COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1974 *

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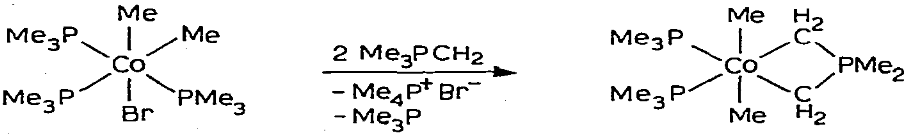
Contents

Metal—carbon σ-bonded complexes

Trimethylmethylenephosphorane, $Me_3\overset{+}{P}$—$\overset{-}{C}H_2$ reacts with $CoBrMe_2(PMe_3)_3$ to give the cobalt dimethylphosphoniodimethylide complex 1 [1], the crystal structure of which has been determined [2]. $[CoCl(PMe_3)_3]$, however, reacts with the Wittig reagent to give $[CoCl_2(CH_2PMe_3)_2]$ and $[Co(PMe_3)_4]$ [1].



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Complexes of type 2 are known to be readily formed via the oxidative elimination reaction of CF_3I with $[MCp(CO)_2]$, (M = Co, Rh or Ir) [3]. However, al-

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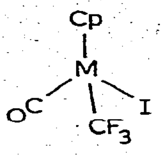
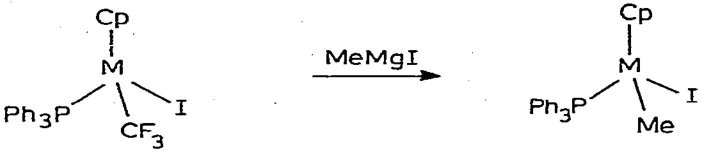
* Cobalt, Rhodium and Iridium, Annual Survey covering the year 1973, see J. Organometal. Chem., in press.



(2)

though attempts to methylate these complexes with methylmagnesium iodide or chloride failed [3], treatment of the triphenylphosphine substituted derivative 3 with the Grignard reagent gives the complex 4. In these reactions the CF_3 group, rather than iodide ligand, is displaced, which has been rationalised in terms of the pseudohalogen nature of the CF_3 ligand [3]. The cobalt derivatives $[Co(Cp)(R_f)(I)(CO)]$ ($R_f = CF_3, C_2F_5, C_3F_7$ and $(CF_3)_2CF$) react with the potassium polypyrazolylborates $K[(C_3H_3N_2)_nBH_{4-n}]$ (n = 2, 3 and 4), at room temperature, to give the red complexes $[Co(Cp)(R_f)\{(C_3H_3N_2)_nBH_{4-n}\}]$ ($n = 2$, $R_f = CF_3, C_2F_5, C_3F_7$ and $(CF_3)_2CF$; $n = 3$, $R_f = CF_3, C_2F_5$ and C_3F_7; $n = 4$, $R_f = C_2F_5$ and C_3F_7), in which the polypyrazolylborates are bidentate ligands in all cases [4]. Interestingly, the complexes $[Co(Cp)(R_f)(I)(CO)]$ remove a pyrazolyl ring from potassium tetrapyrazolylborate to give boron-free compounds formulated as 5. Two stereoisomers of the compounds $[Co(Cp)(C_3F_7)\{(C_3H_3N_2)BH_2\}]$ and $Co(Cp)(C_2F_5)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ can be separated [4]. Similarly, the complexes $[Co(Cp)(C_3F_7)(NN')]^+PF_6^-$ (formed via the reaction of $[Co(Cp)(C_3F_7)(I)(CO)]$ with the Schiff base NN′ derived from S-(—)-α-phenylethylamine and pyridine carbaldehyde-2) and the complexes $[Co(Cp)(NN'')]$, formed via the reaction of the cobalt complex with the sodium salt $Na^+[NN'']^-$ of the Schiff base derived from S-(—)-α-phenylethylamine and pyrrolcarbaldehyde-2) can be separated into diastereoisomeric pairs [5]. Infrared studies on the complex $[Co(Cp)(C_2F_5)(CO)(PPh_3)]ClO_4$ also suggest that diastereoisomers are present in this system, the coordinated phosphine and the cobalt constituting chiral



(M = Co or Rh)

(3)

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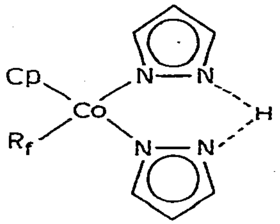
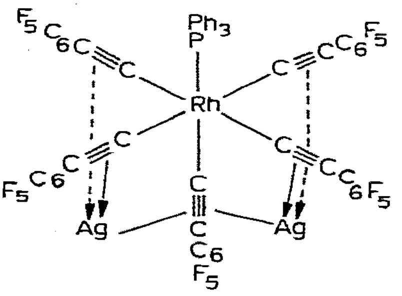


(5) ($R_f = C_2F_5$, C_3F_7, $(CF_3)_2CF$)

centres [6]. Variable temperature proton and fluorine NMR spectra of several of the complexes $[\mathrm{Co(Cp)(R_f)(I)(L)}]$ ($\mathrm{R_f = CF_3, C_2F_5}$, and $\mathrm{(CF_3)_2CF}$; L = phosphorus donor) also provide evidence for hindered rotation about both metal—carbon and phosphorus—aryl bonds [6]. The reaction of $[\mathrm{Co(Cp)(C_3F_7)(I)(CNCHMePh)}]$ with $\mathrm{AgClO_4/NH_4SCN}$ produces a mixture of the nitrogen- and sulphur-bonded isomers of $[\mathrm{Co(Cp)(C_3F_7)(CNS)(CNCHMePh)}]$, which on treatment with pentane can be transformed into (+)-$[\mathrm{Co(Cp)(C_3F_7)(NCS)(CNCHMePh)}]$ [7].

The complexes $[\mathrm{Co(COCH_2F)(CO)_3(PPh_3)}]$ and $[\mathrm{Co(COCH_2F)(CO)_3\{P(OPh)_3\}}]$ are also present as rotational isomers at —100° to +80°C. Theoretical considerations suggest that in these complexes hindered rotation about the C—C bond, rather than about the $\mathrm{Co{-}C_{acyl}}$ bond, is preferred. The complexes are prepared via the reaction of the anhydrides $\mathrm{(CHFXCO)_2O}$ (X = H or F) with $\mathrm{Na[Co(CO)_4]}$ or $\mathrm{Na[Co(CO)_3(PR_3)]}$ at —78°C in dimethyl ether. These acyl complexes undergo decarbonylation between 0° and 70°C [8].

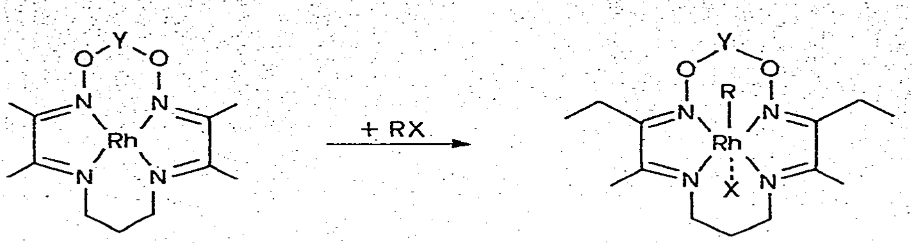
Several square-planar complexes $[\mathrm{IrR(CO)(PPh_3)_2}]$ (R = Me, $\mathrm{CH_2Ph}$, Ph, p-$\mathrm{MeC_6H_4}$, p-$\mathrm{ClC_6H_4}$, p-$\mathrm{Me_2NC_6H_4}$, mesityl, $\mathrm{C_6F_5}$ and $\mathrm{C_6Cl_5}$) have been prepared from reactions of $[\mathrm{IrCl(CO)(PPh_3)_2}]$ with the appropriate aryllithium reagents or arylmagnesium halides [9,10]. The σ-pentahaloaryl complexes undergo reversible oxidative addition reactions with hydrogen halides. Treatment of $[\mathrm{Ir(C_6F_5)(CO)(PPh_3)_2}]$ with diphenylmethylphosphine gives $[\mathrm{Ir(C_6F_5)(PMePh_2)_3}]$ [9]. The reaction between $[\mathrm{RhCl(PPh_3)_3}]$ and $\mathrm{Ag(C{\equiv}CC_6F_5)}$ in tetrahydrofuran gives the hexanuclear cluster $[\mathrm{Rh_2Ag_4(C{\equiv}CC_6F_5)_8(PPh_3)_2}]$ (which is probably isostructural with $[\mathrm{Ir_2Cu_4(C{\equiv}CC_6F_5)_8(PPh_3)_2}]$) and the binuclear complex $[\mathrm{RhAg(C{\equiv}CC_6F_5)_4(PPh_3)_3}]$. However, in 1,2-dimethoxyethane, a third complex $[\mathrm{RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3}]$ (6) can be isolated, the crystal structure of which has been determined [11].



(6)

Studies on the macrocyclic rhodium(I) complex 7a, which appears to be the most reactive neutral d^8 complex toward oxidative addition yet discovered, are complicated by insolubility and side reactions of the hydrogen bridge. However, these problems can be overcome by the preparation of 7b which is more soluble and has a $\mathrm{BF_2}$ bridge [12]. Alkyl halides and sulphonates react readily with 7b to give the *trans* rhodium(III) adduct 8. The rate law for the reaction follows second-order behaviour:

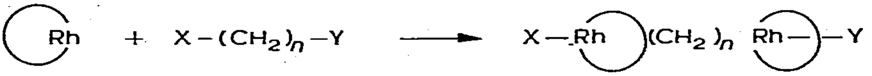
$$\frac{-\mathrm{d}[\mathrm{Rh^I}]}{\mathrm{d}t} = k_2[\mathrm{Rh^I}][\mathrm{RX}]$$



(7 a R = Me, Y = H
7 b R = Et, Y = BF_2)

(8)

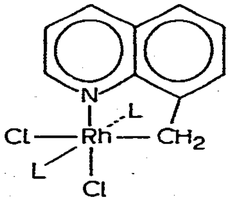
and the observation that reaction of 7b with n-BuBr, in the presence of LiCl, affords *only* the *trans*-alkylchlororhodium complex provides evidence for a cationic rhodium(III) intermediate in these reactions. The order of reactivity Me > Et > secondary > cyclohexyl and the failure of 1-bromoadamantane to react strongly, support an oxidative addition mechanism involving initial nucleophilic attack by rhodium. Treatment of 7b with α, ω-dihalo alkyls affords only the dirhodium complex 9 for X = Y = Br and n = 2, 3, 4 or 6. The



(9)

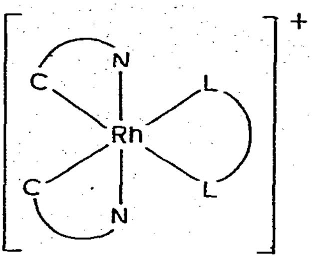
second-order rate constants for the α, ω-dihalides are only slightly different from those of simple alkyl halides, the second oxidative addition is, therefore, presumably much faster than the first [12].

8-Methylquinoline (Hmq) undergoes metallation with hydrated rhodium(III) chloride in boiling 2-methoxyethanol. The insoluble product, $[RhCl_2(mq)(Hmq \cdot HCl)_{0.33}]_n$, reacts with donor ligands (L) to give $[RhCl_2(mq)(L)]$, (L = pyridine, dimethylsulphide or acetonitrile and 10, L = Ph_3As and P-n-Bu_3)



(10)

[13]. Benzo[*h*]quinoline (bhqH) is metallated by both $RhCl_3 x H_2O$ and $Na_3[IrCl_6]$ in boiling ethanol or 2-methoxyethanol respectively, to give, after purification, either $[RhCl(bhq)_2]_2 \cdot 0.25 CHCl_3$ or $[IrCl(bhq)_2]_2 \cdot 0.66 CHCl_3$. Treatment of the rhodium complex with ethylenediamine, 2,2′-bipyridyl, $Ph_2PCH_2CH_2PPh_2$ and other bidentate ligands give the complexes 11 [14]. Both complexes react with donor ligands L to afford the complexes $[MCl(bhq)_2L]$ (M = Rh, L = P-n-Bu_3, Me_2S, py, 4-Me-py, $MeNH_2$; M = Ir, L = P-n-Bu_3, Et_2S) [14,15]. The resonance stabilised ylide $C_5H_5\overset{+}{N}\bar{N}COPh$, is also metallated by salts of rhodium and iridium to give $[Rh(L{-}H)_2(H_2O)_2]Cl$



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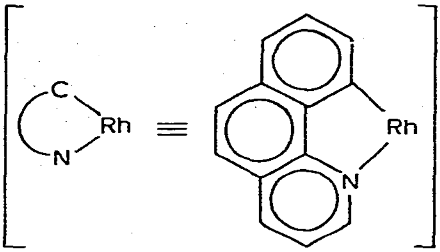
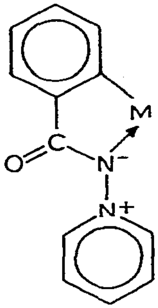


and $[IrCl(L{-}H)_2(H_2O)]3H_2O$ respectively, which contain the formula unit 12. The rhodium complex is unreactive towards carbon monoxide but the



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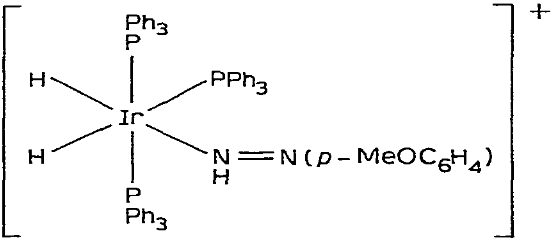
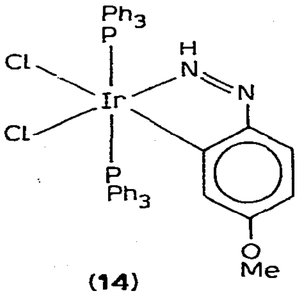


(13)

iridium complex undergoes a rapid reversible reaction to give $[Ir(L{-}H)_2(CO)_2]X$ (X = halogen) [16].

Para-substituted aryldiazonium cations react with $[IrH_3(PPh_3)_3]$ to give salts of the cation 13 [17]. When a salt of the cation 13 is dissolved in chloroform, orange crystals of the *ortho*-metallated product 14 slowly separate; the crystal structure of this complex has been determined [17]. The crystal structure of the *ortho*-metallated azobenzene complex 15 has also been reported [18].



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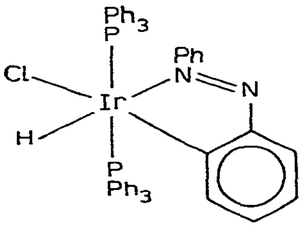
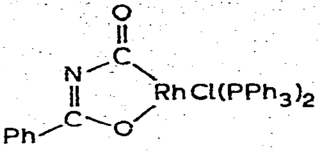


(15)

A metallocyclic complex 16 can be generated via the reaction of benzoyl isocyanate, PhCONCO, with $[RhCl(PPh_3)_3]$. Similarly, reaction of 2-phenylthiazoline-4,5-dione 17 with $[RhCl(PPh_3)_3]$ or *trans*-$[RhCl(CO)(PPh_3)_2]$ gives 18 [19].

Carboxylic acid anhydrides undergo oxidative addition reactions with *trans*-$IrX(CO)L_2$ (X = Cl, Br; $R = CF_3$, C_2F_5; $L = PPh_3$, $PMePh_2$) to give the octa-



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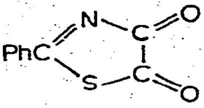
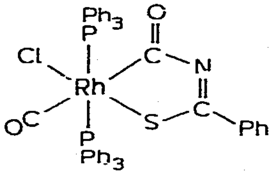


(17)

hedral acyl complexes $IrCl(COR)(OCOR)(CO)L_2$. However, with perfluorosuccinic anhydride insertion into the five membered ring occurs to give **19**. Perfluoroglutaric anhydride reacts with *trans*-$IrCl(N_2)(PPh_3)_2$ to give an orange product, which could not be recrystallised but may be a seven-membered ring complex, $[IrCl\{C(O)(CF_2)_3CO_2\}(PPh_3)_2]$. In refluxing benzene a ring contraction occurs to give **20**. The anhydrides $(RCO)_2O$ react with the dinitrogen complex to afford the complexes **21**, which undergo migration reactions to form the complexes $Ir(OCOR)(R)(Cl)(CO)(PPh_3)_2$. The complexes $[IrClI(CF_3)(CO)_2L_2]$, $[IrCl_2(COCF_3)(CO)L_2]$ and $[IrCl_2(COCF_3)L_2]$ can be obtained by oxidative addition of CF_3I or CF_3COCl to *trans*-$[IrCl(Z)(PPh_3)_2]$ (Z = CO, N_2). The five-coordinated complex $[IrCl_2(COCF_3)L_2]$ undergoes a migration reaction to form $[IrCl(CF_3)(CO)L_2]$ [20]. Further studies have shown that this migration reaction occurs in the solid state and that the enthalpy changes for the conversion of the acyls **22** to the alkyl complexes **23** have been determined [21]. There is



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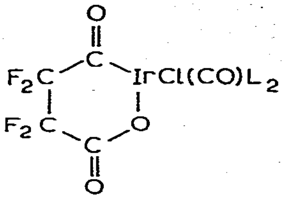

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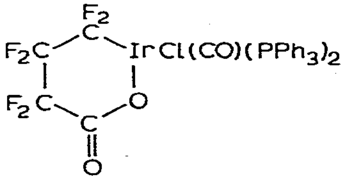

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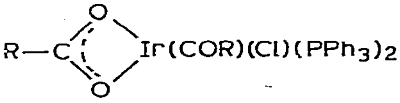

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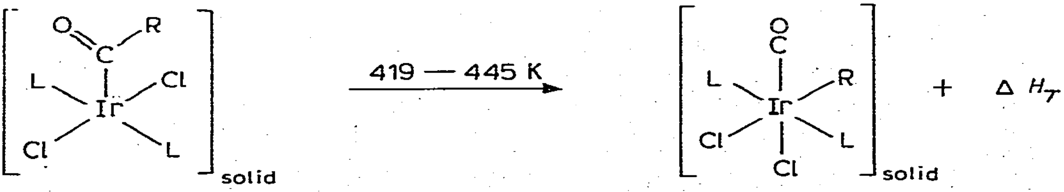
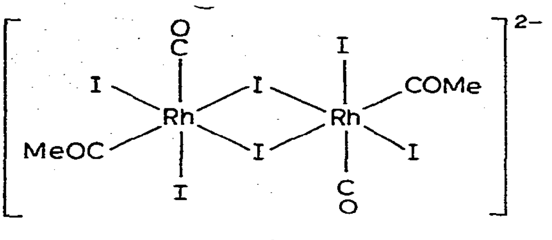


(22) (23)

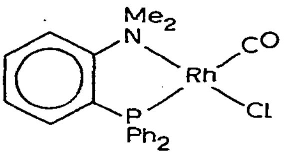
an inverse relationship between the migration rate and the enthalpy change. A rhodium acetyl complex **24** is formed upon addition of methyl iodide to



(24)

$[RhI_2(CO)_2]^-$ and the crystal structure of the $PhMe_3N^+$ salt has been determined [22]. An acyl complex $[RhI_2(COMe)(CO)(PN)]$, which can be separated into two isomers, can be isolated upon treatment of **25** with methyl iodide in the presence of sodium iodide [23]. The addition of methyl iodide to $[Rh(PN)_2]X$, ($X = Cl, PF_6, SbF_6, BPh_4, ClO_4$) gives $[RhI(Me)(PN)_2]X$.

Some highly labile oxidative addition products (**26**) result upon addition of



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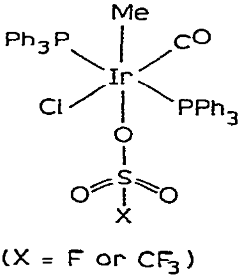
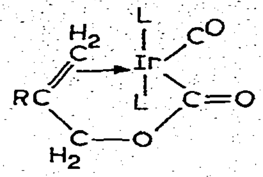


(26)

$MeOSO_2F$ or $MeOSO_2CF_3$ to *trans*-$[IrCl(CO)(PPh_3)_2]$. The OSO_2X group is labile and is readily replaced by F, Cl, Br, I, —NCS, N_3, —ONO, —ONO_2, —$OCOCH_3$, $S_2O_2C_7H_7$, —$(NC)_2Pt(CN)_2$ and —$NCC(CN)_2$ to give a series of iridium(III) complexes which are inaccessible by direct oxidative addition [24]. Kinetic parameters have been reported for the addition reactions of $MeOSO_2F$ with *trans*-$[IrX(CO)(PPh_3)_2]$ (X = Cl or Br) [25].

Treatment of *trans*-$[IrCl(CO)L_2]$ ($L = PPh_3$ or $PMePh_2$) with CO, methanol and triethylamine gives the five-coordinate carbonyls, $[Ir(CO_2Me)(CO)_2L_2]$. However, no analogous reaction occurred for either $[RhCl(CO)(PPh_3)_2]$ or $[CoCl(CO)_2(PPh_3)_2]$. The iridium complexes react with methyl iodide to form $[IrI(CO_2Me)(Me)(CO)L_2]$ [26]. Transesterification reactions of $[Ir(CO_2Me)(CO)_2(PPh_3)_2]$ occur when the iridium complex is treated with $CH_2{=}C(R)CH_2OH$, (R = H, Me), $MeC{\equiv}CCH_2CH_2OH$ and $HOCH_2CH_2OH$, to afford **27**, $[Ir(CO_2CH_2CH_2C{\equiv}CMe)(CO)_2(PPh_3)_2]$ and $[Ir(CO_2CH_2CH_2OH)(CO)_2(PPh_3)_2]$ respectively. However, the acetylenic alcohol, $HC{\equiv}CCH_2CH_2OH$ gives $[Ir(C{\equiv}CCH_2CH_2OH)(CO)(PPh_3)_2]$ [27]. Treatment of **27** with fluoroboric acid, perchloric acid, $Ph_3C^+BF_4^-$ and $Me_3O^+BF_4^-$ gives the cation $[Ir(CO)_3(PPh_3)_2]^+$, while reaction with MeI leads to initial formation of $[IrI(CO)_2(PPh_3)_2]$ but prolonged reaction yields $[IrI_2(Me)(CO)(PPh_3)_2]$. The metal—alkene bond in **27**

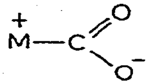


(L = PPh₃)

(27)

is not cleaved by CO or triphenylphosphine [27]. Ethoxycarbonyl(tetraphenylporphinato)rhodium(III), Rh(COOEt)(TPP), is obtained upon treatment of RhCl(CO)(TPP) with sodium ethoxide [28].

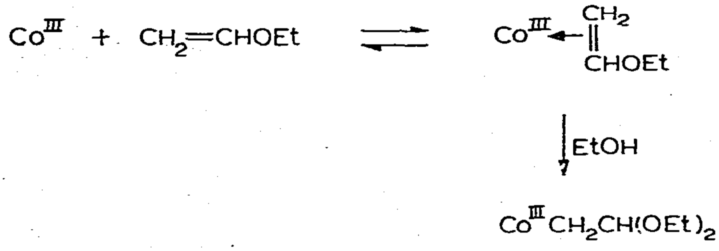
The complexes *trans*-[M(OH)(CO)(PPh$_3$)$_2$] (M = Rh or Ir) and sodium [*NN*′-ethylenebis(salicylideneiminato)cobaltate(I)] reversibly add carbon dioxide to give the complexes [M(OH)(CO)(CO$_2$)(PPh$_3$)$_2$] and [Co(salen)CO$_2$]Na. In pyridine solution the cobalt complex gives [Co(salen)(CO$_2$)(py)]Na [29,30]. The cobalt complex, and possibly the rhodium and iridium complexes, contain CO$_2$ as the reduced species in the bent form (28). The complex [CoH(N$_2$)(PPh$_3$)$_3$] has also been shown to react with carbon dioxide in acrolein solution to produce the complexes [Co(OCOEt)$_2$(PPh$_3$)$_2$] and [Co(CO$_3$)$_n$(CO$_2$Et)(PPh$_3$)] [31].



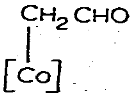
(28)

The reaction of cobaloximes and cobalamines with vinyl ethers, in the presence of alcohols give acetals via intermediate cobalt(III)—alkene complexes (Scheme 1), which has been substantiated by further work [32]. The rearrangement of the cobaloximes β-OH-i-PrCo(D$_2$H$_2$)HOH to β-OH-n-PrCo(D$_2$H$_2$)HOH may also proceed via an alkene—cobaloxime(III) π-complex [33].

Scheme 1



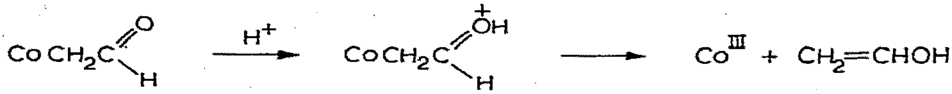
Formylmethylcobalamin (29) is a suggested intermediate in the enzymic con-



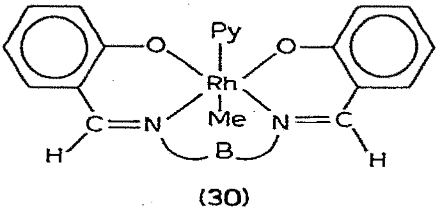
(29)

version of ethylene glycol to acetaldehyde in a coenzyme-B_{12}-dependent reaction, the synthesis of the complex **29** has been achieved [34]. In contrast to previous reports, the complex is acid sensitive and a route for its acid decomposition (Scheme 2) has been proposed [34]. Formylmethylbis(dimethylglyoximato)-(pyridino)cobalt(III) has also been described [35].

Scheme 2

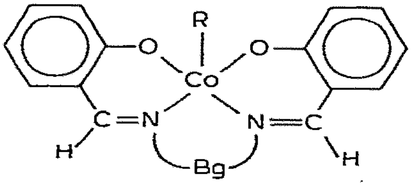


Treatment of $[Rh(SB)py_2]PF_6$ with sodium amalgam, followed by addition of methyl iodide and pyridine, affords the rhodium—methyl complexes **30** [36]. Similarly, the reaction of alkyl halides with $[Co(sal_2Bg)]^-$ generates the alkyl complexes $CoR(sal_2Bg)$ (**31**) (R = Me, Et, n-Pr, i-Pr) [37]. The cobalt—carbon bond in these complexes is cleaved by light, I_2, CN^-, HS^-, RS^- and RSH.



(30)

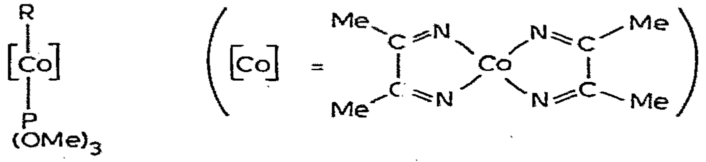
[B = 1,3-propylene (sal-1,3-pn) or 1,2-phenylene (salphen)]



(31)

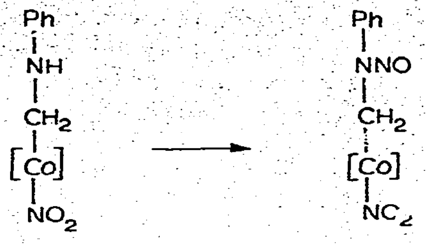
[Bg = $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_3N(CH_2)_3$]

It is known that alkyl substituents, on the axis normal to the planar ligand system of bis(dimethylglyoximato) complexes of cobalt(III) strongly labilise the *trans* position. Further evidence for this effect, using dimethylsulphoxide as solvent, is provided by a comparison of the rates of anation of $[CoMe(dmgH)_2(DMSO)]$ and $[Co(NO_2)(dmgH)_2(DMSO)]$ with NCO^-, N_3^- and NCS^- [38]. Further, it is apparent from studies on the rate of dissociation of $P(OMe)_3$ from the complexes **32**, that substitution of the axial CH_3 by alkylhalo groups results in a decrease in rate which does not follow the expected inductive order. The rates decrease in the order R = $Me_3SiCH_2 > Me > CH_2F > CHF_2 > CH_2Cl > CF_3 \approx CHCl_2 \approx CH_2Br > CHBr_2$ [39].



(32)

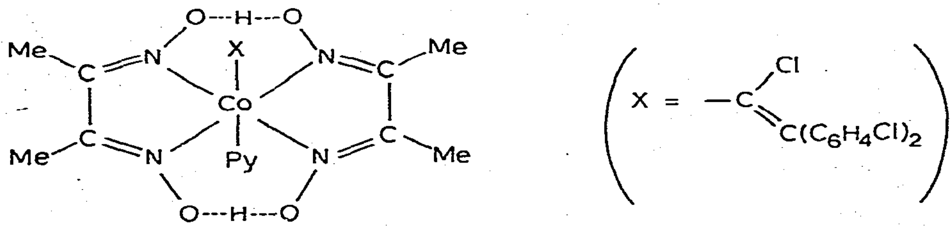
Interestingly, a potent carcinogen, *N*-nitroso-*N*-methylaniline can be prepared employing a bis(dimethylglyoximato)cobaltate template. Thus the complex **33** readily undergoes nitrosation to generate **34**. However, replacement of the axial



(33) **(34)**

nitro group with cyanide inhibits the nitrosation reaction [40]. ^{19}F NMR studies on complexes of the type $[Co(CH_2C_6H_4F\text{-}4)(dmgH)_2(B)]^-$ reveal that the electron-donating ability of the substituent CH_2Co (ligands) is particularly enhanced when B is cyanide [41].

Several cobalt(III) σ-vinyl halide complexes have previously been prepared by reactions of cobalt(I) species with acetylenes or vinyl halides. Such a complex (35) has now been prepared by the reaction of a fully saturated organic

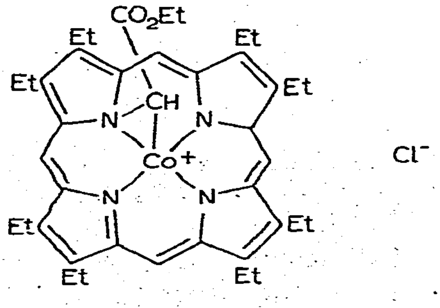


(35)

molecule, 1,1-bis-(*p*-chlorophenyl)-2,2,2-trichloroethane (*p,p'*-DDT) with bis(dimethylglyoximato)pyridinecobalt(I). This complex is presumably formed via S_N2 attack by cobalt(I) on C(2) on DDT followed by HCl elimination. Conjugation of the vinyl group with the benzene rings provides a driving force for the reaction and the Co—C bond is stabilised by the vinylic chlorine [42].

Cobalt-59 nuclear quadrupole and nuclear magnetic resonance spectra of some cobaloximes have been reported [43,44].

The reaction of ethyl diazoacetate with (octaethylporphin)cobalt(II) has been shown to yield a cobalt(III) salt (36), in contrast to reaction with zinc

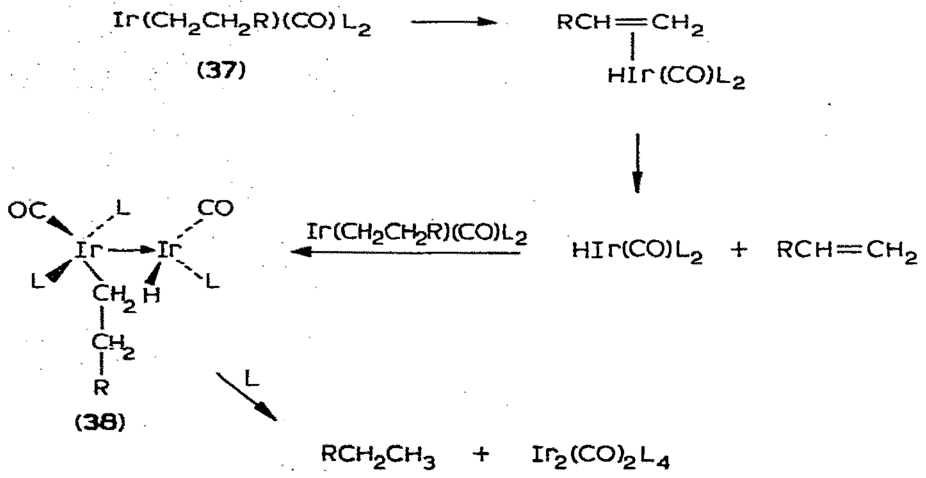


(36)

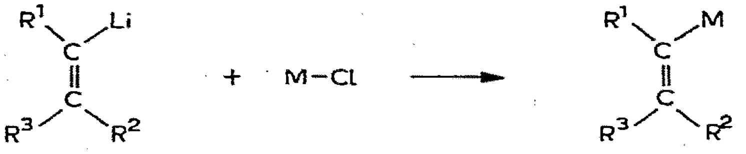
derivatives which do not give metal—carbon bonded products [45].

The thermal decomposition of the octyl iridium complex 37 gives predominantly octene. However, octane is also produced in substantial amounts, which are dependent on the concentration of triphenylphosphine (L). It is suggested, on the basis of a series of experiments, that octane is produced via loss of hydrocarbon from a bimolecular intermediate 38 [46] (Scheme 3).

Scheme 3



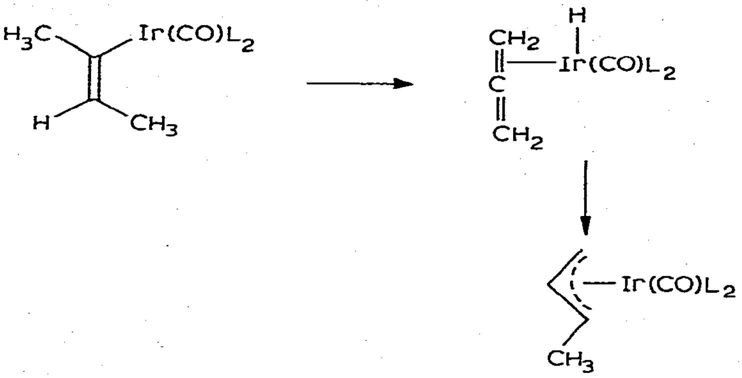
The kinetic isotope effect for β-hydride elimination from $[Ir(CH_2CHDC_6H_{13})(CO)(PPh_3)_2]$ is $K_H/K_D = 2.28 \pm 0.20$. The measured isotope effect suggests a transition state for β-hydride elimination in which the iridium inserts into the βC—H bond of the alkyl group [47]. β-Hydride elimination can also occur from vinyl-iridium(I) and -rhodium(I) complexes. The complexes 39 are readily prepared from the appropriate organolithium reagent. In 39a a β-hydrogen *cis* to iridium is present and on thermolysis dimethylacetylene is eliminated and the hydride 40 is formed. However, there is no β-hydrogen present in 39b, 39d or 39e and an η^3-crotyl species e.g. 41 is formed. From these studies it is apparent



(39)

(a $R^1 = R^3 = Me$, $R^2 = H$, M = *trans* - $Ir(CO)L_2$
b $R^1 = R^2 = Me$, $R^3 = H$, M = *trans* - $Ir(CO)L_2$
c $R^1 = R^3 = H$, $R^2 = Me$, M = *trans* - $Ir(CO)L_2$
d $R^1 = R^2 = Me$, $R^3 = H$, M = *trans* - $Rh(CO)L_2$
e $R^1 = R^2 = Me$, $R^3 = H$, M = RhL_3)
($L = PPh_3$)

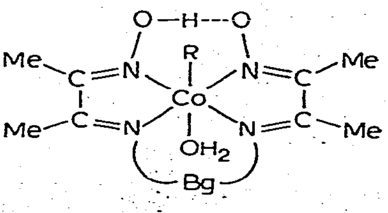
(40)



(41)

that the trend for β-H elimination is β-vinylic H > β-alkylic H [48].

Cleavage of the cobalt—carbon bond in [Co(*erythro*-$CHDCHDCMe_3$)-$(dmgH)_2(py)$] by mercury(II), in aqueous perchloric acid, proceeds with inversion of configuration of the α-carbon. The formation of the cobalt complex from the *threo-p*-bromobenzenesulphonate or *threo*-$Me_3CCHDCHDOH$ and $[Co(dmgH)_2]^-$ also occurs with inversion of configuration at the α-carbon atom [49]. The relative rates of dealkylation of the complexes 42 by mercury(II) decrease in the order R = Me $\gg$ Et > CH_2Ph > n-Bu $\simeq$ n-Pr. This order, together with other evidence, is also consistent with an S_E2 mechanism for Co—C bond cleavage [50]. It should be noted, however, that while transfer of the alkyl group from cobalt to mercury appears to involve one simple step, kinetic



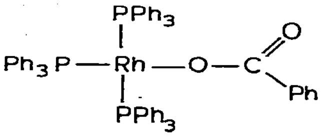
(42)

(R = Me , Et , n-Pr , n-Bu , CH_2Ph
Bg = $(CH_2)_3$, $(CH_2)_2$)

studies on the transalkylation by mercury(II) of alkyl- and aryl-aquo-1,3-bis-(diacetylmonoximeimino)propanatocobalt(III) monocations and of alkylaquo-*N,N'*-ethylenebis(salicylideneiminato)cobalt(III) (RCo) reveal the formation of intermediates $RCoHg^{2+}$ [51]. Chromium(II) in aqueous perchloric acid will also effect cleavage of the cobalt—carbon bond in methyl- and ethyl-cobalamin. The reactions occur with a 1/1 stoichiometry, producing $[CrR(H_2O)_5]^{2+}$ and B_{12}. The reactions follow second-order kinetics [52]. In the methyl transfer from MeB_{12} to $PdCl_4^{2-}$ there are two kinetically distinct steps, the final products being, Pd, MeCl, aquo- and chloro-cobalamin [53]. Exchange of alkyl groups can also occur between organocobalt(III) derivatives containing Schiff-base ligands and related cobalt(II) complexes [54].

Irradiation of the cobaloximes $[CoR(dmgH)_2(py)]$ causes homolytic cleavage of the Co—R bond when R = i-Pr, i-Bu, n-pentyl and cyclohexyl. However, with the methyl and benzyl derivatives electron transfer occurs, in the first instance, from the solvent or from the equatorial ligands [55]. In the presence of oxygen, photo-induced insertion of oxygen into the cobalt—carbon bond can be achieved via a pentacoordinate complex, formed by photolytic cleavage of the cobalt—base bond [56].

Carbon dioxide cleaves the rhodium—phenyl bond of $[RhPh(PPh_3)_3]$ to produce the benzoate 43, the crystal structure of which has been determined [57].

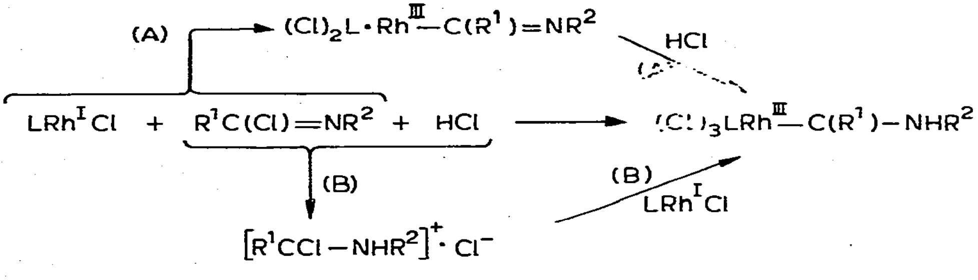


(43)

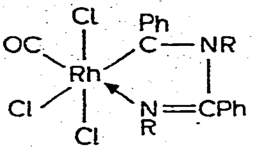
Metal carbene complexes

The new rhodium carbene complexes $[Cl_3(L)Rh—C(R^1)NHR^2]$ (R^1 = Ph, R^2 = Me, Et, or i-Pr; R^1 = Me, R^2 = C_6H_4OMe; L = (tertiary phosphine)$_2$, (tertiary phosphine)(CO), or CO) have been prepared from the reactions of imidoyl chlorides, $RC(Cl)=NR^1$, with rhodium(I) substrates $[Rh(CO)_2Cl]_2$, $[Ph_3PRh(CO)Cl]_2$ and $(Ph_2MeP)_2Rh(CO)Cl$, in the presence of hydrogen chloride [58]. The mechanism may involve either, or both, of the pathways A and B (Scheme 4).

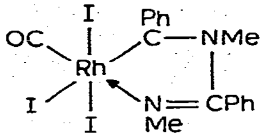
Scheme 4



Further work on this system [59] has shown that the reaction of $[Rh(CO)_2Cl]_2$ with $PhC(Cl){=}NR$ (R = Me, Et), in the absence of hydrogen chloride, yields the rhodium(III) carbene chelates **44**.



(44)

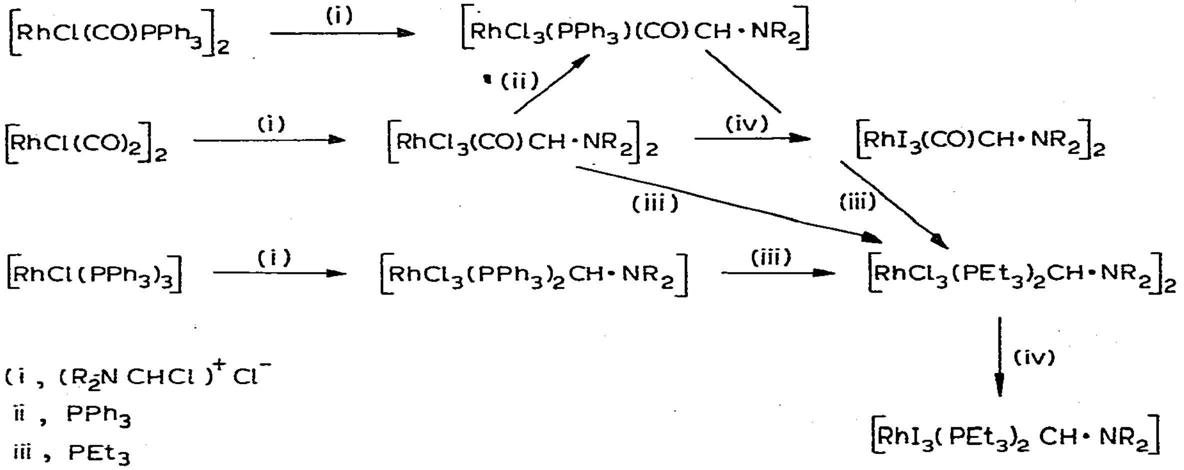


(45)

Reaction of **44** with LiBr or LiI gives replacement of all the chloride ligands by Br^- or I^- respectively. The chelate bridge may be cleaved by a tertiary phosphine. A single crystal X-ray study on **45** shows the Rh atom to have an approximately octahedral environment.

Chloromethyleneammonium chlorides $(R_2NCHCl)^+Cl^-$ (R = Me, Et, i-Pr, or n-Bu) have been found to be useful sources for secondary carbene complexes [60] (Scheme 5).

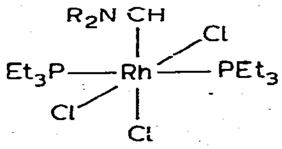
Scheme 5



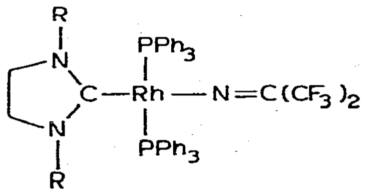
(i , $(R_2NCHCl)^+Cl^-$
ii , PPh_3
iii , PEt_3
iv , LiI)

A single crystal X-ray study of **46** was carried out.

Two rhodium(I) complexes, **47** and **48**, containing both alkylideneamido and

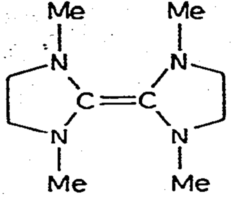


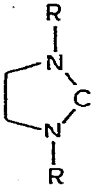
(46)



(**47** , R = p-MeC_6H_4
48 , R = Me)

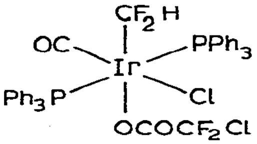
substituted carbene ligands have been prepared [61]. The former was synthesized from a previously known rhodium carbene complex, whereas the latter was prepared from the electron-rich olefin 49. Single crystal X-ray studies on 48 show the Rh atom to have an approximately square-planar environment.


(49)


(50)

Studies on the mechanism of substitution by tertiary phosphines in the square planar complexes $[RhL_n^RP_{2-n}(CO)X]$ ($n = 1, 2$; P = tertiary phosphine; L^R = tertiary carbene), to give cationic carbene complexes $[RhL_n^RP_{3-n}(CO)X]$ (n = 1, 2), with change of configuration at the metal, show that the mechanism is a two step process: substitution with retention, followed by isomerisation [62]. Both of these steps are sensitive to steric effects; in particular, an increase in the size of R on the carbenes 50 causes a reduced isomerisation rate, whereas an increase in the size of the incoming phosphine reduces the rate of substitution. A *cis*-influence and *cis*-effect for the carbene is also demonstrated.

The difluorocarbene precursor $CF_2ClCOONa$ reacts with $IrCl(CO)(PPh_3)_2$ [63,64] to yield initially $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$ (51), which can then decompose to $IrCl_2(CHF_2)(CO)(PPh_3)$ (52). Although these compounds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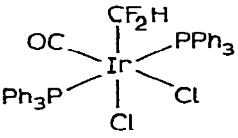
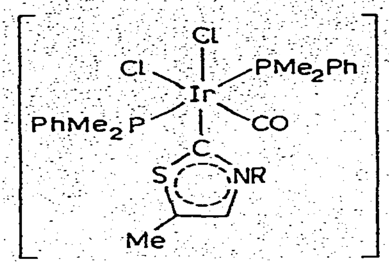
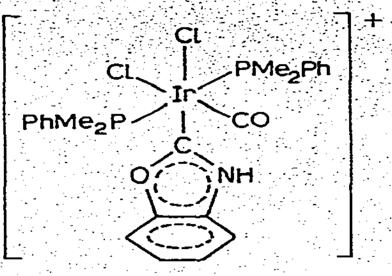

(52)

are not the hoped-for difluorocarbene systems, they do possess two interesting structural features which may have important chemical implications. The first of these is the presence of the difluoromethyl group in both complexes, for which a novel mechanism involving a metallo carbanion is proposed. The second is the decomposition of the coordinated acetate in going from the first complex to the second. The crystal structures of 51 and 52 have been determined. The decomposition reaction is discussed as a means of generating CF_2.

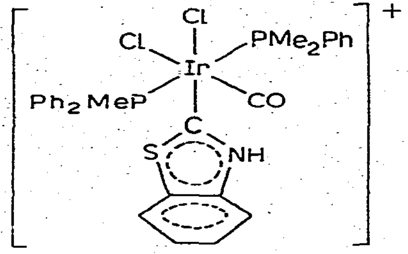
The cationic iridium(III) complexes 53, 54, 55 and 56 have been prepared [65] by reaction of the 2-chloro derivatives of 5-methyl-1,3-thiazole, -benzthiazole, and -benzoxazole with $IrCl(CO)(PMe_2Ph)_2$, followed by protonation of the resulting neutral iridium(III) complexes. Complex 54 is prepared by a similar reaction with the *N*-methyl salt of 2-chloro-5-methyl-1,3-thiazole. All these complexes are inert to ligand substitution.



(**53**, R = H
56, R = Me)

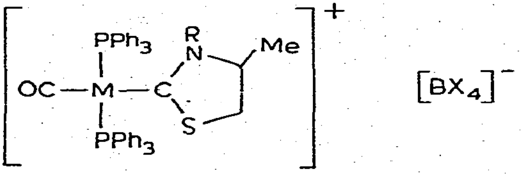


(**54**)

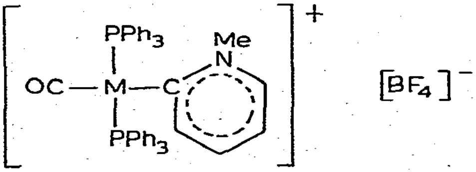


(**55**)

Further examples of compounds containing carbene ligands, in which the carbene carbon atom is part of a ring system, are the cationic iridium(I) and rhodium(I) complexes 57—61, prepared from the anions $[M(CO)_{4-n}(PPh_3)_n]^-$



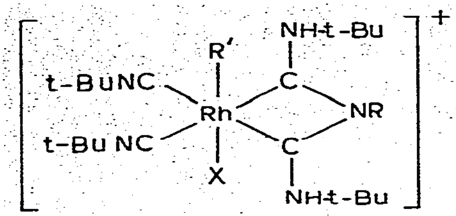
(**57**, M = Ir, R = Me, X = F
58, M = Rh, R = Me, X = F
59, M = Ir, R = Et, X = Ph)



(**60**, M = Ir
61, M = Rh)

(M = Ir, n = 1; M = Rh, n = 2) [66]. The coordinatively unsaturated complex 57 undergoes oxidative addition reactions with hydrogen, hydrogen chloride, chlorine and iodine, and also reacts with lithium chloride or bromide in ethanol, but not in C_6F_6. Some further chemistry of the reactions with methyl iodide, $NaBH_4$, and $Et_4N^+I^-$ was investigated.

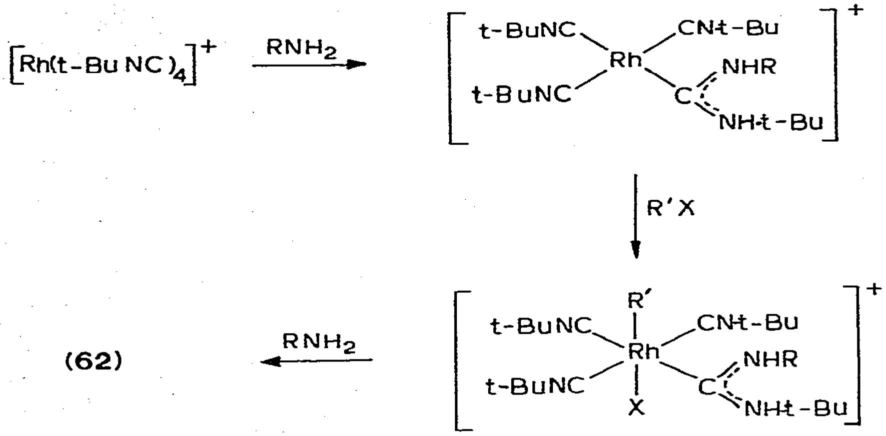
The reaction of the octahedral rhodium(III) complexes $[RhR'(X)(t\text{-}BuNC)_4]^+$ (R′ = alkyl, X = halogen or t-BuNC) or $[RhR'(X)\{C(NHR)(NH\text{-}t\text{-}Bu)\}(t\text{-}BuNC)_3]^+$ with primary amines (RNH_2) gives chelated dicarbene complexes of type 62 [67]. This observation leads to the establishment of a stepwise reaction path



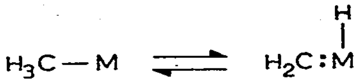
(62)

from rhodium(I) isocyanide complexes to rhodium(III) chelated dicarbene complexes (Scheme 6).

Scheme 6



Evidence for a reversible α-hydrogen abstraction from the methyl groups of $CoCH_3(PPh_3)_3$ and $RhCH_3(PPh_3)_3$ has been presented, based on mass spectrometric evidence [68]. It is postulated that such a process occurs via intermediate metal carbene hydride (63) formation.

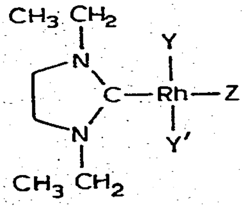


$$H_3C—M \rightleftharpoons H_2C\!:\!\overset{H}{M}$$

(63)

^{13}C NMR and single crystal X-ray studies on the novel rhodiumdiarylcarbene complexes $[Rh(CPh_2)Cl(C_5H_5N)]_2CO$, $[Rh(CPh_2)(\pi\text{-}C_5H_5)]_2CO$ and $[Rh(CPh_2)(\pi\text{-}C_5H_5)]_2$ show that the CPh_2 groups occupy bridging positions [69].

Proton NMR studies on rhodium carbene complexes of type 64 have pro-

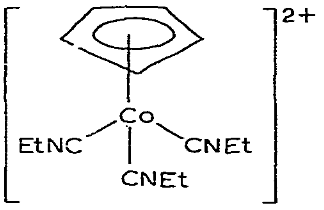


(64)

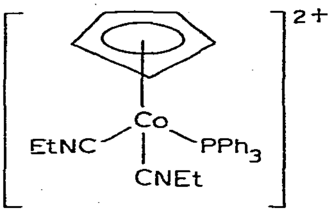
vided a useful probe into the nature of the M—$C_{carbene}$ bond [70]. Restricted rotation on the NMR time scale about the Rh—$C_{carbene}$ bond has been observed for these complexes; in addition, for *trans*-$[Rh(L^{ET})_2(CO)Cl]$ (L^{ET} = $CN(Et)CH_2CH_2NEt$), rotational activation parameters have been obtained, including a relatively low activation energy ($\leqslant$ 10 kcal mol^{-1}) and a negative activation entropy.

Metal isocyanide complexes

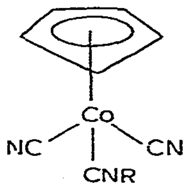
The effect of alkylating agent and solvent on the nature of the products obtained from alkylation of the cyano groups in some cyclopentadienyl cobalt complexes has been studied [71]. Thus, with triethyloxonium tetrafluoroborate, complete alkylation of the species $[C_5H_5Co(CN)_3]^-$ and $C_5H_5Co(CN)_2PPh_3$ occurs, giving **65** and **66** respectively. Use of methyl iodide in acetonitrile, however, resulted only in monomethylation of the tricyanide and the phosphine-substituted complexes $C_5H_5Co(CN)_2L$ (L = PPh_3, PMe_2Ph), giving **67** and **68** respectively. The importance of the nature of the solvent was shown by the methylation of $[C_5H_5Co(CN)_3]^-$ with dimethyl sulphate; in methanol, only dimethylation was observed, whereas in ethanol, in addition to the major dimethylated derivative, mono- and tri-methylated species were found as well as unreacted cobalt tricyanide anion. A comparison of some of these results with those obtained for $[C_5H_5Fe(CO)(CN)_2]^-$ was also made.



(65)



(66)



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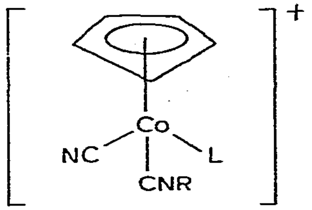


(68)

The complex $C_5H_5 \cdot Co(CO)I_2$ reacts with ligands RNC (R = $C_6H_4 \cdot OMe$-*p* or Me) in dichloromethane solution to give the isocyanide compounds $C_5H_5 \cdot Co(CNR)I_2$ [72]. These stable, crystalline compounds were used in the preparation of a range of cationic isocyanide-containing derivatives, by replacement of one or both of the iodide ions with other 2-electron donors, e.g. with RNC (R =

C_6H_4OMe-*p* or Me), giving $[C_5H_5Co(CNR)_2I]X$ (X = I or PF_6). Addition of excess RNC to the complexes $[C_5H_5Co(CNR)_2I]PF_6$ in acetone, in the presence of one mole of $AgPF_6$, results in the formation of the compounds $[C_5H_5Co(CNR)_3][PF_6]_2$. Other new complexes can be prepared from these mono-, di-. and tri-isocyanide derivatives by replacement of one or more of the isocyanide groups with other carbon-, phosphorus- or nitrogen-donor ligands.

The complexes $[Co(CNC_6H_4Cl\text{-}4)_3(P(OCH_3)_3)_2]BF_4$ and $[Co(CNC_6H_4Cl\text{-}4)_3(P(C_6H_5)_3)_2]ClO_4$ have been prepared by replacement of two molecules of *p*-ClC_6H_4NC from the $[Co(CNC_6H_4Cl\text{-}4)_5]^+$ ions [73].

Isocyanides have been found to displace up to five carbonyl ligands from $[Co_4(CO)_{12}]$, $[(\pi\text{-}C_5H_5)NiCo_3(CO)_9]$, $[YCCo_3(CO)_9]$ (Y = Cl, Me, or Ph), $[SCo_3(CO)_9]$ and $[SCo_2Fe(CO)_9]$ [74]. Displacement of carbon monoxide in various cobalt carbonyl clusters by Group VA ligands has been found to take place with (a) retention of the cluster, or (b) its fragmentation. These reactions with isocyanide ligands usually occur by Route a and even, in some cases, with polymerisation of dicobalt to tetracobalt clusters. Thus, the products from the above clusters are of the type $[Co_4(CO)_{12-n}(CNR)_n]$ (R = alkyl; $n = 1$—5), $[(\pi\text{-}C_5H_5)NiCo_3(CO)_8(CNR)]$, $[YCCo_3(CO)_{9-n}(CNR)_n]$ and $[SFeCo_2(CO)_{9-n}(CNR)_n]$ (n = 2 or 3). No stable products are isolated from $[SCo_3(CO)_9]$, although reaction with isocyanides does occur. With $Co_2(CO)_8$ the products are derivatives of $[Co_4(CO)_{12}]$ or $[(RNC)_5Co][Co(CO)_4]$; $[\{LCo(CO)_3\}_2Hg]$ (L = tertiary phosphine or CO) and $[(R_3P)_2Co(CO)_3][Co(CO)_4]$ also undergo CO displacement. The structures of the products are discussed on the basis of IR spectral evidence.

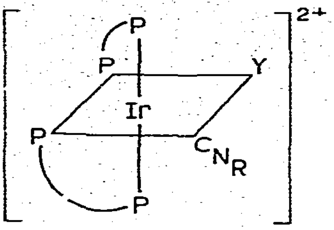
IR spectroscopic studies of the *trans*-α-benzyldioximes $[CoX(HDf)_2(C{\equiv}N{-}C_6H_{11})]$ (**69**) and $[Co(HDf)_2(C{\equiv}N{-}C_6H_{11})_2]X$ (**70**) (X = Cl, Br, I; HDf = α-benzyldioxime) show that the isonitrile coordinates through the C atom [75]. Thermal stability increases in the series Cl < Br < I. Heating a salt of **70** results in gradual cleavage of the isonitrile. Similar studies on the complexes *trans*-$[CoX(DH)_2L]$ (X = Cl, Br, I; DH = dimethylglyoxime; L = MeCN, $C{\equiv}N{-}C_6H_{11}$) show that thermal cleavage of L is easier in the order Cl < Br < I [76]. These studies also indicate that a Co—C bond is stronger than a Co—N bond in this type of compound.

The five-coordinate d^8 iridium complexes $[Ir(CNR)L_2]^+$ (R = Me or *p*-MeO-C_6H_4; L = 1,2-bis(diphenylphosphino)ethane or *cis*-1,2-bis(diphenylphosphino)-ethylene) have been synthesised [77]. These complexes undergo oxidative reactions with addenda XY, but not by either of the usual mechanisms, i.e.

$$[ML_5]^{z+} \xrightarrow{-L} [ML_4]^{z+} \xrightarrow{XY} [MX(Y)L_4]^{z+} \tag{i}$$

$$[ML_5]^{z+} + XY \rightarrow [M(Y)L_5]^{(z+1)+} + X^- \rightarrow [MX(Y)L_4]^{z+} + L \tag{ii}$$

The ligands in these new species, however, are held so tightly that no ligand displacement is observed, which indicates the strength of the Ir—C interaction. Instead, the dicationic adducts $[IrY(CNR)L_2]^{2+}$ (Y = H, Cl, I, or HgCl) are formed, from oxidative addition of proton acids, halogens and $HgCl_2$. These compounds probably have the configuration **71**, and are formed under kinetic control. Addition of dihydrogen and dioxygen does, however, result in slow displacement of the isocyanide ligand to give *cis*-$[IrH_2L_2]^+$ and -$[Ir(O_2)L_2]^+$ respectively. SO_2 gave an unstable product, which dissociated at room temperature.



(71)

Treatment of poly(tricarbonylchloroiridium) [{Ir(CO)$_3$Cl}$_n$] with alkyl and aryl isocyanides gives the square-planar [Ir(CNR)$_4$]$^+$ cations (R = C_6H_{11}, p-MeC_6H_4, p-$MeOC_6H_4$) [78]. Although [{Ir(CO)$_3$Cl}$_n$] undergoes substitution with many neutral ligands, only isocyanide has so far been found to give complete substitution of CO, resulting in four-coordinate cations. The chemistry of these species has been investigated; no five-coordinate compounds were obtained on treatment with CO, $PPhMe_2$ or RNC, and no neutral four-coordinate compounds were isolated in the reaction with Cl^-. However, six-coordinate iridium(III) species have been obtained from oxidative addition reactions with I_2, Br_2 and Cl_2 (although with Cl_2 and R = C_6H_{11}, only intractable materials were obtained; IR spectral evidence did suggest that oxidative addition had occurred). In addition, the complexes [Ir(CNC_6H_{11})$_4$(Me)I]BPh_4, and [Ir(CNC_6H_{11})$_4$(O_2)]$^+$ were formed as oxidative addition products with MeI and O_2 respectively.

Metal carbonyls and related compounds

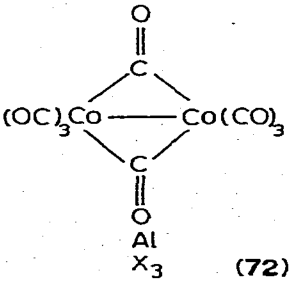
(a). Zero oxidation state compounds

Cobalt carbonyl and its derivatives have been reviewed [79].

The decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ in heptane solution, in the presence of carbon monoxide, is second-order with respect to $Co_2(CO)_8$ and is of an order of −2 with respect to carbon monoxide. This negative second-order dependance suggests that two molecules of carbon monoxide are involved in fast pre-equilibria which are probably the steps [80]:

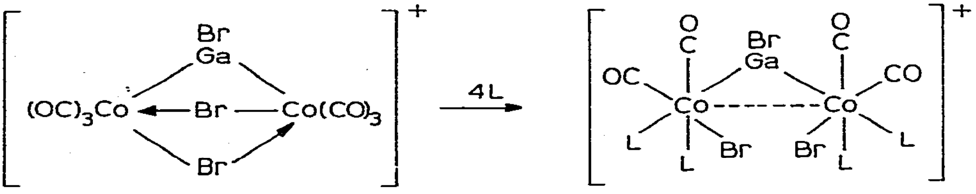
$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO$$
$$Co_2(CO)_7 \rightleftharpoons Co_2(CO)_6 + CO$$

A study has been made on the reactions of $Co_2(CO)_8$ with the boron trihalides, BX_3 (X = Cl, Br, I), $AlCl_3$, $AlBr_3$, $GaBr_3$ and $InBr_3$. The boron trihalides form unstable adducts $Co_2(CO)_8 \cdot BX_3$, but the stable adducts 72 are formed with the



(72)

aluminium halides. $GaBr_3$ and $InBr_3$ behave differently, forming the complexes $MCo_2Br_4(CO)_6$ (M = Ga or In), from which the substituted derivatives $GaCo_2Br_4(CO)_4(THF)_2$ and $GaCo_2Br_4(CO)_4L_4$ (L = H_2O, PPh_3, PCy_3) can be obtained [81]. These complexes, e.g. 73 and 74, may be ionic in character.

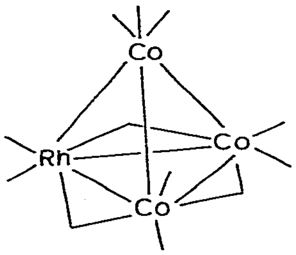


(73) (74)

Trimethylphosphite reacts with $[RhCp(C_2H_4)_2]$ at 60°C to produce the pale yellow crystalline complex $[Rh_2\{P(OMe)_3\}_8]$. This complex, which has a bicapped trigonal antiprismatic structure at room temperature, undergoes a specific equatorial intermolecular ligand exchange at higher temperatures, rather than equatorial—axial ligand exchange [82].

Previous studies have suggested that $Rh_2(CO)_8$ is only stable under high CO pressures and at low temperatures. These studies have now been confirmed by cocondensation reactions of rhodium atoms with CO under high metal concentrations, which yield $Rh_2(CO)_8$. The elusive $Ir_2(CO)_8$ has now also been obtained by this technique. The mononuclear complexes $Rh(CO)_4$ and $Ir(CO)_4$ are also products of these reactions. $Rh_2(CO)_8$ and $Ir_2(CO)_8$ exist in the bridge bonded form, $Rh_2(CO)_8$, disproportionating under dynamic vacuum conditions to the bridge bonded $Rh_4(CO)_{12}$ at —48°C. $Ir_4(CO)_{12}$ is similarly formed at —58°C [83].

^{13}C NMR studies at —85°C on the mixed metal carbonyl $RhCo_3(CO)_{12}$ (75) are consistent with the proposed structure for this complex. Temperature dependent studies further reveal that two types of concerted carbonyl site exchange occur. At low temperatures carbonyl site exchange occurs within the three RhCoCo triangular faces via the complexes 76 and 77. However, at higher temperatures



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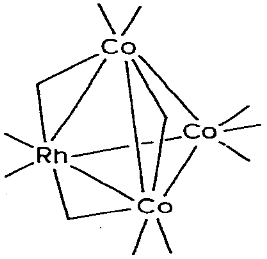

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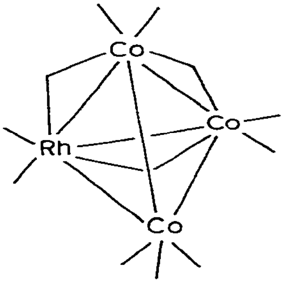
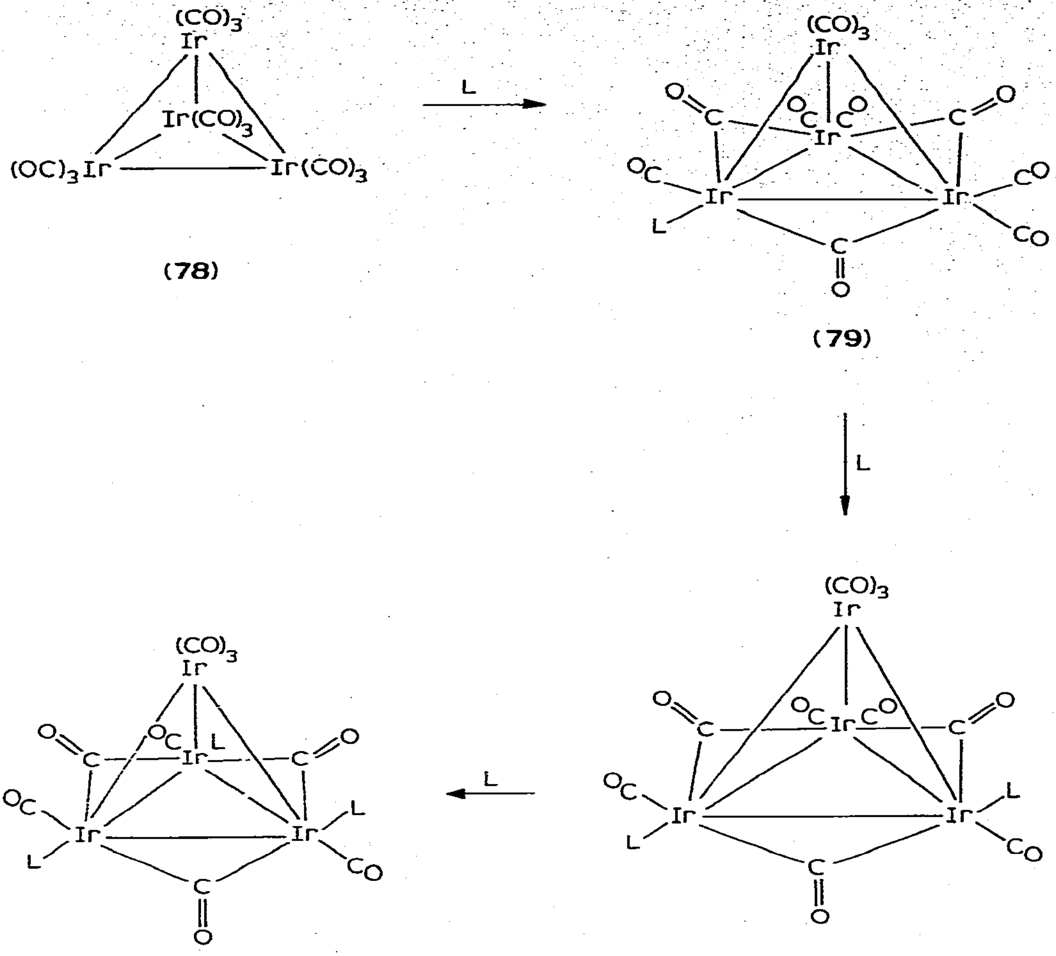


(77)

(> —30°C), interconversion of all carbonyl groups occurs, leading to bridge formation in any one of the four triangular metal faces. This is somewhat different to the exchange mechanism found for $Rh_4(CO)_{12}$ which occurs via a single process through a symmetrical T_d intermediate [84].

The rates of carbonyl substitution by triphenylphosphine in the reactions $78 \rightarrow 79$, $79 \rightarrow 80$ and $80 \rightarrow 81$ are 5.6×10^{-3} mol^{-1} s^{-1}, 8.8×10^{-5} mol^{-1} s^{-1} and 1.4×10^{-3} mol^{-1} s^{-1} respectively. There is thus an increase in the rate of substitution from unsubstituted 78 to disubstituted 80 by a factor of over 42 000 at 75° C. Usually there is a decrease in the rates of successive carbonyl replacements by phosphines in mononuclear carbonyls. The increase in rate of substitution in 79 can be associated with the change from a non-bridged to a bridged system. However, the further increase in the substitution rate of the bridged complex 80 may be a consequence of stabilisation of the dissociative transition state by semi-bridging carbonyl groups. Infrared spectra support the expected Ir—C bond order $78 \leqslant 79 \leqslant 80$ [85].



(78)

(79)

(80)

(81)

Complexes of the type $[Ir_4(CO)_8L_4]$ (L = $PMePh_2$, PMe_2Ph, $PEtPh_2$, $AsMePh_2$, $P(OPh)_3$; 2 L = $Ph_2PCH_2CH_2PPh_2$) may be prepared in good yield by the reaction of the ligand with a suspension of $Ir_4(CO)_{12}$. The complexes do not dissociate in benzene solution and NMR studies show that intramolecular carbonyl exchange processes occur in solution. Diprotonated species which are also stereochemically non-rigid are formed in acid solution [86].

Oxidation of $K_2[Rh_6(CO)_{15}C]$ with iron(III) ammonium sulphate in water, under carbon monoxide, gives an uncharacterised brown precipitate. Treatment of a toluene or CH_2Cl_2 solution of this precipitate with carbon monoxide gives the new carbido carbonyl cluster $[Rh_8(CO)_{19}C]$, which has been characterised by X-ray methods. However, if the oxidation is carried out in a nitrogen atmosphere $[H_3O][Rh_{15}(CO)_{28}C_2]$ is obtained. In methyl cyanide solution a new uncharacterised anionic species is formed, together with $[Rh(CO)_2(MeCN)_2]^+$. However, $[Rh_8(CO)_{19}C]$ in methyl cyanide solution disproportionates to $[Rh_6(CO)_{15}C]^{2-}$ and $[Rh(CO)_2(MeCN)_2]^+$. The cobalt carbido carbonyl cluster $[Co_6(CO)_{15}C]^{2-}$ has also been obtained [87].

Molecular orbital calculations for the octahedral cluster $[Co_6(CO)_{14}]^{4-}$ have been carried out [88].

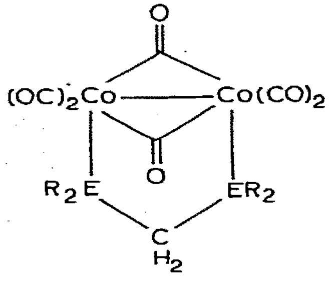
UV irradiation of the dimer $[Co(CO)_3\{P(OEt)_3\}]_2$ in chloroform solution at —30° C, in the presence of the radical trap nitrosodurene, ArNO, (Ar = 2,3,5,6-Me_4C_6H) causes homolysis of the Co—Co bond. The resulting spin adduct $[ArN\{Co(CO)_3P(OEt)_3\}O]^{\cdot}$ can be identified by its ESR parameters [89].

Sublimation of $Co_2(CO)_8$ in the presence of oxygen gives a species which has been identified as $[O_2Co(CO)_4]^{\cdot}$. This species is also formed in the rapid reaction of $[Co(CO)_4]^{\cdot}$ with oxygen [90]. Reduction of $[Ir_4(CO)_{12}]$ generates the radical anion $[Ir_4(CO)_{12}]^{\cdot-}$ [91].

The use of the Karl-Fischer reagent as an oxidising agent can provide a convenient method for the determination of the concentration of, e.g. $[Co_2(CO)_8]$, $[Co(CO)_4]^-$ and $[Rh_4(CO)_{12}]$ [92].

Studies on the infrared spectra of solutions of the complexes $[Co(CO)_3L]_2$ (L = various phosphine, arsines, stibines), reveal that one non-bridged and two CO-bridged isomers are present. The non-bridged isomers are favoured by higher temperatures, polar solvents, bulky ligands and a higher electron density at the cobalt atom [93].

Treatment of $Co_2(CO)_8$ with the ligands $R_2ECH_2ER_2$ (R = Me, Et, *p*-MeC_6H_4, E = Sb, R = Ph, E = Sb, As, P) gives complexes formulated as in 82. The bridging carbonyls in these complexes can be displaced with a diarylacetylene [94].



(82)

A direct synthesis of $[Co(CO)_3(P\text{-}n\text{-}Bu_3)_2]^+[Co(CO)_4]^-$ can be achieved by heating $Co(OAc)_2 \cdot 4\,H_2O$ or Co_3O_4 with P-n-Bu_3 and Me_3CCH_2OH under a pressure of CO [95].

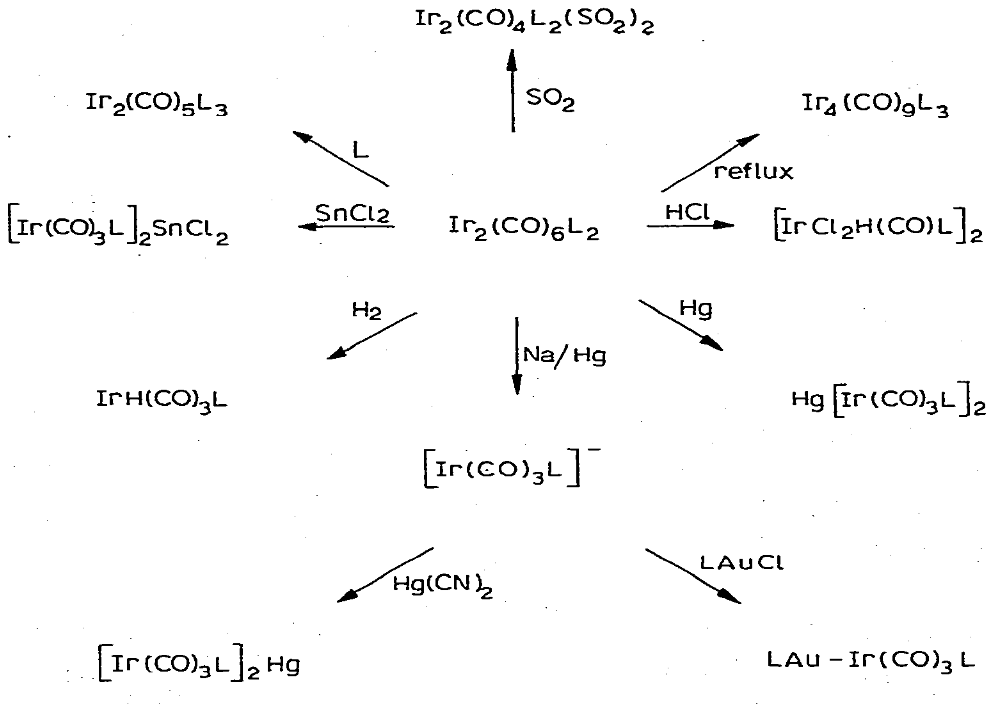
The reactions of $Co_2(CO)_8$ with the phosphites $P(OMe)_3$, $PPh(OMe)_2$ and

PPh_2OMe have been investigated. Treatment of $Co_2(CO)_8$ with $P(OMe)_3$ at −20°C in pentane, gives $[Co(CO)_2\{P(OMe)_3\}_3]^+[Co(CO)_4]^-$. In benzene solution this precipitate gives rise to acyl and alkyl cobalt complexes, the final products being $[CoMe(CO)_3\{P(OMe)_3\}]$ and $[Co_2(CO)_6\{P(OMe)_3\}_2]$. In the presence of PPh_3, the acyl compound $[Co(COCH_3)(CO)_2\{P(OMe)_3\}_2]$ can be isolated. A mechanism for this Michaelis-Arbuzov rearrangement is proposed [96]. Some polymer-bound cobalt carbonyl derivatives, e.g. $[CoH(CO)_3(PPh_2\sim\sim)]$, have been isolated from the reactions of polymeric analogs of benzyldiphenylphosphine and triphenylphosphine with $Co_2(CO)_8$ or $[CoH(CO)_4]$ [97,98].

The action of carbon dioxide on a benzene solution of $[Rh(CO)_2(PPh_3)]_2 \cdot C_6H_6$ in the presence of triphenylphosphine, at room temperature and atmospheric pressure, gives the air-stable carbon dioxide complex $[Rh(CO)_2(CO_2)_2(PPh_3)_3] \cdot C_6H_6$ [99]. Passage of air through a benzene solution of the carbon dioxide complex leads to $[Rh_2(CO)_2(CO_2)(PPh_3)_3] \cdot C_6H_6$ which has previously been obtained by oxygen oxidation of $[Rh(CO)_2(PPh_3)_2]_2$ [100].

The zerovalent iridium compound $[Ir_2(CO)_6(PPh_3)_2]$ can be prepared by the action of sodium ethoxide on the readily available $[IrI(CO)_2(PPh_3)_2]$ in an atmosphere of carbon monoxide. Some reactions of $[Ir_2(CO)_6(PPh_3)_2]$ are summarised in Scheme 7 [101]. The reaction of the iridium dimer with hydrogen halides, in basic solvents, follows a different course resulting in disproportionation:

Scheme 7



(L = PPh3)

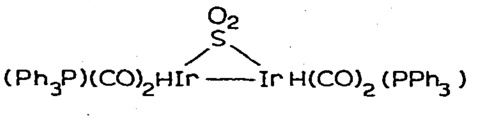
$$Ir_2(CO)_6(PPh_3)_2 + 6\,HX \rightleftharpoons IrX_2H(CO)(PPh_3) + H[IrX_4(CO)_2] + 2\,H_2 + 3\,CO$$

Disproportionation also occurs in ethanolic perchloric acid, the reaction being different in a CO atmosphere to that observed under nitrogen:

$$3\,Ir_2(CO)_6(PPh_3)_2 + 2\,HClO_4 \xrightarrow{CO} 2[Ir(CO)_3(PPh_3)_2]ClO_4 + Ir_4(CO)_{10}(PPh_3)_2 + H_2 + 2\,CO$$

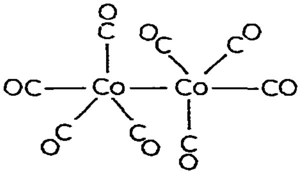
$$3\,Ir_2(CO)_6(PPh_3)_2 + 2\,HClO_4 \xrightarrow{N_2} 2[IrH_2(CO)_2(PPh_3)_2]ClO_4 + Ir_4(CO)_{10}(PPh_3)_2 + 4\,CO$$

With sodium borohydride $[IrH(CO)_2(PPh_3)_2]$ is formed together with a mixture of anionic cluster compounds $[Ir_4(CO)_8L_3H]^-$, $[Ir_4(CO)_9L_2H]^-$ and $[Ir_4(CO)_{10}LH]^-$ [101]. Passage of hydrogen gas through a solution of $[Ir_2(CO)_4(PPh_3)_2(SO_2)_2]$ (Scheme 7) gives $[IrH(CO)_2(PPh_3)_2]_2SO_2$ (83), the crystal structure of which has been determined [102].



(83)

It has been known for some time that two isomers of $Co_2(CO)_8$ exist in solution. One isomer is the bridged carbonyl form, identical to the solid state structure. However, there has been some disagreement as to the structure of the other isomer, structures 84 or 85 being suggested. Studies on the infrared spectra of $Co_2(CO)_8$ enriched with ^{13}CO provide no evidence for structure 85, which must now be abandoned. However, there is evidence for the presence of a third isomer of, as yet, unknown structure [103]. A vibrational analysis of $[Co(CO)_4]^-$ has been undertaken [104]; the ion sites present when $Na[Co(CO)_4]$ is dissolved in Me_2SO, Me_2NCHO, $MeNO_2$, MeCN, pyridine and hexamethylphosphoramide have been investigated by computer aided analyses of the infrared band around 1900 cm^{-1} [105].



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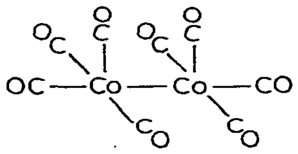


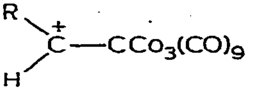
(85)

A review on the ^{13}C NMR spectra of metal carbonyl compounds contains data on cobalt, rhodium and iridium compounds [106], and the ^{13}C NMR spectrum of $[Rh_{12}(CO)_{30}]^{2-}$ has been shown to be consistent with X-ray structural data [107].

Cobalt-59 nuclear quadrupole resonance studies on five-coordinate complexes of the type $[Co(CO)_3L]_2$ have been published [108].

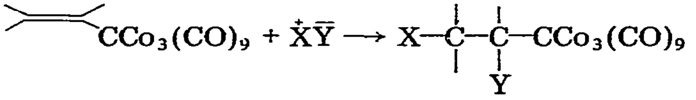
The reaction of diarylmercurials and arylmercury(II) halides with $HCCo_3(CO)_9$ provides a good route to the aryl derivatives $ArCCo_3(CO)_9$ [109]. The corresponding reactions with dialkylmercurials or alkylmercury(II) halides occurs much more slowly and in much lower yield. Arylation of the apical carbon also occurs in the reactions of $XCCo_3(CO)_9$ (X = Cl, Br, I) with $HgPh_2$, and in reactions of $HCCo_3(CO)_9$ with $SnPh_4$ and $PbPh_4$. Analogous reactions with Grignard or organolithium reagents are not good methods for the introduction of alkyl groups. Reduced products $RCH_2CCo_3(CO)_9$ are obtained from the reaction of α-haloalkyl mercurials $(RCHX)_2Hg$ with $HCCo_3(CO)_9$, rather than the expected $RCHXCCo_3(CO)_9$ [109].

Carbonium ions of the type 86, generated from the appropriate alcohols

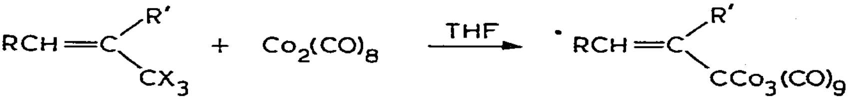


(86)

$RCH(OH)CCo_3(CO)_9$ in strong acid media, are exceptionally stable. This stability appears to be due to extensive delocalisation of the positive charge into the cluster, which is supported by ^1H and ^{13}C NMR studies [110]. Further evidence for the stability of these carbonium ions is provided by protonation studies of the vinyl derivatives $RRC{=}C(R)CCo_3(CO)_9$. Thus, treatment of $CH_2{=}CMeCCo_3(CO)_9$ with $HPF_6/(EtCO)_2O$ precipitated the salt CH_3CMe-$CCo_3(CO)_9PF_6$, which on treatment with methanol gave $MeOCMe_2CCo_3(CO)_9$. In general these reactions proceed in the direction:



The vinyl derivatives 87 were also prepared. Protonation of $Me_3SiCH{=}CH$-



(87)

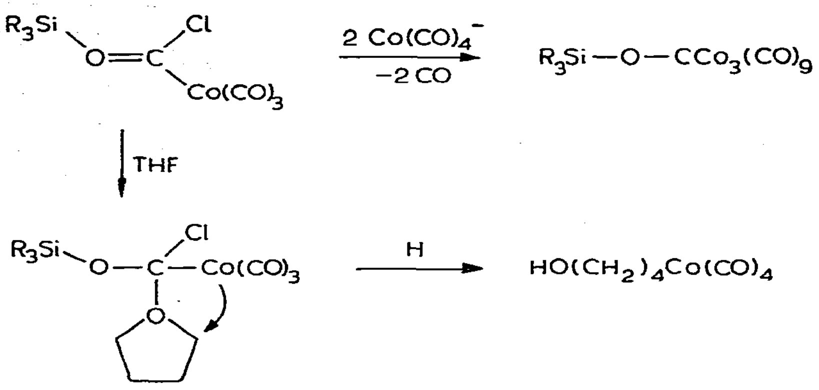
(R′ = H ; R = H , $SiMe_3$, MeCO
R′ = Me ; R = H)

$CCo_3(CO)_9$ results in desilylation to produce $Me\overset{+}{C}HCCo_3(CO)_9$ [111].

The complexes $RCCo_3(CO)_9$ could be regarded as carbyne complexes. Indeed, oxidative and thermal degradation of $RCCo_3(CO)_9$ (R = Ph or $PhCH_2$) gives the acetylenes RC≡CR [112].

The course of the reactions of chlorosilanes with $Co_2(CO)_8$, or $NaCo(CO)_4$, are dependent upon the solvent basicity and the nature of the chlorosilane and cobalt carbonyl species. Thus, although $Co_2(CO)_8$ does not react with either $MeSiCl_3$ or $SiCl_4$ in diethyl ether, $Co(CO)_4^-$ gives the siloxy cluster $R_3SiOCCo_3(CO)_9$. The formation of the cluster is rationalised in terms of initial electrophilic attack by the chlorosilane on the O atom of a carbonyl group. The resulting intermediate can then undergo nucleophilic attack by $Co(CO)_4^-$ to give siloxy clusters, or by tetrahydrofuran (Scheme 8) to give alkyl or alcohol clusters [113]. In reactions involving solvent cleavage acyl intermediates, $RCOCo(CO)_4$, are formed. These acyls can lead to cluster compounds, since on

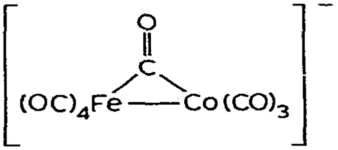
Scheme 8



thermal decomposition the complexes $RCCo_3(CO)_9$ are formed. A novel ether cluster compound, $PrOCCo_3(CO)_9$, can also be obtained from n-PrCOCl and $Co_2(CO)_8$ [113].

(b). Heteronuclear metal—metal bonded carbonyl compounds

An X-ray structural study of $[(Ph_3P)_2N]^+[FeCo(CO)_8]^-$ (88) shows that the anion has a structure intermediate between that of $Co_2(CO)_8$ and $[Fe_2(CO)_8]^{2-}$, containing only one bridging carbonyl [114]. Studies on substitution reactions of the anion $[FeCo_3(CO)_{12}]^-$ suggest that the presence of the negative charge strengthens both the metal—carbon and metal—metal bonds, as compared to those in neutral clusters. Treatment of $[Et_4N][FeCo_3(CO)_{12}]$ with an excess of $PMePh_2$, PPh_3 or $P(O\text{-}i\text{-}Pr)_3$ gives the monosubstituted products $[Et_4N]$-$[FeCo_3(CO)_{11}L]$. Only with $Ph_2PCH_2CH_2PPh_2$ is it possible to replace more than one CO group. Protonation reactions lead to the neutral polynuclear hydrides $HFeCo_3(CO)_{11}L$ and are accompanied by large kinetic isotope effects. Reaction of the anion with PhC≡CPh gives the acetylene complex $[Et_4N]$-$[FeCo_3(CO)_{10}Ph_2C_2]$ which appears to have a different structure to that found for $[Co_4(CO)_{10}(Ph_2C_2)]$. Protonation of $[FeCo_3(CO)_{10}(Ph_2C_2)]^-$ or reaction of tolan with $HFeCo_3(CO)_{12}$ leads to the trinuclear complex $[FeCo_2(CO)_8$-$(Ph_2C_2)]$ [115]. The reactions of phosphines with the bridged arsine complex 89 result in Fe—Co bond cleavage to give the complexes $(OC)_4Fe(AsMe_2)$-



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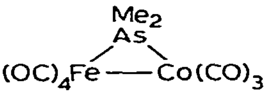
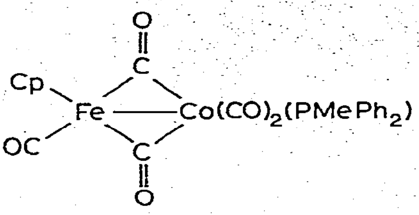


(89)

$Co(CO)_3L$ (L = PPh_3, PMe_2Ph, $P(OMe)_3$, $P(NMe_2)_3$) [116]. Cobalt—gold bond cleavage also results when $Ph_3PAuCo(CO)_4$ is treated with the chelating ligands $Ph_2E(CH_2)_nEPh_2$ (E = P, As, Sb; n = 1 or 2). The salts $[Au(PPh_3)(Ph_2E(CH_2)_n$-$EPh_2)][Co(CO)_4]$ are produced [117].

X-ray structural studies reveal that the complexes **90**, **91** and **92** contain non-planar bridging carbonyl systems [118—120] but **93** has an almost planar



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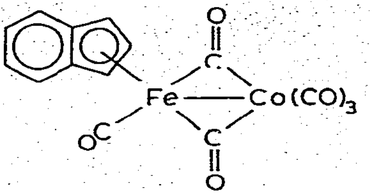

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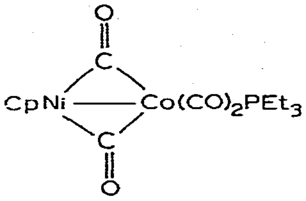

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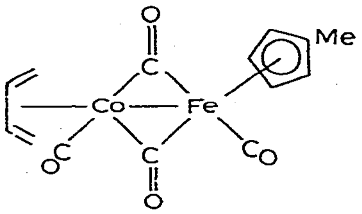
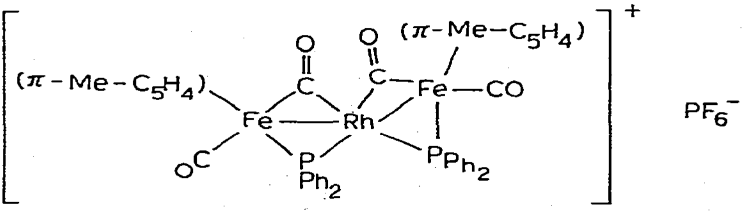


(93)

bridge system [121]. However, in the non-bridged compounds $(CO)_4$-Co—M$(CO)_5$ (M = Mn, Tc or Re) the infrared spectra can be interpreted in terms of a model which allows free rotation about the Co—M bond [122].

The reaction of [Fe(π-MeC$_5$H$_4$)(CO)$_2$(PPh$_2$)] with RhCl$_3$ · xH$_2$O, in the presence of hexafluorophosphate, gives the complex **94**. X-ray crystallographic

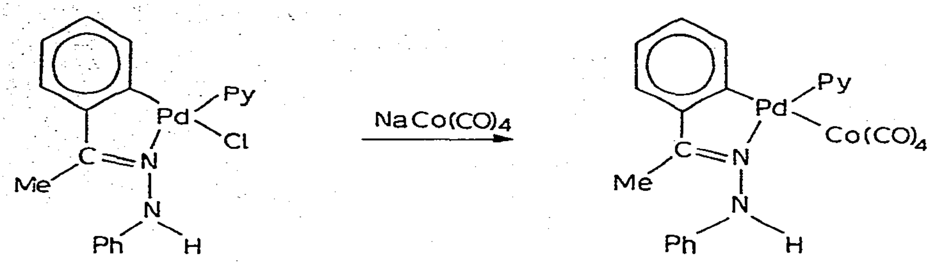


(94)

studies show that the structure contains a trinuclear non-closed rhodium—iron arrangement. It is suggested that the highly basic phosphido bridges destabilise the closed structure observed in related bridged carbonyl systems [123].

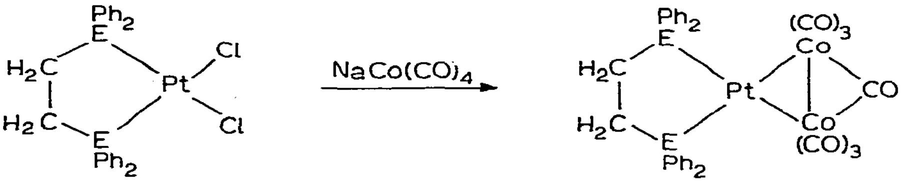
The molecular structure of Co$_2$Ir$_2$(CO)$_{12}$ is very similar to that of Co$_4$(CO)$_{12}$ and Rh$_4$(CO)$_{12}$. Three of the carbonyl ligands are involved in edge bridging about a tetrahedron of metal atoms. It is noteworthy that although the cobalt and iridium are partially disordered at the vertices, the iridium tends to reside in the apical position to which only terminal ligands are coordinated [124].

Treatment of **95** with NaCo(CO)$_4$ gives the air-stable complex **96**. The stabili-



(95) (96)

ty of this complex is ascribed to the weak nucleophile $[Co(CO)_4]^-$ being *trans* to a soft σ-bonded C atom [125]. However, treatment of the platinum(II) complexes **97** with $NaCo(CO)_4$ gives the complex **98**, fromulated as a $PtCo_2$ closed cluster [126].



(97) (98)

(E = P or As)

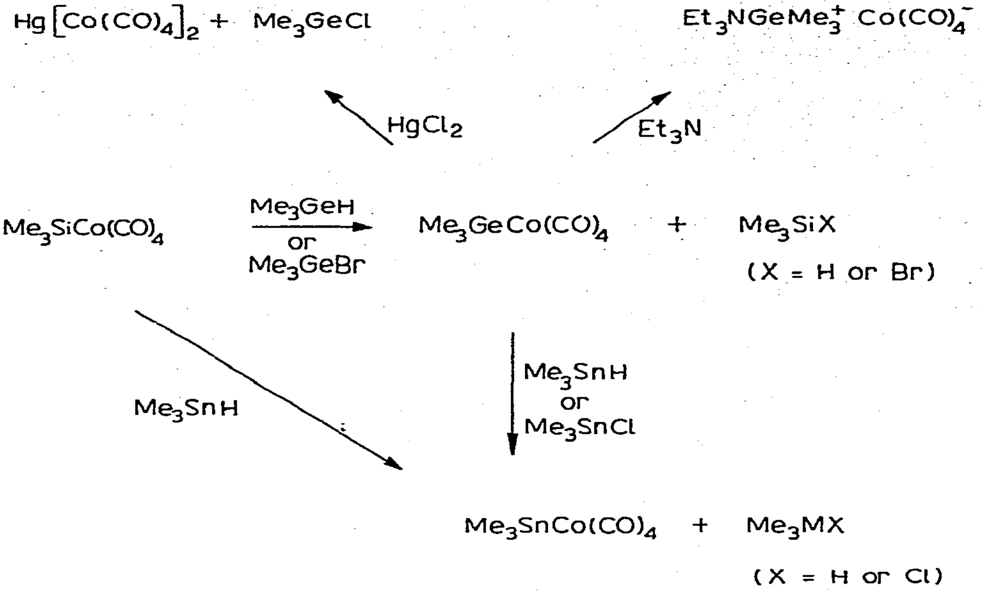
The silanes $MeSiCl_2H$ and Me_2SiClH react with $Co_2(CO)_8$, in the absence of solvent, to give $MeSiCl_2Co(CO)_4$ and $Me_2SiClCo(CO)_4$ respectively. Although $Me_3SiCo(CO)_4$ reacts with HCl and HBr at 90°C/4 atm, the compounds $Me_xCl_{3-x}SiCo(CO)_4$ ($x = 0, 1, 2$) only undergo Si—Co bond cleavage when the pressure of hydrogen halide was increased to 4000 atm. Mercury(II) chloride and bromide cleave the Si—Co bond in all the compounds at 90°C. Attempts to insert CO into the Co—Si linkage were not successful [127]. Treatment of $Co_2(CO)_8$ with $HMe_2SiCH_2CH_2SiMe_2H$ gives $(OC)_4CoSiMe_2CH_2CH_2Me_2SiCo(CO)_4$ [128].

Attempts to abstract halide from complexes of the type $ClPh_2GeCo(CO)_4$, with $AgBF_4$, to generate Ph_2Ge complexes instead results in fluoride exchange [129].

The hydrides R_3MH react exothermically with $Co_2(CO)_8$ at 20°C to give the complexes $R_3MCo(CO)_4$ (R = Me, M = Si, Ge, Sn; R = Et, M = Ge). Reactions of the complexes are summarised in Scheme 9 [130].

In diethyl ether solution, Sn_2Me_6 rapidly reacts with $Co_2(CO)_8$ to give $[Me_3SnCo(CO)_4]$ as the sole product. However, in stronger coordinating solvents, such as tetrahydrofuran, the reaction produces, in addition to $[Me_3SnCo(CO)_4]$, Me_4Sn and $[Me_2Sn\{Co(CO)_4\}_2]$. Reaction of Sn_2Me_6 with a catalytic amount of $Co_2(CO)_8$, in tetrahydrofuran, gave 90% of Me_4Sn, 10% of $Me_3SnCo(CO)_4$ and an insoluble

Scheme 9



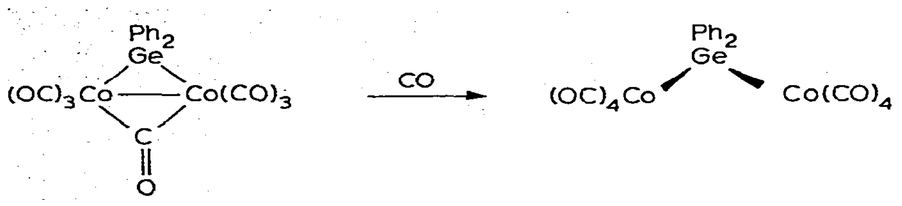
solid. These results are interpreted in terms of a 1,2 methyl shift in Sn_2Me_6, catalysed by $Co_2(CO)_8$ [131]:

$Me_3SnSnMe_3 \rightarrow Me_4Sn + [Me_2Sn]$

Treatment of R_3Sn(indenyl), (R = Me, Ph) [132] or R_3SnOAc (R = Me) [133] with $Co_2(CO)_8$ gives $R_3SnCo(CO)_4$; the trimethyltin derivative also results from an unusual reaction, when Me_3SnCH_2I is treated with $NaCo(CO)_4$ [134].

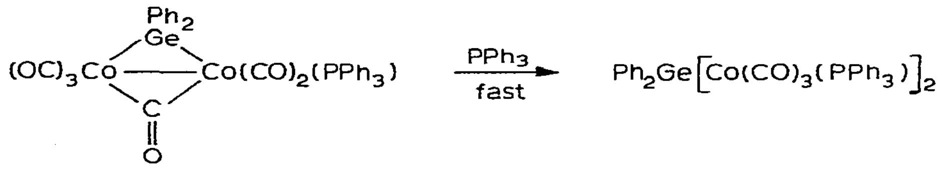
Nucleophilic substitution of the $Co(CO)_4$ group occurs when the compounds $Ph_3MCo(CO)_4$ (M = Sn, Pb) are treated with the carbonylate anions $[FeCp(CO)_2]^-$, $[Re(CO)_5]^-$, $[Mn(CO)_5]^-$ and $[MoCp(CO)_3]^-$. The ease of substitution of the Sn—X bond is $[FeCp(CO)_2]^- \geqslant [Re(CO)_5]^- > [Mn(CO)_5]^- \geqslant [MoCp(CO)_3]^-$ [135]. The carbonyl groups in the complexes $R_3MCo(CO)_4$ and $X_2M[Co(CO)_4]_2$ are also known to undergo substitution reactions with tertiary phosphines and related ligands. Using this approach a variety of substituted complexes, $Ph_3MCo(CO)_3L$ (M = Sn, L = PPh_3, $AsPh_3$, $SbPh_3$; M = Ge, L = PPh_3), $PhX_2MCo(CO)_3(PPh_3)$ (X = Br, M = Ge; X = Cl, M = Sn), $X_3SnCo(CO)_3(PPh_3)$, $Ph_2SnClCo(CO)_3PPh_3$, $X_2Ge[Co(CO)_4][Co(CO)_3PPh_3]$ (X = Cl, CNS), $X_2M[Co(CO)_3(PPh_3)]_2$ (X = Cl, M = Ge; X = Ph, Cl, CNS, M = Sn), $PhClSn[Co(CO)_3(PPh_3)]_2$, $Cl_2Sn[Co(CO)_4][Co(CO)_3(PPh_3)]$, $ClSn[Co(CO)_4]_2$-$[Co(CO)_3(PPh_3)]$ and $ClSn[Co(CO)_4][Co(CO)_3(PPh_3)]_2$ can be prepared [136]. Some of these unsubstituted complexes, e.g. $Ph_3SnCo(CO)_4$, $Ph_2Sn[Co(CO)_4]_2$, $Cl_2Sn[Co(CO)_4]_2$ and $ClSn[Co(CO)_4]_3$, cyclotrimerise PhC≡CPh to hexaphenylbenzene in varying yields. However, p-$(RC{\equiv}C)_2C_6H_4$ reacts with $Hg[Co(CO)_4]_2$ to give $[\{Co_2(CO)_6\}_2\{C_6H_4(C{\equiv}CR)_2\}]$ (R = H, Ph) [137].

The reversible ring-opening reaction of the complex **99** with carbon monoxide to form **100**, in decalin, proceeds by a process which is first-order in concentration

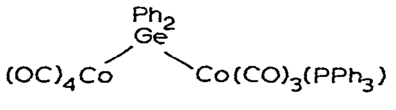


(99) (100)

of the complex and carbon monoxide. However, reaction with triphenylphosphine probably proceeds via a rate-determining CO-dissociative path involving **101**, which undergoes a rapid reaction with phosphine to form **102**. Bimolecular attack by triphenylphosphine also occurs to give **103**. The reaction of triphenylphosphine with **100** proceeds via formation of 99 in a rate-determining step, which subsequently reacts rapidly with phosphine. Attack of the complexes **100** and **103** by $P\text{-}n\text{-}Bu_3$ are bimolecular processes [138].



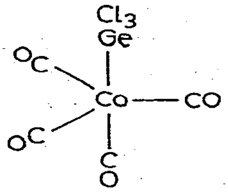
(101) (102)



(103)

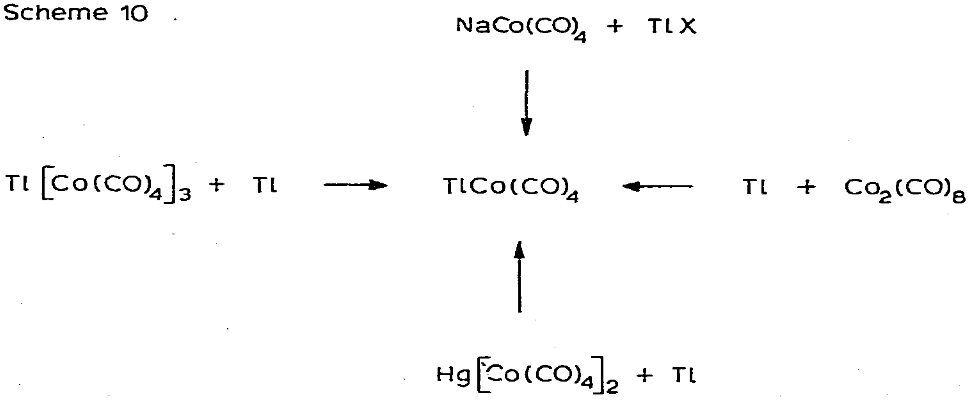
The reactions of tin(II) halides, SnX_2 (X = F, Cl, Br or I), with $[Co(CO)_3(P\text{-}n\text{-}Bu_3)]_2$ can lead to six types of compounds, namely, $[Co(SnX_3)(CO)_3(P\text{-}n\text{-}Bu_3)]$, $X_2Sn[Co(CO)_3(P\text{-}n\text{-}Bu_3)]_2$, $XSn[Co(CO)_3(P\text{-}n\text{-}Bu_3)]_3$, $HSn[Co(CO)_3(P\text{-}n\text{-}Bu_3)]_3$, $Sn[Co(CO)_3(P\text{-}n\text{-}Bu_3)]_4$ and $CoX(CO)_2(P\text{-}n\text{-}Bu_3)_2$. It is proposed that these reactions proceed either by direct insertion of SnX_2 into the Co—Co bond or by cleavage of the Co—Co bond to form $[Co(SnX_3)(CO)_3(P\text{-}n\text{-}Bu_3)]$, which can undergo further reaction with $[Co(CO)_3(P\text{-}n\text{-}Bu_3)]_2$. This latter reaction can be used to obtain mixed metal complexes such as $Cl_2Sn[Fe(NO)(CO)_2(PPh_3)][Co(CO)_4]$. The type of complex formed appears to depend upon the nature of X, the ratio of the reactants and the reaction conditions [139]. The ease of these reactions also depend on the nature of the phosphine, and the rates decrease with changing L in the order $CO > P(OPh)_3 > P\text{-}n\text{-}Bu_3$ [140]. The thermal insertion of $SnCl_2$ into the Co—Co bond of $[Co(CO)_3\{P(OPh)_3\}]_2$ probably occurs via a two stage process, as proposed previously for the reaction with the $P\text{-}n\text{-}Bu_3$ complex. The better π-acceptor $P(OPh)_3$ appears to weaken the Co—Co bond more than $P\text{-}n\text{-}Bu_3$ [140]. The hydride $HSn[Co(CO)_3(P\text{-}n\text{-}Bu_3)]_3$, obtained in the above reactions, is an unusually stable stannane, however, attempts to obtain the corresponding plumbane were unsuccessful. Only $Pb[Co(CO)_3(P\text{-}n\text{-}Bu_3)]_4$ is formed [141]. In contrast to the fairly rapid reaction of tin(II) halides with $Co_2(CO)_8$ the reaction of $Sn(C_5H_4Me)_2$ is complex, $Sn[Co(CO)_4]_4$ being isolated after two days [142].

The crystal and molecular structure of $Cl_3GeCo(CO)_4$ (**104**) has been determined [143] and complete vibrational assignments of the compounds $X_3MCo(CO)_4$ (M = C, Ge, X = H, D, F; M = Si, Ge, Sn; X = H, D, F, Cl, Br, I) have been made [144,145]. The nature of the tin—cobalt bond in the compounds $[Co(CO)_3L]_xSnX_{4-x}$ (L = CO, PPh_3, P-n-Bu_3; X = Cl, Br, I, Et, Ph; $x = 1, 2$) has been studied by obtaining ^{119}Sn Mössbauer parameters [146] and the ^{59}Co NQR spectra of the compounds $Ph_3SnCo(CO)_3L$ and $Ph_3SnCo(CO)_2L_2$ (L = P-n-Bu_3, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$) have been recorded and interpreted [147].


(104)

The thallium compound $TlCo(CO)_4$ can be prepared by several methods outlined in Scheme 10 [148]. The reaction of $TlCo(CO)_4$ with a variety of Lewis bases produces either $TlCo(CO)_3L$ or $Tl[Co(CO)_3L]_3$ and Tl metal. Stable thallium(I) compounds, e.g. $[TlCo(CO)_3\{P(OPh)_3\}]$ appear to be formed with those bases which give anions of low basicity. The p*K*a of $[HCo(CO)_3\{P(OPh)_3\}]$ is 4.95. However, ligands giving more strongly basic anions react to give thallium(III) compounds, e.g. $Tl[Co(CO)_3(PPh_3)]_3$ and thallium metal. Other Lewis bases, e.g. $P(OMe)_3$, $P(OEt)_3$, $AsPh_3$, $SbPh_3$ and P-n-Bu_3, which give substituted hydrides $HCo(CO)_3L$ with p*K*a's > 5, also react to give thallium(III) derivatives [149]. The structure of $TlCo(CO)_4$ consists of discrete Tl^+ and $Co(CO)_4^-$ ions, although in solutions of low dielectric constant $TlCo(CO)_4$ exists as a tight ion-pair [150].

Scheme 10



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

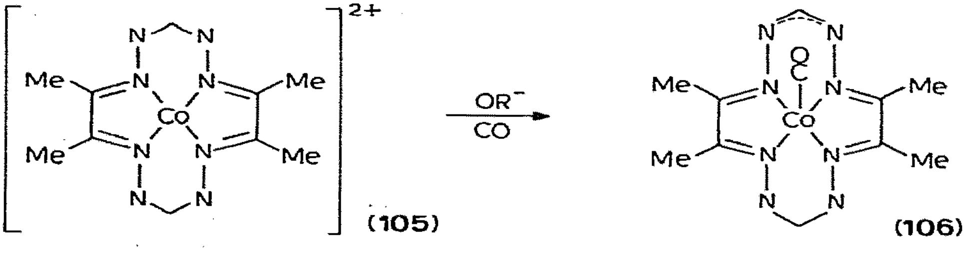
The reaction of carbon monoxide and isocyanides with the cationic complexes $[CoXL_4]^+$ ($L = P(OMe)_3$, $PPh(OEt)_2$; $X = Cl$, Br, I) give the five-coordinate cobalt(I) mixed-ligand complexes $[CoI(CO)_2L_2]$, $[Co(CO)_2L_3]^+$, $[Co(CNR)_2L_3]^+$ and $[Co(CNR)_3L_2]^+$. Trigonal bipyramidal structures with carbonyl or isocyanide ligands in equatorial positions are proposed for these complexes on the basis of infrared and NMR studies. The cations $[Co(CO)_2L_3]^+$ are non-rigid molecules at room temperature [151].

Dry $CoCl_2$ in anhydrous ethanol reacts slowly with triethylphosphite, in the presence of triethylamine, to produce yellow crystals of $[Co\{P(OEt)_3\}_5]Cl$. Additions of small quantities of water to the reaction mixture can lead to the isolation of a green compound, $[Co\{P(OEt)_3\}_5][CoCl_n]^{2-n}$. These compounds have previously been incorrectly formulated as $CoClL_4$ and $CoClL_3$ respectively ($L = P(OEt)_3$). The complexes $CoClL_3$ and $[CoL_2(BPh_4)]$ have also been characterised [152]. Cationic phosphite complexes of the type $[ML_5][BPh_4]$ (M = Co, Rh, Ir) are stereochemically non-rigid. The intramolecular rearrangements involve simultaneous exchange of the axial ligands with a pair of equatorial ligands in the trigonal bipyramidal ground state, consistent with the Berry mechanism. Barriers increase with increasing steric bulk of the ligand until the bulk is too great for pentacoordinate complexes to be formed and the ligand dissociation equilibrium

$$ML_5^+ \rightleftharpoons ML_4^+ + L$$

lies over to the right. For a given phosphite, barriers are not very sensitive to the central metal but the sequence Co > Rh < Ir has been established [153,154]. Treatment of *trans*-$[IrCl(CO)(PPh_3)_2]$ or $[IrCl(C_8H_{12})]_2$ with phosphonite, $P(OR)_2Ph$, and phosphinite, $P(OR)Ph_2$, ligands afford complexes of the type $[IrL_4][BPh_4]$ ($L = P(OR)Ph_2$, $P(OEt)_2Ph$) or $[IrL_5][BPh_4]$ ($L = P(OMe)_2Ph$), hydride formation being prevented in some experiments by the addition of triethylamine to remove traces of HCl. With $[IrHCl_2(C_8H_{12})]_2$, hydride complexes *cis*- and *trans*-$[IrHClL_4][BPh_4]$ and *trans*-$[IrH_2L_4][BPh_4]$ can be obtained [155].

Difluorophenylphosphine reacts with cobalt(II) chloride, via a redox disproportionation reaction, to give $[CoCl(PF_2Ph)_4]$ and $[CoCl_3(PF_2Ph)_3]$. Excess PF_2Ph and cobalt(II) bromide give the analogous bromo derivatives. The phosphine also forms stable complexes of the type $[CoX_2(PF_2Ph)_2]$ (X = Br or I) [156]. Treatment of tertiary phosphine complexes of the type $[CoX_2(PR_3)_2]$ yield cobalt(II) and cobalt(I) complexes $CoX_2(CO)L_2$ and $CoX(CO)_2L_2$ [157]. However, the low spin cobalt(II) compound **105** does not react with CO, but it does react with alkoxide anions to produce a cobalt(I) complex **106** which does add CO.



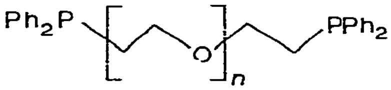
(105) (106)

The complex **106** oxidatively adds MeI [158].

The reactions of Lewis bases with $[RhCl(CO)_2]_2$ are known to be dependent on the Lewis base, on the ratio of reactants and on the solvent. Amines react to give *cis* dicarbonyl compounds, *cis*-$[RhCl(CO)_2(amine)]$, while phosphines in excess give *trans*-$[RhCl(CO)(PR_3)_2]$; the details of the latter reactions have been reviewed [159]. Tricyclohexylphosphine oxide, Cy_3PO, has now been shown to also give a *cis* dicarbonyl complex, *cis*-$[RhCl(CO)_2(Cy_3PO)]$, which has been the subject of an X-ray structure determination [160]. The crystal structure of the related complex *cis*-$[IrCl(CO)_2py]$ has also been reported [161].

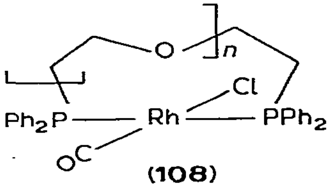
The complex $[RhCl(CO)(C_2H_4)]_2$ may have a bent halogen-bridged structure as is found in $[RhCl(CO)_2]$ and the complexes $[RhCl(CO)L]_2$ ($L = PF_2$-n-Pr, $P(OMe)_3$, PPh_3, $P(NMe_2)_3$, PMe_2Ph, PMe_3 or PEt_3) which can be obtained from the ethylene complex and may have similar bent structures. Triphenylphosphine and tertiary phosphite complexes $[Rh_2Cl_2(CO)L_3]$ and $[Rh_2Cl_2(CO)_3L]$ may also be obtained [162].

Treatment of $[RhCl(CO)_2]_2$ with the stibine ligands L ($L = Ph_3Sb$, *o*- or *p*-$MeC_6H_4)_3Sb$) gives either the four- or five-coordinate complexes $[RhCl(CO)L_2]$ or $[RhCl(CO)L_3]$, depending upon the solvent and size of L. The steric influence of *ortho* substituents in the phenyl rings favour four-coordinate complexes and in solution there is dissociation of the five-coordinate complexes. During the addition of L to $[RhCl(CO)_2]_2$ the intermediate $[RhCl(CO)_2L]$ can be detected in solution and *cis*-$[RhCl(CO)_2L]$ can be obtained upon reaction of CO with $[RhCl(cod)L_2]$ and $RhClL_3$. $[Rh(acac)(CO)_2]$ reacts with the stibine ligands to produce $[Rh(acac)(CO)L_2]$ [163]. The β-phosphino ether (**107**) displace CO from $[RhCl(CO)_2]_2$ to give the complexes **108**. These complexes show no great tendency to react with O_2, H_2 or CO but **108** ($n = 1$) forms an adduct with SO_2 and oxidatively adds HCl. Treatment of the complexes **108** with $AgPF_6$ gives the complexes **109**, **110** and **111**, the latter being an example of a macrocyclic aquo-complex [164]. Tri- and tetra-pyrazolylborate anions react with $[RhCl(CO)_2]_2$ to give the insoluble complexes $[Rh_2\{HB(Pz)_3\}_2(CO)_3]_n$ and $[Rh_2\{B(Pz)_4\}_2(CO)_3]_n$, where n is probably one [165], which are formally related to $[Rh_2Cp_2(CO)_3]$. Reaction with iodine yields the complexes $[RhI_2(CO)$-



(107)

(n = 1,2,3)



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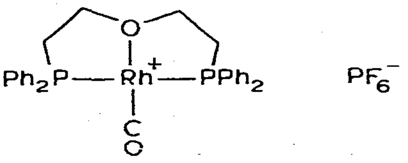

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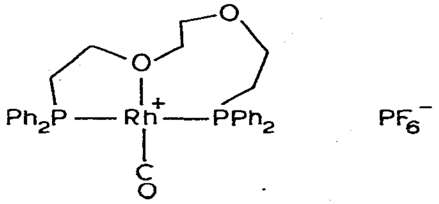

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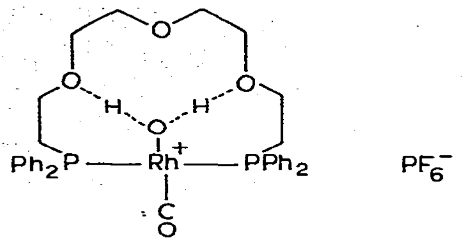
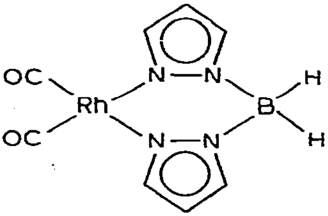


(111)

{RB(Pz)$_3$}] (R = H or Pz). However, in contrast to these results, KHB(Me$_2$Pz)$_3$ reacts with [RhCl(CO)$_2$]$_2$ to give [Rh(Me$_2$Pz)(CO)$_2$]$_2$, a reaction which involves B—C bond cleavage. This complex and [Rh(Pz)(CO)$_2$]$_2$ can be obtained from the pyrazole and [RhCl(CO)$_2$(py)$_2$] in the presence of triethylamine. Both complexes exhibit fluxional behaviour [166]. Chlorocarbonylrhodium dimer also reacts with KH$_2$B(Pz)$_2$ to give 112 [167]. Treatment of [RhCl(CO)$_2$]$_2$ with aziridine,



(112)

which is highly toxic, gives [RhCl(CO)$_2$(Az)$_2$], analogous to the known dipyridine complex [RhCl(CO)$_2$(py)$_2$]. However, in contrast to studies with other N-donor ligands, a complex of stoichiometry [RhCl(CO)(Az)$_3$] can be isolated with an excess of the aziridine ligand. This complex reacts with hydriodic acid to give [RhI(Az)$_3$] [168]. Octaethylporphin, oepH$_2$, and [RhCl(CO)$_2$]$_2$ react in hot chloroform to give a complex which is shown by X-ray analysis to be $[\text{oepH}]_4^{2+}[cis\text{-RhCl}_2(\text{CO})_2]_2^{2-}$ [169].

The reactions of [RhCl(CO)$_2$]$_2$, in aqueous hydrochloric acid, with dichromate, hexachloroplatinic acid, cerium(IV) sulphate or *p*-benzoquinone [170] proceed by consumption of four equivalents of oxidising agent according to the equation:

$$\text{Rh}^{\text{I}}(\text{CO})_2 + \text{H}_2\text{O} \rightarrow \text{Rh}^{\text{III}}(\text{CO}) + 2\,\text{H}^+ + \text{CO}_2 + 4e$$

Intermediates of the type Rh$_2$ICl(CO)$_4$ and Rh$_2$Cl(OAc)(CO)$_4$ have been detected in exchange reactions of the type:

$$[\text{Rh}_2\text{X}_2(\text{CO})_4] + 2\,\text{MY} \longrightarrow [\text{Rh}_2\text{Y}_2(\text{CO})_4] + 2\,\text{MX}$$

$(\text{X} \neq \text{Y}; \text{X,Y} = \text{halogen, OCOR}^-, \text{SR}^-)$

The reaction of [RhCl(CO)$_2$]$_2$ with thiols give the dimers [RhSR(CO)$_2$]$_2$ (R = Ph, t-Bu) which, upon treatment with tertiary phosphines, form the five-coordinate dimers [RhSR(CO)$_2$(PR$_3$)]$_2$ [172]. The kinetics of the carbonylation reaction:

$$2\,\text{RhCl}_3 \cdot x\text{H}_2\text{O} + 4\,\text{CO} = [\text{RhCl}(\text{CO})_2]_2 + 2\,\text{Cl}_2 + 2x\text{H}_2\text{O}$$

in the presence of methanol at 383—423 K have been studied [173].

A more detailed study of the reaction of [Rh(bipy)(cod)] [PF_6] with CO show that this complex takes up three moles of gas to give the pentacoordinated complex [Rh$(CO)_3$(bipy)] [PF_6]. This complex was previously reported to be a dicarbonyl, [Rh$(CO)_2$(bipy)] [PF_6], which is produced upon bubbling nitrogen gas through a methyl cyanide solution of the tricarbonyl. The tricarbonyl complexes [Rh$(CO)_3$(bipy)] [PF_6] and [Rh$(CO)_3$(*o*-phen)] [PF_6] react with lithium halides to give neutral derivatives [RhX(CO)(chelate)]. In the presence of CO [RhX$(CO)_2$(bipy)] can be obtained [174].

Passage of carbon monoxide gas through an ethanolic solution of rhodium perchlorate followed by addition of bipyridyl or *o*-phenanthroline, is reported to give the ionic derivatives $[Rh(CO)_2(N—N)]^+[ClO_4]^-$. However, in view of the discussion above, these are probably tricarbonyl salts. The tetrafluoroborate derivatives can be obtained by treating an ethanolic solution of rhodium trichloride with excess $NaBF_4$, followed by addition of the ligand. Using rhodium perchlorate the salts $[Rh(CO)_2L_3][ClO_4]$ (L = tertiary phosphine or arsine) have also been obtained. The bulky tri-*o*-tolylphosphine gives a four-coordinate *trans* species, *trans*-$[Rh(CO)_2L_2][ClO_4]$ [175,176]. Some cationic iridium complexes $[Ir(CO)_2L_2]^+$ (L = PPh_3, $P(C_6H_4Me\text{-}o)_3$, $P(CHMe_2)_3$, $P(C_6H_{11})_3$, PPh_2CMe_3) can be obtained upon addition of $AgBF_4$ or $NaBPh_4$ and the ligand L to $[IrCl(CO)_3]_n$. Phosphine basicity appears to be important in promoting pentacoordination since all the cations, except when L = PPh_3 or $P(C_6H_4Me\text{-}o)_3$, absorbed CO to give $[Ir(CO)_3L_2]^+$ [177].

Treatment of [Rh(acac)$(CO)_2$], in dimethylformamide, with $NaBH_4$ is reported to give Na_4[(acac)Rh$(O_2)_2$Rh(OH)(DMF)], which when treated with water and acetone gives NaH_3[(acac)Rh$(O_2)_2$Rh(OH)(H_2O)]. In anhydrous dimethylformamide a bridged carbonyl complex is obtained [178].

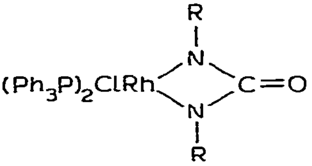
The UV and visible spectra and electrical conductivity measurements on the compounds [IrCl$(CO)_2$L] (L = CO, *p*-$H_2NC_6H_4F$, *p*-$H_2NC_6H_4NMe_2$) and [Ir$(CO)_2$X′] (HX′ = 1-(phenyliminomethyl)-2-naphthol and 1-(phenylazo)-2-naphthol) reveal that increasing the ligand size reduced the intermolecular metal—metal interactions in these complexes [179].

An attempt to prepare *trans*-[IrF(CO)$(AsPh_3)_2$] by treatment of *trans*-[IrCl(CO)$(AsPh_3)_2$] with ammonium fluoride and silver carbonate, in methanol, leads to [IrF$(AsPh_3)_3$]. However, the fluorocarbonyl complex can be obtained via the acetonitrile-coordinated cation $[Ir(CO)(MeCN)(AsPh_3)_2]^+$ [180].

The reaction of sodium cyanamide, Na_2NCN, with *trans*-[IrCl(CO)$(PPh_3)_2$] gives $[(Ph_3P)_2(OC)IrN{=}]_2C$, and the complex [Ir(NHCN)(CO)$(PPh_3)_2$] can be similarly obtained with NaNHCN [181]. Treatment of [RhCl(CO)$(PPh_3)_2$] with [Ph_4As] [CNO] gives the fulminato complex [Rh(CNO)(CO)$(PPh_3)_2$] [182]. However, reaction of [RhCl(CO)$(PPh_3)_2$] with nitromethane gives the isocyanato complex [Rh(NCO)(CO)$(PPh_3)_2$], and Vaska's complex and nitromethane may give [IrH(CO)(N_2)$(PPh_3)_2$] [183]. Treatment of [IrX(CO)$(PPh_3)_2$] (X = N_3 or NCO) with SO_2, in benzene, gives the adducts [IrX(CO)$(PPh_3)_2$] · SO_2. Bis-adducts [IrX(CO)$(PPh_3)_2$] · 2 SO_2 are formed in methanol [184]. Linkage isomerism has been observed with the complexes [Rh(NCO)$(PPh_3)_3$] and Rh(OCN)$(PPh_3)_3$ [185].

A wide range of thioiridium complexes [IrSR(CO)$(PPh_3)_2$] can be obtained by oxidative addition of thiols to *trans*-[$IrCl(CO)(PPh_3)_2$], followed by strong base (NaOMe) elimination of HCl from the unstable intermediates [$IrHCl(SR)(CO)(PPh_3)_2$]. The complexes [$Ir(SR)(CO)(PPh_3)_2$] add oxygen irreversibly [186]. Monothio- and monoseleno-carbamate complexes [$Rh\{SC(O)NR_2\}(CO)(PPh_3)_2$] and [$Rh\{SeC(O)NR_2\}(CO)(PPh_3)_2$] have also been described [186a]. The siloxane derivative [$Ir(OSiMe_3)(CO)(PPh_3)_2$] can be prepared via the reaction of Vaska's complex with $NaOSiMe_3$ [187].

Treatment of [$RhH(PPh_3)_4$] and [$RhH(CO)(PPh_3)_3$] with 1,3-diaryltriazenes affords [$RhH_2(ArNNNAr)(PPh_3)_2$] and [$Rh(ArNNNAr)(CO)(PPh_3)_2$] respectively. It is not clear whether the latter complex is four-coordinate, or whether the diaryltriazenido ligand is bidentate thus making the rhodium five-coordinate. However, since the acetate ligand in [$Rh(OCOMe)(CO)(PPh_3)_2$] is unidentate the triazenido ligand may also be unidentate. The complexes [$RhCl(ArNNNAr)_2(PPh_3)$] and [$Rh(ArNNNAr)_2(NO)(PPh_3)$] have also been described [188]. A somewhat analogous complex (113) to those described above has been obtained from the reaction of [$RhCl(PPh_3)_3$] with either RNCO or RNHCONHR (R = toluene-*p*-sulphonyl). The reaction of toluene-*p*-sulphonyl azide with [$RhH(Ph_2PCH_2CH_2PPh_2)_2$] affords 114 which probably contains a diimide bridge [189].



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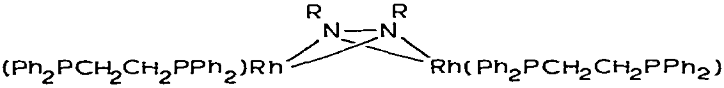


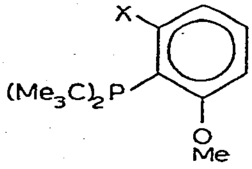
(114)

Some dinitrogen cobalt complexes of the type [$Co(N_2)L_3$] (L = triaryl-phosphine, -arsine, or -stibine) can be obtained by the reduction of $Co(acac)_2$ with n-BuMgBr in the presence of L under a nitrogen atmosphere [190].

Further studies have appeared on the alkene hydrogenation catalysts [$RhClL_3$] (L = PPh_3 or P(*p*-tolyl)$_3$). It is now apparent that these complexes do not dissociate to a spectroscopically detectable extent, but that despite its low concentration a species of composition [$RhClL_2$] must be postulated, as previously reported, in order to explain the kinetics of hydrogen reactions with solutions of [$RhClL_3$]. The triphosphine complexes are in equilibrium with the dimers which react with hydrogen to form [$L_2RhCl_2RhH_2L_2$]; the dimers can be readily cleaved by ethylene or L, but not cyclohexene, to form [$RhCl(C_2H_4)L_2$] or [$RhClL_3$] [191].

Tricyclohexylphosphine reacts with [$RhCl(cyclooctene)_2]_2$ to give [$RhCl(C_8H_{14})(PCy_3)_2$], but with excess phosphine the solvated complex [$RhCl(PCy_3)_2S$] is slowly formed in solution. Solutions of the complex react with CO, N_2, C_2H_4, O_2 (L) to give [$RhCl(L)(PCy_3)_2$] and with H_2 to give [$RhClH_2(PCy_3)_2$]. Steric requirements of phosphine may stabilise the N_2 complex [192]. The complexes [MX_3L_3], [$MX(CO)L_2$], [$IrHX_2(CO)L_2$], [$MX_3(CO)L_2$] and [$IrX(CO)(O_2)L_2$] (M = Rh, Ir; X = halogen) have been obtained with the arsine $AsPh_2Pr$ (L) [193]. The phosphines $P(COMe)Ph_2$ and $P(COCF_3)Ph_2$ are decarbonylated by [RhCl(PPh$_3$)$_3$] to give [RhCl(CO)(PPh$_3$)$_2$] and PRPh$_2$ (R = Me or CF$_3$) [194].

Passage of carbon monoxide through a boiling propan-2-ol solution of **115** (X = H) and [IrCl$_6$]$^{3-}$ gives the demethylated phosphine complex **116**. A benzene solution of **116** in air rapidly becomes blood red, carbon dioxide is evolved and the iridium(II) complex **117** (X = H) is formed, together with the hydride **118** (X = H). The phosphine **115** (X = OMe) forms analogous complexes **117** and **118** [195].



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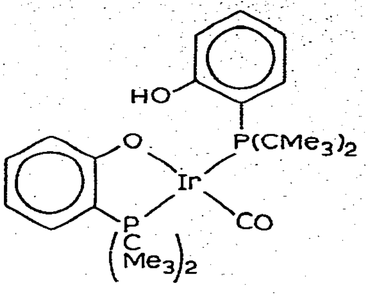

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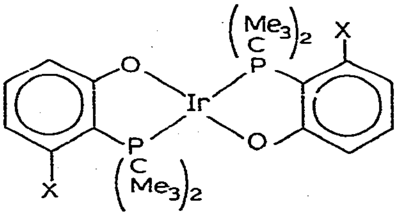

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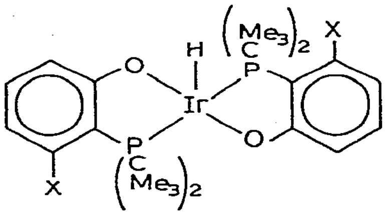
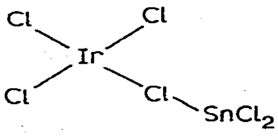


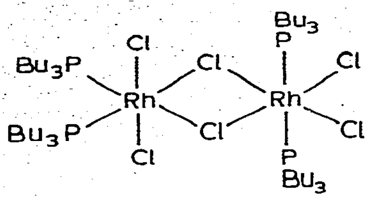
(118)

The reaction of triphenylphosphine with [IrCl$_6$]$^{2-}$ in dimethylformamide gives [IrCl$_3$(CO)(PPh$_3$)$_2$]; the iodide [IrI$_3$(CO)(PPh$_3$)$_2$] has been obtained from [IrCl(CO)(PPh$_3$)$_2$] and excess potassium iodide. X-ray structural studies reveal that both complexes have a *trans* configuration [196]. Treatment of K$_2$IrCl$_6$, in formic acid, with SnCl$_2$ gives K[IrCl$_4$SnCl$_2$] which, on the basis of Mössbauer and infrared studies is formulated as **119**. The complexes [Et$_4$N]$_2$[IrCl$_3$(CO)(SnCl$_3$)$_2$] and [Et$_4$N]$_3$[IrCl$_3$(SnCl$_3$)$_3$] have aslo been obtained [197]. The iridium(III) or rhodium(III) tertiary phosphine or arsine complexes of the type MX$_3$L$_3$] (both isomers) form adducts with mercury(II) halides [MX$_3$L$_3$HgY$_2$)] which are believed to have a double halide bridge between the metal atoms. The adducts often easily dissociate and SnCl$_2$ reacts with [IrCl$_3$(PEt$_3$)$_3$(HgCl$_2$)] to



(119)

give $[IrCl_2(SnCl_3)(PEt_3)_3]$, a reaction which can be reversed by the addition of $HgCl_2$ [198]. The crystal structure of the bridged rhodium(III) complex **120**



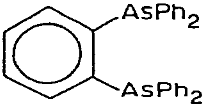
(120)

has been determined [199]. In contrast to the reactions of tertiary phosphines or arsines, Ph_3Sb reacts with $RhCl_3 \cdot xH_2O$ in ethanol, regardless of the ratios of reactants, to yield only the product *mer*-$[RhCl_3(SbPh_3)_3]$. This complex is also significantly different to related complexes in that metathetical reactions do not proceed to completion but stop at *mer*-$[RhCl_2X(SbPh_3)_3]$ (X = Br, I, NCS, $SnCl_3$) [200]. Reactions of the complex *mer*-$[RhCl_3(PMe_2Ph)_3]$ with excess of $(S{-}S)^-$ ion $[(S{-}S)^- = {}^-S_2CNMe_2, {}^-S_2PMe_2, {}^-S_2PPh_2, {}^-S_2COEt]$ also give monosubstituted complexes, *mer*-$[RhCl_2(S{-}S)(PMe_2Ph)_3]$, which contain a unidentate dithio acid group. Recrystallisation of these complexes from non polar solvents gives *trans*-$[RhCl_2(S{-}S)(PMe_2Ph)_3]$ [201].

Rhodium and/or iridium complexes of the chelating ligands **121** [202], **122** [203], **123** [203], **124** [204], **125** [205], **126** [206], **127** [206], **128** [206], **129** [207,208], **130** [207,208], **131** [208], **132** [208], have been described.

$Ph_2SbCH_2CH_2SbPh_2$

(121)



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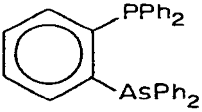
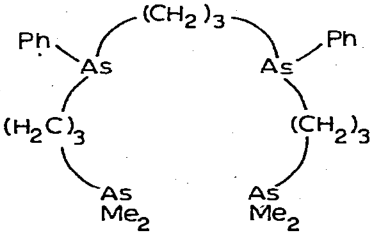


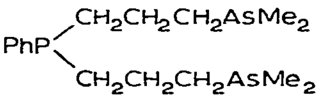
(123)

$Ph_2AsCH_2CH_2AsPh_2$

(124)

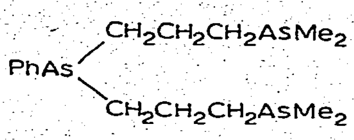


(125)
(lqa)



$PhP(CH_2CH_2CH_2AsMe_2)_2$

(126)
(dap)



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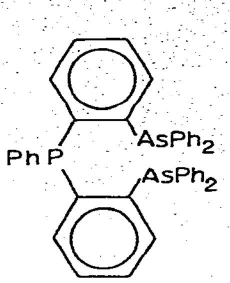

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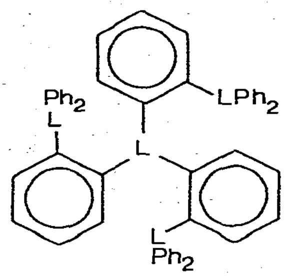
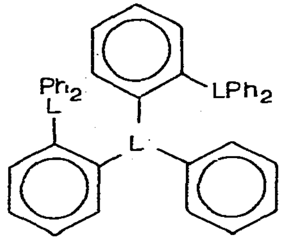
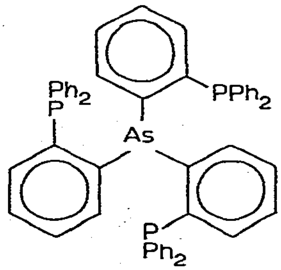


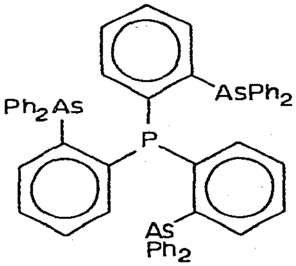
(129)
(L = P
L = As)



(130)
(L = P
L = As)



(131)

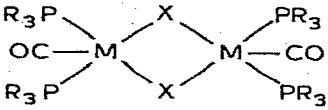


(132)

The reaction of **125** (lqa) with *trans*-$[IrCl(CO)(AsPh_3)_2]$ gives $[Ir(CO)(lqa)]Cl$, and the chelate complexes $[Ir(CO)(Ph_2AsCH_2CH_2AsPh_2)]Cl$ and $[IrCO(Ph_2AsCH{=}CHAsPh_2)]Cl$ can similarly be obtained [205]. Treatment of *trans*-$[IrX(CO)(EPh_3)_2]$ (X = F, Cl, Br, I; E = P, As) with **127** (tas) also gives ionic complexes $[Ir(CO)(tas)]Cl$, but in contrast, **126** (dap) reacts to give a mixture of $[IrX(CO)(dap)]$ and $[Ir(CO)(dap)]X$ ($X \neq F$). The fluoride analogue gives only $[IrF(CO)(dap)]$. The cation $[Ir(CO)(tas)]^+$ undergoes slow oxygenation but $[IrCO(dap)]^+$ does not react with oxygen gas [206].

Treatment of $[IrHCl_2(COD)]_2$ with the ligands $P(OR)_2Ph$ and $P(OR)Ph_2$ (R = Me, Et) gives the derivatives $[IrHCl_2L_3]$ [209], whilst reaction of α-$[RhHX_2L_3]$ (X = Cl, Br; L = $AsMePh_2$, $AsEtPh_2$, $PEtPh_2$) with bipyridyl or *o*-phenanthroline, in the presence of perchloric acid, gives the salts $[RhHX(N{-}N)L_2][ClO_4]$. However, the β-isomers give $[RhX_2(N{-}N)L_2][ClO_4]$ [210].

Intermolecular redistribution of carbonyl, halide and phosphine ligands has been found to occur in systems of the type $[MX(CO)(PR_3)_2]$ (M = Rh, Ir; X = Cl, Br). These exchange reactions probably proceed via halogen- and carbonyl-bridged intermediates of the type 133 and 134 [211].



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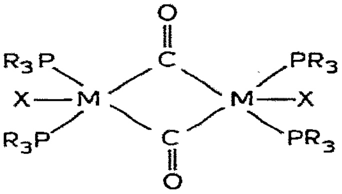


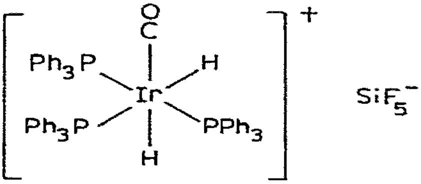
(134)

Phosphorus NMR studies on complexes of the type *fac*-$[MX_3(PR_3)_3]$ (M = Rh, Ir) have been reported [21], and the application of $^1H\{^{31}P\}$INDOR spectroscopy to the determination of P—P coupling in rhodium(III) and iridium(III) complexes has been described [213].

Considerable amounts of benzene are formed upon heating the triphenylphosphine complexes $[RhCl(PPh_3)_3]$ $[RhH(PPh_3)_4]$ and $[RhCl(CO)(PPh_3)_2]$ in several types of organic solvents, especially amines which have high hydrogen-donating ability [214].

Treatment of chloroiridic acid with dimethyl sulphoxide leads to the hydride complex $[IrHCl_2(DMSO)_3]$ [215].

The close correspondence between the activation parameters for the addition of triphenylphosphine and oxidative addition of silanes to the intermediate $[IrH(CO)(PPh_3)_2]$, suggests that on the approach to the transition state there is a π-donation of electrons from the metal to the addendum. To obtain evidence for this type of interaction the reaction of $[IrH(CO)(PPh_3)_3]$ with SiF_4 has been investigated. However, the reaction leads to the formation of the salt 135 which has been characterised by an X-ray structure determination. The same complex can also be obtained by the addition of concentrated hydrofluoric acid to a stirred suspension of high surface area silica, in a benzene/methanol solution of $[IrH(CO)(PPh_3)_3]$. Treatment of the latter with BF_3 gives $[IrH_2(CO)(PPh_3)_3]^+[BF_4]^-$ [216]. Boron trihalides react with certain rhodium(I) complexes in a number of different ways. Thus, BF_3 forms an adduct 136 with $[Rh(diphos)_2][BPh_4]$, but the nature of the adducts formed with $[RhCl(PPh_3)_3]$ remain obscure. The predominant species in solu-



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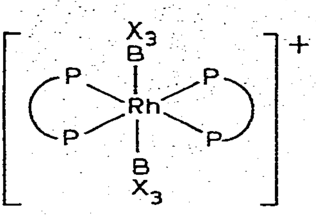
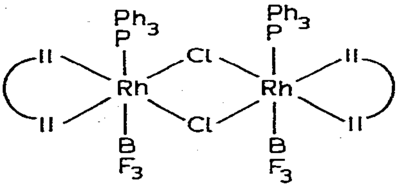


(136)

tion when $[RhCl(C_8H_{12})(PPh_3)]$ is treated with BF_3 is probably **137**, but the 1/1 adduct formed with *trans*-$[RhCl(CO)(PPh_3)_2]$ is probably **138** [217].



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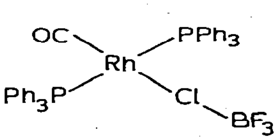
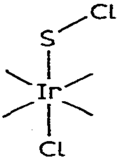


(138)

The hydride $[CoH(diphos)_2]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) is reported to react with the chlorosilanes $HSiCl_3$, $HSiMe_2Cl$, $HSiMeCl_2$ and $HSiPh_2Cl$ to give the salts $[CoH_2(diphos)_2]SiX_3$ (X_3 = Cl_3, $MeCl_2$, Me_2Cl, Ph_2Cl respectively) [218]. However, other results suggest that these salts do not contain silicon anions but that the reactions initially lead to $[CoCl(diphos)_2]$, which reacts with HCl present in the system to give the salt $[CoClH(diphos)_2]^+Cl^-$ [219]. The dinitrogen complex $[CoN_2(PPh_3)_3]$ reacts with $SiHCl_3$ to give $[CoCl(PPh_3)_3]$ and $[CoCl_2(PPh_3)_2]$ [218]. In contrast to these results, silanes oxidatively add to the complexes $[RhClL_3]$ to give $[RhClHSiR_3L_2]$ [220].

Sulphur dichloride reacts with *trans*-$[IrX(CO)(PPh_3)_2]$ (X = Cl, Br, NCS) to give oxidative products $[IrX(CO)(PPh_3)_2SCl_2]$, which are thought to have structures of type **139** rather than **140**. The rhodium compound $[RhCl(CO)(PPh_3)_2]$, however, reacts to give $[RhCl_3(CO)(PPh_3)_2]$ [221]. Treatment of $[IrCl(N_2)(PPh_3)_2]$, $[Ir(NCMe)(CO)(PPh_3)_2][PF_6]$ and $[RhCl(PPh_3)]$ with $CSCl_2$ results in a three-fragment oxidative addition to generate iridium(III) and rhodium(III) thiocarbonyl complexes $[MCl_3(CS)(PPh_3)_2]$ and $[IrCl_2(CO)(CS)(PPh_3)_2][PF_6]$ [222].



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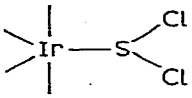
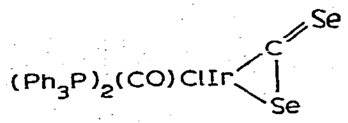


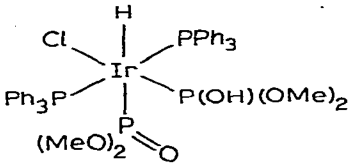
(140)

Carbon diselenide adds to *trans*-$[IrCl(CO)(PPh_3)_2]$ to give the complex **141**. The areneselenol *p*-MeC_6H_4SeH oxidatively adds to give $[IrClH(CO)(SeC_6H_4Me\text{-}p)$-



(141)

$(PPh_3)_2]$ [223]. The red solution obtained by treating the cyclooctene complex $[IrCl(C_8H_{14})_2]_2$ with two equivalents of triphenylphosphine, which is thought to contain $[IrCl(PPh_3)_2]$, reacts with $(MeO)_2P(O)H$ to give a complex of structure 142 or 143. Oxidative addition products $[IrHCl\{P(O)(OMe)_2\}\{P(OH)(OMe)_2\}$-



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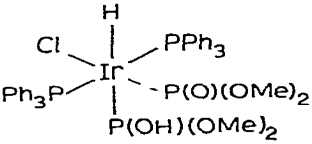
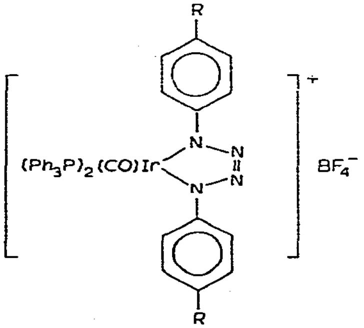


(143)

$(AsPh_3)_2]$, and $[MHCl\{P(O)(OMe)_2\}(PMe_2Ph)_3]$ are also produced by the action of tertiary phosphine or arsine and dimethylphosphite upon $[MCl(C_8H_{14})_2]_2$ (M = Rh or Ir). With phosphorous acid, $[IrHCl\{P(O)(OH)_2\}\{P(OH)_3\}(AsPh_3)_2]$ can be obtained. A complex $[IrHCl\{P(O)(OMe)_2\}\{P(OH)(OMe)_2\}_3]$, obtained from dimethylphosphite and $[IrCl(C_8H_{14})_2]_2$, catalyses the stereoselective reduction of 4-t-butylcyclohexanone [224].

Treatment of Vaska's complex with various aryldiazonium tetrafluoroborates give aryltetrazene complexes 144, the properties and synthesis of which have been given [225].

A comparison of the oxidative addition reactions of *trans*-$[IrCl(CO)(PMe_2$-$(o\text{-}MeC_6H_4))_2]$ and *trans*-$[IrCl(CO)\{PMe_2(p\text{-}MeC_6H_4)\}_2]$ with *trans*-$[IrCl(CO)$-$(PMe_2Ph)_2]$, suggests that the dominant effect increasing the reactivity and nucleophilic power of the $PMe_2(o\text{-}MeC_6H_4)$ complex is a direct interaction of the methoxy group with the iridium, as shown in 145 [226].



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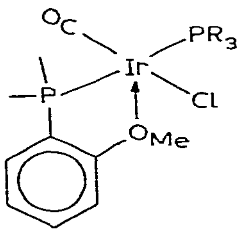
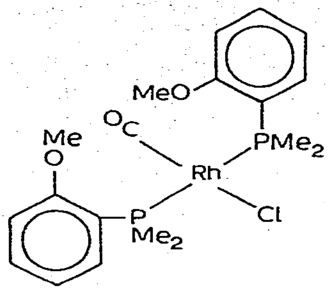


(145)

The complex 146 also undergoes rapid oxidative addition reactions with HCl, MeCl, MeI, CCl_4, Cl_2 and PhCOCl, the reactions being facilitated by the *o*-methoxy group. Allyl chloride adds reversibly in benzene solution possibly because of steric effects, but in polar solvents isomerisation to the acyl complex $[RhCl_2$-



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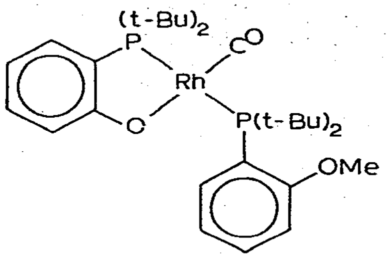
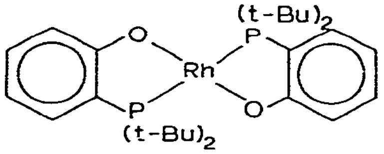


(147)

$(COCH_2CH{=}CH_2)L_2]$ occurs. The complex *trans*-$[RhCl(CO)\{P\text{-}t\text{-}Bu_2\text{-}(o\text{-}MeOC_6H_4)\}_2]$ resists oxidative addition but in boiling propan-2-ol demethylation of one ligand occurs to give **147**. Hydrated rhodium(III) chloride reacts with this ligand to give the rhodium(II) species **148** [227]. The crystal structure of bis(*o*-metalated)tris(triphenylphosphine)iridium(III) hydride has been determined [228]. Oxidative addition reactions of the complexes $[Rh(PN)_2]X$ ($X = Cl$, PF_6, SbF_6, BPh_4, ClO_4; PN = **149**) with HCl_2, MeI, O_2 and $(CN)_2$ have



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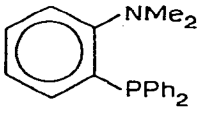
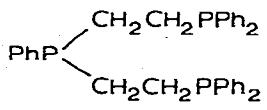


(149)

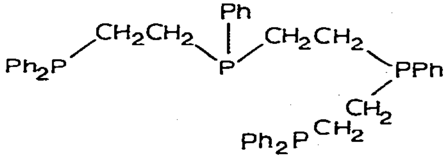
been described, the nitrogen donor ligand increasing the nucleophilicity of the metal. Allyl chloride and $[RhCl(CO)(PN)]$ gave $[RhCl_2(\sigma\text{-}C_3H_5)(CO)(PN)]$. An iridium complex $[IrHCl(PN)_2][PF_6]$ can be obtained by addition of PN to $[IrCl(cyclooctene)_2]$ and $[NH_4][PF_6]$ [23]. The reactions of acyl halides with *trans*-$[RhCl(CO)(PR_3)_2]$ (R = OMe or Me) [229] and the addition of MeI to $[RhX(CO)(N{-}N)]$ (X = Cl, Br, I; N—N = bipy, *o*-phen) have been reported [174].

Usually, oxidative addition reactions of *trans*-$[IrCl(N_2)(PPh_3)_2]$ result in loss of the dinitrogen ligand. However, reaction of the iridium complex with $MeOSO_2CF_3$ affords the octahedral complex $[IrCl(OSO_2CF_3)(Me)(N_2)(PPh_3)_2]$, the dinitrogen ligand being retained [230].

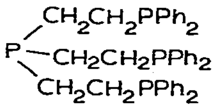
Treatment of the rhodium and iridium complexes *trans*-$[MCl(CO)(PPh_3)_2]$ with **150**, **151** and **152** give the complexes [M(CO)(triphos)]Cl, [M = (tetra-



(150)
(triphos)



(151)
(tetraphos-1)



(152)
(tetraphos-2)

phos-1)] Cl and [M(CO)(tetraphos-2)] Cl respectively. These complexes undergo oxidative addition reactions with H_2, HCl and MeI. With molecular oxygen [M(CO)(triphos)] Cl] undergoes oxidation of the coordinated carbonyl to the carbonate group [231]. This is in contrast to the ion $[Ir(CO)(tas)]^+$ (see 127), which only forms a dioxygen adduct [206]. The salts [M(tetraphos-1)] Cl and [M(CO)(tetraphos-2)] Cl similarly form dioxygen complexes [231]. Studies on the square-planar cationic rhodium(I) and iridium(I) complexes containing chelating tertiary diphosphine ligands, reveal that their photoluminescence properties are quenched when they form adducts with O_2, H_2 and CO [232].

The relative rates of dioxygen absorption by the complexes *trans*-$[IrX(CO)(PPh_2R)_2]$ (X = F, Cl, Br, I; R = Ph, Me) in dichloromethane solution follow the order R = Ph < Et < Me; X = F < Cl < Br < I. The energy of the ν(CO) stretching frequency does not reflect the basicity of the iridium(I) complexes, and the complex basicity is not proportional to $1/\nu$(CO) [233].

The arsine complexes *trans*-$[IrX(CO)L_2]$ (X = Cl, Br; L = $AsMePh_2$, $AsEtPh_2$), prepared by treatment of $[IrHX_2(CO)L_2]$ with NaOMe, also add dioxygen or X_2 [234]. The rates of oxygenation of $[RhCl(PPh_3)_3]$ in benzene solution, obtained from ESR measurements, suggest the presence of a rhodium(II)$\cdots O_2^-$ species [235]. The rate-controlling step in thermal deoxygenation of solid $[IrCl(CO)(O_2)(PPh_3)_2]$ has been found to be one of nucleation and growth of product [236].

Metal nitrosyl complexes

Secondary phosphines HPR_2 (R_2 = Ph_2, PhCy, Cy_2; Cy = cyclohexyl) react with $Co(NO_3)_2 \cdot 6\,H_2O$ in propan-2-ol, at room temperature, to give red crystalline $Co(NO)(HPR_2)_3$ [237]. Under the same conditions $HPEt_2$, HPMePh and HPEtPh give red oils, the IR spectra of which suggest the presence of the $Co(NO)(HPR_2)_3$ species. Refluxing $Co(NO_3)_2 \cdot 6\,H_2O$ with the tertiary phosphines PMe_2Ph and $PMePh_2$ gives red crystalline $Co(NO)(PR_3)_3$, but with PEt_3 and PEt_2Ph red oils are obtained; the IR spectra of these oils suggest the presence of $Co(NO)(PR_3)_3$ complexes.

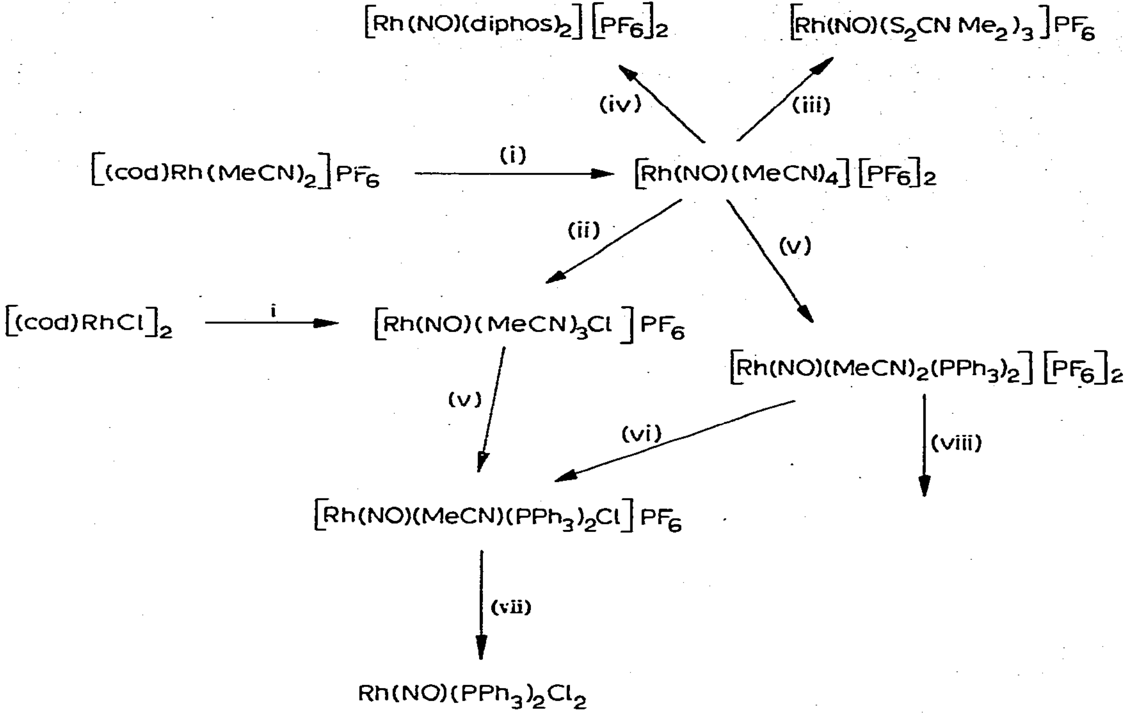
Reaction of $Co(NO)(CO)_2P(C_6H_5)_3$ with excess $[(CH_3)_3CN]_2S$, in refluxing toluene, gives the metal cluster compound $Co_4(NO)_4[\mu_3\text{-}NC(CH_3)_3]_4$ in 5—10% yield [238]. A structural determination of this compound shows it to have a cubane-like framework, with the cobalt and nitrogen atoms occupying alternate corners of a distorted cube; the geometry does not conform to that predicted by a first-order Jahn-Teller effect.

Reaction of nitric oxide with $Co(SacSac)_2$ (SacSac = "dithioacetylacetone", $C_5H_7S_2$) yields the two new nitrosyl complexes $Co(NO)(C_5H_7S_2)_2$ and $Co(NO)_2(C_5H_7S_2)$ which have been characterised by spectroscopic and magnetic techniques [239]. The mononitrosyl disproportionates in solution to $Co(NO)_2(C_5H_7S_2)$ and $Co(C_5H_7S_2)_3$; this interconversion has been studied by NMR and IR techniques.

The mercaptide-bridged cobalt(II) dimer of *N,N'*-dimethyl-*N,N'*-bis(β-mercaptoethyl)ethylenediamine (CoL_2) reacts with nitrosonium salts to give the $[(CoL)_2NO]^+$ cation [240]. The cation is believed to contain a bridging nitrosyl group, by analogy with $[(FeL)_2NO]^+PF_6^-$, for which a single crystal X-ray structure determination has been made. The cobalt derivative is not, however, thought to contain a metal—metal bond.

The cationic rhodium nitrosyl complex $[Rh(NO)(MeCN)_4][PF_6]_2$ has been prepared from $[Rh(cod)(MeCN)_2]^+PF_6^-$ and $NO\cdot PF_6$ in MeCN [241]. Reactions of this complex with uninegative and neutral ligands were investigated (Scheme 11).

Scheme 11



Reagents: i, $NOPF_6$ in MeCN; ii, Cl^-; iii, $Na[S_2CNMe_2]$
iv, diphos ($Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2$); v, PPh_3; vi, Cl^- (mol.eq.);
vii, Cl^- (excess); viii, $Na[S_2CNEt_2]$.
(cod = cycloocta-1,5-diene)

$Rh(CO)NO_2(PPh_3)_2$ in $CHCl_3$ reacted with HCl or KCl, HBr, HNO_3 or KNO_3 and KSCN to give $Rh(NO)Cl_2(PPh_3)_2$, $Rh(NO)Br_2(PPh_3)_2$, $Rh(NO)NO_3(PPh_3)_2$ and $Rh(NO)(CNS)_2(PPh_3)_2$ respectively [242]. Reaction mechanisms were discussed.

A crystal structure determination for the complex $Co(NO)_2[PPh_2(CH_2)_2\text{-}PPh_2O]I$ showed it to have a distorted tetrahedral coordination around cobalt [243]. This is the first example of a distinctly bent M—N—O linkage in a four-coordinate nitrosyl complex.

The crystal and molecular structure of $Co(CO)_2(NO)(SbPh_3)$ was determined, showing that the Co and Sb atoms both have distorted tetrahedral geometries [244]. A crystal structure study on a second isomer of hydridonitrosyltris(triphenylphosphine)iridium(I) perchlorate, $[IrH(NO)\{P(C_6H_5)_3\}_3]ClO_4$ [245], shows that the cation adopts a distorted trigonal-bipyramidal arrangement, with two PPh_3 ligands in the apical positions; the complex is best formulated as an NO^+ complex of iridium(I).

Some reactions of nitrosyl fluorophosphine complexes of cobalt with alkoxide and hydroxide ions have been studied [246]. Thus, $Co(NO)(PF_3)_3$ reacts with ROH (R = Me, Et, Pr, Me_2CH, Bu and Ph), with total F exchange, to give $Co(NO)[P(OR)_3]_3$ complexes. $Co(NO)(PF_3)_3$ also reacts with a $(Me_2CH)_2 \cdot NH/H_2O$ mixture to yield $(Me_2CH)_2NH_2[Co(NO)(PF_3)_2PF_2O]$, and with $Ba(OH)_2$ in THF to give $Ba[Co(NO)(PF_3)_2PF_2O]_2$, the latter reacts under stronger conditions partially to form $Ba[Co(NO)(PF_3)(PF_2O)_2]$. The difluorophosphito complexes can be alkylated with Et_3OBF_4 to give $Co(NO)(PF_3)_2PF_2OEt$.

Nitric oxide has been found to react with $Co(en)_2(NO)Cl_2$ giving *cis*-$Co(en)_2(NO_2)Cl_2$ and N_2O [247]; similarly $Co(NO)(DMG)_2 \cdot CH_3OH$ (DMG = dimethylglyoximate anion) yields $Co(NO_2)(DMG)_2(py)$ in the presence of pyridine (py). This represents the first example of attack by free NO on coordinated NO which is uncomplicated by other oxidations and, as such, can be thought of as catalysis by cobalt of the disproportionation:

$$3\,NO \longrightarrow N_2O + NO_2$$

In the presence of added ligands B (B = 4-t-butylpyridine, 4-cyanopyridine, 1-methylimidazole and $P(C_6H_5)_3$), cobaloxime nitrosyl $Co(DH)_2NO$ (DH = monoanion of dimethylglyoxime) reacts with molecular oxygen giving the oxygen-bonded nitrato compounds $BCo(DH)_2NO_3$ in amounts greater than 50%, as well as the expected nitro compound and small amounts (<10%) of side products [248]. This compares with the reaction in the absence of ligands B when the nitro complex $(H_2O)Co(DH)_2NO_2$ is formed. The reaction mechanism has not, as yet, been determined.

Polarographic reduction of pentacyanonitrosylcobalt(III) complex is found to be a one electron process, in which one mole of H^+ is consumed by one mole of the complex molecule [249].

The complexes $[Ir(X)_5NO]^-$ (X = Cl or Br) are susceptible to nucleophilic attack at the nitrosyl nitrogen atom; the following reactions have been observed [250]:

$$[Ir(X)_5NO]^- + 2\,OH^- \longrightarrow [Ir(X)_5NO_2]^{3-} + H_2O$$
$$[Ir(X)_5NO]^- + NH_2OH \longrightarrow [Ir(X)_5H_2O]^{2-} + N_2O + H^+$$
$$[Ir(X)_5NO]^- + N_3^- + H_2O \longrightarrow [Ir(X)_5H_2O]^{2-} + N_2O + N_2$$
$$[Ir(X)_5NO^-] + 2\,NH_3 \longrightarrow [Ir(X)_5NH_3]^{2-} + N_2 + H_3O^+$$

Hydrazine hydrate and $[Ir(Br)_5NO]^-$ give $[IrBr_3(N_2H_4)_3] \cdot 0.5\,H_2O$ by an unknown route.

Certain dinitrosyl complexes have been found to be unexpectedly reactive, and the conversion of NO into N_2O and CO into CO_2 in their presence is catalytic and general in scope [251]. To test the generality of reaction i it was carried out in the presence of $IrP_2(NO)_2Br$, $[IrP_2(NO)_2][PF_6]$, $IrP_2(CO)$-

(solvent)$^+$, and their rhodium analogs. The reaction proceeds catalytically, albeit

$$2\,\mathrm{NO} + \mathrm{CO} \xrightarrow{\text{“M(NO)}_2\text{”}} \mathrm{N_2O} + \mathrm{CO_2} \qquad \Delta H(298) = -91.3 \text{ kcal mol}^{-1} \qquad \text{(i)}$$

$$\Delta G(298) = -78.2 \text{ kcal mol}^{-1}$$

slowly, at 20° C. $IrP_2(NO)Br_2$, $CoP_2(NO)_2Br$ and $[CoP_2(NO)_2][PF_6]$ were found to be inactive. It was suggested that the reaction proceeds via intermediates which are best formulated as 18-electron, N—N bonded *cis*-dinitrogen dioxide complexes. Further studies from a different source have led to the same conclusion, and a mechanism has been proposed (Scheme 12) [252].

SCHEME 12.

$$\begin{array}{lcl}
\mathrm{M(NO)_2L_2^+ + CO} & \rightleftharpoons & \mathrm{M(N_2O_2)L_2CO^+} \\
\mathrm{M(N_2O_2)L_2CO^+ + CO} & \rightleftharpoons & \mathrm{ML_2(CO)_2^+ + N_2O_2} \\
\mathrm{M(N_2O_2)L_2CO^+ + 2\,CO} & \rightleftharpoons & \mathrm{ML_2(CO)_2^+ + N_2O + CO_2} \\
\mathrm{N_2O_2} & \rightleftharpoons & \mathrm{2\,NO} \\
\mathrm{ML_2(CO)_2^+ + CO} & \rightleftharpoons & \mathrm{ML_2(CO)_3^+}
\end{array}$$

(M = Rh or Ir)

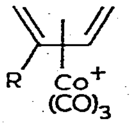
The kinetics of the ^{15}NO exchange with $Co(NO)_2IL$ ($L = P(C_6H_5)_3$ or $As(C_6H_5)_3$) in toluene have been studied; activation parameters have been measured, and the results compared with those for $Fe(NO)_2IL$ [253]. The effect of L on the rate constant indicates that the nitrosyl group behaves in a similar way to the CO group of carbonyl complexes.

The ^{31}P NMR spectra of the catalytically active nitrosyl complexes $MNO(PPh_3)_3$ (M = Co, Rh) and $Rh(NO)Cl_2(PPh_3)_2$ have been measured [254]. Phosphine exchange in $RhNO(PPh_3)_3$ is shown to occur via a dissociative mechanism; the three phosphines in this molecule are chemically equivalent, a result which is consistent with the pseudotetrahedral structures determined for $IrNO(PPh_3)_3$ and $RhNO(PF_3)_3$.

The concept of an inorganic functional group has been applied to the problem of understanding the properties of the $[CoNO]^8$ group in ligand fields of C_{4v}, C_{2v}, and C_s symmetry [255].

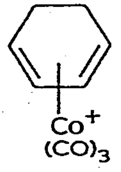
Metal alkene and alkyne complexes

Oxidation of the dimers $[Co(CO)_2(diene)_2]_2$ with $Ph_3C^+BF_4^-$ or iron(II) chloride gives the cations $[Co(CO)_3diene]^+$, 153 (diene = 2-methylbut-1,3-diene or but-1,3-diene) and 154 (diene = cyclohexa-1,4-diene). In the presence of tri-



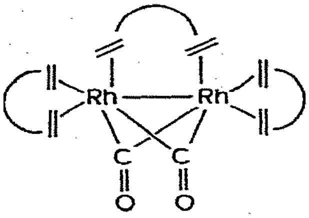
(153)

(R = H, Me



(154)

phenylphosphine mono- and di-substituted salts are obtained [256]. Although the reactions of [$Co_4(CO)_{12}$] or [$Rh_4(CO)_{12}$] with monoalkenes do not afford alkene complexes, reactions with dienes give the complexes [$Rh_6(CO)_{14}$(diene)] (diene = 1,5 COD, NBD, cyclohexa-1,4-diene, 2,3-dimethylbut-1,3-diene), which are best obtained from $Rh_6(CO)_{16}$. Reaction of norbornadiene with $Rh_4(CO)_{12}$ at room temperature gives a complex which may have the structure 155. Reactions of [$Co_4(CO)_{12}$] with dienes give the complexes [$Co_2(CO)_4$(diene)$_2$] which are identical to the complexes prepared from [$Co_2(CO)_8$]. With cycloheptatriene and [$Co_4(CO)_{12}$] two complexes, [$Co_4(CO)_9(C_7H_8)$] which may have structure 156 and [$Co_4(CO)_6(C_7H_8)_2$] are obtained. Cyclooctatetraene gives the fluxional complexes [$Co_2(CO)_4(C_8H_8)$] and [$Rh_4(CO)_8(C_8H_8)_2$] [257]. The dinitrogen complex [$CoH(N_2)(PPh_3)_3$] reacts with $CH_2{=}C(Me){-}C(Me){=}CH_2$ to give 157



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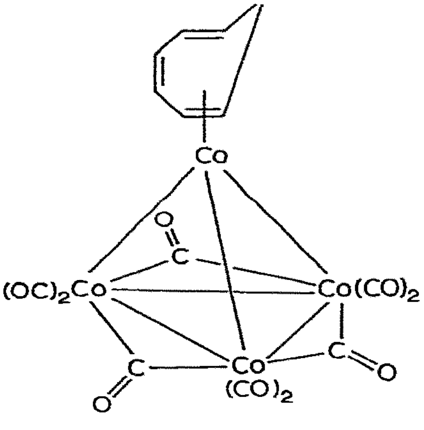

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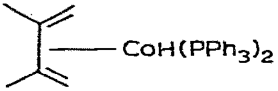
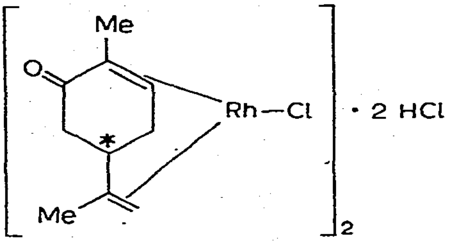


(157)

[258], while the cathodic reduction of cobalt(II) chloride, in the presence of butadiene and P-n-Bu_3, gives [Co(η^3-butenyl)(η^4-butadiene)(P-n-Bu_3)] [259]. However, with triphenylphosphine, heptadienyl complexes are obtained [259].

The hydrides $[CoH(N_2)(PPh_3)_3]$ and $[RhH(PPh_3)_4]$ readily release ethylene from vinyl acetate [260].

Hexa-1,5-diene reacts with aqueous ethanolic $RhCl_3 \cdot xH_2O$ to give [RhCl(hexa-1,5-diene)]$_2$ [261]. The chiral dienone carvone also forms a stable complex with rhodium(I) (158). Analytical data suggest the presence of a di-HCl adduct. The complex **158** undergoes typical bridge splitting reactions with acetylacetonate and cyclopentadienide [262]. The addition of limonene (159) and α-phellandrene (160) to $[RhCl(C_2H_4)_2]_2$, followed by treatment with TlC_5H_5, similarly gives the cyclopentadienylrhodium complexes of these alkenes. These alkenes permit a clear differentiation between the *endo* and *exo* faces of the coordinated diene; protonation in CF_3CO_2H can be shown to occur via *endo* attack to yield monocationic π-allyl species [263].



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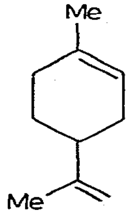

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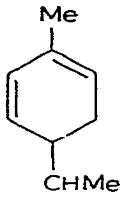
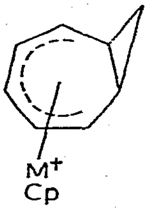


(160)

Although (η-cyclooctatetraene)(η-cyclopentadienyl)-cobalt(I) and rhodium(I) are known to form unstable solutions in concentrated sulphuric acid, the less vigorous protonic acid CF_3CO_2H generates the stable cationic species $[MCp(C_8H_9)]^+$. Initially, the bicyclic cation **161** is produced which subsequently isomerises to **162**. It is proposed that the proton attacks with *endo* stereospecificity. At low temperatures protonation of the iridium complex gives the hydride $[IrH(Cp)(C_8H_8)]^+$ [264].



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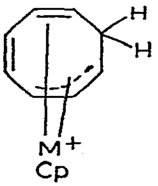
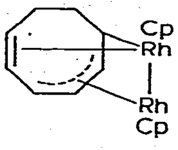


(162)

The complexes **163** and **164** have both been prepared and in solution the complexes undergo an oscillation, **165** ⇌ **166** (X = CH_2 or CH_2CH_2). Protonation



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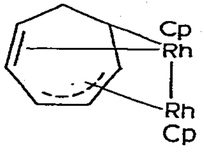

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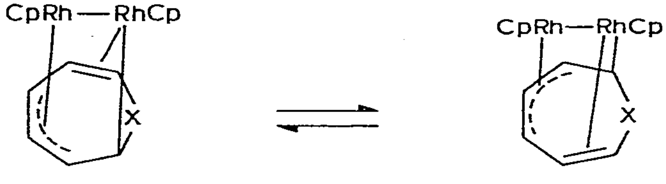


(165) (166)

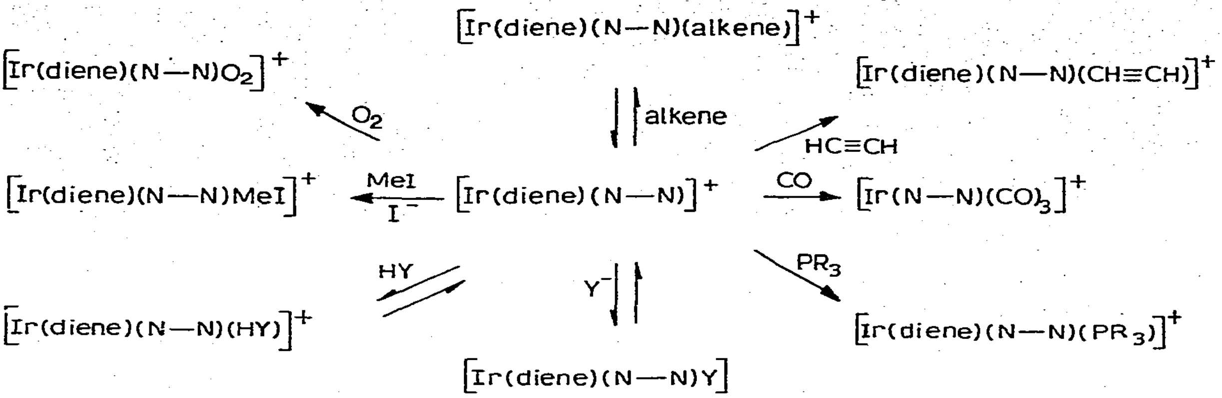
(X = CH_2 or CH_2CH_2)

gives the bridged hydride cationic complexes $[CpRh(\mu\text{-}C_7H_8)(\mu\text{-}H)RhCl]^+$ and $[CpRh(\mu\text{-}C_8H_{10})(\mu\text{-}H)RhCp]^+$. This causes an increase in the energy barrier to oscillation for the cyclooctadienyl complex whilst the bonding in the cycloheptadienyl complex changes to the 1-3η : 4-6η type [265].

Acetylacetonatorhodium(I) complexes of *meso*- and (±)-3,4-dimethylhexa-1,5-diene do not undergo thermal interconversion or Cope rearrangements and their stability is probably kinetic in origin [266].

Although $[RhCl(CO)_2]_2$ does not react under reflux with cyclopentene, cyclohexene or *trans*-cyclododecene, *cis*-cyclooctene readily reacts to give $[RhCl(CO)(C_8H_{14})]_2$. Mixed carbonyl-cyclooctene complexes also result via ligand exchange reactions ($[RhCl(CO)_2]_2$ + $[RhCl(C_8H_{14})_2]_2$ and $[Rh(acac)(CO)_2]$ + $[Rh(acac)(C_8H_{14})_2]$) and it appears that cyclooctene forms strong complexes with rhodium(I). The reaction of norbornene with $[RhCl(CO)_2]_2$ does not lead to CO displacement but gives the adduct $[RhCl(CO)_2(nb)]_2$. An interesting reaction occurs with norbornene and rhodium(III) chloride to give the rhodium(III) complex $[RhCl_2(C_7H_9)(C_7H_{10})]_2$ [267]. The complex $[RhCl(CO)(C_2H_4)]_2$ reacts with amine ligands to produce the dinuclear five-coordinate complexes $[RhCl(CO)(C_2H_4)(amine)]_2$ (amine = 2,6-lutidine, $NHEt_2$) [172, 268]. The rates of displacement of piperidine by a series of amines from the complex [RhCl(COD)(piperidine)] in methanol have been determined [269]. The cations $[Ir(diene)(N—N)]^+$ undergo various substitution and oxidative reactions, some of which are illustrated in Scheme 13. In general, complexes with norbornadiene react more rapidly than the corresponding cycloocta-1,5-diene derivatives. They also give more stable oxidative addition products and pentacoordinated adducts [270]. Some unusual tricoordinated complexes, $[Rh(N—N)(alkene)]PF_6$, result from the action of fumaronitrile and tetracyanoethylene upon the complexes $[Rh(CO)_3(N—N)]PF_6$ (N—N = bipy or *o*-phen). The fumaronitrile ligand but not TCNE is displaced by CO, cycloocta-1,5-diene and norbornadiene. Complexes of the type $[Rh(N—N)_2(alkene)]PF_6$ (alkene = CH_2=CHCN, CHCN=CHCN, TCNE, maleic

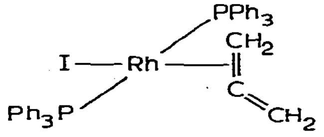
Scheme 13



(diene = 1,5-COD, NBD
N—N = bipyridyl or *o*-phenanthroline
alkene = C_2H_4, C_3H_6, CH_2=CHCN, CHCN=CHCN, TCNE, butadiene)

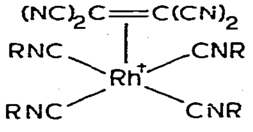
anhydride) result from the action of the alkene and the N—N ligand upon $[Rh(CO)_3(N—N)]PF_6$ [174].

The dimers $[RhClL_2]_2$ (L = PPh_3, $P(C_6H_4Me\text{-}p)_3$) are cleaved by ethylene, but not cyclohexene, to give the ethylene complexes $[RhCl(C_2H_4)L_2]$ [191]; the tricyclohexylphosphine complex has also been obtained [191]. The crystal structure of $[RhI(allene)(PPh_3)_2]$ (167) has been described [271]. The isocyanide



(167)

complexes $[Rh(CNR)_4]X$, $[Rh(CNR)_2(PPh_3)_2]X$ and $[Rh(CNR)(PPh_3)_3]Cl$ react with tetracyanoethylene or fumaronitrile to give the alkene complexes $[Rh(CNR)_4(TCNE)]X$ (168) (X = BPh_4, R = Me; X = ClO_4, R = *p*-$MeOC_6H_4$, *o*- and *p*-MeC_6H_4, *p*-ClC_6H_4) $[RhI(CNR)_2(PPh_3)(alkene)]$ and $[Rh(CNR)_2(PPh_3)_2(alkene)]ClO_4$ and $[RhCl(CNR)(PPh_3)_2(TCNE)]$. The TCNE adduct 168 exhibits temperature dependent NMR spectra which have been interpreted in terms of rotation of the TCNE in a square-pyramidal complex. The other complexes are rigid and it is suggested that these may have structures based on a trigonal-bipyramidal co-



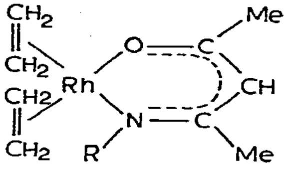
(168)

ordination [272]. Enthalpies of the dissociation reactions:

$$[IrX(CO)(PPh_3)_2L]\,(s) \longrightarrow [IrX(CO)(PPh_3)_2]\,(s) + L(g)$$

reveal that the stabilities of tetrafluoroethylene and hexafluorobut-2-yne (L) adducts follow the order F > Cl > Br < I [273]. This is somewhat different to the trends found for dioxygen complexes [233].

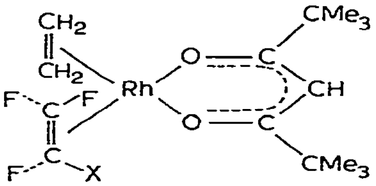
Diethylene complexes of the type **169** have been prepared. An examination



(169)

$(R = Me, Ph, MeC_6H_4, ClC_6H_4, BrC_6H_4, MeOC_6H_4, O_2NC_6H_4)$

of their ^1H NMR spectra indicate that the mobility of coordinated ethylene about the coordination bond is greater in 2,4-pentanedione complexes than in the complexes **169**. In these latter complexes, ethylene *cis* to nitrogen is more mobile than that in the *trans* position [274, 275]. The fluoroolefin complexes **170** have been prepared and ^{19}F NMR studies show that the fluoroolefin ligand is rigidly bound,



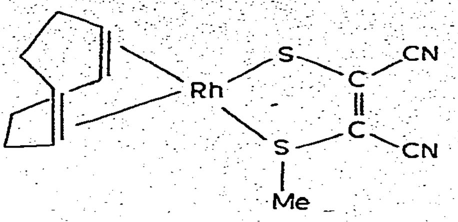
(170)

$(X = F, CF_3, Cl, Br)$

and that the X substituent lies in an "outside" position with respect to the ethylene ligand [276]. The polypyrazolylborate complexes $[Rh(C_2H_4)_2(RBPz_3)]$ (R = H, Pz) and the corresponding cycloocta-1,5-diene complexes exhibit fluxional behaviour. The ethylene ligands are displaced by phosphines, N_2 and CO but only the latter yields stable adducts. Mercury(II) chloride adducts $[Rh(alkene)_2(HBPz_3) \cdot HgCl_2]$ can also be obtained [166, 167].

Treatment of the chloro-bridged dimers $[RhCl(diene)]_2$ (diene = 1,5-COD, NBD) with $Na_2(mnt)$ gives the dithiolene complexes $[Rh(diene)(mnt)]^-$. Treatment of the anions with MeI gives the fluxional molecules [Rh(diene)(mnt)Me] which are shown by X-ray crystal structure analysis to possess a methylated sulphur (**171**). Reversible adducts of the anions with SO_2 are formed [277]. The crystal structures of the pentacoordinated fluxional molecule $[IrSnCl_3(NBD)(PMe_2Ph)_2]$ [278], which has a geometry midway between trigonal-pyramidal and square-pyramidal, and **172** [279] have been determined.

Treatment of the appropriate π-ethylene metal complex of rhodium(I) or iridi-



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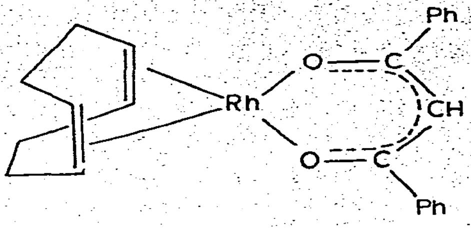
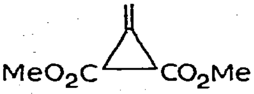


(172)

um(I) with *trans* and *cis* isomers of Feists acid dimethyl ester (**173a** and **173b**) gives the complexes [Rh(alkene)$_2$L] (alkene = **173a**, **173b**; L = Cl, acac, Cp) and [Ir(alkene)$_2$(acac)] (alkene = **173a**) [280]. Treatment of [Rh(acac)(C$_2$H$_4$)$_2$] with allene at —78° C gives a yellow precipitate of [Rh(acac)(C$_3$H$_4$)$_3$], unstable at 0° C, which reacts with pyridine to give **174**. However, if the triallene intermediate is kept at 0° C, a polymeric product [Rh(acac)(C$_3$H$_4$)$_2$] is formed which reacts with triphenylphosphine to give **175**. The complexes **174** and **175** have



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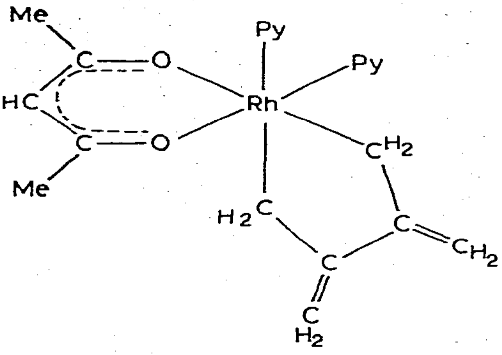

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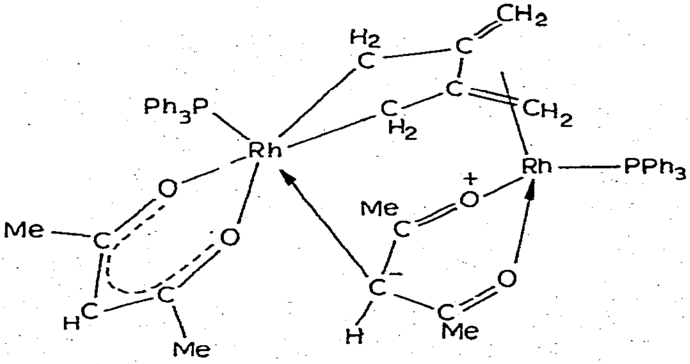


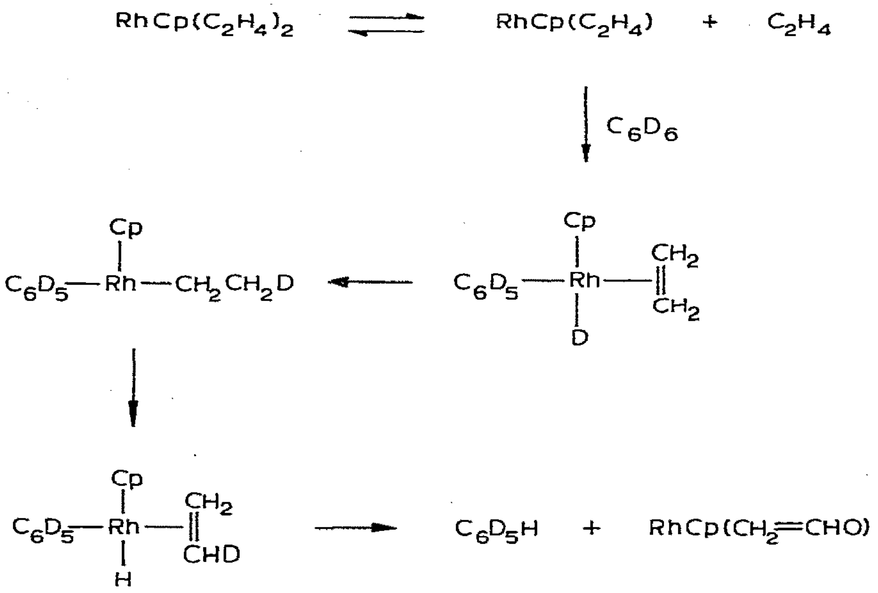
(175)

been characterised by X-ray methods, both products containing a metallocyclopentane ring; which is considered to be involved in certain catalytic reactions of allene. The complex **175** contains a rather unusual bridging acac ligand [281].

The reaction of acrolein with [RhCl(cyclooctene)$_2$]$_2$ in the presence of diphos or bipyridyl is reported to give the complexes [$RhCl(CO)(CH_2{=}CH_2)(CH_2{=}CHCHO)(diphos)$] and [$RhCl(CH_2{=}CHCHO)_2(bipy)$] [282]. Sodium diethyldithiocarbamate cleaves the dimers [$MCl(C_8H_{14})_2$] (M = Rh, Ir) to give the cyclooctene complexes [$M(dtc)(C_8H_{14})_2$]. Similarly from [$IrCl(COD)(C_2F_4)]_2$, [$Ir(dtc)(COD)(C_2F_4)$] can be obtained. An interesting product [$Ir(dtc)_3(COD)$], which may contain one bidentate and two monodentate ligands, can be obtained from [$Ir(dtc)(COD)$] and tetraethylthiuram disulphide [283].

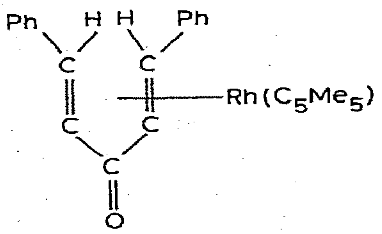
An interesting hydrogen—deuterium exchange reaction occurs when [$Rh(C_2H_4)_2(\eta^5\text{-}C_5H_5)$] is heated with C_6D_6. At 130°C deuterium is introduced into both the cyclopentadienyl and ethylene groups. The reaction may proceed via oxidative addition of C_6D_6 to the rhodium (Scheme 14) [284].

Scheme 14



The crystal structure determination of **176** shows that the dibenzylideneacetone ligand is in the *s-cis,s-cis* conformation [285].

Hexaphenylcarbodiphosphorane ($Ph_3P{=}C{=}PPh_3$) induces self metallation of [$Ir(COD)$]PF_6 and [$Ir(cyclooctene)$]PF_6 to give products formulated as **177** and **178** [286].



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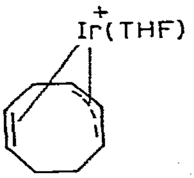

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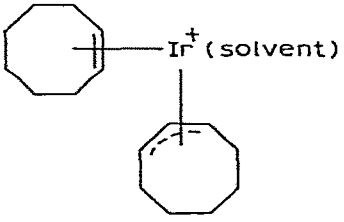


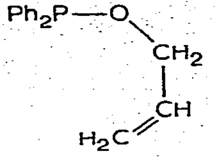
(178)

The phosphines bdpp (179) and dppp (180) react with either $[RhCl(C_2H_4)_2]_2$ or $[RhCl(C_8H_{12})]_2$ to give the halogen-bridged complexes 181 and 182, which undergo halogen bridge cleavage reactions with TlCp. The acetylacetonato derivatives, which react with air in the solid state, are best obtained via $[Rh(acac)(C_2H_4)_2]$. Two possible configurations for the phosphorusbutene part of the ligand has been established by X-ray structure determinations on $[RhCl(bdpp)]_2$ and $[RhClP(CH_2CH_2CH{=}CH_2)_3]$ [287, 288]. The preferred configuration, in which the C=C axis is perpendicular to the Rh—P bond, is found for both complexes, but a second configuration in which the C=C bond is parallel to the Rh—P bond also occurs in $[RhCl(bdpp)]_2$.

$Ph_2PCH_2CH_2CH{=}CH_2$

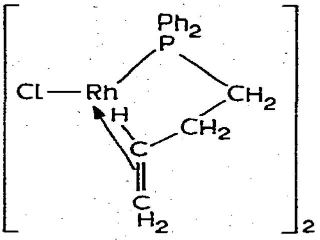
(179)

(bdpp)



(180)

(dppp)



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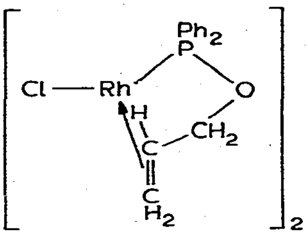
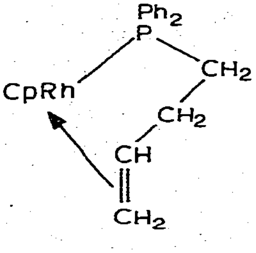


(182)

The complexes 183 and 184 react with chlorine or bromine to yield dihalide adducts with a non-coordinating alkene linkage. Methyl halides primarily give ionic products which contain Rh—alkene and Rh—Me bonds. However, in reaction with 183 small amounts of the cyclic complexes 185 and possibly 186 are formed. Treatment of the ionic product 187 with methoxide also yields a cyclic product (188). The complex 184 does not react with organo halides but, in contrast to 183, does react with CO [289].



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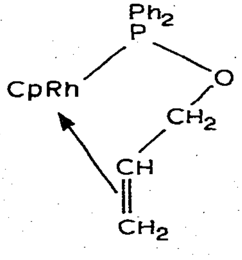

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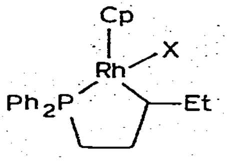

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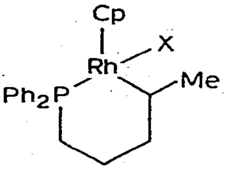

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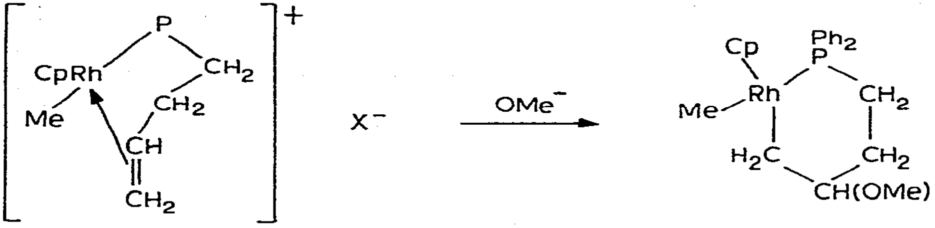
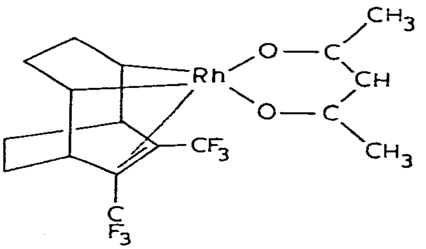


(187) (188)

Hexafluorobut-2-yne reacts with $[RhCl(COD)]_2$ to give the adduct $[RhCl(COD)(C_4F_6)]$ in which the hexafluorobut-2-yne has added 1,4 to the coordinated diene. Treatment of the adduct with sodium acetylacetonate gives **189** which has been characterised crystallographically. In contrast, [Ir(acac)(COD)] reacts with hexafluorobut-2-yne to give the metallocyclopentene **190**, in which a second molecule



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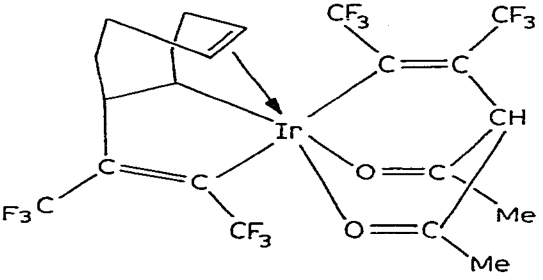
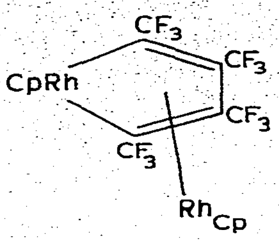


(190)

of hexafluorobut-2-yne has been added 1,4 to the β-ketoenolate ring [290]. A review of the compounds derived from alkynes and carbonyl complexes of cobalt has been published [291]. In reactions between $[MCp(CO)_2]$ (M = Co, Rh) and but-2-yne, a cyclopentadienone complex $[MCp(C_4Me_4CO)]$ is usually formed as a major product. Much smaller amounts of duroquinone complexes $[MCp(C_4Me_2\text{-}C_2O_2)]$ are obtained. However, with reactions involving hexafluorobut-2-yne a tetrahaptobenzene complex $[MCp\{C_6(CF_3)_6\}]$ is formed as a major product when M = Rh and as a minor product when M = Co. A metallocyclopentadiene complex **191** exhibits fluxional behaviour, as has been found previously for this type of complex [292].

Treatment of the alkyne complex **192**, which is a possible intermediate in the formation of cyclobutadiene complexes, gives **193** which can also be obtained from



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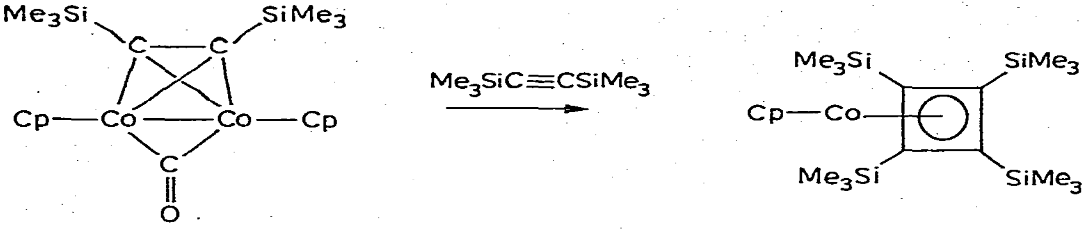
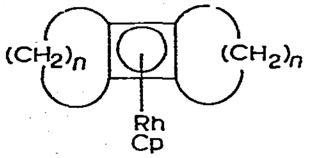


(192) **(193)**

cobaltocene and the alkyne [293]. Cyclobutadiene complexes **194** also result from the reaction of the macrocyclic acetylenes **195** with [RhCp(CO)$_2$]. Simple acetylenes, however, do not give cyclobutadiene complexes. Thus, hex-3-yne gives **196** and **197**, diphenylacetylene gives **198**, analogous to [Fe$_3$(CO)$_9$-(PhC≡CPh)]. In these reactions, carried out in boiling cyclooctane, some of the cycloocta-1,5-diene complex [RhCp(COD)] is formed, apparently arising via a



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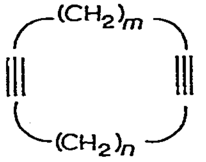
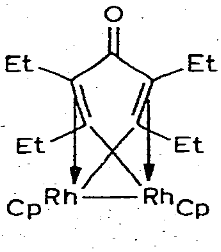


(195)

($m = 4$; $n = 4,5,6$
$m = 5$; $n = 5$)



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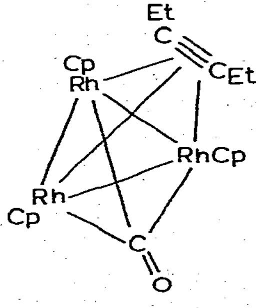

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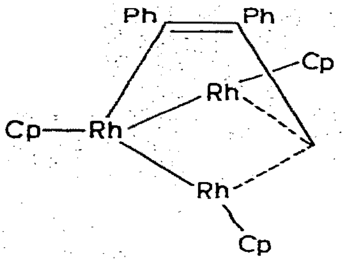

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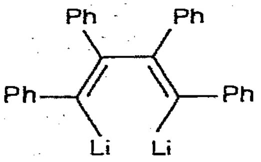
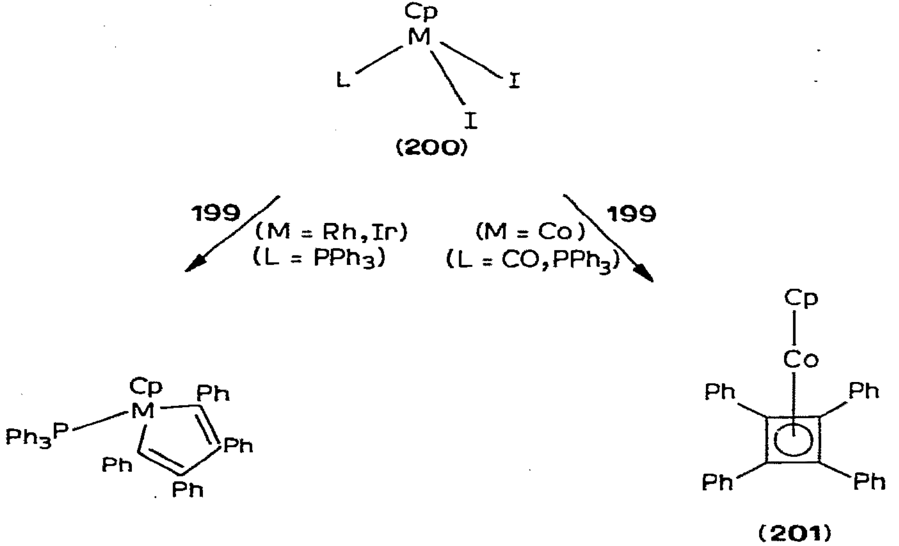


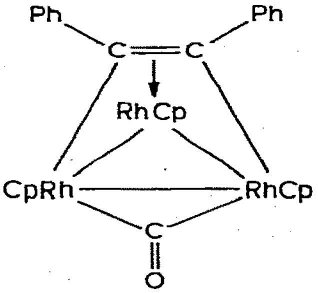
(199)

hydrogen abstraction reaction from the solvent [294].

The reactions of alkynes with low-valent metal complexes often lead to metallocyclopentadiene complexes (Scheme 15). Complexes of this type have now been obtained from the action of the dilithiocompound **199** upon the rhodium and iridium diiodides **200**. However, reaction of the cobalt complexes **200** (L = CO, PPh_3) with **199** gives the cyclobutadiene complex **201**, a result which lends support to the idea that metallocyclopentadiene complexes could be intermediates in the formation of cyclobutadiene complexes. Similarly, the observation that the reaction of $[RhI_2Cp(CO)]$ with the dilithio reagent **199** gives **202**, analogous to **197**,

Scheme 15

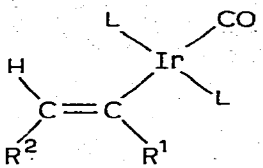




(202)

which again suggests that metallocyclic intermediates are involved in the reaction of acetylenes with low-valent metal complexes [295].

Four-coordinate alkenyl complexes **203** result when $[IrH(CO)(PPh_3)_3]$ is treated with hexafluorobut-2-yne and dimethyl acetylenedicarboxylate. The four-coordinate complexes react avidly with oxygen. At higher temperatures (50—80° C), and using an excess of the alkyne, σ-alkenyl-π-alkyne complexes **204** are formed which react further to give the metallocyclic complexes **205**.



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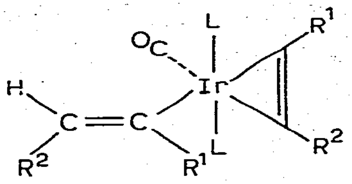
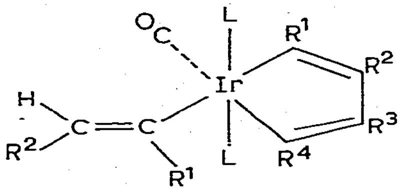


(204)

($R^1 = R^2 = CN, CF_3, COOMe, Ph$; $R^1 = Ph$, $R^2 = COOEt$)

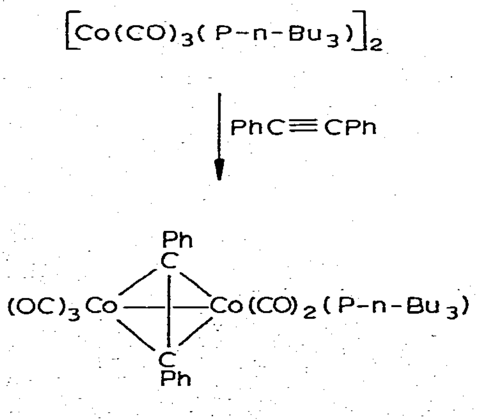


$R^1 = R^2 = CF_3$,
$R^3 = R^4 = COOMe$;
$R^1 = R^2 = COOMe$; $R^3 = Ph$,
$R^4 = COOEt$

(205)

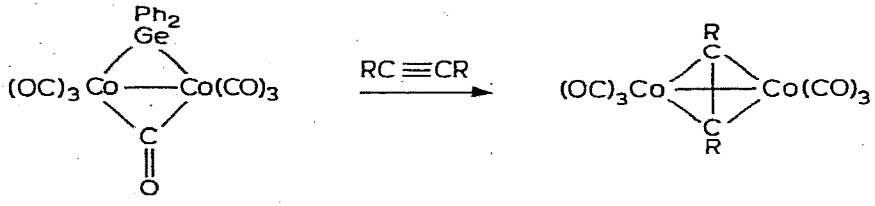
These complexes are excellent catalysts for the cyclotrimerisation of disubstituted alkynes and they are more effective catalysts than complexes in which the alkenyl ligand is replaced by chloride [296].

Kinetic studies on the reaction of diphenylacetylene with $[Co(CO)_3(P\text{-n-}Bu_3)]_2$ in decalin reveal that the reaction occurs in two stages. The initial product is the alkyne-bridged complex **206** which then reacts with the released tri-n-butyl-



(206)

phosphine to form $[Co_2(\mu\text{-}C_2Ph_2)(CO)_4(P\text{-}n\text{-}Bu_3)_2]$ [297]. Bridged alkyne complexes $[(CO)_3Co(\mu\text{-alkyne})Co(CO)_3]$ also result from the action of C_2Ph_2, MeC_2Ph, PhC_2H and $C_2(CO_2Et)_2$ upon **207**. Kinetic studies on these reactions are consistent with a process that involves initial reversible ring opening of **207** to form $(CO)_3Co(\mu\text{-}GePh_2)Co(CO)_4$, analogous to the reactions of **207** with CO and phosphines [298]. Kinetic studies on the carbonyl substitution reaction of **208** (R = Ph), with $P\text{-}n\text{-}Bu_3$ have also been published [299]. Electron impact measurements suggest that dissociation energies of Co—CO bands in complexes of type **208** are mainly dependent upon the π-acceptor ability of the ligand and exhibit the sequence $R = CF_3 < H < Me$ [300]. The ^{13}C NMR spectrum of **208** (R = Ph) has been studied [301].



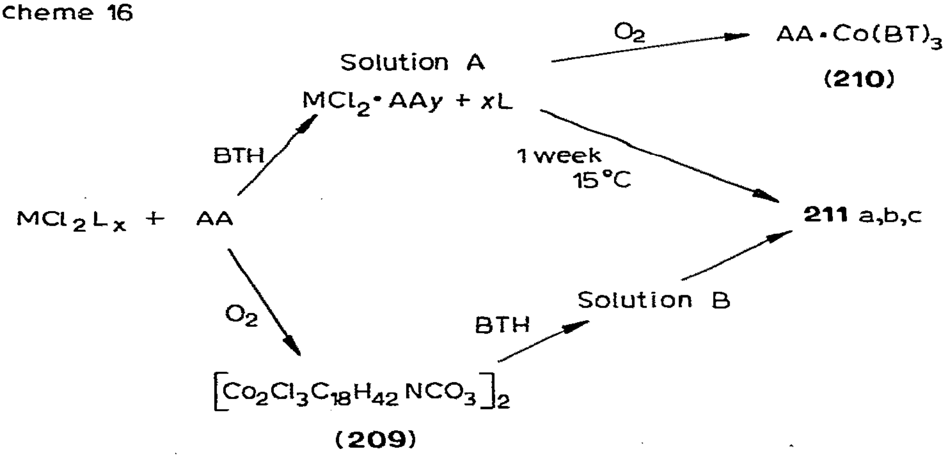
(207) (208)

Metal π-allyl complexes

A review of metal π-allyl compounds has been published [302].

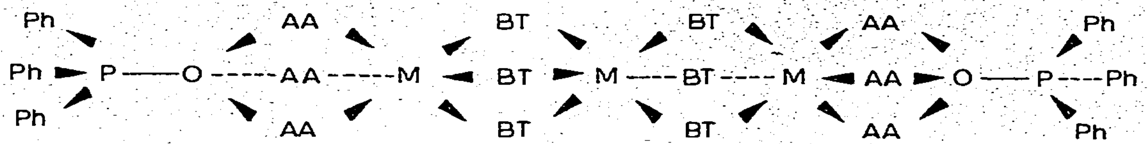
The absorption of oxygen by solutions of $(PPh_3)_2CoCl_2$ in allylamine, in the presence of heterocyclic ligands, has been studied [303]. (Scheme 16). The nature of the various reactions is discussed, but the most striking observation is the formation of a binuclear complex **211** from Co (or Ni).

Scheme 16



(M = Co or Ni, L = PPh , $x = 2$; L = α,α'-bipyridyl, $x = 1$

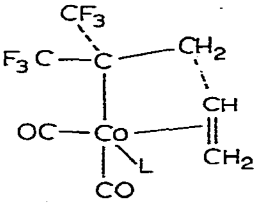
AA = allylamine, BT = benzotriazole)



(**211** a , M = Co ; b , M = Ni ;
c , M = Ni , PPh_3 as ligand instead of Ph_3PO)

A series of complexes $[CoL(PF_3)_3]$ (L = 1,3-π-(1-methylallyl),-(1,1-dimethylallyl), -(1,2-dimethylallyl), -(1,3-dimethylallyl), -cyclooctenyl, and -cycloheptadienyl) have been prepared by low-pressure ligand displacement reactions [304]. ^1H and ^{19}F NMR studies indicate the absence of intermolecular phosphine exchange. These complexes react with hydrogen chloride over several weeks at room temperature, giving cobalt(II) chloride, trifluorophosphine and a chloroalkane. Treatment of the 1,1-dimethylallyl derivative with dihydrogen and excess PF_3 did not lead to any detectable amounts of $[CoH(PF_3)_4]$. These reactions with hydrogen chloride and dihydrogen contrast sharply with those of the analogous rhodium complexes. The 1-3-π-(1,1-dimethylallyl) complex undergoes a novel thermal isomerisation to the *anti*-1,2-complex. The compound $[Co(\pi\text{-}C_7H_9)(PF_3)_2]$ contains a 1-5-π-cycloheptadienyl group.

Bis(trifluoromethyl)diazomethane, $(CF_3)_2CN_2$, reacts with tricarbonyl-(π-allyl, π-2-methylallyl or π-1-methylallyl)cobalt to form compounds **212**, **213**, **214** and **215** respectively (L = CO), the latter being a minor product only [305].



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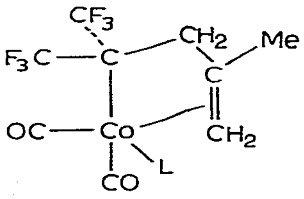

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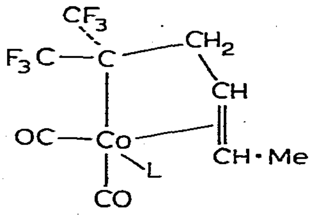

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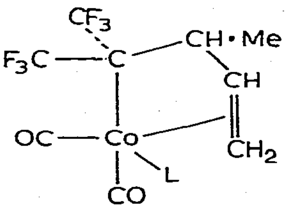
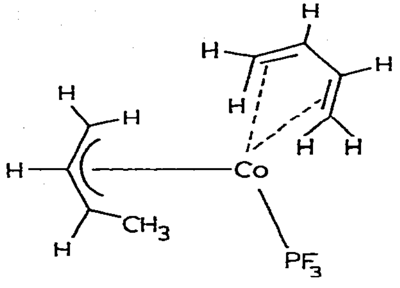


(215)

These complexes all react with triphenylphosphine or triphenylarsine, by displacement of carbon monoxide, to give **212**, **213**, **214**, **215** (L = PPh_3 or $AsPh_3$).

Tris(π-pentenyl)iron was obtained in 13% yield by treatment of an ethereal solution of pentenylmagnesium chloride with $FeCl_3$; tris(π-pentenyl)cobalt was prepared in 30% yield by an analogous procedure [306]. A toluene solution of the cobalt complex is stable up to 23° C.

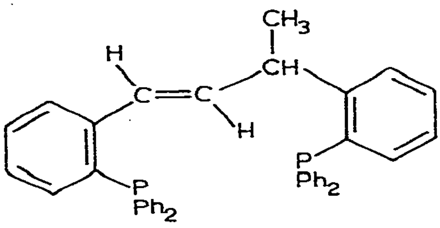
The new hydrido complexes $CoH(PF_3)_{4-n}(PPh_3)_n$ (n = 1—3) have been prepared by low pressure routes [307]. Reaction of $CoH(PF_3)(PPh_3)_3$ with butadiene, in a sealed tube at 60° C for two hours, yields the volatile complex *anti*-1-methyl-π-allylbutadiene(trifluorophosphine)cobalt(I), $Co(\pi\text{-}C_4H_7)(C_4H_6)(PF_3)$, (216). The hydrido complexes are active catalysts for the isomerisation of



(216)

1-octene to 2-octene under hydrogen or nitrogen.

Reaction of the ligand 217 with $RhCl_3$ in 1/1 mole ratio results in deprotonation and coordination of the double bond, giving the allylic complex 218 [308].



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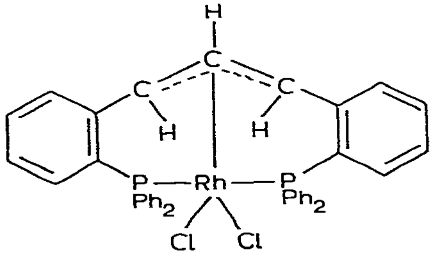


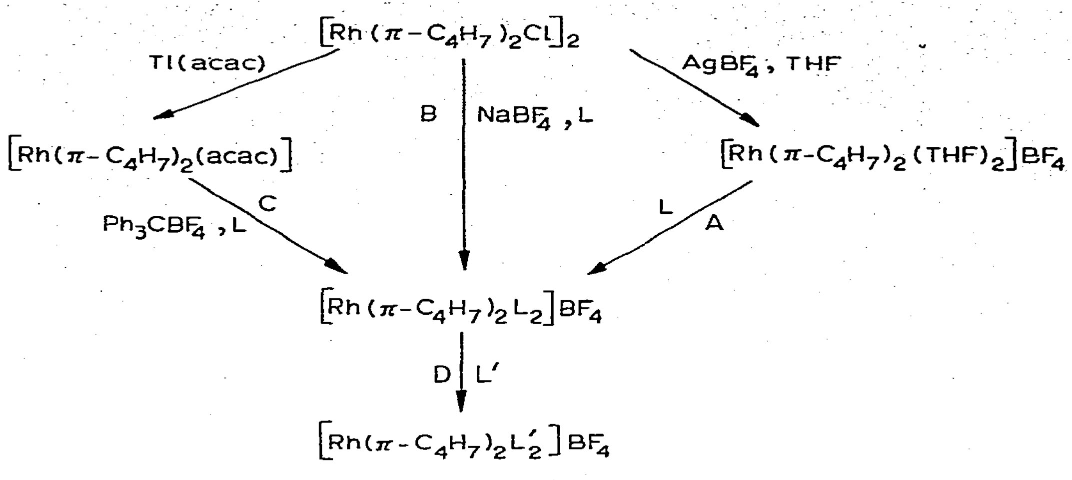
(218)

In contrast to this, $IrCl_3$ gives a chelate olefin complex in which the methine proton remains intact.

A series of (1-3-η-allyl)tris(trifluorophosphine)rhodium(I) complexes have been prepared [309]. Thus, tris(1-3-η-allyl)rhodium(III) reacts with a large excess of PF_3 to give (1-3-η-allyl)tris(trifluorophosphine)rhodium(I); this can also be prepared from $[RhH(PF_3)_4]$ and allene, or from $K[Rh(PF_3)_4]$ and allyl bromide. Addition of $[RhH(PF_3)_4]$ to buta-1,3-diene, or of $L[Rh(PF_3)_4]$ to but-2-enyl bromide gives the 1-3-η-methallyl complex in both *syn* and *anti* forms In a similar way the 1-3-η-cyclohexenyl, 2-methylallyl, 1,2-dimethylallyl (*syn* and *anti* forms) 1,1-dimethylallyl, 1,3-dimethylallyl (*syn,syn* and *anti,syn* forms) and 1-ethyl-3-methylallyl (*syn,syn* and *syn,anti* forms) complexes were prepared. NMR evidence establishes that these complexes undergo inter- and intramolecula phosphine ligand exchange.

The cationic bis-(π-allyl) or -(π-2-methylallyl) complexes $[M(all)_2L_2]BF_4$ (M = Rh or Ir; L = phosphine, phosphites, arsine, pyridines, and MeCN), the neutral complexes $[M(all)_2(tpl)]$ (M = Rh or Ir; tpl = tropolonate) and $[Rh(all)_2(pyc)]$ (pyc = pyridine-2-carboxylate) have been made (Scheme 17) [310]. The scheme

Scheme 17. Cationic complexes

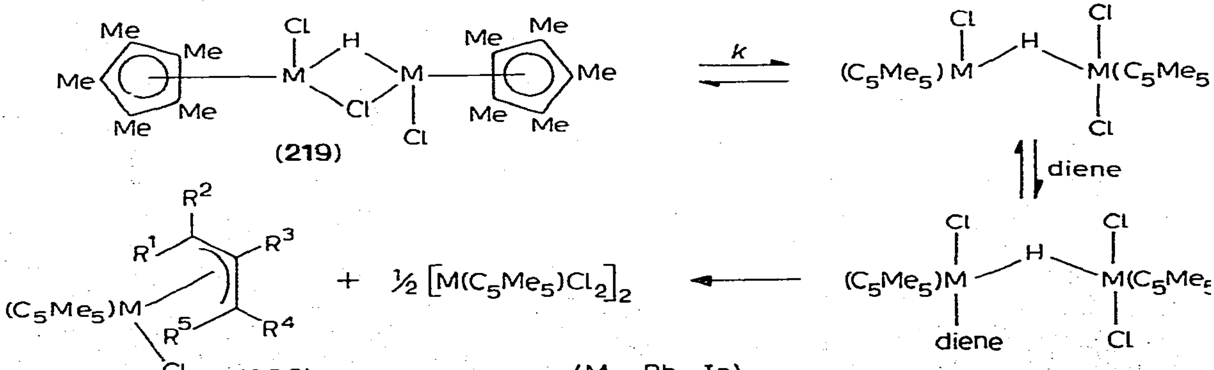


(THF = tetrahydrofuran)

shows the methods used to prepare the cationic complexes, using the 2-methylallyl system as an example. Method A was the most useful, whereas method B could only be used for the stronger ligands. Route C involved isolation of the intermediate acetylacetonate complex, and D involved replacement of the more weakly bonded ligands by other ligands. The iridium cations were prepared by route A. The tropolone species were prepared by reaction of $[M(all)_2Cl]_2$ with tropolone in the presence of base; similarly $[Rh(all)_2(pyc)]$ was made from $[Rh(\pi\text{-2-methylallyl})_2Cl]_2$, 2-picolinic acid and base. NMR spectra of these complexes show that two equivalently bonded π-allyl ligands are asymmetrically bonded to each atom. The dynamic behaviour of the complexes in solution has been studied by variable temperature ^1H NMR spectroscopy.

Reaction of the bridged metal hydrides **219** with a series of 1,3-dienes, gives the η-allylic complexes **220** [311], data obtained for a series of dienes (e.g. isoprene, 2,3-dimethylbutadiene, cycloocta-1,3-diene etc.) are consistent with the mechanism shown in Scheme 18. The ease with which these compounds (**220**) undergo elimination (—HCl) to give $[M(C_5Me_5)diene]$ depends on the positions of the substituents on the allyl ligand.

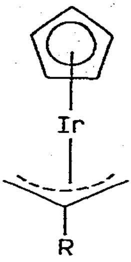
Scheme 18



(220)

(M = Rh, Ir)

Allylation of $[(\pi\text{-}C_5H_5)IrI_2]_2$ with $CH_2{=}C(R)CH_2 \cdot HgCl$ (R = H, Me) in MeOH at 25° C affords 61—62% of adducts 221 → HgI_2, which can be converted to 221



(221)

by the action of $Na_2S_2C_3$ in acetone at 25° C [312].

The crystal structure of di-μ-chlorobis[chloro{2-hydroxymethyl)pent-4-enyl}-rhodium(III)] · methanol has been determined [313]. The complex is dimeric, but the central Rh_2Cl_2 ring is non-planar. The hydroxyl groups of the organic ligands and of the solvent methanol molecule are involved in hydrogen bonding.

Further studies on the structure of di-π-cyclopentadienylmolybdenumbis-(μ-methanethiolato)di-π-allylrhodium hexafluorophosphate, $C_{18}H_{26}MoRhS_2PF_6$, show that the compound does not have an intramolecular metal—metal bond [314]. Single crystal X-ray studies on π-allylbis(triisopropylphosphine)iridium(I) indicate that the coordination of the Ir atom is distorted planar [315].

The σ- and π-allylcobalt(III) polycyanides $K_3[\sigma\text{-}C_3H_4RCo(CN)_5]$, $K_2[\pi\text{-}C_3H_4\text{-}RCo(CN)_4]$ and $K[\pi\text{-}C_3H_4RCo(CN)_3PPh_3]$ (R = H or Me) have been fully characterised after preparation as shown [316]:

$$\pi\text{-}C_3H_4RCo(CO)_3 + I_2 + 4\ KCN \rightarrow K_2[\pi\text{-}C_3H_4RCo(CN)_4] + 3CO + 2\ KI$$

$$\pi\text{-}C_3H_4RCo(CO)_2PPh_3 + I_2 + 3\ KCN \rightarrow K[\pi\text{-}C_3H_4RCo(CN)_3PPh_3] + 2CO + 2\ KI$$

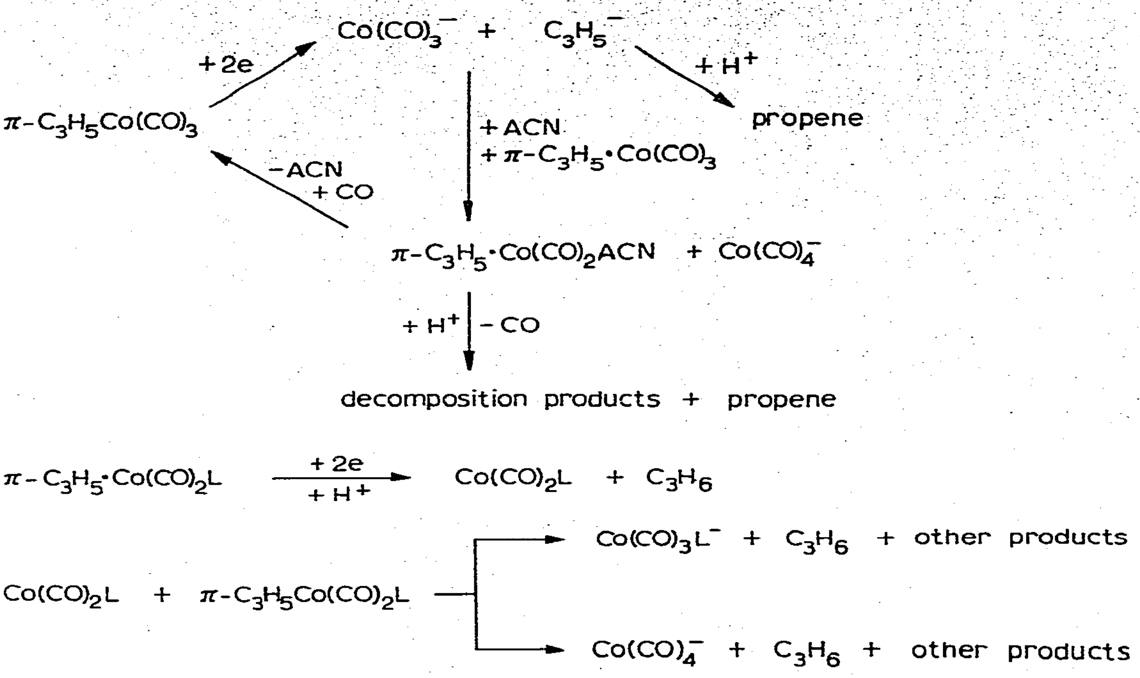
Use of excess cyanide gave the salts of the σ-complexes $K_3[C_3H_5Co(CN)_5]$ and $K_3[C_3H_4MeCo(CN)_5]$.

The polarographic reduction in acetonitrile (ACN) of $\pi\text{-}C_3H_5Co(CO)_3$ and $\pi\text{-}C_3H_5Co(CO)_2L$ (L = $P(OPh)_3$, $P(OCH_2)_3CC_2H_5$, $P(Ph)_3$, $P(OEt)_3$, P-n-Bu_3, $P(C_6H_{11})_3$) has been studied [317]. The proposed reduction mechanisms are illustrated in Scheme 19. The first step corresponds to a transfer of two electrons into an orbital of the metal—allyl bond, leading to homolytic cleavage of the bond.

The first unequivocal demonstration of catalysis of aromatic hydrocarbon hydrogenations with a discrete metal complex has been reported [318]. Using π^3-C_3H_5-$Co[P(OCH_3)_3]_3$, catalytic hydrogenation of benzene to cyclohexane, alkylbenzenes to alkylcyclohexanes, anisole to methoxycyclohexane, ethyl benzoate to ethyl cyclohexenylcarboxylate and furan to tetrahydrofuran was achieved. A mechanism has been proposed for these hydrogenation reactions.

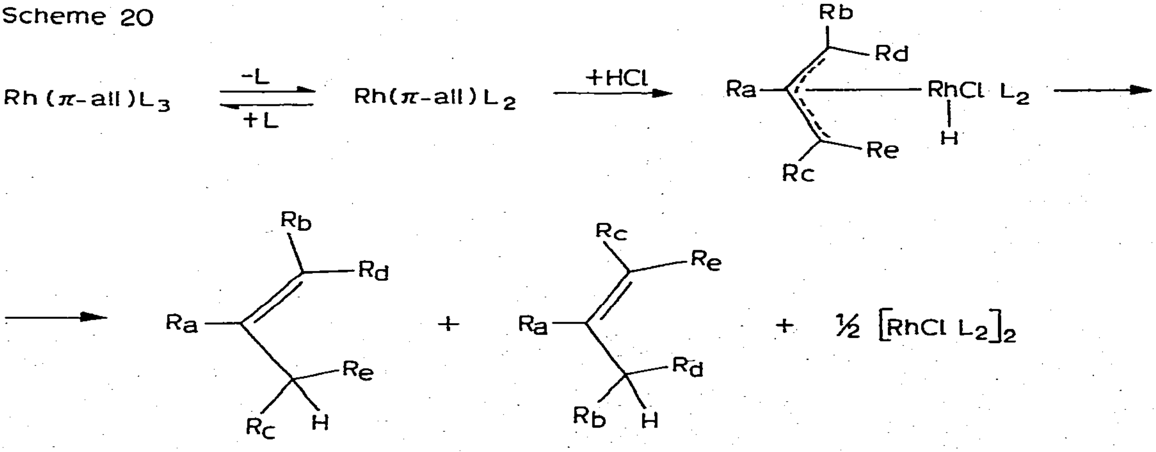
π-Allylic hydridorhodium(III) intermediates have been postulated in the reaction of hydrogen chloride with π-allylic tris(trifluorophosphine)rhodium(I) complexes $Rh(\pi\text{-all})(PF_3)_3$ (all = C_3H_5, cyclohexenyl, 2-methyl-π-allyl, *syn*-1-methyl-π-allyl, 1,1-dimethyl-π-allyl, *syn*-1,2-dimethyl-π-allyl, *syn*-1,3-dimethyl-π-allyl

Scheme 19



and *syn*-1-ethyl-3-methyl-π-allyl) to yield $[RhCl(PF_3)_2]_2$, PF_3 and the corresponding olefin [319]. For the case when all = C_3H_5, a π-allylic hydridorhodium(III) intermediate has been characterised by ^{19}F and ^1H NMR spectroscopy, leading to a proposed mechanism (Scheme 20). Reaction of $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ with hydrogen and PF_3 at room temperature gives $RhH(PF_3)_4$, and with NO or NOCl gives $Rh(NO)(PF_3)_3$.

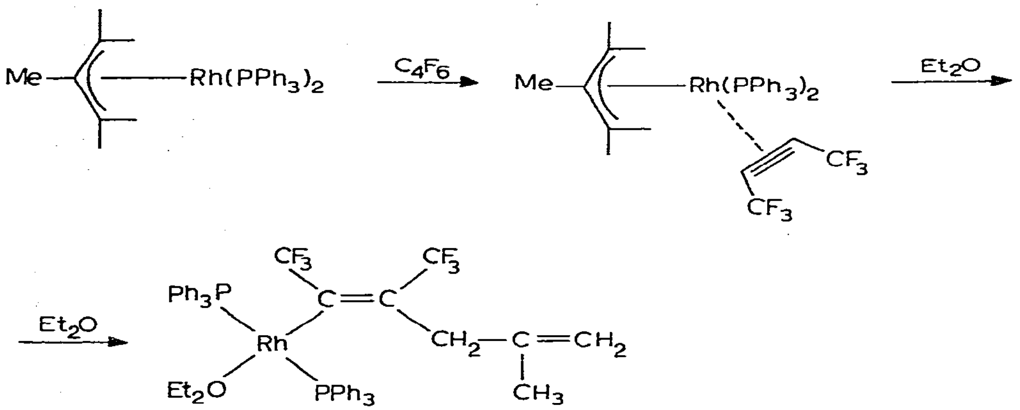
Scheme 20



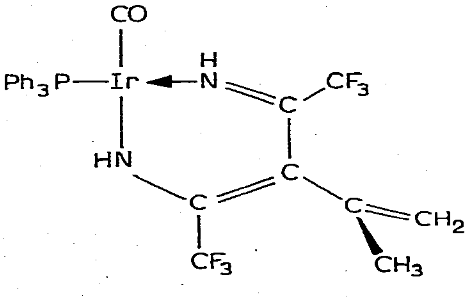
2-Methylallylrhodium dichloride reacts with $Ph_2PCH_2CH_2PPh_2$ in EtOH under hydrogen, with partial or complete hydrogenation of the allyl groups, to give

$[(Ph_2PCH_2CH_2PPh_2)RhCl_2]$ and *trans*-$[RhClH(Ph_2PCH_2CH_2PPh_2)_2]Cl$ [320]. The complexes $Rh(\pi\text{-allyl})(PPh_3)_2$ (π-allyl = C_3H_5, 1-methylallyl, 2-methylallyl) have a vacant coordination site which can be occupied by a carbonyl, trifluorophosphine, or dimethylaminodifluorophosphine ligand [321]. One of the complexes so formed, $Rh(\pi\text{-}C_3H_5)(PPh_3)_2(PF_3)$, reacts with chloroform, giving *trans*-$RhCl(PPh_3)_2(PF_3)$. Reaction of hexafluoro-2-butyne with one of the starting complexes, $Rh(\pi\text{-2-methylallyl})(PPh_3)_2$, leads to the compound shown, probably via an intermediate involving the C_4F_6 occupying the vacant coordination site (Scheme 21). $Rh(\pi\text{-}C_3H_5)(PPh_3)_2$ also acts as a catalyst for the hydrogenation of 1-octene and cyclohexene.

Scheme 21



Reaction of a solution of carbonyl(π-2-methylallyl)bis(triphenylphosphine)iridium in benzene with an excess of trifluoroacetonitrile results in formation of complex 222 [322]. The $CH_3CH{=}CH_2$ group is inclined at nearly 90° to the plane of the heterocyclic ring. In contrast, reaction of carbonyl(π-1-methylallyl)bis(triphenylphosphine)iridium with trifluoroacetonitrile yields complex 223. The corresponding reaction of carbonyl-π-allylbis(triphenylphosphine)iridium with CF_3CN gives an analogue of 222, together with a variable low yield of 224.



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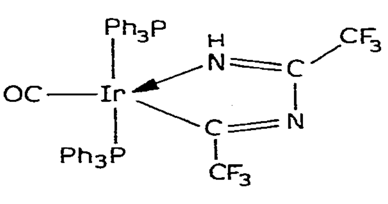

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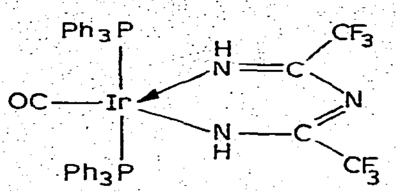
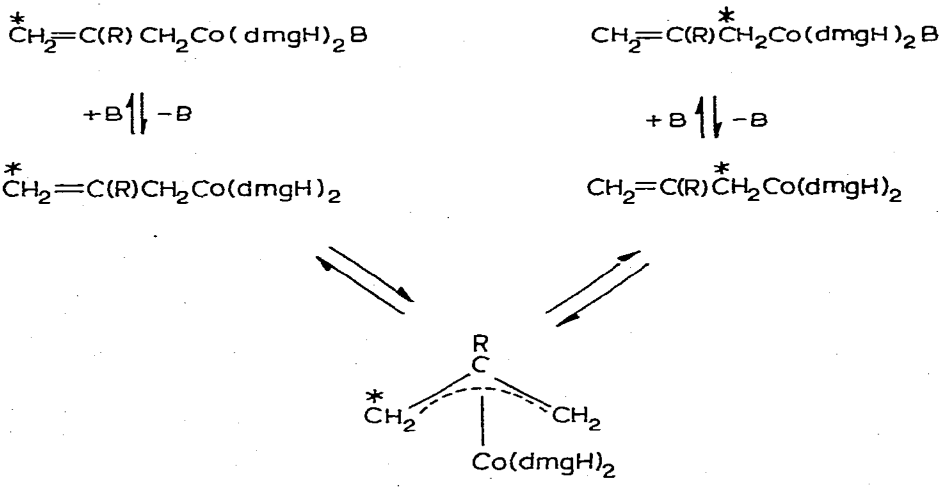


(224)

The NMR spectra and carbonyl vibrational frequencies of $(\pi\text{-}C_3H_4X)Co(CO)_2$-$PPh_3$ (X = H, 1-CH_3, 2-CH_3, 2-Cl) show that the electronic effects are similar to those found in the parent $(\pi\text{-}C_3H_4X)Co(CO)_3$ compounds [323]. The nature of the allyl—metal bond does not change significantly, and there is no evidence of asymmetric π,σ-bonding in $(\pi\text{-}C_3H_4X)Co(CO)_2PPh_3$.

Proton NMR studies on some allylcobaloximes have been carried out [324]; these show that the character of the allylcobaloxime is dependent upon the nature of the other axial ligand, and in some cases dynamic σ-allylcobaloximes are formed in solution. The formation of these species has been ascribed to the fact that transient intermediate five-coordinate allyl complexes can adopt the π-allyl configuration (Scheme 22). Thus, when B is weakly coordinating, the rate of formation and the proportion of the five-coordinate species are large.

Scheme 22



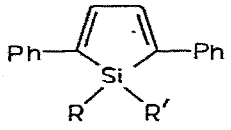
[$(dmgH)_2$ = conjugate base of dimethylglyoxime
B = axial ligand]

The π-allyl group of $\pi\text{-}C_3H_5Co(CO)_3$ has two angles of tilt; the factors accounting for the stability of each of these have been worked out from semiempirical molecular orbital calculations [325]. The $Co(CO)_3$ moiety has asymmetric bonding, with one CO group more weakly bonded to the Co atom. This fact accounts for the relatively high reactivity of π-$C_3H_5Co(CO)_3$, compared to the reactivity of π-$C_3H_5Fe(CO)_2NO$, $Co(NO)(CO)_3$ or $Ni(CO)_4$.

IR and Raman spectral data indicate that the three ligands in tri-π-allylrhodium are equivalent [326], and that the redistribution of electron density in the allyl groups of dimeric di-π-allylrhodium bromide and chloride is negligible. The dimer of chloro(bis-1-methyl-π-allyl)rhodium has also been studied.

Metal carbocyclic complexes

Trans,trans-$C_6H_5BrC{=}CCHCH{=}CBrC_6H_5$ when heated with butyllithium and $C_6H_5SiCl_2R$ ($R = CH_3$ or C_6H_5) gives silacyclopentadienes 225 ($R = CH_3$, $R' = C_6H_5$; $R = R' = C_6H_5$). In addition, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane when treated with *N*-bromosuccinimide gives 225 ($R = R' = CH_3$). 225 when treated with $Fe_2(CO)_9$ and π-$C_5H_5Co(CO)_2$ gives 226 and 227 respectively [327].



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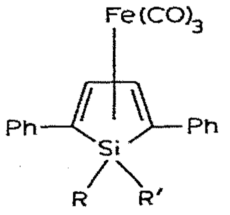

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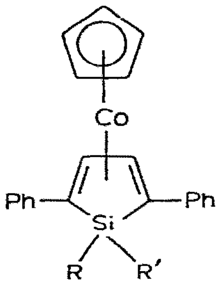


(227)

Mass spectra indicate an aromatic silacyclopentadiene species.

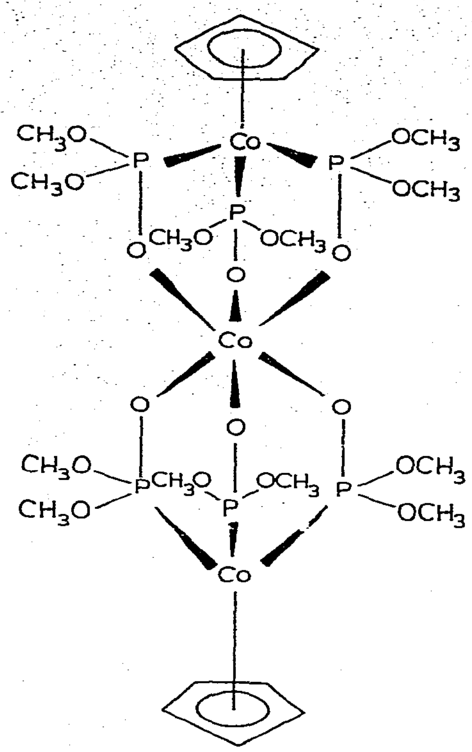
π-$C_5H_5Co(CO)_2$ reacts with (dimethylamino)dimethylphosphine, $(CH_3)_2P$—$N(CH_3)_2$, with substitution of a carbonyl group, to give π-$C_5H_5Co(CO)$—$[(CH_3)_2P$—$N(CH_3)_2]$ [328]. Similar reaction with octacarbonyldicobalt does not give a straightforward substitution; instead the product $[(CO)_3Co\{(CH_3)_2P$—$N(CH_3)_2\}_2]^+[Co(CO)_4]^-$ is formed.

The trinuclear cobalt complexes $(\pi$-$C_5H_5)_2Co_3[P(O)(OR)_2]_6$ ($R = CH_3$ or C_2H_5) have been prepared from $Co(C_5H_5)_2$ and $P(OR)_3$ (via. $C_5H_5Co[P(OR)_3]_2$ as intermediates) and also from $Co(C_5H_5)_2$ and $HP(O)(OR)_2$ [329]. The structure of $(C_5H_5)_2Co_3[P(O)(OCH_3)_2]_6$ (228) has been solved from single crystal X-ray data.

$[CoH(N_2)(PPh_3)_3]$ reacts with cycloheptatriene in diethyl ether, giving $[Co(1\text{-}5\text{-}\pi\text{-}C_7H_9)(PPh_3)_2]$ (229) [330]. This compound reacts with carbon monoxide in ether, giving $[Co(1\text{-}3\text{-}\pi\text{-}C_7H_9)(CO)_2(PPh_3)]$ (230). Both compounds have been characterised by ^1H NMR and IR spectra.

Refluxing bis(1-phenylborinato)cobalt (231) for 24 h with $Ni(CO)_4$ in toluene, followed by chromatography and vacuum sublimation, gives 35% of dicarbonyl(1-phenylborinato)cobalt (232) [331]. The analogous reaction using $Co_2(CO)_8$ instead of $Ni(CO)_4$ does not work.

Trimethylsilylnitrene, formed from trimethylsilylazide by elimination of nitrogen, has been trapped as μ_3-trimethylsilylimido complexes of ruthenium,



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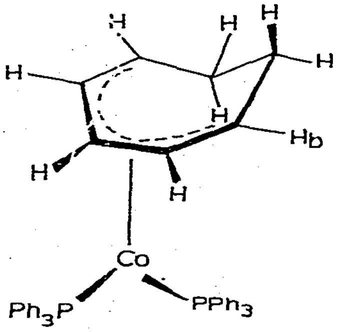

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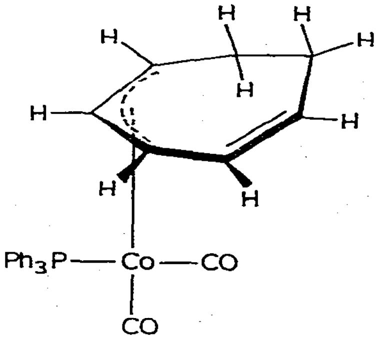

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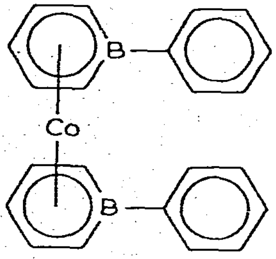

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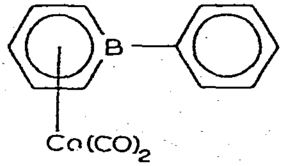
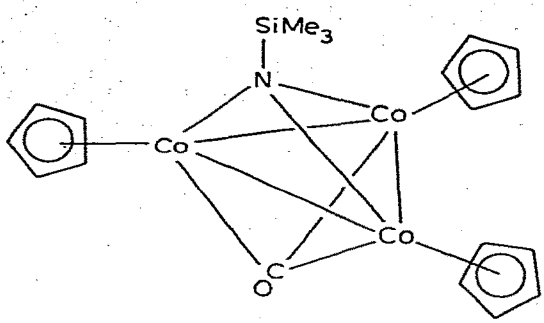


(232)

cobalt and rhodium, in which the fixed nitrene acts as a four-electron donor [332]. The cobalt complex **233** was prepared by reacting trimethylsilyl azide with $(\pi\text{-}C_5H_5)Co(CO)_2$; the analogous rhodium complex **234** was prepared from trimethylsilyl azide and $(RhC_5H_5)_3(CO)_2$.



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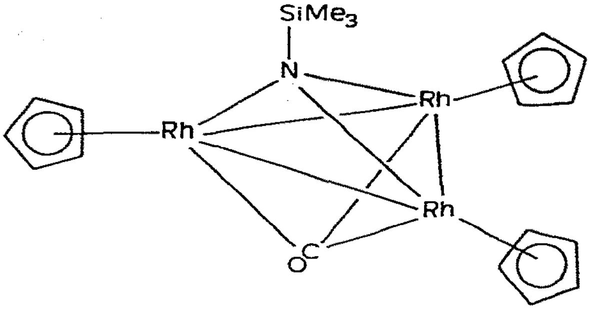

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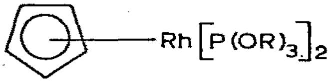
Exposure of a petroleum ether solution of $(\pi\text{-}C_5H_5)Rh(CO)_2$ to dry air for ten days gives red crystals of $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ [333]. This compound had previously been formulated as $(\pi\text{-}C_5H_5)_2Rh_2(CO)_4$, and was thought to be the only example of a polynuclear metal carbonyl with bridging carbonyl groups but no metal—metal bond. In fact, $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ has one bridging CO ligand and also a Rh—Rh bond.

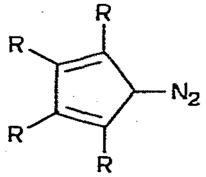
The rhodium phosphite complexes **235** have been prepared (R = CH_3, C_2H_5,



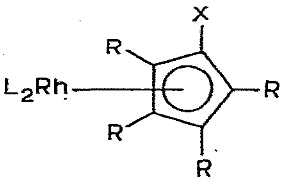
(235)

C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$) [334]. Thus, $[C_8H_{12}RhCl]_2$ was treated with $P(OR)_3$ to give $[ClRh[P(OR)_3]_2]_2$, which, when treated with NaC_5H_5 gave **235**.

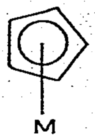
The diazocyclopentadienes **236** insert into halogen-bridged dirhodium species to give new halo-substituted cyclopentadienyl complexes **237a—e** [335]. The

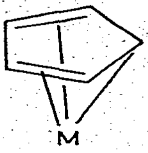


(**236** a, R = C_6H_5
b, R = H)



(**237** a, R = C_6H_5, L_2 = COD, X = Cl
b, R = C_6H_5, L_2 = COD, X = Br
c, R = C_6H_5, L_2 = $(C_2H_4)_2$, X = Cl
d, R = C_6H_5, L_2 = $(CO)_2$, X = Cl
e, R = H, L_2 = COD, X = Cl)
(COD = cycloocta-1,5-diene)



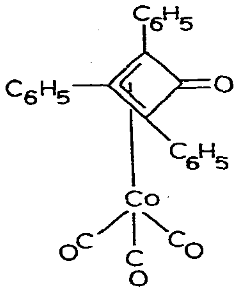


(A) (237c) (B)

crystal structure of **237c** has been determined. Two extreme bonding models can be envisaged for pentahaptocyclopentadienyl metal derivatives. A is the symmetrical π-type model; B is the previously unreported localised type, involving two olefin π bonds and one σ-alkyl bond to the metal. **237c** is unique in having an appreciable contribution from the B form.

Crystal structures of two π-areneenneacarbonyltetracobalt compounds have been determined [336]. In the first, the arene is a disordered 1/1 mixture of *ortho* and *meta* xylenes. The mixed complex $C_6H_4(CH_3)_2Co_4(CO)_9$ was obtained as a side product in the reaction of octacarbonyldicobalt with 2,2,5,5-tetramethyl-3-hexyne to form $(CH_3)_3CC{\equiv}CC(CH_3)_3Co_2(CO)_6$. The second complex, $C_6H_6.Co_4(CO)_9$, was obtained by refluxing octacarbonyldicobalt in benzene for 21 h. Both structures consist of a tetrahedral cobalt cluster; one cobalt atom is π-bonded to the arene moiety, whilst the other three are each bonded to two terminal and two bridging carbonyl groups.

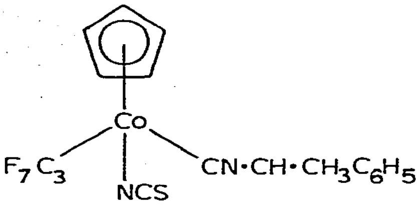
An X-ray crystal structure of the compound $(C_6H_5)_3C_3COCo(CO)_3$ shows it to be the first example of a complex containing a keto-π-cyclobutenyl ligand (238) [337].



(238)

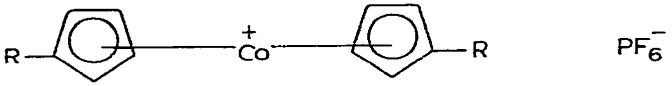
The crystal and molecular structures of (π-cyanocyclopentadienyl)tetraphenylcyclobutadienecobalt, (π-iodocyclopentadienyl)tetraphenylcyclobutadienecobalt and (π-1,2-diiodocyclopentadienyl)tetraphenylcyclobutadienecobalt have been determined [338]. In these compounds cobalt is sandwiched between parallel π-cyclopentadienyl and tetraphenylcyclobutadiene rings, which are planar within experimental error. The crystal structure of bis(trimethylphosphite)(tetraphenylboron)rhodium(I) has also been determined [339]; one carbon ring of the tetraphenylboron group is π-bonded to the rhodium, which is situated symmetrically with respect to the ring. In $(\pi\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$ the cyclopentadienyl ring centre, triphenylphosphine, and carbonyl groups form a planar, triangular array with the central iridium atom [340].

The reaction of $(\pi\text{-}C_5H_5)Co(C_3F_7)(CNCHCH_3C_6H_5)I$ (diastereomeric mixture) with $AgClO_4/NH_4SCN$ gave a mixture of the N- and S-bound $(\pi\text{-}C_5H_5)Co(C_3F_7)(CNCHCH_3C_6H_5)CNS$ diastereoisomers [341]. These were separated by pentane to give pure 239, which is stable in the solid state and in tetrahydrofuran but undergoes epimerisation and structural isomerisation in benzene and toluene.



(239)

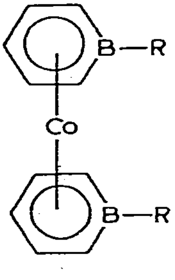
Some reactions of the R group in compounds 240 have been carried out [342]. Reaction of 240a with potassium permanganate in acid medium gives 240b. Treating 240a with aqueous nitric acid and potassium permanganate at 45° C gives 240b and the 1-acetyl-1′-carboxycobaltocenium salt, separated by chromatography on alumina. 240a was prepared by heating sodium cyclopentadienide with ethyl bromide in THF, metallating the resulting $C_2H_5C_5H_5$ with sodium in THF/xylene, and treating with $[Co(NH_3)_6]^+Cl^-$.



(240 a , R = C_2H_5,
b , R = CH_3CO, HO_2C)

The chemical and electrochemical oxidation of several substituted cyclopentadienylcyclopentadienecobalt compounds, $(RC_5H_5)Co(C_5H_4R')$, has been studied [343]. When R = R′ = H, CH_3 or CO_2CH_3 the corresponding cobaltocenium ion is obtained. When R = CH_3 and R′ = H a splitting of the molecule occurs. In the presence of H^+ ions the oxidation is first-order in the cobalt complexes.

Reaction of the diborinato cobalt complexes $Co(C_5H_5B{-}R)_2$ (R = C_6H_5, CH_3) (241) with iron carbonyls gives diborinatodiiron tetracarbonyl complexes $[Fe(CO)_2(C_5H_5B{-}R)]_2$ (R = C_6H_5, CH_3) (242) [344].



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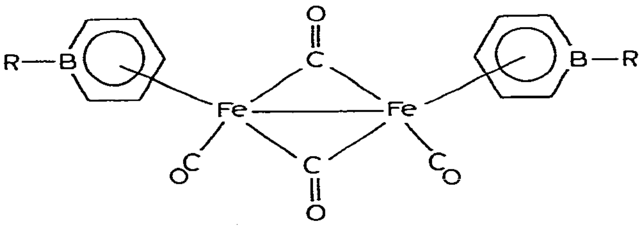


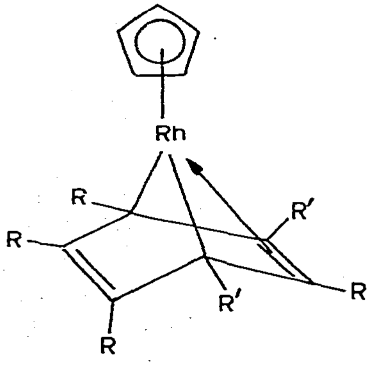
(242)

When (π-C_5H_5)Co(CO)$_2$ (or (π-C_5H_5)V(CO)$_4$) or (π-C_5H_5)Mn(CO)$_4$) was introduced into the ion source of a mass spectrometer together with σ or π donor molecules L, e.g. PF_3, H_2S, H_2O, $(C_2H_5)_2O$, $(CH_3OCH_2)_2$, NH_3, $(C_2H_5)_2NH$, butadiene, cyclooctadiene, cyclooctatriene or cyclooctatetraene, secondary ions (π-C_5H_5)CoL$^+$ and fragment ions were formed [345] according to the equation:

$$(\pi\text{-}C_5H_5)Co(CO)_2^+ + L \rightarrow (\pi\text{-}C_5H_5)CoL^+ + 2CO$$

The course and the relative cross sections of the ion-molecule reactions, as well as the nature of the fragment ions, is dependent on L.

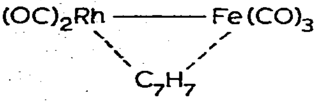
Some reactions of (π-C_5H_5)Rh[P$(C_6H_5)_3$]$_2$ have been studied, for comparison with reactions of (π-C_5H_5)Co[P$(C_6H_5)_3$]$_2$ and also to examine a new route to rhodium complexes having a π-cyclopentadienyl group [346]. Reaction with methyl iodide gives the oxidative addition product [(π-C_5H_5)Rh$(PPh_3)_2CH_3$]I, but with isopropyl iodide the alkyl substituted cyclopentadienyl complex (π-i-$C_3H_7C_5H_4$)Rh$(PPh_3)I_2$ is formed. Reaction with olefins or acetylenes in a nitrogen atmosphere affords the compounds (π-C_5H_5)Rh(PPh_3)L (L = CH_2=CH-CN, CH_2=$CHCO_2CH_3$, $CH_3O_2CC{\equiv}CCO_2CH_3$) by displacement of one triphenylphosphine ligand. In the presence of air, however, complexes of the composition (π-C_5H_5)Rh(L)$_2$ (L = CH_2=CHCN, CH_2=$CHCO_2CH_3$, CH_2=C(CH_3)CN) are formed, and with L = $CH_3O_2CC{\equiv}CCO_2CH_3$ or $C_6H_5C{\equiv}CCO_2CH_3$ complexes of composition (π-C_5H_5)Rh(L)$_3$ (243a and b respectively) are obtained. Reaction of (π-C_5H_5)Rh$(PPh_3)_2$ with carbon disulphide or sulphur gives (π-C_5H_5)Rh(PPh_3)L (L = CS_2, CS_3, S_5).



(243 a, R = R' = CO_2CH_3
b, R' = CO_2CH_3, R = C_6H_5)

Studies on the relationship between the structure of sandwich type organometallic compounds and their electronic absorption spectra, show that introducing ethyl substituents into ferrocene and cobaltocenium chloroplatinate results in similar spectral changes [347]. The rate of hydrogen—deuterium exchange in the rings of cobaltocene, in basic media, was slower than that for cobaltocenium tetrafluoroborate, and was thus affected by the positive charge on the cobalt atom [348].

The resonance Raman spectrum of the novel complex $(CO)_2RhC_7H_7Fe(CO)_3$ (244), which contains an Rh—Fe bond, has been obtained [349]. A chloroform solution of the complex exhibits a band at 172 ± 2 cm^{-1}, assigned to the Rh—Fe stretching vibration.

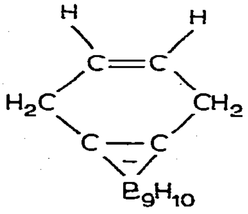


(244)

The ^{13}C NMR spectra of indene (HL) and some of its complexes, including $[CoL_2]PF_6$, were analysed with respect to the hapto ligand properties [350].

Metal carborane complexes

Two new benzocarborane anions 245 and 246 have been prepared; deprotonation of these anions with sodium hydride yields the (1,4-dihydrobenzo)dicarbollide ion (247) and the benzodicarbollide ion (248) respectively [351].



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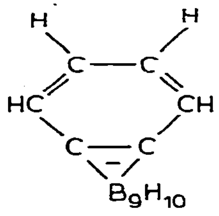

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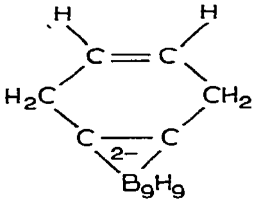

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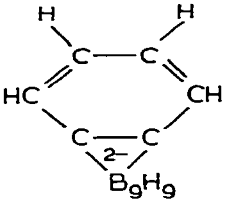
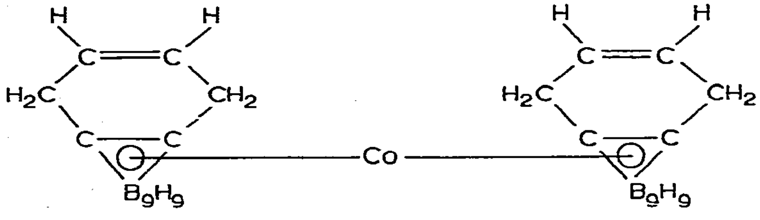


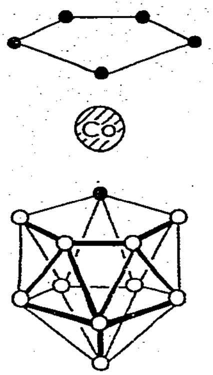
(248)

Manganese and cobalt complexes of 247 and manganese, cobalt and nickel complexes of 248 have been prepared. Anhydrous cobalt(II) chloride reacts with 248 in THF giving the bis(benzodicarbollyl)cobaltate(III) monoanion, which is isolated as the tetramethylammonium salt. The reaction with 247 in refluxing diglyme gives 249.



(249)

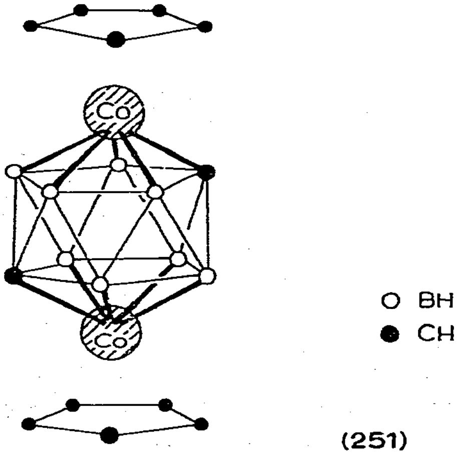
A π-cyclopentadienyl cobalt complex of the π-7-$B_{10}CH_{11}{}^{3-}$ carbollide ligand has been prepared [352]. NMR data suggest the structure 250 for this compound. The ion was isolated as the tetramethylammonium salt.



(250)

Several cobalt sandwich complexes of the cyclic $C_2B_3H_7^{2-}$ and $C_2B_3H_5^{4-}$ ligands have been prepared from 2,3-$C_2B_4H_8$ and 1,6-$C_2B_4H_6$ [353]. Thus, the reaction of $Na^+C_2B_4H_7^-$ with $CoCl_2$ and NaC_5H_5, followed by exposure to air, water and acetone gave (π-2,3-$C_2B_4H_6$)Co(π-C_5H_5), (π-2,3-$C_2B_3H_7$)Co(π-C_5H_5) and (π-2,3-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$. C-methyl and C,C′-dimethyl derivatives were prepared analogously from $Na^+CH_3C_2B_4H_6^-$ and $Na^+(CH_3)_2C_2B_4H_5^-$. Reduction of 1,6-$C_2B_4H_6$ with sodium naphthalide, followed by reaction with $CoCl_2$, NaC_5H_5, air and water, gave (π-2,4-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$, (π-$C_2B_4H_6$)Co_2-(π-C_5H_5)$_2$, and [σ-5-(1-$C_{10}H_7$)(π-$C_2B_4H_5$)]Co(π-C_5H_5) with a trace of (π-2,4-$C_2B_4H_6$)Co(π-C_5H_5). 2,4-$C_2B_5H_7$ reacted with sodium naphthalide and $CoCl_2$ to give probably a (π-2,4-$C_2B_4H_6$)$_2$Co$^-$ anion. Some nickel metallocarboranes were also prepared.

Heating 1-(π-C_5H_5)-1-Co-2,3-$C_2B_8H_{10}$ for 7 h, at 235°C in hexadecane gives five new red isomers and a green isomer of $(C_5H_5)_2Co_2C_2B_8H_{10}$ [354]. Five of these isomers can also be obtained by heating [(π-C_5H_5)$_2$Co]$^+$[1,1′-Co(2,3-C_2-B_8H_{10})$_2$]$^-$ interspersed on ceramic saddles at 525°C under high vacuum, or by heating in hexadecane at 270°C. NMR data specifies the structure of one of these as 2,9-(π-C_5H_5)$_2$-2,9-Co_2-1,12-$C_2B_8H_{10}$ (251), whilst another has been

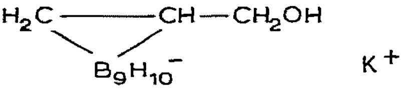


(251)

previously obtained and structurally characterized as 2,3-(π-C_5H_5)$_2$-2,3-Co_2-1,7-$C_2B_8H_{10}$. Atomic arrangements are proposed for the other four isomers.

Reduction of the *closo* metallocarborane 2,1,6-$C_5H_5CoC_2B_7H_9$ with Na in the presence of naphthalene, followed by addition of $CoCl_2$ and NaC_5H_5, gave the new compounds $(C_5H_5)_2CoC_2B_nH_{n+2}$ (n = 5 or 7; for n = 7, three isomers were formed) and $(C_5H_5)_3Co_3C_2B_7H_9$ [355]. Similar reduction of 1,2,3-C_5H_5-$CoC_2B_5H_7$ did not yield any new products. Polyhedral expansion of 1,2,4-C_5H_5-$CoC_2B_8H_{10}$ gave three main neutral products, only one of which was characterized, $(C_5H_5)_2Co_2C_2B_8H_{10}$. 3,1,2-$C_5H_5CoC_2B_9H_{11}$ gave two isomers of $(C_5H_5)_2$-$Co_2C_2B_9H_{11}$ as well as $[(C_5H_5)_2Co][3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$.

Treatment of 252 with cyclopentadiene and $CoCl_2$ in KOH/EtOH for 10 h at



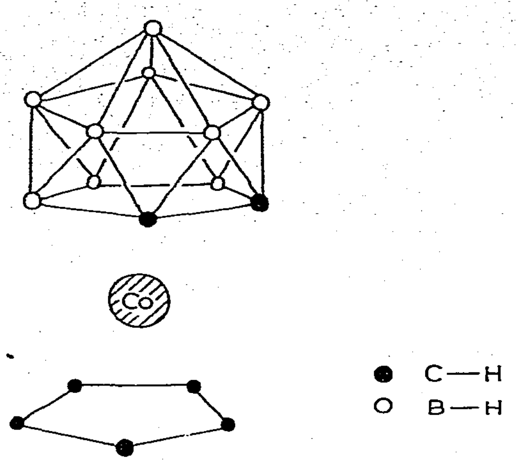
(252)

20°C, followed by boiling for 6 h, gave $(\pi\text{-}C_5H_5Co)_2[\pi\text{-}(3,6)1,2\text{-}B_8H_8CHCCH_2OH]$ in 73% yield [356]. Oxidation of this by CrO_3 at 20°C gave 32% of $(\pi\text{-}C_5H_5Co)_2$-HCB_8H_8CCHO.

The reaction of 13-vertex cobaltacarboranes (π-C_5H_5)$CoC_2B_{10}H_{12}$ with ethanolic potassium hydroxide, in the presence of cyclopentadiene and an appropriate metal salt, produces new 13-vertex bimetallocarboranes [357]. This reaction is a polyhedral subrogation reaction; i.e. removal of a formal BH^{2+} unit from the polyhedral framework by base degradation in the presence of excess metal, resulting in insertion of the metal ion into the hole left by the departing boron atom. The two homobimetallocarboranes (4,5-(π-C_5H_5)$_2$-4,5-$Co_2$1,8-C_2-B_9H_{11}) and (4,5-(π-C_5H_5)$_2$1,8-$(CH_3)_2$-4,5-Co_2-1,8-$C_2B_9H_{11}$) were prepared in this way; both these compounds undergo thermal rearrangements. A similar reaction, but in the absence of cyclopentadiene, gave $[\{(\pi\text{-}C_5H_5)CoC_2B_9H_{11}\}_2Co]^-$, isolated as the tetramethylammonium salt. Replacement of cobaltous chloride by ferrous chloride in the original reaction yielded 4,5-(π-C_5H_5)$_2$-4-Co-5-Fe-1,8-$C_2B_9H_{11}$; the C,C′-dimethyl derivative was also prepared.

Direct reaction of small polyhedral carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ or 2,4-$C_2B_5H_7$ with organometallic reagents in the gas phase or solution, yielded metallocarboranes of Co, Fe and Ni, without the use of a prior cage-opening step [358]. Novel 6-vertex cages as well as 7-vertex species were obtained, including mono-, di-, and tri-metallocarborane species. Reaction of $C_2B_3H_5$ with (π-C_5H_5)-$Co(CO)_2$ in the gas phase at elevated temperatures, gave (π-C_5H_5)$CoC_2B_3H_5$ and (π-C_5H_5)$Co_2C_2B_3H_5$. With $C_2B_4H_6$, (π-C_5H_5)$Co(CO)_2$ gave primarily seven-vertex cobaltacarboranes containing a $Co_2C_2B_4$ cage. The cobalt reagent and $C_2B_5H_7$ gave mono-, di-, and tri-cobaltacarborane species, including two isomers of the novel (π-C_5H_5)$_3Co_3C_2B_5H_7$ system. Direct reaction of (π-C_5H_5)$Co(CO)_2$ with 1,2-$C_2B_{10}H_{12}$ at 30°C gave a mixture of cobaltacarboranes, which were predominantly isomers of (π-C_5H_5)$CoC_2B_9H_{11}$. Fine structure in the carborane-CH proton NMR signals, exhibited by several of the compounds, was attributed to H—C—B—H proton—proton coupling.

(π-C_5H_5)Co(π-HCB_9H_9CR) (253; R = CH_2OH) was prepared by boiling Tl_2-



(253)

HCB_9H_9CR, dry $CoCl_2$ and C_5H_5Tl in THF for 3 h, and also from $KHCB_9H_{10}$-CCH_2OH, cyclopentadiene and $CoCl_2$ [359]. The compounds with R = CH_2CN, CO_2Me, $CH{=}CH_2$, $CF{=}CFCF_3$ were analogously obtained. Some chemistry of the R group in 253 (R = CH_2OH) was investigated.

Oxidation of (π-$B_{10}H_{10}C_2RR'$)Co (R = H, R' = H, Me; R = R' = Me; R = Ph, R' = H) containing *nido* carborane, by $CuCl_2$ in THF for 30 min at 20°C gave 95% *o*- and 5% *m*-$B_{10}H_{10}C_2RR'$ which had the *closo* configuration [360]. Increasing the time to 100 h gave more of the *m*-isomer.

The new carborane $(CH_3)_4C_4B_8H_8$ is formed in the synthesis of $[2,3\text{-}(CH_3)_2\text{-}C_2B_4H_4]_2Co^{III}H$ from $Na^+[2,3\text{-}(CH_3)_2C_2B_4H_5]^-$ and $CoCl_2$ in THF [361]. It is formed via decomposition of the metal complex, and does not appear to be formed directly from the $(CH_3)_2C_2B_4H_5^-$ ion.

Four novel rhodium(I) carborane complexes of general formula $[(C_6H_5)_3P]_2$-Rh(σ-carb) [carb = 2-R-1,2-$B_{10}C_2H_{10}^-$ and 7-R-1,7-$B_{10}C_2H_{10}^-$ (R = CH_3, C_6H_5)] containing a rhodium—carbon σ bond have been obtained, by treating a suspension of $[(C_6H_5)_3P]_3RhCl$ in diethyl ether with an excess of the C-monosubstituted lithium derivative of the carborane [362]. The reactions of these complexes with carbon monoxide are shown in Scheme 23. The compounds 1-[$(PPh_3)_2$-

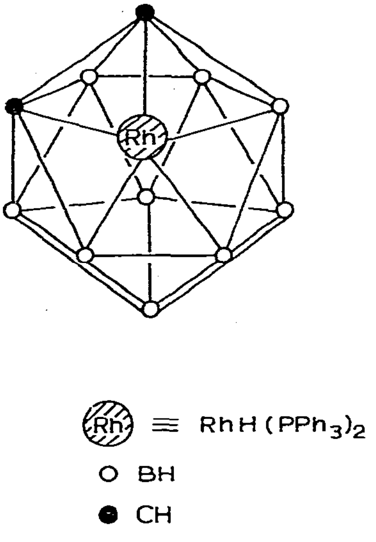
Scheme 23

$$\begin{tikzcd}
(PPh_3)_3RhCl \arrow[r, "Li(carb)"] \arrow[d, "+CO"', "-PPh_3"] & (PPh_3)_2Rh(\sigma\text{-}carb) \arrow[r, shift left, "+2CO,-PPh_3"] & (PPh_3)Rh(CO)_2(\sigma\text{-}carb) \arrow[l, shift left] \\
trans\text{-}(PPh_3)_2Rh(CO)Cl \arrow[rr, "Li(carb)"] & & trans\text{-}(PPh_3)_2Rh(CO)(\sigma\text{-}carb) \arrow[u, "+CO", "-PPh_3"']
\end{tikzcd}$$

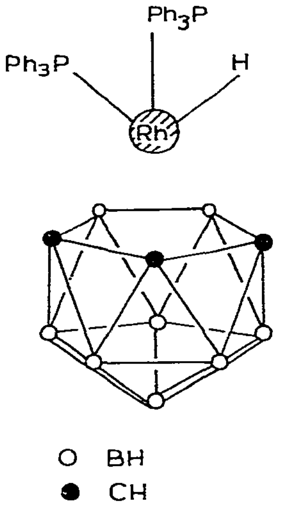
($Li(carb)$ = $1\text{-}Li\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{10}$)

Rh(CO)]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$) and 1-[(PPh_3)Rh$(CO)_2$]-2-C_6H_5-1,2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$) were made as indicated in Scheme 23, the latter crystallising with a half molecule of CH_2Cl_2. Reaction of 1-[$(PPh_3)_2$Rh]-2-Ph-1,-2-(σ-$B_{10}C_2H_{10}$) with benzonitrile gave the four-coordinate adduct 1-[$(PPh_3)_2$-Rh(C_6H_5CN)]-2-Ph-1,2-(σ-$B_{10}C_2H_{10}$).

Two new hydridometallocarboranes have been prepared and some of their catalytic properties have been investigated [363]. A methanol solution of tris-(triphenylphosphine)rhodium(I) cation was allowed to react at 60°C with a methanol solution of either $(CH_3)_3NH^+$ [7,8-$C_2B_9H_{12}$]$^-$ or $(CH_3)_3NH^+$ [7,9-$C_2B_9H_{12}$]$^-$. IR spectra, elemental analyses, and ^1H, ^{11}B, and ^{31}P NMR data confirmed the products as 3,3-[$(C_6H_5)_3P$]$_2$-3-H-3,1,2-Rh$C_2B_9H_{11}$ (254) and 2,2-[$(C_6H_5)_3P$]$_2$-2-H-2,1,7-Rh$C_2B_9H_{11}$ (255) respectively. The complexes were formulated as d^6 rhodium(III) hydrides, with triphenylphosphine ligands in two coordination sites and the $C_2B_9H_{11}{}^{2-}$ ligand symmetrically bonded to the rhodium. Benzene solutions of the complexes catalyse the isomerisation of 1-hexene to *cis*-2-hexene, *trans*-2-hexene, *cis*-3-hexene and *trans*-3-hexene; they also catalyse the hydrogenation of 1-hexene. In addition, the complexes catalyse the deuterium exchange of terminal BH groups in boranes, carboranes and metalloboranes, as well as the hydrosilation of ketones. The chemistry has been expanded to include the iridium congeners.

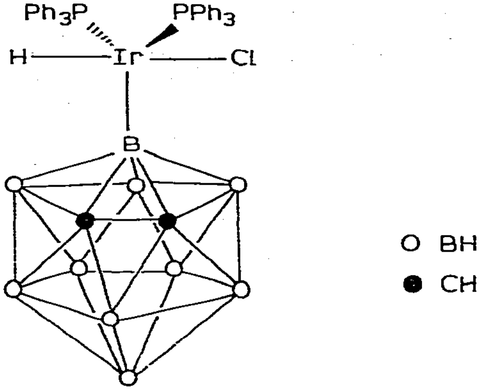


(254)



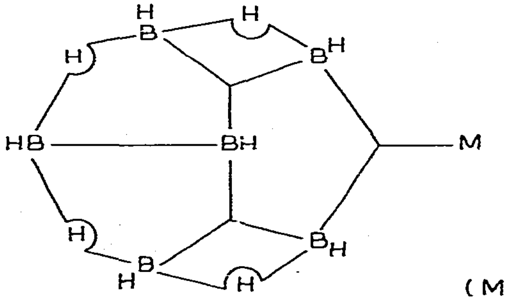
(255)

More detailed studies on the catalytic activity of complexes 254 and 255 in the deuterium exchange of terminal BH groups have been presented [364]. Similar exchange, catalysed by $(PPh_3)_3$RuHCl, has been observed in 3-(π-C_5H_5)-3,1,2-Co$C_2B_9H_{11}$ and 1-(π-C_5H_5)-1,2,4-Co$C_2B_8H_{10}$; complexes 254 and 255 are, however, the two most active catalysts so far examined. Intermediates formed by oxidative addition of the B—H bonds to a transition metal complex were postulated; stable boron σ-metallocarboranes have since been prepared in this manner [365]. Slow addition of hexane to a cooled solution, prepared by heating $(PPh_3)_3IrCl$ with a three-fold excess of 1,2-$C_2B_{10}H_{12}$ in toluene, produced a small quantity of 3-[$(PPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$. The low yield is probably due to the strength of the Ir—P bond; thus, similar reaction in benzene with $(PPh_3)_2IrCl$, formed in situ, yielded 80% of **256**. Similar complexes have been formed with 1,7-$C_2B_{10}H_{12}$ and 1,12-$C_2B_{10}H_{12}$. **256** has been shown to arise from oxidative addition of a carboranyl B—H bond to the metal atom; these complexes were also shown to be good models for intermediates in the transition metal-catalysed exchange reactions.



(256)

Hexaborane(10) has been shown to form the complexes μ-$Fe(CO)_4B_6H_{10}$, *trans*-$Pt(B_6H_{10})_2Cl_2$, $Rh(B_6H_{10})_2(acac)$, $[Rh(B_6H_{10})_2Cl]_2$ and $[Ir(B_6H_{10})_2Cl]_2$ [366]. These have been characterised by elemental analysis and IR, ^1H NMR and ^{11}B NMR spectral studies. The metal is thought to have inserted into the anomalously short boron—boron bond along a basal edge of the pentagonal pyramidal structure of hexaborane(10), forming a three-centre, two-electron bond (**257**).

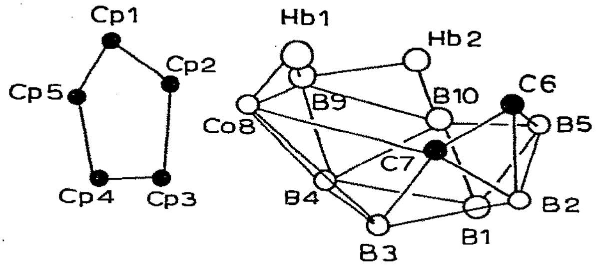


(M = Fe, Rh, Pt, Ir)

(257)

The addition of bromopentaborane(9) and pentaborane(9) to *trans*-$IrCl(CO)(PMe_3)_2$ has been studied [367]. In all cases the iridium atom is linked to B2, regardless of the stereochemistry of the starting borane. With excess 1- or 2-BrB_5H_8 the compound 2-[$IrBr_2(CO)(PMe_3)_2$]B_5H_8 was obtained, and its crystal structure determined by single crystal X-ray methods. The intermediate $IrClH(CO)(PMe_3)_2(BrB_5H_7)$ was postulated for the reaction. The reaction with B_5H_9 gave 2-$[IrClH(CO)(PMe_3)_2]B_5H_8$.

In the polyhedral contraction of the complex 1-(π-C_5H_5)-1-Co-2,4-$C_2B_8H_{10}$ a product formulated as $C_5H_5CoC_2B_7H_{11}$ was isolated. A single crystal X-ray structure determination of this compound shows it to have the structure 258,



(258) 8-(π-C_5H_5)-8-Co-6,7-$C_2B_7H_{11}$

involving two bridging hydrogen atoms [368]. Mechanistic aspects of the synthesis and chemistry of the compound have been discussed in light of the atomic arrangement observed. The "red" isomer of (π-C_5H_5)Co($B_{10}C_2H_{12}$), synthetised and found to be "fluxional" by Hawthorne and coworkers, has been subjected to an X-ray crystallographic study [369].

The polyhedral expansion of 1,6-$C_2B_8H_{10}$ at —80°C yields two isomers of $(\pi\text{-}C_5H_5)_2Co_2C_2B_8H_{10}$, and a bimetallocarborane anion $[(\pi\text{-}C_5H_5)CoC_2B_8H_{10}\text{-}CoC_2B_8H_{10}]^-$. The structure of the tetraethylammonium salt of this anion has been determined by ^1H NMR, ^{11}B NMR and X-ray diffraction studies [370]. The anion contains a bimetallic $Co_2C_2B_8H_{10}$ unit, in which one cobalt atom is shared with a terminal $C_2B_8H_{10}$ group.

Oxidation of metal complexes of carborane dianions, e.g. (*o*-, *m*-, *p*-$C_2B_{10}H_{12})_2M$ (M = Fe, Co, Ni), by $CuCl_2$ in aqueous acetic acid gave mixtures of *m*-, *o*- and *p*-carboranes [371]. Oxidation of dianions, obtained by reduction of *o*-, *m*- and *p*-carboranes, is the rate-determining step in the formation of *o*-carboranes from *m*-carboranes and *m*-carboranes from *p*-carboranes.

Treatment of [1-(π-C_5H_5)-2,4,1-$C_2CoB_8H_{10}$] or $[1,2\text{-}C_2B_9H_{11}\text{-}3,1'\text{-}Co\text{-}2,4'\text{-}C_2B_8H_{10}]^-$ with pyridine gave the *nido* adducts [9-(π-C_5H_5)-11-(C_5H_5N)-7,8,9-$C_2CoB_8H_{10}$] and $[1,2\text{-}C_2B_9H_{11}\text{-}3,9'\text{-}Co\text{-}11'\text{-}(C_5H_5N)\text{-}7',8'\text{-}C_2B_8H_{10}]^-$ respectively [372]. Oxidation with $FeCl_3$ afforded the substituted *closo* compounds. Analogous compounds were prepared from [1-(π-C_5H_5)-2,4,1-$C_2CoB_8H_{10}$] and piperidine. The unsubstituted *nido* metallocarboranes $[9\text{-}(\pi\text{-}C_5H_5)\text{-}7,8,9\text{-}C_2CoB_8H_{11}]^-$ and $[1,2\text{-}C_2B_9H_{11}\text{-}3,3'\text{-}Co\text{-}1',2'\text{-}C_2B_9H_{11}]^-$ were prepared by degradation of icosahedral compounds [3-(π-C_5H_5)-1,2,3-$C_2CoB_9H_{11}$] and $[1,2\text{-}C_2B_9H_{11}\text{-}3,3'\text{-}Co\text{-}1',2'\text{-}C_2B_9H_{11}]^-$. These *nido* compounds could be reversibly protonated.

(π-C_5H_5)CoB_9H_9(C_2H_2-π) has been metallated by butyl lithium (1/1) in ether at —35°C; carboxylation of this intermediate gave (π-C_5H_5)$CoB_9H_9C_2H$(CO_2H-π) [373]. Analogous metallation in a 1/2 (complex/n-BuLi) ratio gave (π-C_5H_5)$CoB_9H_9C_2(CO_2H)_2$-π. Metallation with butyllithium in THF at —30° C gave (π-n-BuC_5H_4)CoB_9H_9(C_2H_2-π). Analogous metallation with $C_6H_5C{\equiv}CLi$ gave (π-C_6H_5)$C{\equiv}C$-$C_5H_4CoB_9H_9$(C_2H_2-π).

Electrophilic bromination of $(\pi\text{-}C_5H_5)CoC_2B_9H_{11}\text{-}\pi$ by bromine in a 1/1 ratio gave $C_5H_5CoC_2B_9H_{10}Br$ [374]. With a 1/2 ratio (complex/Br_2), $C_5H_5CoC_2B_9H_9Br_2$ was obtained; a 1/5 ratio gave $C_5H_5CoC_2B_9H_8Br_3$. 1-methyl-*o*-carborane when treated with $CoCl_2$ and cyclopentadiene gave $C_5H_5CoB_9H_9C_2HCH_3$, which was brominated (1/1) to $C_5H_5CoB_9H_8BrC_2HCH_3$. A 1/2 (complex/Br_2) ratio gave $C_5H_5CoB_9H_7Br_2C_2HCH_3$.

The following empirical rules governing the thermal rearrangements of nonicosahedral cobaltacarboranes of the type $(\pi\text{-}C_5H_5)CoC_2B_nH_{n+2}$ (n = 6,7,8 and 10) have been presented [375]. (*a*) The cobalt atom will occupy the vertex of highest polyhedral coordination, and remain there. (*b*) The carbon atoms will not decrease their mutual separation. (*c*) Carbon atoms will migrate to vertices of lowest polyhedral coordination number. Once so located, they will migrate to an alternate low-coordination vertex. (*d*) Carbon atoms will tend to migrate away from the cobalt atom providing rules *b* and *c* are not violated. It does seem that the attainment of vertices of favourable coordination number dominates the migration of carbon atoms, and may even dominate these thermal rearrangements entirely.

The thermal polyhedral rearrangements of some 10-, 11- and 12-vertex bimetallic cobaltcarboranes, $(C_5H_5)_2Co_2C_2B_nH_{n+2}$ have been investigated [376]. Rearrangements involving migration of cobalt, as well as boron and carbon atoms, were observed, demonstrating the mobility of the C_5H_5Co vertex in the polyhedral surface. This investigation of bimetallic cobaltacarboranes revealed several similarities to the chemistry of monocobaltacarboranes, $C_5H_5CoC_2B_nH_{n+2}$, and also carboranes, $C_2B_nH_{n+2}$, as well as some chemical behaviour which could only be observed because of the two transition metal vertices. The general rules derived for monometallic rearrangements [375] appear to be valid in bimetallic systems, although here the isolation of isomers of intermediate stability, e.g. 1,4,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ from 1,8,2,3-$(C_5H_5)_2CoC_2B_7H_9$, becomes possible, emphasising the mobility of the C_5H_5Co vertex. Several new bi- and tri-metallic species were synthesised during this work, and improved syntheses of known metallocarboranes were discovered.

The recognition of the similarity of the bonding capabilities of $C_2B_9H_{11}{}^{2-}$ and $C_5H_5{}^-$, i.e. each moiety having six electrons in five molecular orbitals for "π-bonding" to various transition metals, allows an analogy to be made between the electron delocalisation in paramagnetic metallocenes and metallocarboranes. For this reason the isotropic shifts of the ^{11}B and ^{13}C nuclear resonances in paramagnetic metallocarboranes $(C_5H_5)M(C_2B_nH_{n+2})$ and $M(C_2B_nH_{n+2})_2$ (M = chromium(III), iron(III), nickel(III) and cobalt(II); n = 9,8,7 and 6) have been evaluated [377]. Electron delocalisation is primarily ligand-to-metal charge transfer, except for icosahedral cobalt(II) where it is metal-to-ligand. The magnitude and direction of the ^{13}C isotropic shifts are similar to those in metallocenes implying that the energetics of the metal—ligand interaction are similar, i.e. the highest filled molecular orbital is primarily metal centred, and non-bonding in nature.

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