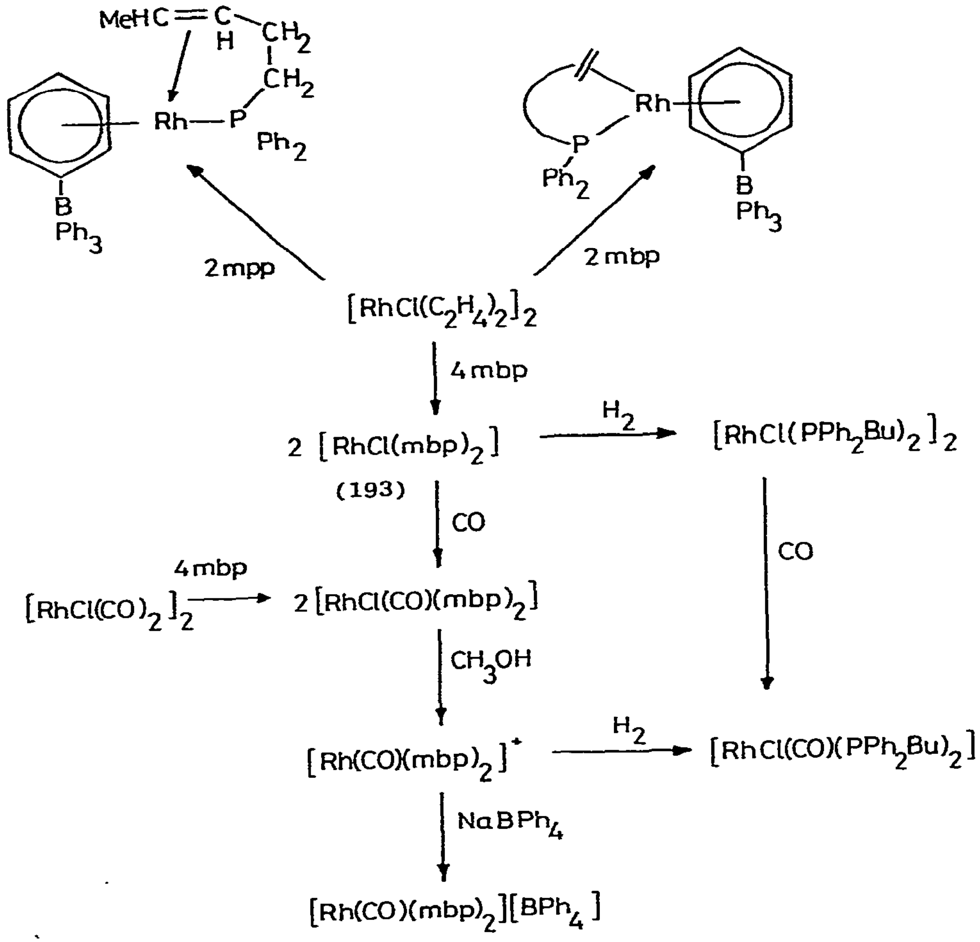
Scheme (41)

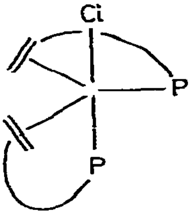


tbp = $P(CH_2CH_2CH{=}CH_2)_3$

tpp = $P(CH_2CH_2CH_2CH{=}CH_2)_3$

Scheme (42)





(193)

mbp = $Ph_2PCH_2CH_2CH{=}CH_2$

mpp = $Ph_2PCH_2CH_2CH_2CH{=}CH_2$

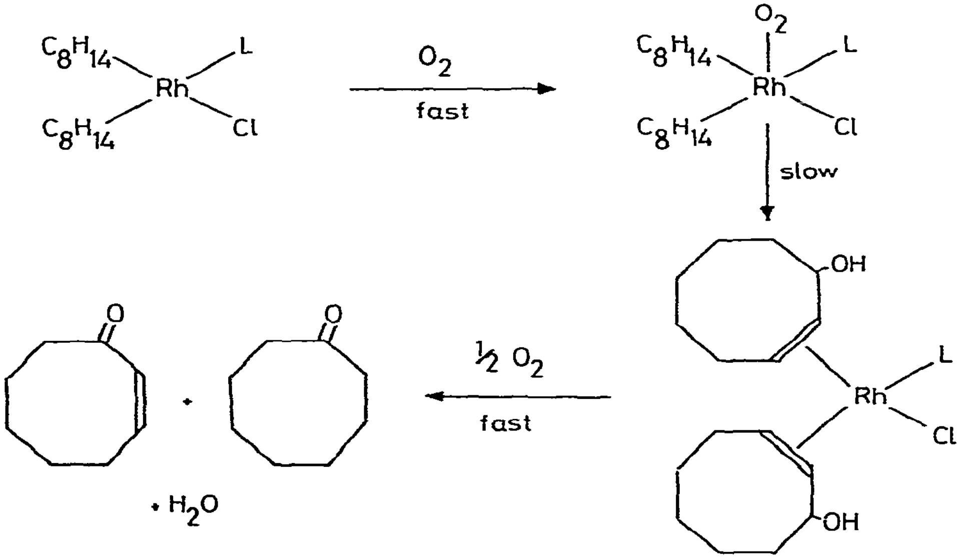
Scheme (43)

triallylphosphite, (194), gives the complex [RhCl(triallylphosphite)$_3$] in which all the double bonds are co-ordinated

$$\mathrm{P\text{-}(OCH_2CH{=}CH_2)_3} \qquad (194)$$

to the rhodium. However, reaction of (194) with [RhCl(PPh$_3$)$_3$] gives trans-[RhCl(CO)(PPh$_3$)$_2$].[239] No evidence for the co-ordination of the double bonds in the unsaturated acids, $\mathrm{RCH(CO_2H)_2}$, $\mathrm{RCH_2CO_2H}$, and $\mathrm{RN(CH_2CO_2H)_2}$, (R is $\mathrm{CH_2{=}CHCH_2}$, $\mathrm{CH_2{=}CHCH_2CH_2}$, $\mathrm{CH_2{=}CHCH_2CH_2CH_2}$) to cobalt(II) has been obtained.[240]

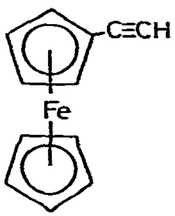
The rhodium(I) promoted autoxidation of cyclo-octene gives non-catalytic yields of cyclo-oct-1-en-3-one and cyclo-octanone, Scheme (44).[241]



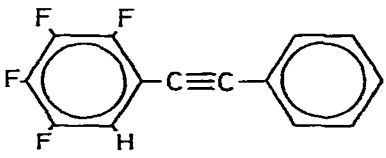
Scheme (44)

The i.r. and Raman spectra of $[RhCl(norbornadiene)]_2$ have been assigned.[242]

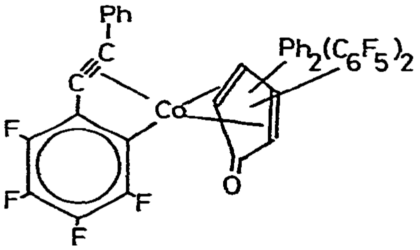
The reaction of alkynes with $Co_2(CO)_8$ to give μ-alkyne complexes, $[Co_2(CO)_6(alkyne)]$ is well known and the kinetics of these reactions have been reviewed in a lecture.[243] Further examples of this type of reaction have been observed with the alkynes (195)[244] and (196).[245] Thermal degradation of the complex formed with (196) gives the free alkyne, asymmetric and symmetric isomers of the cyclopentadienone, $C_4(C_6F_4H)_2Ph_2CO$, a hexa-substituted benzene, $C_6(C_6F_4H)_3Ph_3$, a small amount of 2,2', 3,3', 4,4', 5,5',-octafluorobiphenyl and an oligomer $(C_6F_4HC_2Ph)_n$ where n is between 3 and 4. Free alkyne is implicated in the formation of these organic products.[245] Similar products result upon thermolysis of the bridged complexes formed with $C_6F_5C{\equiv}CC_6F_5$, $PhC{\equiv}CC_6F_5$, $PhC{\equiv}CH$ and $PhC{\equiv}CPh$. One of the organometallic complexes formed in



(195)

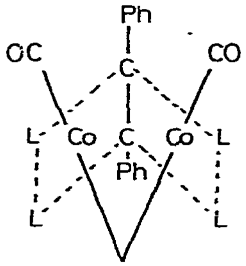


(196)



(197)

the degradation of $[Co_2(CO)_6(C_6F_5{-}C{\equiv}CPh)]$ may be a rare example of a four-co-ordinate cobalt(I) complex, (197). Thermolysis of $[Co_2(CO)_6(PhC{\equiv}CH)]$ gives several complexes of general formula $Co_3(CY)(CO)_9$. Degradation of the diyne complex, $[Co_2(CO)_6]_2[PhC{\equiv}CC{\equiv}CPh]$ occurs relatively quickly at 185°C to give $[Co_2(CO)_6(PhC{\equiv}CPh)]$ as a major product possibly via a radical mechanism.[246] The acetylene complexes $[Co_2(CO)_6(RC{\equiv}CR)]$, ($R = H, CH_2OH, Ph$) undergo replacement of one or both axial CO groups on heating with monodentate phosphines, phosphites, and arsines. Bulky ligands do not react. Trimethylphosphite can displace up to four carbonyl ligands in a series of reversible reactions to give ultimately (198).

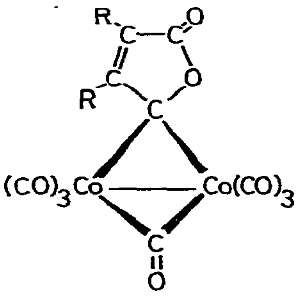


L = $P(OMe)_3$

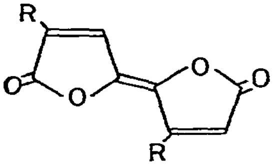
(198)

Bidentate fluorocarbon- and hydrocarbon- bridged ligands tend to occupy equatorial positions about the metal atoms either by bridging two cobalt atoms in the same molecule or by chelating to one of them.[247]

The alkyne complexes, $[Co_2(CO)_6(RC{\equiv}CR')]$ as well as $[Co_2(CO)_8]$ plus an alkyne are known to react with carbon monoxide to give the lactone complexes (199). Further studies on these reactions reveal that the formation of these

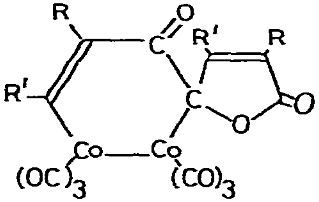


(199)



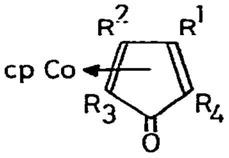
(200) (R′ = H)

complexes is stereospecific, the bulkier substituent R always being in the 2-position of the lactone ring.[248,249] The route from the complex (199) to unsymmetrical bifurandiones (200) probably involves successive insertion of carbon monoxide, alkyne and again carbon monoxide, an intermediate of type (201) being proposed.[249]



(201)

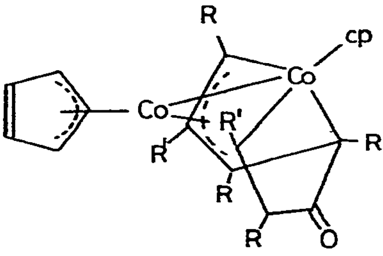
A variety of complexes are formed in reactions of the alkynes $C_6F_4HC{\equiv}CPh$, $C_6F_5C{\equiv}CC_6F_5$, $C_6F_5C{\equiv}CPh$, $C_6Cl_5C{\equiv}CPh$, and $C_6Cl_5C{\equiv}CC_6Cl_5$ with $[MCp(CO)_2]$, (M = Co,Rh). The complexes isolated include cyclopentadienone and cyclobutadiene complexes as well as trinuclear complexes, $[Rh_3Cp_3(CO)(acetylene)]$.[243,245,250] The fluxional solution characteristics of these and similar complexes have been studied using ^{13}C n.m.r.[251] and in addition the crystal structure of $[Cp_2Rh_2(CO)_2(CF_3C{\equiv}CCF_3)]$ formed by reacting $[RhCp(CO)_2]$ with $CF_3C{\equiv}CCF_3$ reveals that the bridging alkyne unit is σ-bonded to the two rhodium atoms and that some metal-metal bonding occurs.[252] Reaction of the diynes $MeC{\equiv}C{-}C{\equiv}CMe$ and $PhC{\equiv}C{-}C{\equiv}CPh$ with $[CoCp(CO)_2]$ give three isomers of the cyclopentadienone complexes, (202), and a novel complex, $Co_2Cp_2(CO)(RC_2C_2R)_3$. The complex (R=Ph) can be separated into two isomers and one of the isomers has been assigned the novel structure (203).



(202)

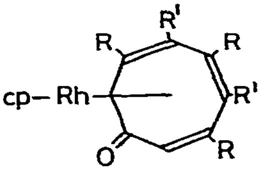
R^1	R^2	R^3	R^4
R	C≡CR	C≡CR	R
C≡CR	R	C≡CR	R
C≡CR	R	R	C≡CR

(R = Me, Ph)



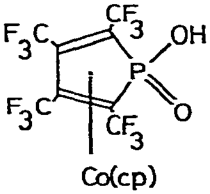
(203)

The second isomer may have a similar structure with different arrangements of the PhC_2- and Ph- substituents. However, it appears not to have a trihapto-cyclopentadienyl ligand. The complex (R=Me) exists in two isomeric forms and they may have structures based on (203). These complexes are surprisingly stable and can be recovered unchanged after treatment with bromine in CCl_4. They are not degraded at 300°C. The diyne MeC≡C-C≡CMe reacts with $RhCp(CO)_2$ to give two isomers of a tetrahapto-cycloheptatrienone complex (204).[253]

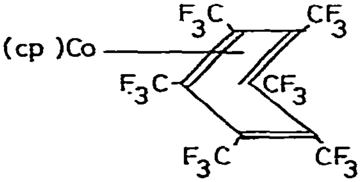


(204)

Treatment of $[CoCp(PF_3)_2]$ with hexafluorobut-2-yne leads to (205) which has been characterised crystallographically.[254]

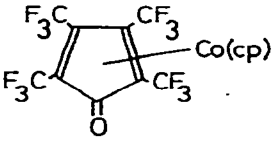


(205)

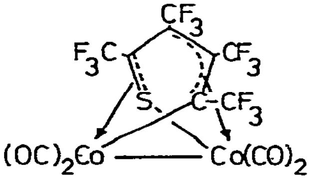


(206)

The highly electrophilic hexafluorobut-2-yne also reacts with $[CoCp(SR)_2]$, (R = CF_3,C_6F_5) to give a complicated mixture of products, but only (206) could be identified. This complex has previously been isolated from the reaction of the alkyne with $[CoCp(CO)_2]$. Hexafluorobut-2-yne reacts with $[CoCp(SC_6F_5)_2(CO)]$ to give the known cyclopentadienone complex (207) but with $[Co(SC_6F_5)(CO)_3]_2$ (208) is formed together with the known complexes, $[Co_2(CO)_6(CF_3C{\equiv}CCF_3)]$ and $[Co_2(CO)_4\{C_6(CF_3)_6\}]$. The complex (208) has been characterised by an X-ray structure determination.[255]

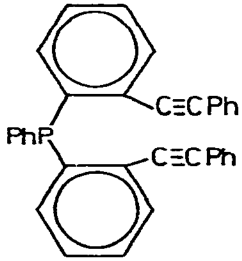


(207)



(208)

The reaction of the bis-alkyne (209) with $[RhCl(PPh_3)_3]$[256] leads to the cyclobutadiene complex (210). The ^{31}P n.m.r. spectra of rhodacyclopentadiene and cyclobutadienylrhodium complexes have been compared[257]. The ^{31}P n.m.r. spectrum of (210) is in agreement with the proposed structure. The



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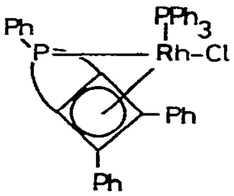
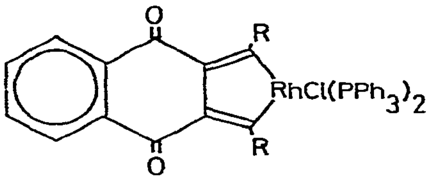
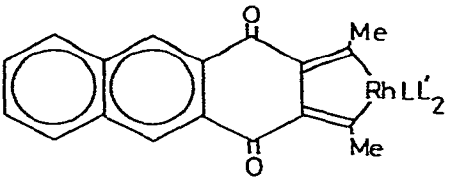


(210)

reactivity of the rhodacyclopentadiene complexes (211) and (211a)

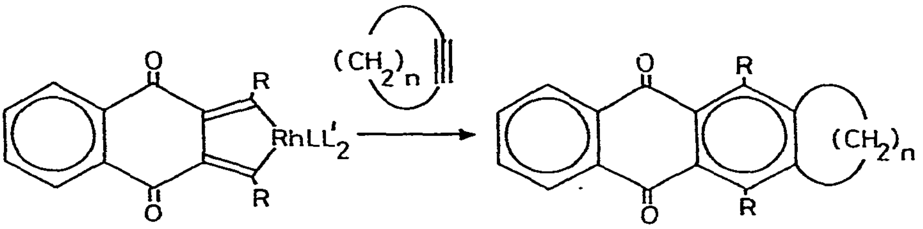


(211) (R = Me, Ph)



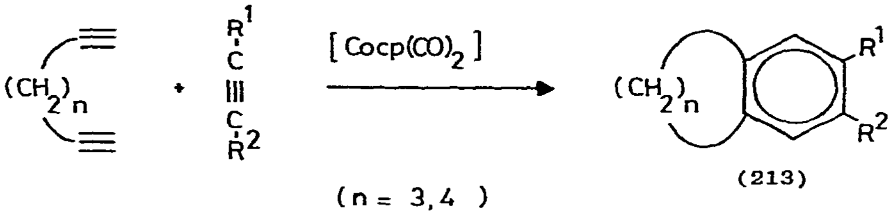
(211a) L = Cl
L' = PPh$_3$

towards strained cycloalkynes has been examined. Such reactions lead to quinone derivatives, e.g. (212), but benzyne does not react with the rhodium complexes.[258] An extension



(212)

of this reaction has been used to give a general synthesis of indans and tetralins, (213), via the co-oligomerization of hepta-1,6-diyne (n=3) or octa-1,7-diyne with substituted monoalkynes catalysed by $[CoCp(CO)_2]$. In reactions involving $Me_3SiC{\equiv}CSiMe_3$ the cobalt complex (213a) is also formed.[259] Some cyclic diacyl complexes can be obtained by the reaction of $[IrX(CO)_3]$, (X = Br,Cl) with PhC≡CPh and EtC≡CEt. Some reactions of the complexes are summarised in Scheme (45).[260]



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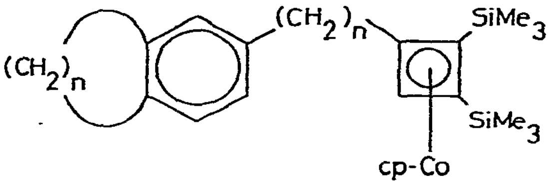
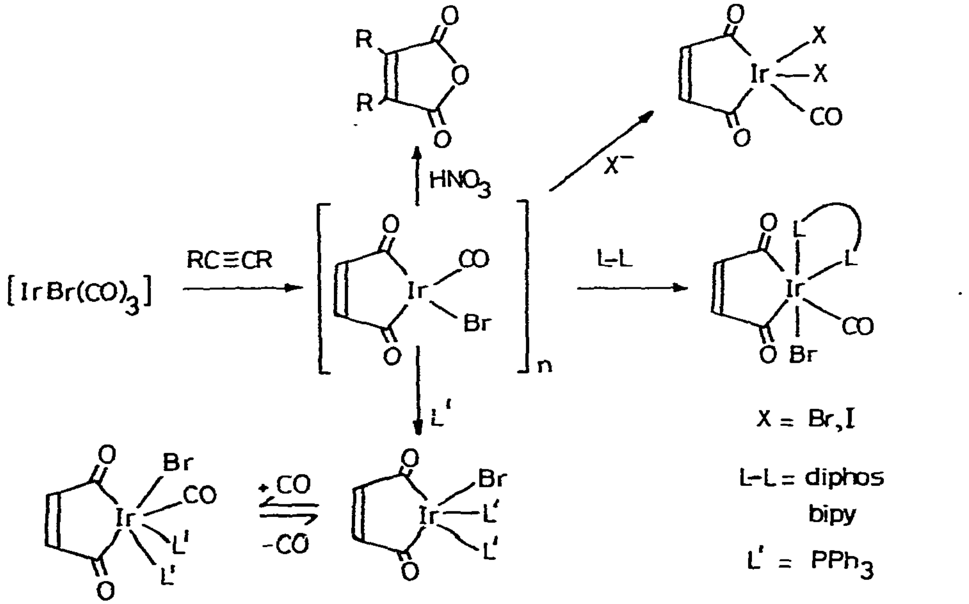
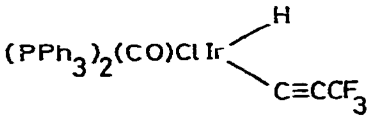


(213a)

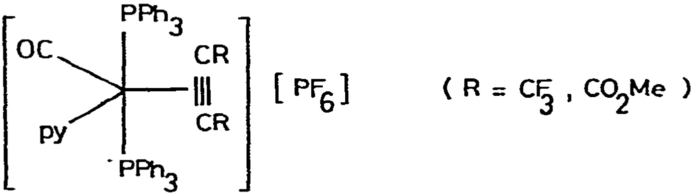


Scheme (45)

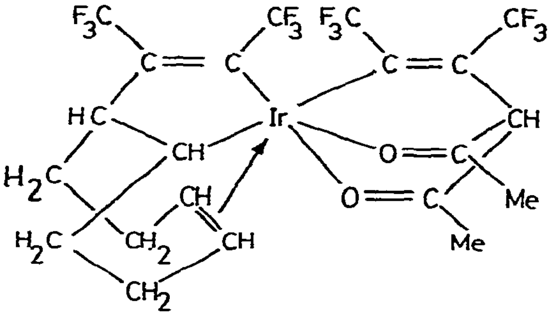
Treatment of trans-$[IrCl(CO)(PPh_3)_2]$ with $CF_3C{\equiv}CH$ gives the acetylide complex (214). Reaction of the iridium(I) complex with (195) gave a similar acetylide complex. However, the ethynylferrocene (195) is easily removed from the iridium on attempted recrystallisation.[244] Attempts to obtain cationic rhodium(I) or iridium(I) alkyne complexes from $[M(CO)(acetone)(PPh_3)_2][PF_6]_2$ (M = Rh,Ir) and alkynes have not been successful. However, the iridium complexes, (215), can be isolated with electrophilic alkynes if one equivalent of pyridine is introduced into the reaction mixture.[47] Treatment of [Ir(acac)(COD)] with hexafluorobut-2-yne results in the alkyne adding 1,4- to the acetylacetonate ring and incorporation of one double bond of the diene together with a second molecule of the alkyne into an iridacyclopentene ring (216). The product has been characterised by an X-ray structure determination.[261]



(214)

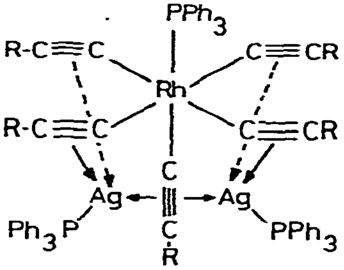


(215)



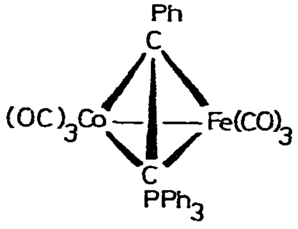
(216)

The reaction of $[AgC{\equiv}CC_6F_5]$ with $[RhCl(PPh_3)_3]$ gives the heteronuclear trimetallic complex (217) and the full paper on the X-ray structure of this compound has now appeared.[262]



(217)

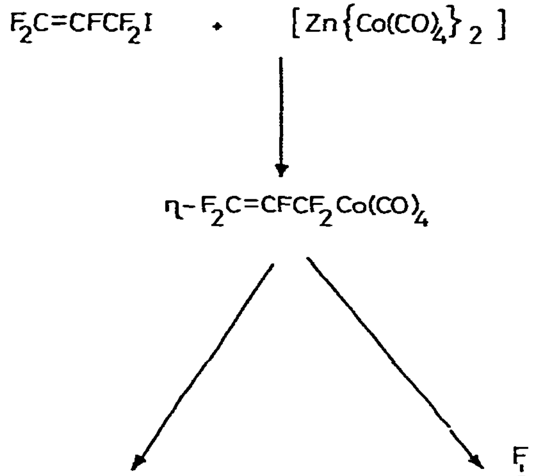
The mixed metal complex, $[CoFe(CO)_6(Ph_3PC_2Ph)]$, which probably has the structure (218) results from the reaction of $[Ph_3PC{\equiv}CPh]Br$ with $Co_2(CO)_8$ and $Fe(CO)_5$.[263]



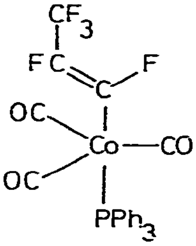
(218)

Metal π-allyl complexes.

The first η^3-perfluoroallyl compound (219) has been isolated from the reaction of perfluoroallyl iodide and $[Zn\{Co(CO)_4\}_2]$. The allyl complex (219) is an air sensitive



yellow liquid which decomposes rapidly at 35°C in vacuo. The propenyl complex (220) is also formed in this reaction. The reaction of (219) with triphenylphosphine proceeds without evolution of carbon monoxide to give a mixture of (221) and (222).[264]



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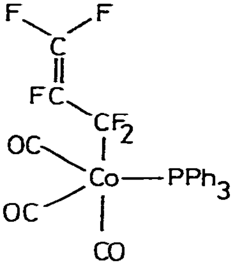
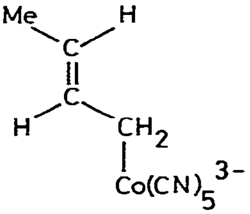


(222)

The reaction of buta-1,3-diene with $[CoH(CN)_5]^{3-}$ in aqueous solution has been investigated by Raman spectroscopy. The results are in agreement with previous ^1H n.m.r. studies. At high initial CN^-/Co ratios the butenyl complexes (223) and (224) are present. At lower ratios a η³-(butenyl)tetracyanocobaltate(III) complex can be detected.[265]



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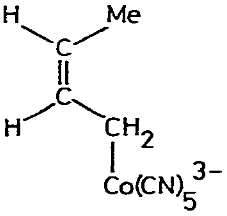
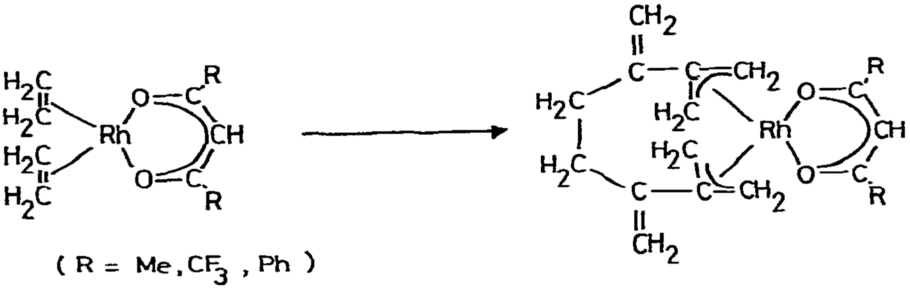


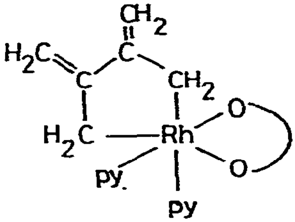
(224)

Allene reacts with the β-diketonato complexes (225)


(R = Me, CF_3, Ph)

(225) (226)

at -35°C to give the bis(η^3-allylic) complexes (226). At -78°C liquid allene reacts with $[Rh(acac)(C_2H_4)_2]$ to give a precipitate of stoichiometry $[Rh(acac)(C_3H_4)_3]$ which could be formulated as indicated in structure (227). Indeed the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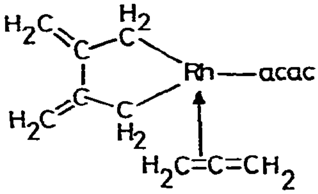
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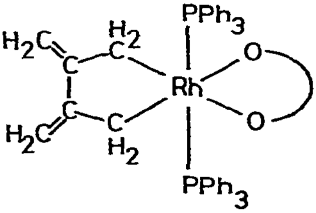
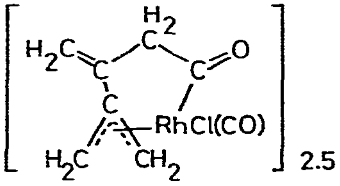
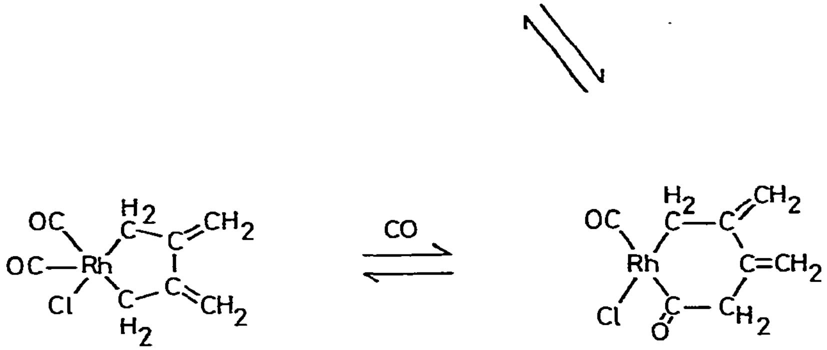

(229)

product reacts with pyridine and triphenylphosphine to form the complexes (228) and (229) respectively. Presumably (227) is an intermediate in the formation of the bis(η^3-allylic) complex (226), (R = Me).[266] An allylic complex (230) also results from the reaction of allene with $[RhCl(CO)_2]_2$ and the formation of (230) can be rationalised in terms of the mechanism outlined in Scheme (46).[267]

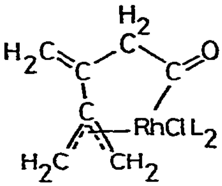


(230)



Scheme 46

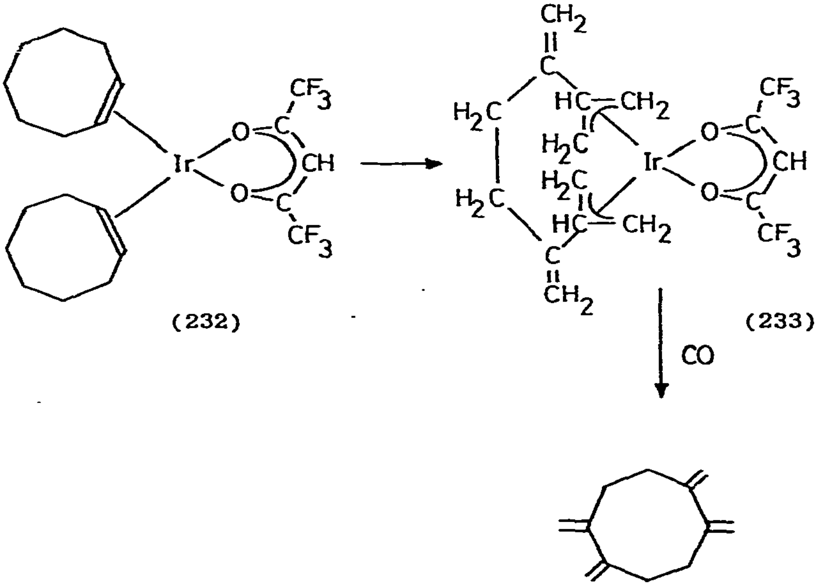
A similar mechanism would account for the formation of (226). Treatment of (230) with excess triphenylphosphine gives <u>trans</u>-$[RhCl(CO)(PPh_3)_2]$ and 3,4-dimethylene cyclopentanone but under less vigorous conditions triphenylphosphine and -arsine react to give the complexes (231).[267] An iridium analogue



(L = PPh_3,$AsPh_3$)

(231)

of (226) can be isolated from the reaction of allene with (232). The structure of (233) has been established by X-ray

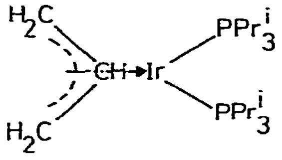


(232)

(233)

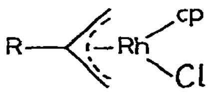
(234)

crystallography and the complex reacts with carbon monoxide to give (234).[268] The X-ray structure of the iridium(I) allyl complex, (235), has also been reported.[269]



(235)

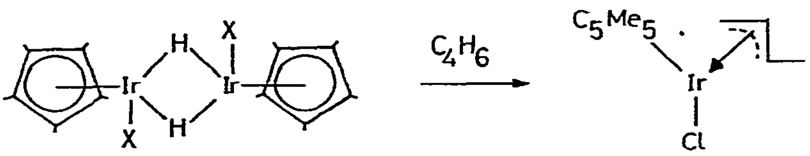
The allyl complexes (236) can be obtained by treating hydrated rhodium(III) chloride with CH_2=$CRCH_2HgCl$ followed by addition of TlCp.[270] Analogous pentamethylcyclopentadienyl



(R = H , p- or m- FC_6H_4)

(236)

complexes are formed on treating the di-µ-hydrido complex (237) with butadiene in a polar solvent such as ethanol or acetone.[271]

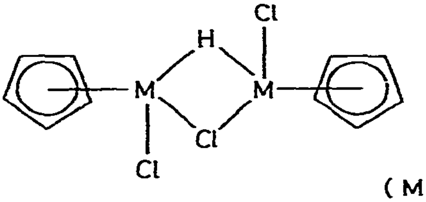


(X = Cl Br)

(237)

(238)

These allyl complexes (238) are obtained more readily from the mono-μ-hydrido complexes (239),[272] a feature consistent with the proposal that the rate determining step is opening of the metal-halide bridge and not the metal-hydride bridge.[273]

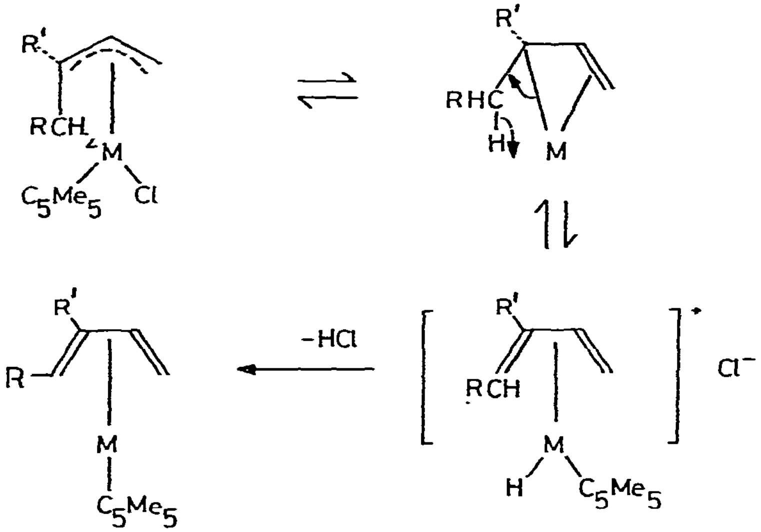


(M = Rh, Ir)

(239)

The reactions of (239) with butadiene, penta-1,3-diene, isoprene, 1,1-dimethylallene, 2,3-dimethyl butadiene, trans-2-methylpenta-1,3-diene and 2,5-dimethylhexa-2,4-diene have been reported. The η-allylic complexes so formed may be divided into three groups dependent upon the ease with which they undergo reductive elimination of HCl to give diene complexes Group A complexes all possess syn- and anti-1-methyl groups and eliminate HCl so rapidly that they are only just detectable in the absence of base and not at all in its presence. It is proposed that the presence of the anti-1-methyl or -methylene group provides a cisoid arrangement of the carbon skeleton which is close to the conformation of the cis-diene, Scheme (47).

Group B complexes only eliminate HCl with difficulty and they all possess alkyl groups in both the syn-1 and the -2 position. Since it is known that with increasing bulk of 1- and 2-substituents, the anti-1-isomers become thermodynamically more stable it is suggested that this group, which has relatively small substituents at the 1- and particularly at the

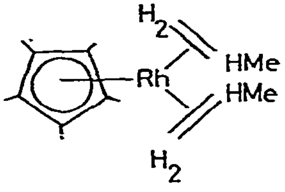


Scheme(47)

2- positions, will need extra activation energy to form the anti-1-isomers.

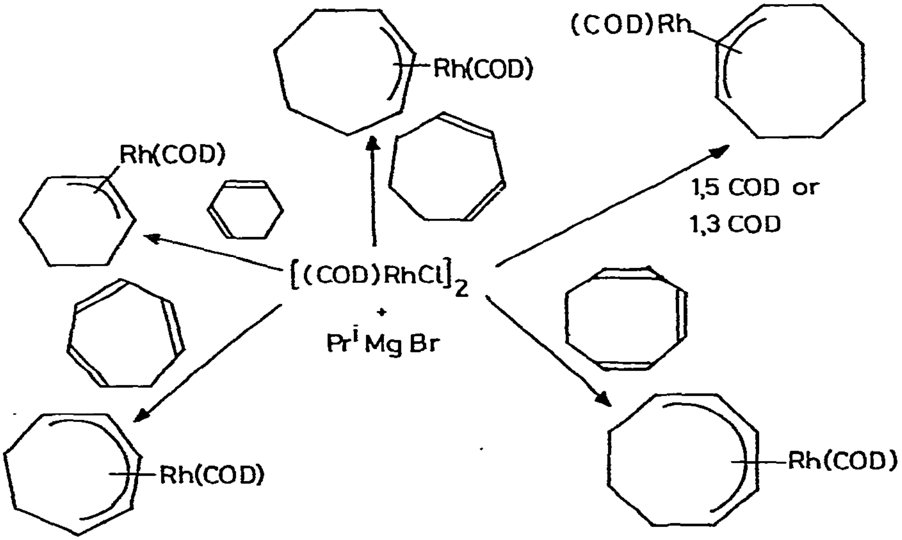
Group C complexes do not eliminate HCl under any conditions. These complexes only contain alkyl groups in the syn-1 position and hydrogen in the -2 position and as steric effects will be less in these examples a prohibitively higher activation energy will be required for reorganisation.[272,273] Cyclo-octa-1,3- and -1,5-diene, cyclohexa-1,3- and -1,4-diene similarly react with (239) to give cyclic η-allylic complexes which reductively decompose to give $[M(C_5Me_5)(diene)]$. Cyclopentadiene gives a cyclopentyl complex which loses 2H to give $[M(C_5Me_5)(C_5H_5)]^+$ while norbornadiene gives a σ-η-norbornenyl complex which loses HCl to form $[M(C_5Me_5)(norbornadiene)]$. The ready formation of these diene complexes is in accord with the mechanism depicted in

Scheme (47).[273] The cyclo-octa-1,5-diene complex $[Rh(C_5Me_5)(COD)]$ can also be obtained from the reaction of $[RhCl_2(C_5Me_5)]_2$ with Pr^iMgBr in the presence of the diene while reaction of the rhodium complex with the Grignard reagent gives (240). Various allyl and dienyl complexes result



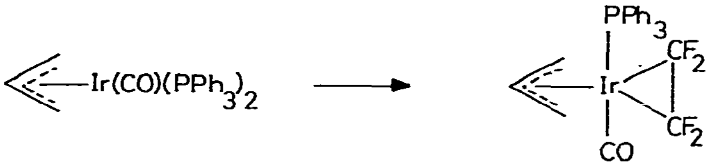
(240)

if the complexes $[RhCl(diene)]_2$, (diene = cyclo-octa-1,5-diene, cyclohepta-1,3-diene, norbornadiene) are treated with Pr^iMgBr-cyclo-alkenes. Some reactions of the cyclo-octa-1,5-diene complexes are illustrated in Scheme (48).[274]



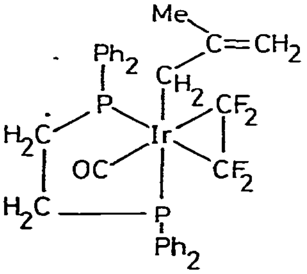
Scheme (48)

The allyl complex (241) reacts with tetrafluoroethylene with replacement of triphenylphosphine to yield the adduct (242).



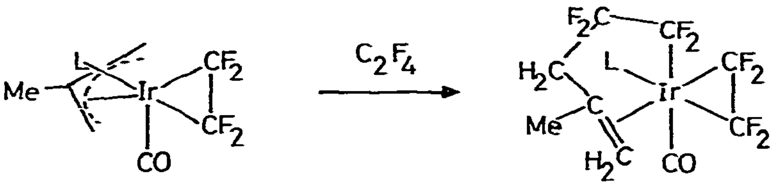
(241) (242)

Analogous reactions occur with the 1-methallyl and 2-methallyl derivatives of (241). In all these reactions a phosphine ligand is displaced and no linking of the allyl group with the tetrafluoro-ethylene is observed. An attempt to obtain an insertion product by the reaction of tetrafluoroethylene with $[Ir(\eta^3\text{-}2MeC_3H_4)(CO)(diphos)]$ gives the σ-allyl complex, (243).

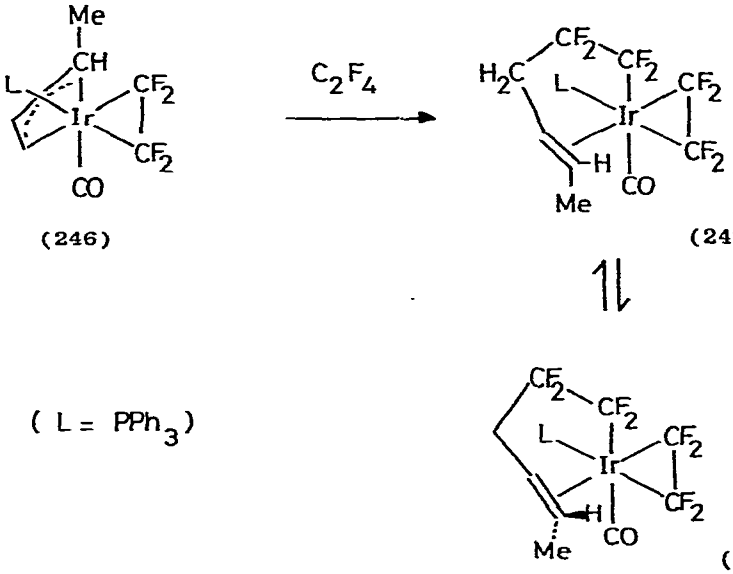


(243)

However, further treatment of the adduct (244) with tetrafluoroethylene affords an insertion product (245) and analogous products can be obtained with the triphenylarsine derivative of (244). The allyl complex (246) reacts with tetrafluoroethylene in a similar way but the product exhibits a temperature

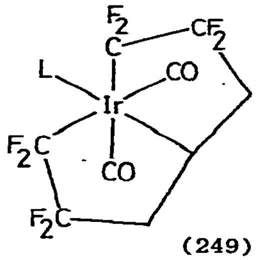

(244) (L = PPh_3,$AsPh_3$) (245)

dependent n.m.r. spectrum which is consistent with interconversion of the isomers (247) and (248) via alkene rotation


(246) (247) (248)

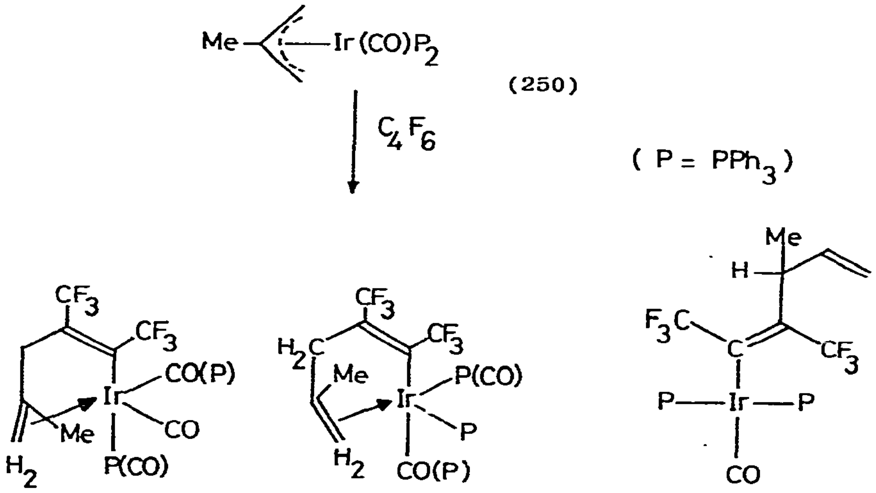
(L = PPh_3)

The absence of this effect in (245) is attributed to an interaction between the methyl group and the ligand L. When the adduct (242) is heated with tetrafluoroethylene an iridabicyclo(3.3.0)octane complex (249) can be isolated.[275]



(249)

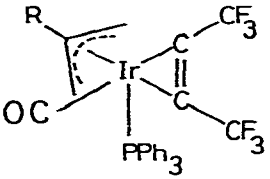
A variety of products result from analogous reactions with hexafluorobut-2-yne and it is apparent that there is a solvent effect on the reaction. Treatment of (250) with hexafluorobut-2-yne in toluene at -30^{o}C affords three complexes, (251), (252) and (253). The complex (251) is a dicarbonyl species but the



(250)

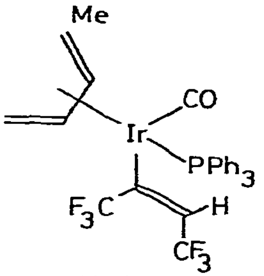
(251) (252) (253)

exact stereochemistry is not clear. The complex (252) exhibits a temperature dependent n.m.r. spectrum and it is suggested that (252) exists as single isomer in solution at room temperature but intramolecular isomerisation, caused by rotation about the alkene-iridium bonding axis occurs at higher temperatures. Surprisingly a similar isomerisation does not occur with (251). The corresponding reaction of hexafluorobut-2-yne with $[Ir(\eta^3-C_3H_5)(CO)(PPh_3)_2]$, (241), gives only one adduct, isolated in low yield and characterised as the trans-insertion product analogous to (253). The formation of both cis- and trans-insertion products suggests that the reactions can proceed via at least two reaction paths. In a methanol-toluene solvent medium hexafluorobut-2-yne reacts with (250) to give only one product, (254), (R = Me), and the

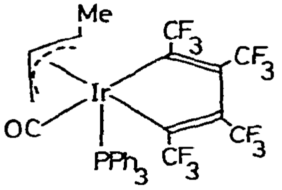


(254)

corresponding reaction of C_4F_6 with (241) in dry methanol proceeds similarly to give (254), (R = H). The complexes (254) are presumably precursors of the cis-addition products (251) and (252) and treatment of (254), (R = Me) with triphenylphosphine affords the cis-insertion complexes (251) and (252). However, it seems unlikely that an intramolecular mechanism would operate in the formation of the trans-insertion product (253). The reaction of hexafluorobut-2-yne with $[Ir(\eta^3-1-MeC_3H_4)(CO)(PPh_3)_2]$ in toluene at $-30^{\circ}C$ also gives only a trans-insertion product in low yield. However, prolonged reaction of the 1-methallyl complex with the alkyne gives two products (255) and (256). Treatment of

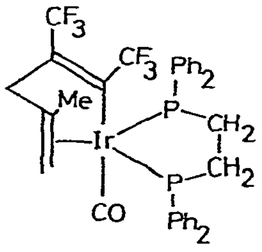


(255)

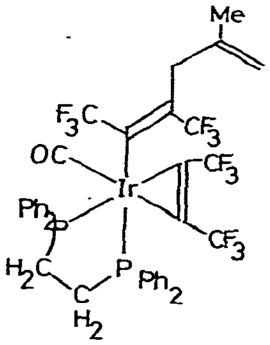


(256)

$[Ir(n^3\text{-}2\text{-}MeC_3H_4)(CO)(diphos)]$ with hexafluorobut-2-yne gives (257) and (258).[276]

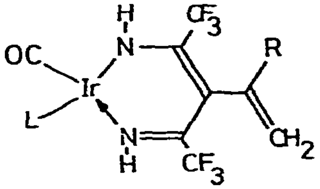


(257)



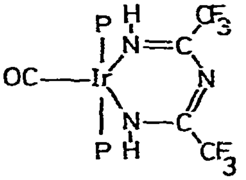
(258)

Some reactions of trifluoroacetonitrile with (250) have also been reported. The product (259), (L = PPh_3, R = Me) obtained from this reaction has been characterised by an X-ray crystallographic study and the corresponding triphenylarsine complex has been similarly obtained. However, two products are obtained from the reaction of CF_3CN with (241). These



(259)

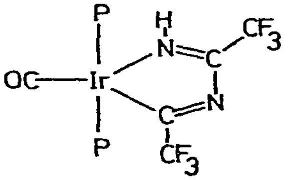
have been characterised as (259), ($R = H$, $L = PPh_3$) and the other complex has been tentatively given the structure (260).



($P = PPh_3$)

(260)

In contrast to the formation of (260) a five-membered ring complex (261) results from the action of CF_3CN upon $[Ir(\eta^3\text{-}1\text{-}MeC_3H_4)(CO)(PPh_3)_2]$. The formation of (261) presumably involves an intermediate iridium-hydride complex

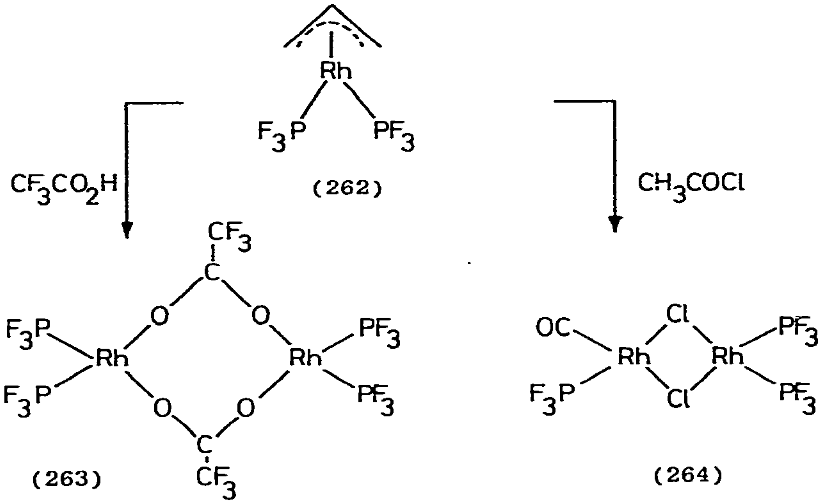


($P = PPh_3$)

(261)

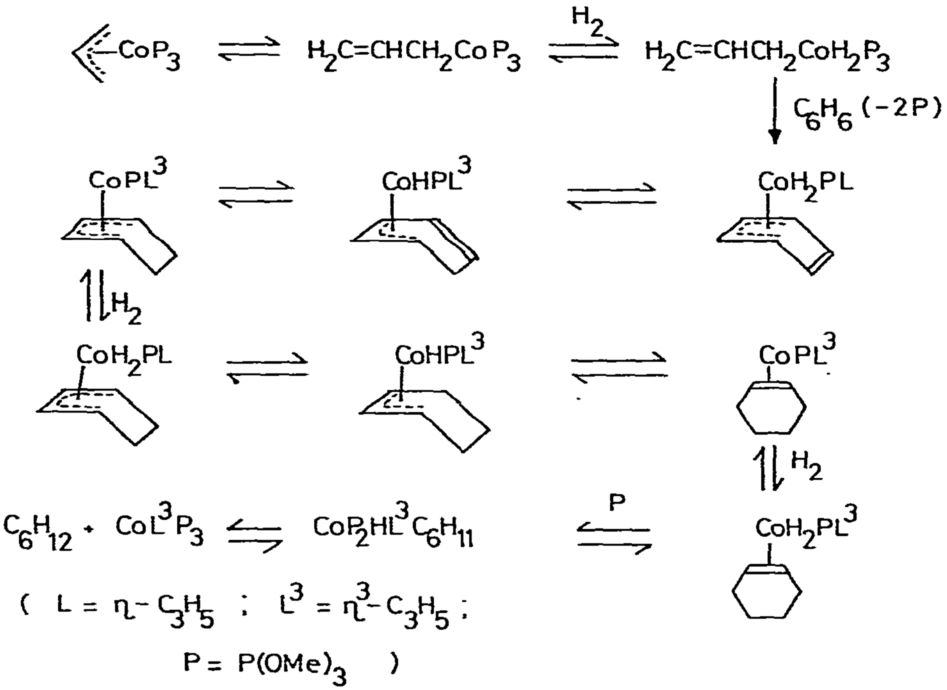
generated by elimination of butadiene from the allyl ligand. This proposal is supported by the observation that (261) is formed in improved yields by the reaction of $[IrH(CO)_2(PPh_3)_2]$ or $[IrH(CO)(PPh_3)_3]$ with CF_3CN.[277]

Trifluoroacetic acid and acetyl chloride react with $[Rh(\eta^3\text{-}C_3H_5)(PF_3)_2]$, (262), to form the bridged carboxylate complex, (263) and (264) respectively. In both reactions



propene is evolved. t-Butyl bromide and (263) react to give $[RhBr(PF_3)_2]_2$ and a mixture of propene and 2-methylprop-1-ene and this mixture of propenes also results from the action of t-butyl bromide upon $[Rh(\eta^3\text{-}C_3H_5)(PPh_3)_2]$. n-Propyl bromide and (263) give $[RhBr(PF_3)_2]_2$ and propene. In these reactions a mechanism involving a β-hydrogen abstraction and hydrogen migration via an intermediate metal to carbon bonded species is proposed. Treatment of $[Rh(\eta^3\text{-}C_3H_5)(PPh_3)_2]$ with Me_3SnCl gives $Me_3SnC_3H_5$ and $[RhCl(PPh_3)_2]_2$.[278]

Further studies on the arene hydrogenation catalyst, $[Co(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}_3]$, reveals that this catalyst exhibits a unique selectivity towards arenes over alkenes. Thus hydrogenation of benzene to cyclohexane occurs at a rate three-four times that of cyclohexene to alkene. The mechanism depicted in Scheme (49) is proposed.[279]

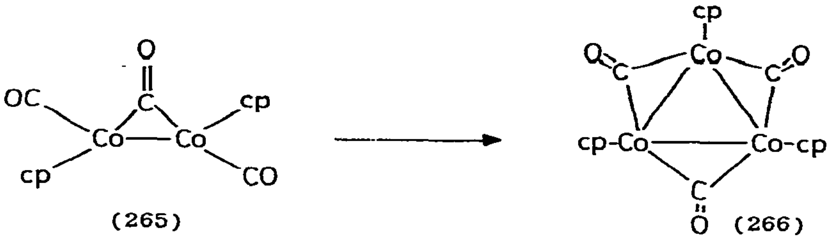


Scheme(49)

Metal carbocyclic complexes.

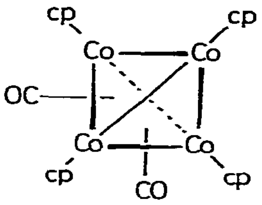
The single crystal X-ray structure of $[Co_4H_4Cp_4]$ has been reported. The compound contains a slightly distorted tetrahedron of cobalt atoms, each atom co-ordinated to a planar η^5-bonded cyclopentadienyl ring. All four faces of the Co_4-cluster are bridged by hydrogen atoms.[280]

Photolysis of $[CoCp(CO)_2]$ gives the reactive binuclear complex (265). This complex is labile and decomposes in



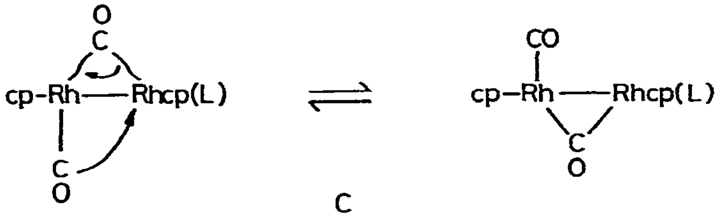
(265) (266)

solution at ambient temperature to give (266) with liberation of a molecule of $[CoCp(CO)_2]$. At 130°C (266) also decomposes with extrusion of $[CoCp(CO)_2]$ to give (267). Both (265) and (266) catalyse the trimerisation of alkynes at much lower



(267)

temperatures than $[CoCp(CO)_2]$.[281] Bridge-terminal carbonyl site exchange is known to occur in the rhodium analogue of (265). Three mechanisms have been envisaged for the exchange process in this complex, Scheme (50).



(L = CO P(OMe)$_3$)

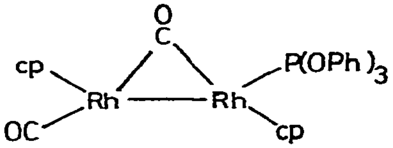
Scheme (50)

(a) via a triply bridged intermediate (A),

(b) via an unbridged intermediate (B),

(c) a synchronous process (C).

Further insight into this problem has been obtained by studying the bridge-terminal carbonyl exchange in (268) which can be obtained by addition of a stoichiometric amount of triphenylphosphite to [$Rh_2Cp_2(CO)_3$]. The temperature

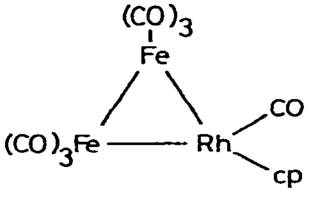


(268)

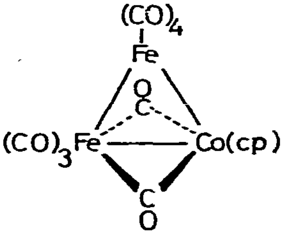
dependent ^{13}C n.m.r. spectrum obtained for (268) reveals that the Rh-P bond is not broken during the process and the synchronous process, C, is favoured for the carbonyl exchange. A similar mechanism could operate in the complex, [$Rh_2Cp_2(CO)_3$]

although mechanism A nas been previously stressed.[232]

The room temperature ^{13}C n.m.r. spectra of (269) and (270) indicate that total scrambling of the carbonyl ligands occurs

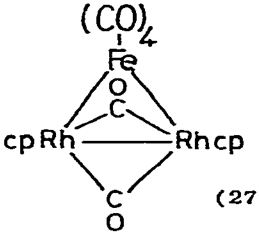


(269)

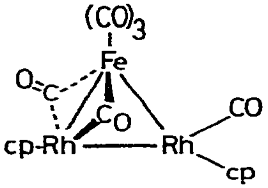


(270)

in solution. However, limiting low temperature spectra cannot be obtained. A low temperature limiting spectrum can be observed for $[FeRh_2Cp_2(CO)_6]$ and the structure (271) adopted by this molecule in solution is different from that proposed for the solid state structure (272). These complexes are



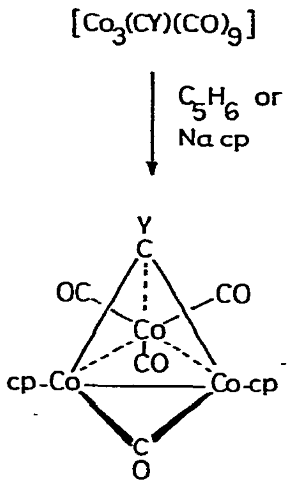
(271)



(272)

related structurally to $Fe_3(CO)_{12}$ and it is apparent that increasing substitution of MCpCo , (M = Co,Rh) in $Fe_3(CO)_{12}$ results in a decrease in rate of carbonyl site exchange.[283]

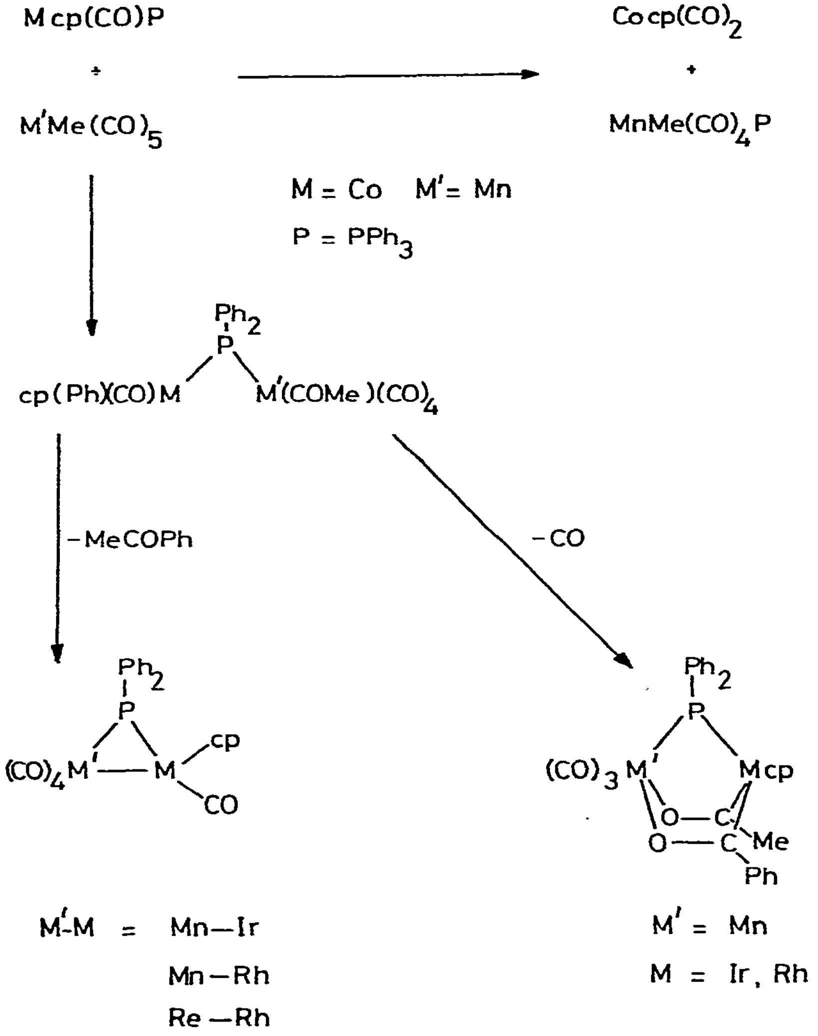
The dark green air-stable cyclopentadienyl complexes (273) have been prepared by the routes indicated in Scheme (51).



(273) (Y = Ph, Me, $C_{10}H_7$, $C_{12}H_{10}$)

Scheme (51)

The spectroscopic data for these complexes in solution are consistent with the same configuration which has been established by an X-ray structure determination. A unique structural feature is the bridging carbonyl group which is at 90^{o}C to the basal cobalt plane. This conformation has not been previously observed in triangular or tetrahedral carbonyl clusters. A very low ν(CO) value (1795 cm^{-1}) is observed for this bridging carbonyl and electrophiles such as $AlBr_3$ rapidly attack the nucleophilic carbonyl oxygen to give unstable 1:1 adducts. Labile phosphine derivatives $[Co_3(CY)Cp_2(CO)_3PR_3]$, can be obtained and it is suggested that the phosphine is in an equatorial configuration, the bridged-carbonyl absorption moving to lower frequencies. Steric congestion may account for the lability of the phosphine ligand and the failure to isolate complexes of the type



(274)

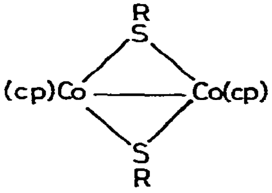
Scheme (52)

[$Co_3(CY)Cp_2(CO)_2$(diene)]. Attempts to acylate a cyclopentadienyl ligand of (273) failed although acylation of the phenyl group of (273), (Y = Ph), can be achieved.[203]

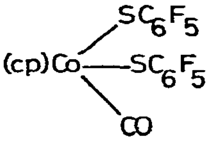
The ability of the $\underline{d}^8$ complexes [$MCp(CO)(PPh_3)$], (M = Rh,Ir), to act as Lewis-bases and form 1:1 adducts with mercury(II) halides has prompted an investigation of the donor ability of these $\underline{d}^8$ complexes towards [$MMe(CO)_5$] (M = Mn,Re). The results of these studies are summarised in Scheme (52).[284] The structure of complex (274), (M' = Mn, M = Ir), has been confirmed by a single crystal X-ray study.[285]

The reaction of [$CoCp(CO)_2$] with $C_6F_5SSC_6F_5$ in the absence of solvent gives (275), (R = C_6F_5). However, in solution and upon irradiation, the complex (276), (R = C_6F_5), is formed. A solution of (276) heated above 50°C gives (275), (R = C_6F_5), and a green complex, [$Co_2Cp(SC_6F_5)_3$] of unknown structure. The complex (275), (R = CF_3) can similarly be obtained with CF_3SSCF_3.[286]

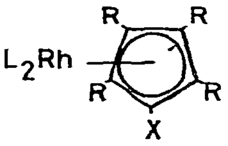
Both 2,3,4,5-tetraphenyldiazocyclopentadiene and diazocyclopentadiene insert into the halogen bridges of [$RhCl(COD)]_2$ and [$RhCl(C_2H_4)_2]_2$ to give the halogen substituted cyclopentadienyl complexes (277).[287]



(275)



(276)



(277)

R = Ph ; L_2=COD

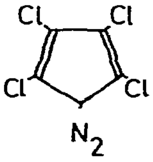
R = Ph ; $L_2=(C_2H_4)_2$

R = Ph ; $L_2=(CO)_2$

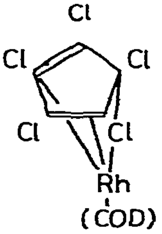
R = H ; L_2= COD

A similar reaction of (278) with $[RhCl(COD)]_2$ gives the pentachlorocyclopentadienyl complex (279).[288] A single crystal X-ray study on (279) reveals the presence of localised bonding in the η^5-C_5Cl_5 ring which suggests appreciable contribution from a bonding model where the ring is co-ordinated to the rhodium by two alkene π-bonds and one σ-alkyl bond.[289]

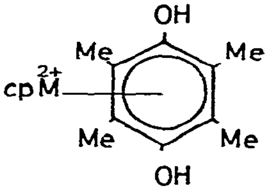
^{13}C n.m.r. studies on the η^4- duroquinone complexes, $[(MCp)C_{10}H_{12}O_2]$, (M = Co,Rh,Ir) suggest that in strongly acidic solution the complexes are protonated to produce the dications (280).[290]



(278)

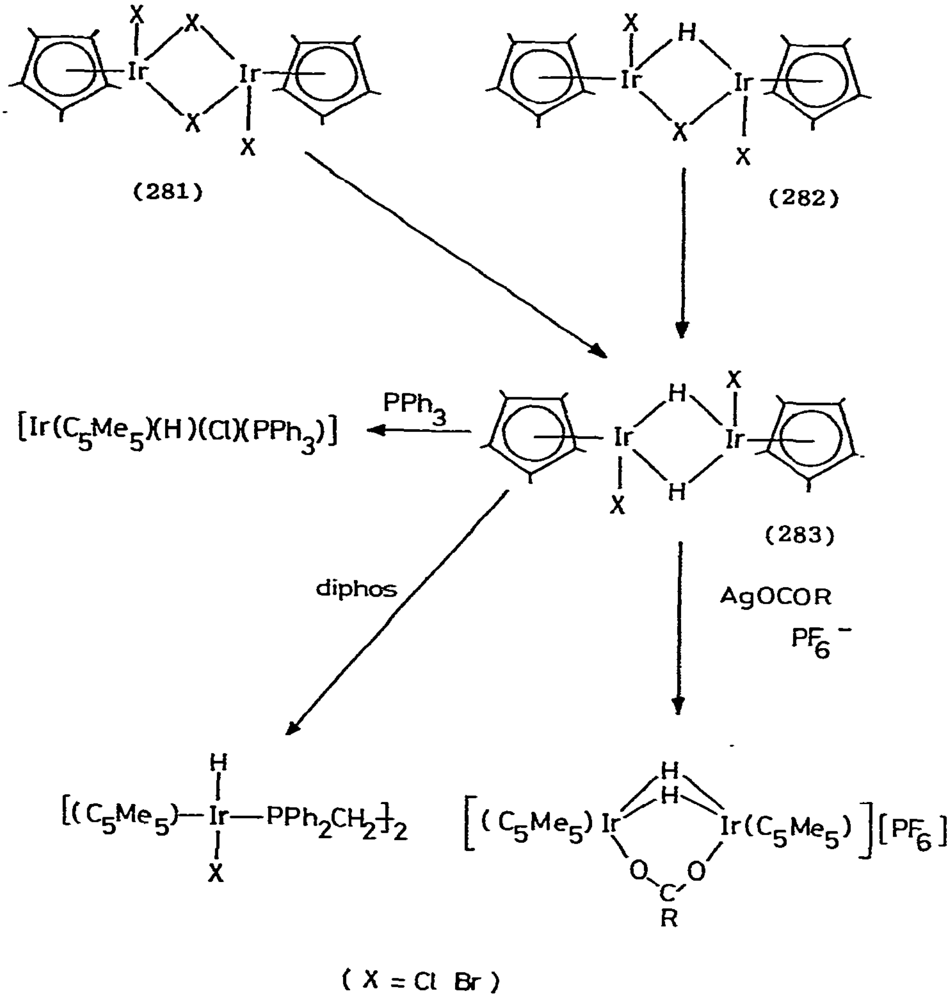


(279)



(280)

Treatment of either (281) or (282) in benzene with isopropanol and triethylamine gives the novel di-μ-hydrido-iridium complexes (283) and some reactions of the complexes are summarised in Scheme (53). Similar methods can be used to obtain the complexes $[M(C_5Me_5)Br_2]_2$, $[Ir(C_5Me_5)I_2]_2$,

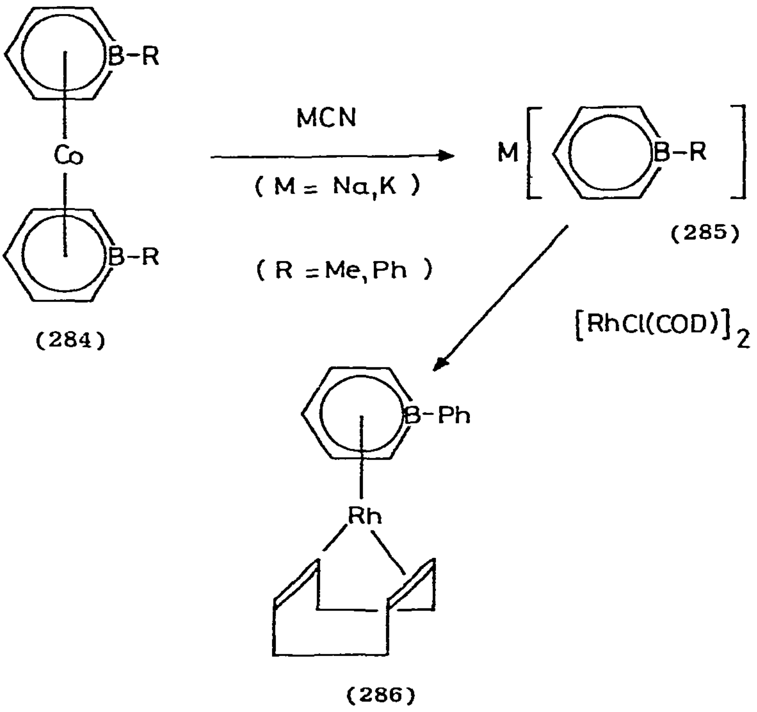


Scheme (53)

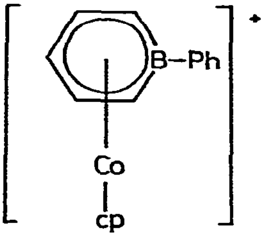
$[Rh(C_5Me_5)(PMe_2Ph)_2X]^+$, (X = Cl,I), $[Rh(C_5Me_5)(NO_3)_2]_n$, $[H\{M(C_5Me_5)\}_2Br_3]$ and $[H\{Ir(C_5Me_5)\}_2I_3]$, (M = Rh,Ir).[271]

Treatment of $[Rh(C_5Me_5)Cl_2]_2$ with potassium hydridotris-(1-pyrazolyl)borate followed by addition of NH_4PF_6 gives $[Rh(C_5Me_5)BH(pz)_3]PF_6$ and the structure of this complex has been determined by an X-ray study.[291]

The bis-borabenzene complexes (284) react with sodium or potassium cyanide in acetonitrile to give the alkali-metal borinates, (285). These salts provide a good route into other borabenzene complexes and the complex (286) can be obtained via $[RhCl(COD)]_2$.[292] The borabenzene complex (284), (R = Ph), undergoes a novel ring contraction when treated with aqueous iron(III) to give the cyclopentadienyl derivative (287)



and this product is also formed on the reaction of methanol with $[Co(C_5H_5BPh)_2]^+$ [293]



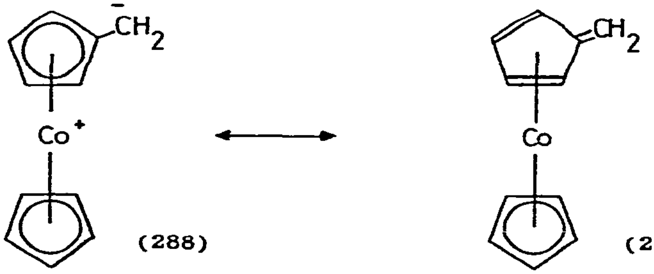
(287)

The e.s.r. spectrum of (284), (R = Ph) has been reported and interpreted.[294]

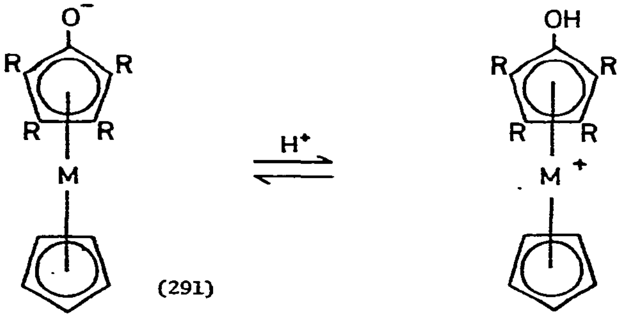
The crystal structure of cobaltocene has been refined[295] and the structure has also been determined by gaseous electron diffraction.[296] The combustion enthalpy of $[CoCp_2]$ has been determined and the standard enthalpy of formation and dissociation energy of the compound have been calculated.[297] The quantum yield of decomposition has been measured for the photolysis of $[CoCp_2]$ and the results have been discussed in terms of the electronic structures of the compounds.[298] The e.s.r. spectrum of cobaltocene in various diamagnetic host systems has been studied.[299] Introducing ethyl substituents into the cyclopentadienyl rings of $[CoCp_2]_2.PtCl_6$ and ferrocene result in similar electron absorption spectral changes[300] and ^{13}C n.m.r. spectra of phenyl- and ethyl-substituted cobaltocenes have been recorded.[301]

Cobaltocene can be intercalated in the layered compound TaS_2 and the orientation arrangement and temperature dependent dynamics of the cobaltocene molecules have been determined by proton n.m.r. measurements.[302]

The cobalticinium nucleus exerts strong electron-withdrawing, inductive and resonance effects and can stabilise negative charge as indicated in the resonance hybrids (288) and (289). Indeed the acidity of alkylcobalticinium salts is greatly enhanced and the basicity of aminocobalticinium salts is greatly reduced in comparison to alkyl- and amino-benzenes and ferrocenes.[303] Similar effects operate in the hydroxy-2,3,4,5-tetra-substituted cobalticinium and rhodicinium salts (290) which are in proteolytic equilibrium with the stable cyclopentadienone complexes (291). The acidity increases with increasing electronegativity of the R group and decreases slightly from cobalt to rhodium. The complexes (290), (R = C_6F_5), are comparable in strength to the mineral acids.[304]



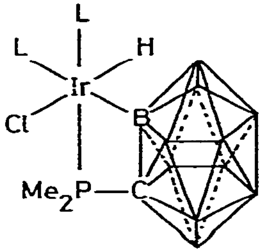
(288) (289)



(291) (290)

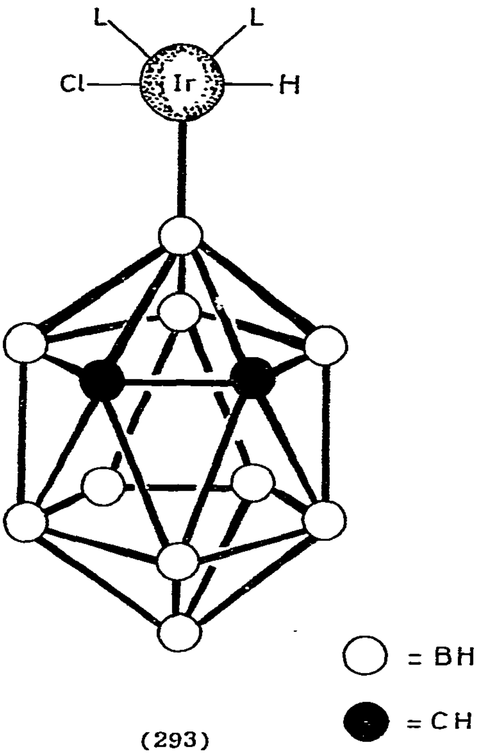
Metal carborane complexes.

Oxidative-addition of terminal boron-hydrogen bonds to low-valent metal complexes provides a useful route to complexes containing a metal-boron σ-bond. Thus the phosphine 1-PMe_2-1,2-$C_2B_{10}H_{11}$, L, reacts with $[IrCl(C_8H_{14})_2]_2$ in cyclohexane to give $[IrClL_3]$ which readily undergoes intramolecular oxidative addition to give (292). Prolonged reaction of 1,2-$C_2B_{10}H_{12}$ with $[IrCl(CO)(PPh_3)_2]$ fails to yield a stable oxidative-addition product. However, $[IrClD_2(CO)(PPh_3)_2]$ is an effective catalyst for deuterium exchange in this carborane implying that oxidative-addition occurs in this reaction but the product is presumably not favoured thermodynamically. The orthometallated complex, $[IrHCl(o\text{-}C_6H_4PPh_2)(PPh_3)_2]$ is the major product of the reaction of $[IrCl(PPh_3)_3]$ with 1,2-$C_2B_{10}H_{12}$ but a small yield of (293), (L = PPh_3) is also obtained. However, the compound $[IrCl(PPh_3)_2]$ formed in situ from $[IrCl(C_8H_{14})_2]_2$ and two equivalents of PPh_3 reacts readily with 1,2-$C_2B_{10}H_{12}$ to give (293). The corresponding triphenylarsine complex can similarly be obtained and 1,7- and



(L = 1-PMe_2-1,2-$C_2B_{10}H_{11}$)

(292)

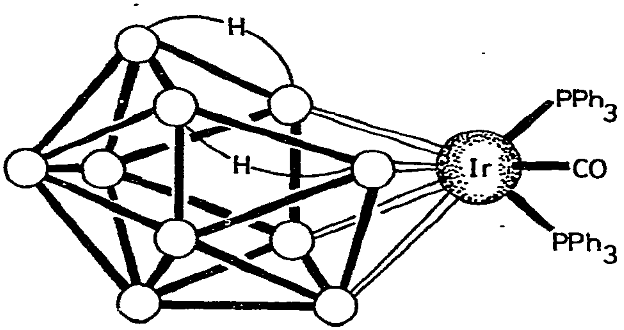


(293)

1,12-$C_2B_{10}H_{12}$ also react with the iridium complex. Both carbon monoxide and triphenylphosphine displace 1,2-$C_2B_{10}H_{12}$ from (293), (L = PPh_3).[305] A full account of the crystal structure of $[Ir(B_5H_8)Br_2(CO)(PMe_3)_2]$ formed by oxidative-addition of 1- or 2-BrB_5H_8 to trans-$[IrCl(CO)(PMe_3)_2]$ has been published.[306]

Quaternary ammonium salts of $[Ir(B_{10}H_{12})(CO)(PPh_3)_2]^-$, (294), react with deuterium gas at ambient temperature and pressure.

Reversible H-D exchange occurs at two terminal B-H sites in the $B_{10}H_{12}$ ligand and the exchange is thought to occur at



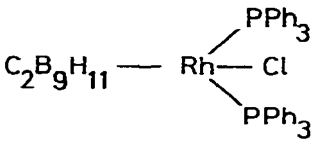
(294)

○ = BH

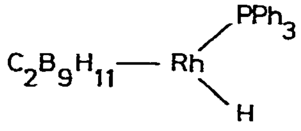
the 5,10 boron atoms. A mechanism involving oxidative-addition of D_2 followed by intramolecular H-D exchange is proposed.[307]

Transition metal complexes containing 2-R-1,2- and 7-R-1,7-$C_2B_{10}H_{10}^-$, (R = H,Me,Ph) ligands bonded through metal-carbon σ-bonds, $[Rh(\sigma\text{-carb})(PPh_3)_2]$, $[Ir(\sigma\text{-carb})(CO)(PPh_3)_2]$ have been prepared by the action of lithium-carborane derivatives with $[RhCl(PPh_3)_3]$ and trans-$[IrCl(CO)(PPh_3)_2]$ respectively.

The phosphine ligands in these carborane complexes undergo exchange reactions with phosphorus donor ligands and the results have been reviewed.[28] However, although 1-Li-2-R-1,2-$C_2B_{10}H_{10}$, (R = Me,Ph), gives σ-bonded carborane complexes the corresponding reactions with $[IrCl(PPh_3)_3]$ lead to the metallated complex, $[Ir(\underline{o}\text{-}C_6H_4PPh_2)(PPh_3)_2]$.[27] Addition of a tetrahydrofuran solution of Na_2-7,8-$C_2B_9H_{11}$ to a suspension of trans-$[RhCl(CO)(PPh_3)_2]$ in benzene produces a deep orange solution which on exposure to air becomes green and then brown. Thin layer chromatographic analysis indicates the presence of ten components. From this mixture the rhodium(III) complex, (295), can be isolated together with a



(295)

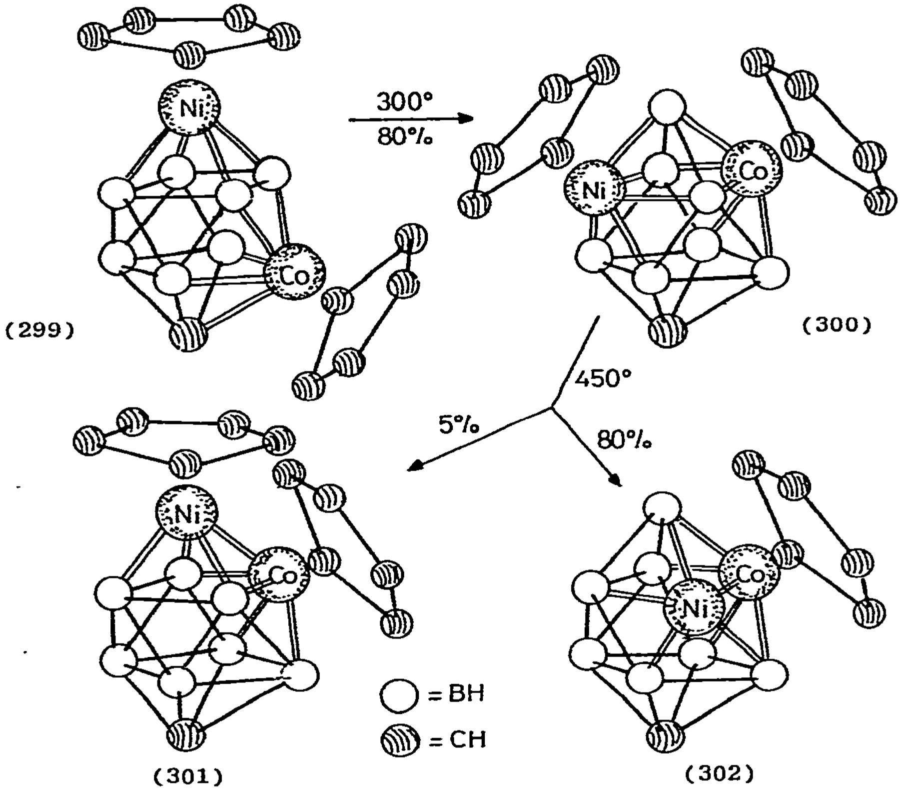


(296)

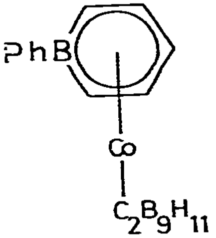
small yield of a complex, $[Rh(C_2B_9H_{11})(C_6H_6)(PPh_3)]_2$ which is considered to be a dimer with a Rh-Rh bond. The reaction of Na_2-7,8-$C_2B_9H_{11}$ with $[RhCl(PPh_3)_3]$ gives a larger yield of the dimer and from this reaction a small amount of (296) may be obtained.[308] Friedel-Crafts acetylation of $[Co(1,2\text{-}C_2B_9H_{11})Cp]$ results in the formation of $[Co(1,2\text{-}C_2B_9H_{10}Cl)Cp]$, $[Co(1,2\text{-}C_2B_9H_{10}\text{-}8\text{-}OCOMe)Cp]$, $[Co(1,2\text{-}C_2B_9H_{10}\text{-}8\text{-}OH)Cp]$, and $[Co(1,2\text{-}C_2B_9H_{10}\text{-}8\text{-}COMe)Cp]$.[309] However, the Grignard reagents RMgBr, (R = Ph,*m*-,*p*-FC_6H_4) attack the cyclopentadienyl ring to give $[Co(1,2\text{-}C_2B_9H_{11})\text{-}(\eta\text{-}C_5H_4R)]$.[310]

Alkyl- or aryl-boron dihalides have been shown to react with cobaltocene to produce borabenzene complexes, e.g. (287). However, an attempt to insert C_6H_5B into the carborane cage of $[Co(1,2\text{-}C_2B_9H_{11})Cp]$ to produce a 13-vertex metallocarborane gives the phenylborinato complex (297).[311]

A mixed-metal trimetallic metallocarborane (298) can be obtained by the reaction of $Fe(CO)_5$ with $[1,2,3\text{-}CpCoMe_2C_2B_4H_4]$.



Scheme (54)



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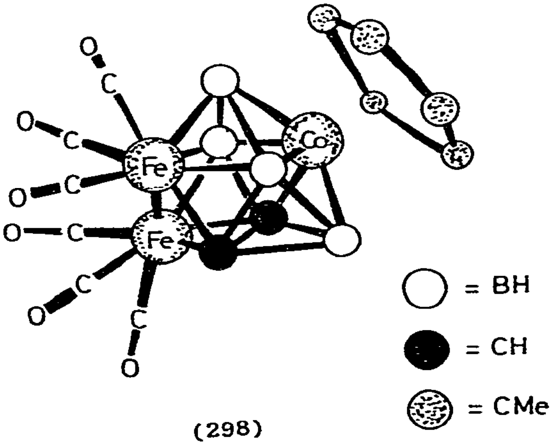


(298)

The complex (298) is cage isoelectronic with other 9-vertex carboranes and metallocarboranes containing 20 skeletal valence electrons, e.g. $[Co_2Cp_2C_2B_5H_7]$ and is presumed to adopt a similar gross tricapped trigonal prismatic geometry.[312] Treatment of $[3\text{-}Cp\text{-}3\text{-}Co\text{-}4\text{-}CB_7H_8]^-$ with sodium naphthalide followed by subsequent reaction with NaCp and nickel(II) leads to four isomers (299)-(302) of the bimetallocarborane $[Cp_2CoNiCB_7H_8]$. These isomers undergo thermal polyhedral rearrangements, the metal atoms migrating to adjacent polyhedral vertices, Scheme (54). {A Cp ring has been omitted from (302).}

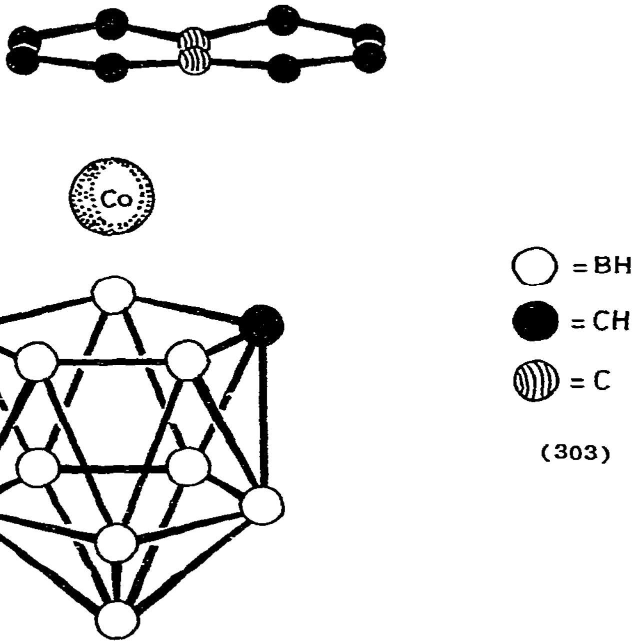
Table 1

Major Processes in Cobaltacarborane Pyrolyses

Cage System	No. of vertices	Intramolecular rearrangements observed	Groups involved in intramolecular transfer
CoC_2B_3	6	None	$(C_5H_5)Co$,BH
CoC_2B_4	7	1,2,3→1,2,4	$(C_5H_5)Co$,BH
CoC_2B_5	8	None	$(C_5H_5)Co$
$Co_2C_2B_3$	7	1,7,2,3⇌1,2,4,5→ 1,2,3,5→1,7,2,4	None detected
$Co_2C_2B_4$	8	None	$(C_5H_5)Co$,BH
$Co_2C_2B_5$	9	1,7,5,6⇌1,8,5,6	$(C_5H_5)Co$
$Co_3C_2B_5$	10	2,3,8,1,6→2,3,4,1,10[A]	$(C_5H_5)Co$

[A] Trace

Bromination of (299) and (300) with 1 or 2 mol of bromine in carbon tetrachloride gives a single isomer of mono- or dibromo-derivative in high yield. Substitution occurs exclusively at boron. Treatment of $[2\text{-Cp-}2\text{-Co-}1\text{-CB}_{10}H_{11}]^-$ with sodium naphthalide, Cp^- and nickel(II) leads to (303), the first metallocarborane containing a neutral arene π-bonded to the metal.[313] The thermal isomerisations of the metallocarboranes, $[1,2,4\text{-CpCoC}_2B_3H_5]$, $[1,2,3\text{-CpCoC}_2B_4H_6]$, $[1,7,2,3\text{-Cp}_2Co_2C_2B_3H_5]$, $[3,1,7\text{-CpCoC}_2B_5H_7]$, $[Cp_2Co_2C_2B_5H_7]$, and $[2,3,8,1,6\text{-Cp}_3Co_3C_2B_5H_7]$ are summarised in Table 1.[314]



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