COBALT, RHODIUM, AND IRIDIUM
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[*] No reprints available. Previous review see J. Organometal. Chem., 211 (1981) 279-396.

Metal carbon σ-bonded compounds

Although methyltetracarbonylcobalt, $CoMe(CO)_4$, has been known for more than two decades little information concerning its chemical and physical behaviour has been reported. IR spectroscopic results are consistent with a trigonal bipyramidal structure with the methyl group in an axial position and a complete Wolfsberg-Helmholtz (Extended Hückel) MO analysis of $CoMe(CO)_4$ has now been reported. The parameters of this study have been fitted to the UV absorption bands and the data predict the methyl group as the site of electrophilic attack and the equatorial CO groups as the site of nucleophilic attack (ref. 1). An unstable rhodium analogue, $RhEt(CO)_4$, has been detected in the hydroformylation of ethylene catalyzed by a range of rhodium(I) carbonyl derivatives, including $Rh_2Cl_2(CO)_4$, $RhCl(CO)_2py$, $Rh_2(OAc)_2(CO)_4$ and $Rh(acac)(CO)_2$ under mild conditions, e.g. 35^oC and 20 - 100 atm total pressure (ref. 2).

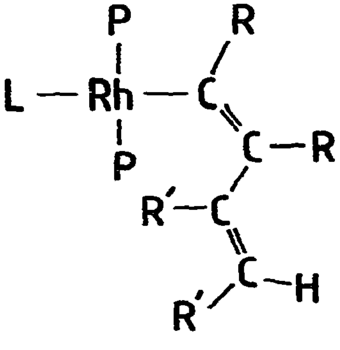
A convenient route to acylcobalt carbonyl complexes has been developed using the tetracarbonylcobalt anion, free from NaOH, in a two phase or three phase system, equation (1). The absence of NaOH is important since this reagent cleaves

$$RCH_2X + NaCo(CO)_4 \xrightarrow[\substack{R_4N^+Cl^- \\ H_2O \\ CO\ (1\ atm),\ 1100\ r.p.m.\ 20^oC}]{CH_2Cl_2} Co(COCH_2R)(CO)_4 \tag{1}$$

the cobalt carbon bond of acyls of the type $Co(COR)(CO)_4$. The complexes $Co(COCH_2R)(CO)_4$ formed in equation (1) are isolated as their more stable triphenylphosphine derivatives $Co(COCH_2R)(CO)_3(PPh_3)$ (ref. 3). The reactions of imidoyl chlorides with tricarbonyltriphenylphosphinecobalt$^-$ or the tetracarbonylcobalt anion in the presence of triphenylphosphine affords iminoacylcobalt carbonyl complexes in 19 - 85% yields, equation (2) (ref. 4).

$$RClC{=}NR \xrightarrow[\substack{or \\ NaCo(CO)_3PPh_3}]{NaCo(CO)_4\ +\ PPh_3} Co(CR{=}NR)(CO)_3PPh_3 \tag{2}$$

Some *ortho*-substituted aryliridium(I) complexes $Ir(C_6H_{5-n}R_n)(CO)L_2$ ($C_6H_{5-n}R_n$ = 2-EtC_6H_4, 2, 6-$Et_2C_6H_3$, 2-Et-6-MeC_6H_3; L = PPh_3, $PMePh_2$) have been prepared from the appropriate aryllithium reagent and *trans*-$IrCl(CO)L_2$. These compounds, with the exception of *trans*-$Ir(2\text{-}EtC_6H_4)(CO)(PPh_3)_2$ exhibit *cis*-*trans* isomerism (ref.5). A similar reaction of $1,1^1$-dichloro-2-lithioferrocene with *trans*-$IrCl(CO)(PPh_3)_2$ affords $Ir(FcCl_2)(CO)(PPh_3)_2$ ($FcCl_2$ = $ClC_5H_4FeC_5H_3Cl$) (ref. 6). Some thiocarbonyl derivatives $MR(CS)(PPh_3)_2$ (M = Rh, R = C_6F_5 or C_6Cl_5; M = Ir, R = C_6F_5 or C_6Cl_5) have also been prepared by the action of aryllithium reagents or arylmagnesiumhalides with $MCl(CS)(PPh_3)_2$. None of these pentafluorophenyl or pentachlorophenyl compounds afford dioxygen adducts but some of them afford stable oxidative addition adducts with HCl, halogens and mercury(II) chloride. The iridium(III) complex $Ir(C_6F_5)I_2(CS)(PPh_3)_2$ reacts with p-toluidine via nucleophilic attack of the amine on the carbon of the CS ligand, to give the isocyanide complex $Ir(C_6F_5)I_2(CNtol)(PPh_3)_2$, and treatment of $Ir(C_6F_5)(CS)(PPh_3)_2$ with methyliodide gives the thiocarbene derivative $Ir(C_6F_5)I_2(carbene)(PPh_3)_2$, carbene = CMe(SMe) (ref. 7). The reactions of electrophilic acetylenes $RC{\equiv}CR$ (R = CF_3 or CO_2Me) with $RhH(L)(PPh_3)_3$ (L = CO or PF_3) afford vinyl complexes trans - $Rh(CR{=}CHR)(L)(PPh_3)_2$ which undergo further acetylene insertion. Thus trans - $Rh(CR{=}CHR)(L)(PPh_3)_2$ (R = CF_3) reacts with DMAD and trans - $RH(CR{=}CHR)(L)(PPh_3)_2$ (R = CO_2Me) reacts with hfb to give the same double insertion product (1).

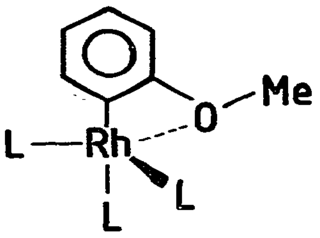


(1)

L = CO, PF_3
P = PPh_3
R = CO_2Me
R' = CF_3

$Rh(CR{=}CHR)(PF_3)(PPh_3)_2$ and t - butyl bromide give $CF_3CH{:}CHCF_3$, isobutene and trans - $RhBr(PF_3)(PPh_3)_2$ (ref. 8).

Solutions of the cobalt(I) methyl compounds, $CoMe(PAr_3)_3$, (Ar = Ph, 4-MeC_6H_4, 3-MeC_6H_4) in THF, benzene or chlorobenzene decompose to yield biaryls. It is suggested that in these compounds the triarylphosphine rearranges via a three-centred oxidative-addition with subsequent coupling to biaryl by reductive elimination from an arylcobalt intermediate (ref. 9). Further evidence for this mechanism is provided by a study of the decomposition of $CoMe(PPh_3)_3$ in chlorobenzene solution which yields biphenyl, triphenylphosphine, methyldiphenylphosphine and diphenylphosphine. It is clear that $CoMe(PPh_3)_3$ has a very strong tendency to undergo oxidative-addition reactions (ref. 10). A rhodium derivative, $RhPh(PMe_3)_3$, can be obtained in high yield by the interaction of $Rh_2(OAc)_4$, Ph_2Mg, and PMe_3 in diethyl ether. In contrast to the triphenylphosphine analogue, $RhPh(PMe_3)_3$, is readily obtained pure and in high yield. The 2-methoxyphenyl derivative (2) is thermally more stable and less air-sensitive than $RhPh(PMe_3)_3$

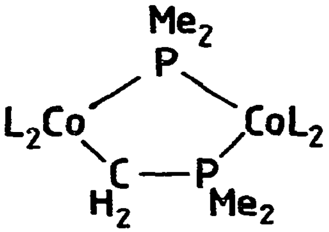


(L = PMe$_3$)

(2)

since the methoxyl group probably coordinates to the rhodium as in (2) (ref. 11).

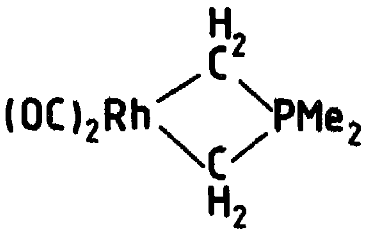
The dinitrogen cobaltates, $Mg(THF)_4(CoN_2L_3)$ and $KCoN_2L_3$ ($L = PMe_3$) react with $CoClL_3$ or $NiCl_2L_2$ to give the novel binuclear complex (3). This complex reacts



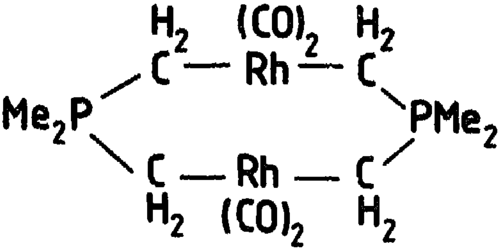
(L = PMe$_3$)

(3)

with carbon monoxide to give $L(CO)_2Co(CH_2PMe_2)(PMe_2)Co(CO)_2L$ but there is no insertion into the cobalt–carbon bond. A cleavage reaction by trimethylphosphite (L') affords $CoP(O)(OMe)_2L_2L'_2$ (ref. 12). The reaction of $Ir_2Cl_2(cod)_2$ with $MeBu^t_2PCH_2$ gives the mononuclear ylide chelate $Ir(CH_2)_2PBu^t_2(cod)$ (ref. 13) and an analogous complex $Ir(CH_2)_2PMe_2(cod)$ can be obtained from $Ir_2Cl_2(cod)_2$ and $Me_2P(CH_2)_2Li$ (ref. 14). Treatment of $Ir_2Cl_2(cod)_2$ with Me_3PCH_2 affords $Ir(CH_2)_2PMe_2(CH_2PMe_3)_2$ and the reactions of $Me_3PNPMe_2CH_2$ with $Ir_2Cl_2(C_8H_{14})_4$ and *trans* - $IrCl(CO)(PPh_3)_2$ gives $\overline{IrCH_2PMe_2NPMe_2CH_2}(cod)$ and $\overline{IrCH_2PMe_2NPMe_2CH_2}(CO)(PPh_3)_2$ respectively (ref. 14). NMR measurements on the rhodium ylide chelate complex $Rh(CH_2)_2PMe_2(CO)_2$ indicate the presence of the mononuclear species (4) and the dinuclear species (5) in a toluene-$\underline{d}^8$ solution (ref. 15).



(4)



(5)

Relatively few alkynyl complexes of cobalt(II) are known. However, some cyclohexylethynyl complexes of cobalt(II), which are sufficiently stable for chemical analysis and spectroscopic measurements, have been reported. Thus $Co(NCS)_2.2NH_3$ reacts with KC_2Cy in liquid ammonia to give $K_4[Co(C_2Cy)_6].2NH_3$ and $K_2[Co(C_2Cy)_4(NH_3)_2]$. The four coordinate square planar complex, $Co(C_2Cy)_2(PPh_3)_2$, has also been claimed. All these complexes of cobalt(II) are low spin and the magnetic moments of the octahedral cobalt(II) complexes, measured at various temperatures, are intermediate between low- and high-spin values (ref. 16).

The cobalt(III) alkyl, $CoMe_3(PMe_2Ph)_3$ has been prepared by the reaction of $CoMe_2(acac)(PMe_2Ph)_2$ with MeLi in the presence of one equivalent of PMe_2Ph. The reaction of $CoMe_3(PMe_2Ph)_3$ with acacH affords methane according to the equation (3) (ref. 17). Two types of dialkylcobalt(III) complexes containing

$$\underline{mer} - CoMe_3L_3 + acacH \longrightarrow CoMe_2(acac)L_2 + CH_4 + L \qquad (3)$$

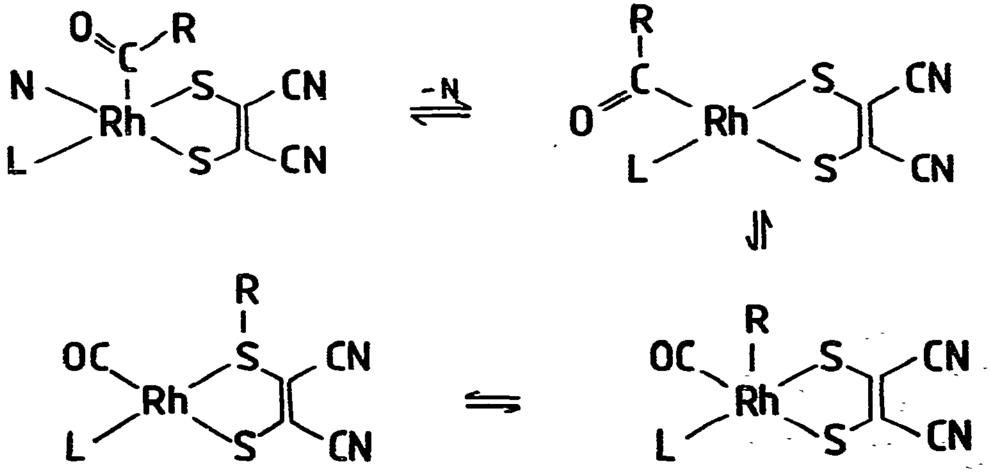
$$(L = PMe_2Ph)$$

bipy have been isolated from reactions of $Co(acac)_3$, bipy, and aluminium alkyls in diethyl ether. With Al:Co ratios greater than 7 the ionic complexes $[CoR_2(bipy)_2]AlR_4$ (R = Me, Et) are obtained. However, at lower Al:Co ratios of 1.5 - 2.0 the neutral complexes $CoR_2(acac)(bipy)$ (R = Me, Et, Pr^n, Pr^i) are formed. Interestingly the cationic complexes are stable at room temperature under nitrogen and in dry air and their inertness towards water is also surprising. Strong acids such as concentrated sulphuric acid cleave both the alkyl-cobalt and -aluminium bonds but dry hydrogen chloride reacts only with the aluminate anion, equation (4).

$$[CoR_2(bipy)_2]AlR_4 + \underset{\text{excess}}{HCl} \longrightarrow [CoR_2(bipy)_2]Cl + 4RH \tag{4}$$

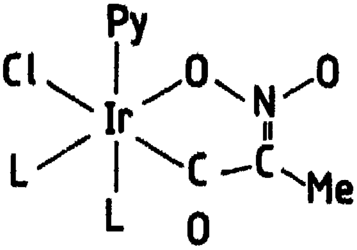
A dark-blue compound, presumably $CoMe(bipy)_2$, is formed by dissolving $[CoMe_2(bipy)_2]AlMe_4$ in tetrahydrofuran and $CoEt(bipy)_2$ can similarly be obtained from $[CoEt_2(bipy)_2]AlEt_4$. These dark-blue cobalt(I) alkyls have previously been erroneously formulated as cobalt(II) alkyls, $CoR_2(bipy)_2$ (ref. 18).

The addition of PEt_3 to solutions of $[Rh(mnt)(CO)_2]^-$ gives $[Rh(mnt)(CO)(PEt_3)]^-$ which readily reacts with a variety of alkyl iodides and bromides to form acyl complexes which are isolated as neutral bis(phosphine) complexes of formula $Rh(COR)(mnt)(PEt_3)_2$, (mnt = maleonitriledithiolate, R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, $\underline{n}$-$C_{10}H_{21}$, Bz, allyl, propargyl). These rhodium(III) acyl complexes, $Rh(COR)(mnt)(PEt_3)_2$, possess a square pyramidal geometry with the acyl group in the apical position. The anion $[Rh(mnt)(CO)(PEt_3)]^-$, in the presence of excess PEt_3, can also be protonated by perchloric acid to give the rhodium(III) hydride, $RhH(mnt)(CO)(PEt_3)_2$. However, the addition of acid to the rhodium(I) complex anion in methyl cyanide in the presence of ethylene slowly leads to the formation of an acyl complex which can be isolated as $Rh(COEt)(mnt)(PEt_3)_2$ upon addition of excess PEt_3. This propionyl complex is formed through a sequence of olefin coordination, insertion into an M-H bond, and migratory insertion of CO (ref. 19). The action of heat upon neutral acyl complexes of the type Rh(COR)(mnt)LN (L = PEt_3 and N = py, $C_6H_{11}NH_2$) in certain cases leads to the S-alkylated complexes $Rh(R\text{-}mnt)(CO)(PPh_3)$, alkyl group migration occurring by a succession of two 1,2 shifts with a rhodium(III) alkyl carbonyl dithiolate (6) as an intermediate (ref. 20).



(6)

The oxidative addition of $MeCH(NO_2)Cl$ to *trans* - $IrCl(CO)(PMe_2Ph)_2$ followed by treatment of the initial product with pyridine affords the iridium(III) acyl (7), the reaction occurring via a radical-chain process.



(7) (L = PMe_2Ph)

The reaction of $MeCH(NO_2)Br$ with *trans* - $IrBr(CO)(PMe_2Ph)_2$ yield two isomers of $IrRBr_2(CO)(PMe_2Ph)_2$, R = $CH(NO_2)Me$, which do not react with pyridine (ref. 21). The reaction of $ClCH_2COCl$ with *trans* - $IrCl(CO)(PPh_3)_2$ affords $IrCl_3(CO)(PPh_3)_2$ quantitatively rather than an iridium acyl complex (ref. 22). The crystal structure determination of $Rh(COPh)Cl_2P_2$ (P_2 = $Ph_2PCH_2CH_2CH_2PPh_2$), which is obtained by the reaction of PhCOCl with bis(1,3-diphenylphosphinopropane)rhodium(I) chloride, reveals a square-pyramidal geometry about the rhodium with the benzoyl group occupying the apical position (ref. 23). Various metallacylic complexes have also been obtained by oxidative-addition type reactions. Thus the Vaska complexes *trans* - $RhCl(CO)(PR_3)_2$ (R_3 = Me_3, Me_2Ph, $MePh_2$) react with triphenylcyclopropenium salts to generate blue-green rhodiacyclic complexes, $\overline{Rh(C_3}Ph_3)Cl_2(PR_3)_2$ via oxidative-cleavage of a C-C bond (ref. 24). A metallocyclic intermediate has also been isolated in the $Ir_2Cl_2(CO)_6$ catalyzed rearrangement of 1,3-bishomocubane (ref. 25).

The compoun $RhMeCl_2(CO)(PPh_3)_2$ has been shown to reductively eliminate methyl chloride by a first order, intramolecular process with an activation energy of 95.0 kJ mol^{-1}. Interestingly in the presence of free triphenylphosphine, S_N2 attack on the methyl group by the phosphine occurs to give $Ph_3PMe^+Cl^-$ and *trans* - $RhCl(CO)(PPh_3)_2$ (ref. 26). A study of the reactions of various cobalt(II) compounds e.g. $CoBr_2$, $CoBr_2(PPh_3)_2$, $CoCl_2$ + CO, $CoCl_2$ + ethylene with $PhMe_2CCH_2MgX$ under varying conditions gives mainly $PhMe_2CCH_2CH_2CMe_2Ph$ or $PhMe_2CH_2C_6H_4$-*o*-Bu^t (ref. 27) and a general symmetry analysis of reductive elimination from transition metal alkyls has been carried out (ref. 28).

Several metallation reactions involving rhodium and iridium complexes, including a review on organometallic intramolecular-coordination containing a nitrogen donor ligand (ref. 29), have appeared during the year. Thus, although $Bu^t_2PCH(Me)OMe$ does not yield a platinum(II) metallated derivative, $Ir_2Cl_2(C_8H_{14})_4$ reacts at 25°C with both $Bu^t_2PCH_2OMe$ and $Bu^t_2PCH(Me)OMe$ to give iridium(III) metallated complexes by oxidative addition to the methyl C-H bond, the coordinatively unsaturated compounds reacting with carbon monoxide to give octahedral iridium(III) carbonyl hydride complexes, equation (5) (ref. 30).

$$\tfrac{1}{2}\mathrm{Ir_2Cl_2(C_8H_{14})_4} \xrightarrow[2.\mathrm{CO}]{1.2\mathrm{L}} \overline{\mathrm{IrH(CH_2OCH_2P}}\mathrm{Bu^t{}_2)(Cl)(CO)L} \qquad (5)$$

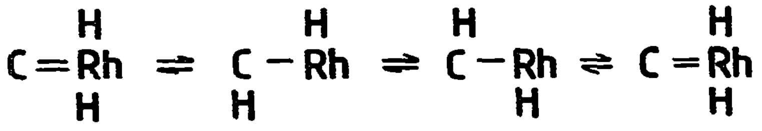
$$(\mathrm{L = Bu^t{}_2PCH_2OMe})$$

The phosphines R_2PCH_2Ph (R = Cy, Bu^t) also react with $M_2Cl_2(C_8H_{14})_4$ (M = Rh, Ir) to give cyclometallated complexes, e.g. equation (6). Studies with $PdCl_2$ and $PtCl_2$(benzonitrile)$_2$ show that the reactivities of the phosphines decrease in the order Ir(I) > Rh(I) $\gg$ Pd(II), Pt(II), suggesting a different mechanism for univalent and bivalent $\underline{d}^8$ metal complexes.

$$\tfrac{1}{2}\mathrm{Ir_2Cl_2(C_8H_{14})_4} \xrightarrow[\mathrm{N}]{2\mathrm{L}} \overline{\mathrm{IrH(C_6H_4CH_2P}}\mathrm{Cy_2)(Cl)(L)(N)} \qquad (6)$$

$$(\mathrm{L = Cy_2PCH_2Ph},\quad \mathrm{N} = \gamma\text{-picoline})$$

Reactions of the metal chlorides with $\underline{m}$-$FC_6H_4CH_2PR_2$ reveal that for rhodium(I) and iridium(I) complexes a nucleophilic mechanism operates in the C-H bond cleavage reaction while for palladium(II) an electrophilic mechanism is involved. Steric effects also have a large influence on the reaction rates (ref. 31). An interesting rapid and reversible C-H fission in $\overline{\mathrm{RhHCl(Bu^t{}_2P}}\mathrm{CH_2CH_2}\overline{\mathrm{CHCH_2CH_2P}}\mathrm{Bu^t{}_2)}$ has been established by n.m.r. spectroscopy. Thus treatment of $RhCl_3 3H_2O$ with $Bu^t{}_2P(CH_2)_5PBu^t{}_2$ in ethanol gives the 16-atom ring hydride complex $Rh_2H_2Cl_4(Bu^t{}_2CH_2CH_2CH_2CH_2CH_2PBu^t{}_2)$ which upon treatment with 2-methylpyridine gives the cyclometallated complex $\overline{\mathrm{RhHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2P}}\mathrm{Bu^t{}_2)}$. This cyclometallated complex does not show a hydride resonance in its proton NMR spectrum at room temperature but the resonance can be observed at low temperatures. The inability to detect the hydride resonance at room temperature has been ascribed to the rapid interconversion of (8) and (9) which may be either a concerted

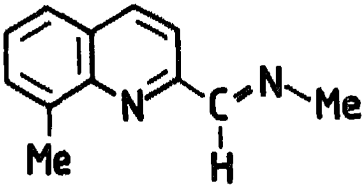


$$\mathrm{C{=}\overset{H}{\underset{H}{Rh}}} \rightleftharpoons \mathrm{\underset{H}{C}{-}\overset{H}{Rh}} \rightleftharpoons \mathrm{\overset{H}{C}{-}\underset{H}{Rh}} \rightleftharpoons \mathrm{C{=}\overset{H}{\underset{H}{Rh}}}$$

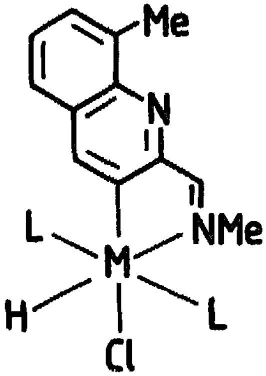
(8) (9)

process or a stepwise process involving a carbenoid-ylide intermediate. As expected the hydride complex $\overline{\mathrm{RhHCl(Bu^t{}_2PCH_2CH_2CMeCH_2CH_2P}}\mathrm{Bu^t{}_2)}$ is not fluxional but it very slowly loses dihydrogen to give the olefin complex $\overline{\mathrm{RhCl(Bu^t{}_2PCH_2CH_2C({=}CH_2)CH_2CH_2P}}\mathrm{Bu^t{}_2)}$ (ref. 32).

In addition to the metallation of ligands which contain phosphorus atoms a number of ligands containing nitrogen donor atoms have also been shown to undergo metallation reactions. Thus metallation of 2-(CHR^2=CR^1)py occurs on reaction with $Rh_2X_6(PBu^n_3)_4$ to afford $RhX_2(CR^2{=}CR^1C_5H_4N)(PBu^n_3)_2$ (R^1,R^2 = H or Me; R^1 = H, R^2 = Ph or C_6H_4OMe-p; X = Cl or Br), the derivative $RhBr_2(CH{=}CHC_5H_4N)(PBu^n_3)_2$ reacting with bromine to give $RhBr_2(CH{=}CBrC_5H_4N)(PBu^n_3)_2$ (ref. 33). Metallation



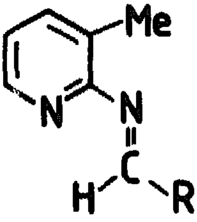
(10)



(L=PCy_3)

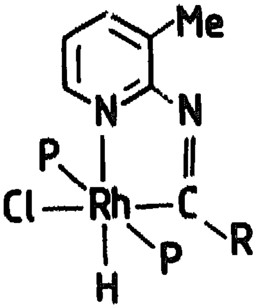
(11)

of the ligand (10) occurs on treatment of $M_2Cl_2(C_8H_{14})_4$ (M = Rh, Ir) with PCy_3 and (10) in refluxing benzene to give (11) (ref. 34), and treatment of the aldimines (12) with $RhCl(PPh_3)_3$ in THF at 55°C gives the yellow air-stable complexes (13). The use of these derivatives in hydroacylation has been



R = Ph, p-$MeOC_6H_4$, p-ClC_6H_4

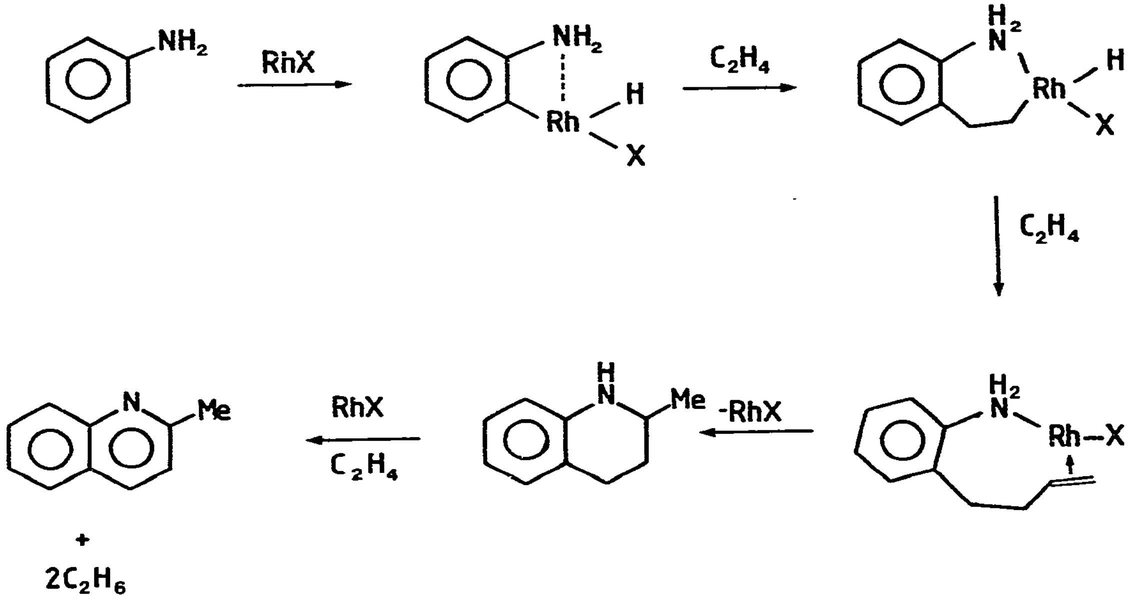
(12)



(P=PPh_3)

(13)

demonstrated. Thus reaction of (12, R = Ph) with a catalytic amount of $RhCl(PPh_3)_3$ in THF under a pressure of ethylene followed by hydrolysis of the reaction mixture affords propiophenone (ref. 35). Metallation reactions are also of importance in the formation of N-ethylaniline and 2-methylquinoline from aniline and ethylene catalyzed by $RhCl_3.3H_2O$ and PPh_3 as illustrated below (ref. 36).



An unusual set of complexes $[\overline{Ir_2(C_6H_3RN{=}NH}\,)_2(CO)_4(PPh_3)_2][BF_4]_2$ results from the reaction $Ir_2(CO)_6(PPh_3)_2$ with p-substituted aryldiazonium salts. These complexes are diamagnetic and presumably contain iridium-iridium bonds. They undergo deprotonation with KOH in ethanol e.g. $[\overline{Ir_2(C_6H_3RN{=}NH}\,)_2(CO)_4(PPh_3)_2][BF_4]_2$ affords the neutral complexes $\overline{Ir_2(C_6H_3RN{=}NH}\,)_2(CO)_4(PPh_3)_2$ and reactions of the dicationic species with halide ions results in cleavage of the iridium-carbon bonds to afford $Ir_2Cl_2(N{=}NC_6H_4R)_2(PPh_3)_2$ (ref. 37).

The complex $\overline{Rh(C_6H_4PPh_2}\,)(PPh_3)_2$ has been shown to catalyze the decomposition of formic acid to CO_2 and H_2, equations (7) - (9) (ref. 38).

$$\overline{Rh(C_6H_4PPh_2}\,)P_2 + HCO_2H \longrightarrow Rh(HCO_2)P_3 \tag{7}$$

$$Rh(HCO_2)P_3 \longrightarrow RhHP_3 + CO_2 \tag{8}$$

$$RhHP_3 + HCO_2H \longrightarrow Rh(HCO_2)P_3 + H_2 \qquad (9)$$

$$(P = PPh_3)$$

An effective new approach has been described for the determination of some transition metal–alkyl bond dissociation energies and it has been applied to determine the first direct estimation of cobalt–carbon bond dissociation energies in some organocobalt compounds. Thus determination of ΔH^o for the reaction described in equation (10) in combination with available data for the heats of

$$Co(CHMePh)(dmgH)_2py \rightleftharpoons Co(dmgH)_2py + PhCH = CH_2 + \tfrac{1}{2}H_2 \qquad (10)$$

formation of styrene and of the PhCHMe radical gives a value of 19.9 kcal/mol for the cobalt–carbon bond dissociation energy of $py(dmgH)_2Co\text{-}CHMePh$ using the thermochemical cycle:

	ΔH^o
$py(dmgH)_2CoCHMePh \rightleftharpoons py(dmgH)_2Co + PhCH = CH_2 + \tfrac{1}{2}H_2$	22.1
$PhCH = CH_2 + \tfrac{1}{2}H_2 \rightleftharpoons Ph\dot{C}HMe$	−2.2
$py(dmgH)_2CoCHMePh \rightleftharpoons py(dmgH)_2Co + Ph\dot{C}HMe$	19.9

The reaction in equation (10) probably proceeds via rate-determining homolytic cleavage of the cobalt–carbon bond and since the reverse of this reaction proceeds with very small activation barriers, the activation enthalpy for equation (10) should be close to the cobalt–carbon bond dissociation energy. Studies of this type suggest that the cobalt–carbon bond dissociation energies in organocobaloximes are higher than those in corresponding organocobalamins and that the cobalt-carbon bond dissociation energies of alkylcobalamins do not exceed the range 20–30 kcal/mol (ref. 39). Steric effects of the corrin ring are considered to be important in promoting homolytic cleavage of the cobalt–carbon bond of organocobalamins and the unusually long cobalt–carbon bond found in $CoPr^i(dmgH)_2py$ together with other data show that there is a clear relationship between cobalt-carbon bond length and the number of substituents joined to the carbon (ref. 40). X-ray studies on the complex $CoMe(dmgH)_2PPh_3$ together with other data also show that ligand steric size is an important factor in determining the degree of bending of the dmgH ligand (ref. 41), and the coordination of the axial 5,6-dimethylbenzimidazole ligand of alkylcobalamins is dependent on the size of the alkyl group, most secondary alkylcobalamins existing mainly in the "base-off" form in neutral solution (ref. 42).

Various secondary alkyl- and cycloalkylcobalamins have been prepared by reactions of olefins, alkyl iodides and bromides with hydridocobalamin. The secondary and higher primary alkylcobalamins undergo sterically induced spontaneous dealkylation via syn beta-elimination. In general they are more stable in acidic media while in neutral or alkaline solution the axial base is coordinated and resulting conformational changes of the corrin ligand accelerates cobalt-carbon bond cleavage (ref. 42). Organocobalamins have also been obtained by oxidation of straight-chain aliphatic carboxylic acids and certain dicarboxylic as well as branched carboxylic acids to organic radicals in the presence of vitamin B_{12r}. As a consequence of steric effects and the instability of secondary and tertiary alkylcobalamins, vitamin B_{12r} acts as a selective scavenger of primary alkyl and omega-carboxyalkyl radicals (ref. 43). Fluoroalkylcobalamins have been prepared by the alkylation of cobalamin with CF_3I, CHF_2Cl or related compounds and cobalamin reacts with trifluoromethylcobalamin to give successively the CHF_2, CH_2F and Me cobalamins (ref. 44).

The cobalt(I)-phthalocyanine anion has been shown to be different from cob(I)alamin and other strong nucleophiles by not undergoing nucleophilic additions. Instead the cobalt(I)-phthalocyanine anion only reacts via nucleophilic substitution, resembling I^- in its selective behaviour and is thus to be regarded as a very strong soft nucleophile (ref. 45). Prolonged reaction of methyl-*p*-bromobenzoate with cob(I)inamide has been shown to give a low yield of the methyl ester of *p*-carboxyphenylcobinamide (ref. 46). Reduction of Co(salen) with lithium and sodium metals in THF affords the bimetallic systems Co(salen)Na(THF) and Co(salen)Li(THF)$_{1.5}$ which are active in carbon dioxide fixation (ref. 47).

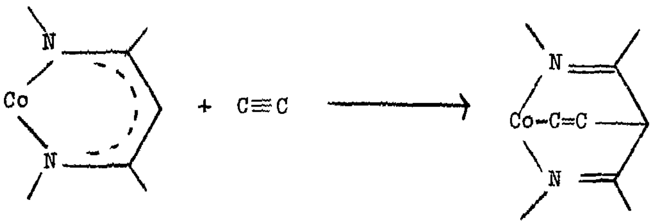
An organocobaloxime has been used to obtain isotopically labelled amino acids, equations (11) and (12) (ref. 48).

$$(Co)\overset{*}{C}H_2R \xrightarrow[\overset{*}{C}O_2]{DTE} R\overset{*}{C}H_2\overset{*}{C}O_2H \qquad (11)$$

$$R\overset{*}{C}H_2\overset{*}{C}O_2H \xrightarrow{N_2H_4} H_2N\overset{*}{C}H_2\overset{*}{C}O_2H \qquad (12)$$

(DTE = dithioerythyritol, R = phthalimido)

A novel cycloaddition reaction of acetylene with cobalt(III) complexes of a tetraaza[14]annulene complex was mentioned in the Annual Survey for 1976 and the full paper on the synthesis and X-ray structure of the product, equation (13) has now appeared (ref. 49).


(13)

(C≡C is acetylene)

The reactions of radicals with cobalt(II) complexes can provide a route to organocobalt(III) complexes and a study has been made of the reactions of cobalt(II) tetraphenylporphyrin and (IR,2R)-N,N^1-disalicylidene-1,2-cyclohexanediaminato-cobalt (II) using (S,S)-(-)-,R,R)-(+)-, and meso-1,1^1-diphenylazoethane, PhMeCHN=NCHMePh, as a radical source. It appears that the PhCHMe radical is stereoselectively stabilized by the cobalt(II) complexes (ref. 50). The reaction of $Co(dmgH)_2py$ with reactive alkyl halides e.g. alpha-halogenoesters and related compounds in the presence of zinc in a non-aqueous solvent gives alkylcobaloximes in yields which are generally superior to those of conventional synthesis. The proposed mechanism of the reaction is outlined in equations (14) - (16) (ref. 51).

$$Co(dmgH)_2py_2 + RX \longrightarrow CoX(dmgH)_2py + R + py \qquad (14)$$

$$\dot{R} + Co(dmgH)_2py_2 \longrightarrow CoR(dmgH)_2py + py \qquad (15)$$

$$2CoX(dmgH)_2py + Zn \longrightarrow 2Co(dmgH)_2py + 2X^- + Zn^{2+} \qquad (16)$$

The negative ion mass spectra of the cobalt complexes Co(oaben), Co(salen) and Co(salophen) in the presence of methane leads to incorporation of a methyl group into the cobalt(II) compounds, e.g. equations (17) - (19) (ref. 52).

$$Co(salen) + \bar{e} \longrightarrow Co(salen)^- \qquad (17)$$

$$Co(salen)^- + CH_4 \longrightarrow CoH(Me)(salen)^- \qquad (18)$$

$$CoH(Me)(salen)^- \longrightarrow H + CoMe(salen)^- \qquad (19)$$

Pseudohalides have been shown to react with alkylcobaloximes to give labile complexes $CoR(CNX)(dmgH)_2$ (X = O,S,Se), the linkage isomers preference being dependant upon X, the alkyl group R, and the solvent. The inert pseudo halide complexes $Co(CNS)(dmgH)_2N$ (N = nitrogen donor ligand) and $Co(SeCN)(dmgH)_2N$ react with alkylcobaloximes $CoR(dmgH)_2(H_2O)$ and $CoR(dmgH)_2$ to form neutral pseudohalide-bridged dicobaloximes $\mathrm{(dmgH)_2RCo{-}(CNS){-}Co(dmgH)_2N}$ and $\mathrm{(dmgH)_2RCo{-}(NCSe){-}Co(dmgH)_2N}$, both linkage isomers of the thiocyanato-bridged system existing. The ligand bridged dicobaloximes partially dissociate in chloroform solution, the degree of dissociation being dependent upon R, CNX, and N, more stable dimers being formed when R = $\mathrm{CF_3}$ rather than Me and N = pyridine rather than piperidine. Oligomers of the type (14) are formed by the reaction of $\mathrm{Co(CNS)(dmgH)_2N}$ or $\mathrm{Co(SeCN)(dmgH)_2N}$ with $\mathrm{CoR(dmgH)_2}$ in the presence

$$\mathrm{(dmgH)_2RCo[-(CNX)Co(dmgH)_2-]_n(CNX)Co(dmgH)_2N} \qquad (14)$$

$$(n = 2,3;\ X = S,\ Se)$$

of trace quantities of cobalt(II) (ref. 53). Chelate cobalt(III) complexes containing the pseudohalides, $\mathrm{C{\equiv}CR}$, $\mathrm{C(CN)_3}$, $\mathrm{CH_2NO_2}$ have also been reported (ref. 54) and azidochelate cobalt(III) complexes $\mathrm{CoN_3(N{-}N)PPh_3}$, N-N = dianion of N,N^1-o-phenylenebis(salicylidenimine), have been shown to react with isocyanides to give cobalt-carbon bonded tetrazolate complexes e.g. (15). The compound 2-isocyanoethanol affords tetrazolato or azidooxazolidin-2-ylidene

$$\mathrm{Co\overline{C{=}N{-}N{=}N{-}N}Cy(N{-}N)(CNCy)} \qquad (15)$$

complexes (16), depending on the nature of the chelate ligand, the solvent and the trans - basal ligand (ref. 55).

$$\mathrm{Co\overline{CNHCH_2CH_2O}(N_3)(chelate)} \qquad (16)$$

Organocobalt(III) complexes can undergo cobalt-carbon bond cleavage by any of the three reaction types illustrated in equations (20) - (22). Results of a

$$\mathrm{CoR(chelate)} \longrightarrow \mathrm{R^+ + Co(I)(chelate)} \qquad (20)$$

$$\mathrm{CoR(chelate)} \longrightarrow \mathrm{\dot{R} + Co(II)(chelate)} \qquad (21)$$

$$\mathrm{CoR(chelate)} \longrightarrow \mathrm{R^- + Co(III)(chelate)} \qquad (22)$$

study on the mechanism of the base-catalyzed methane formation from methyl(aquo)cobaloxime have shown that all simple alkyl(aquo)cobaloximes undergo cobalt-carbon bond cleavage in aqueous base with generation of cobalt(III) complex (ref. 56).

Homolytic cleavage of a cobalt-carbon bond, equation (21), upon photolysis of an organocobalt complex is a well documented process but much remains to be clarified concerning the nature and the fate of the radical pair initially formed and the effects of equatorial and axial ligands. Photolysis of alkylated cobalt complexes of 1,19-dimethyl-ad-bisdehydrocorrinato, CoR(BDHC), results in an apparent heterolytic cleavage of the cobalt-carbon bond, the radical pair generated upon photolysis undergoing electron transfer to give the cobalt(III) complex and a carbanionic intermediate which is readily protonated, equations (23) (ref. 57).

$$\mathrm{RCo(III)} \overset{h\nu}{\rightleftharpoons} \mathrm{R{\cdot}Co(II)} \longrightarrow \mathrm{R^{-}Co(III)} \xrightarrow{H_2O} \mathrm{RH + Co(III)} \qquad (23)$$

The photolysis of several alkylcobaloximes, cobalamins, methyl salen, and coenzyme B_{12} in protic solvents has been studied by ESR and spin-trapping techniques and it is apparent that during photolysis hydrogen atoms are probably abstracted from the C(10) position of the corrin equatorial ligand in the case of coenzyme B_{12} and cobalamin derivatives (ref. 58). Photohomolysis studies of alkylcobalamins show that there are no long-lived homolysis precursors in either methyl- or adenosylcobalamin and previously observed variations in the cobalt(II) EPR signal are a consequence of secondary radical reactions (ref. 59).

Whereas (hydroxyalkyl)cobaloximes are stable in both acidic and basic media (β-hydroxyethyl)cobaloxime readily decomposes under these conditions, equations (24) and (25). Kinetic studies have been carried out on the cleavage and

$$\mathrm{Co(CH_2CH_2OH)(dmgH)_2(H_2O)} \xrightarrow{H^+} \mathrm{Co(dmgH)_2(H_2O)_2{}^{+} + C_2H_4} \qquad (24)$$

$$\mathrm{Co(CH_2CH_2OH)(dmgH)_2(H_2O)} \xrightarrow{OH^-} \mathrm{Co(dmgH)_2{}^{-} + MeCHO + 2H_2O} \qquad (25)$$

rearrangement reactions of (β-hydroxyalkyl)cobaloximes in acid solution and it is apparent that although β-hydroxyethyl derivatives evolve ethylene, β-hydroxy-n-propyl and β-hydroxyisopropyl derivatives undergo reversible isomerization prior to olefin release by a mechanism in which the olefin is π-bonded to the cobalt complex. Cleavage reactions of the BF_2-substituted macrocycle are much slower than for the bis(dimethylglyoximato) complexes (ref. 60).

The hemiacetal of formylmethylcobalamin, ethoxy-2-hydroxyethylcobalamin (17) has been shown to be formed from both the deacetalization of the 2,2-diethoxyethylcobalamin (18) and from the catalyzed acetalization of (19) in alcoholic solutions containing Et_3N. Formylmethylcobalamin (19) can also be formed from the alkaline deacetalization of (17) and (18) (ref. 61).

$$\mathrm{[Co]CH_2CH(OH)(OR)} \qquad (17)$$

$$[Co]CH_2CH(OR)_2 \qquad (18)$$

$$[Co]CH_2CHO \qquad (19)$$

The electrochemical reduction at mercury and platinum electrodes of a number of perfluoroalkyl (R_f) and alkyl (R_h) cobalt(III) complexes containing quadridentate salicylaldimines CoR(salen) have been studied. Each class of complex undergoes reduction as indicated in equation (26), the perfluoroalkyl complexes

$$Co(III)R(salen) \xrightarrow{e^-} Co(II)R(salen)^- \xrightarrow{e^-} Co(I)R(salen)^{2-} \qquad (26)$$

being reduced most readily. The $CoR_f(salen)^-$ species are more stable than the alkyl complexes but they do decompose to perfluorocarbanions and Co(salen). The alkyl anions $CoR_h(salen)^-$ rapidly give $Co(salen)^-$ and the alkyl radical. The dianions $CoR_f(salen)^{2-}$ and $CoR_h(salen)^{2-}$ are exceedingly unstable and decompose rapidly to $Co(salen)^-$ (ref. 62).

Oxidative cleavage of the cobalt-carbon bond of organocobaloximes occurs with inversion at the alpha-carbon. The mechanism of this reaction occurs via one-electron oxidation of the organocobaloxime followed by nucleophilic attack at the alpha-carbon resulting in the observed inversion of configuration, equation (27). The radical cations $CoR(dmgH)_2L^+$ have been generated by chemical oxidation e.g. with Br_2, PbO_2, and Ce(IV) or electrochemical oxidation of the

$$CoR(dmgH)_2(H_2O) \xrightarrow{X_2} CoR(dmgH)_2(H_2O)^+ \xrightarrow{X^-} Co(II) + RX \qquad (27)$$

cobalt(III) complexes $CoR(dmgH)_2L$ and EPR studies of the radical cations $CoR(dmgH)_2L^+$ support their formulation as organocobalt(IV) complexes (ref. 63). A study of the cleavage reaction of organocobaloximes with iodine in chloroform

$$CoR(dmgH)_2(H_2O) + I_2 \longrightarrow RI + CoI(dmgH)_2(H_2O) \qquad (28)$$

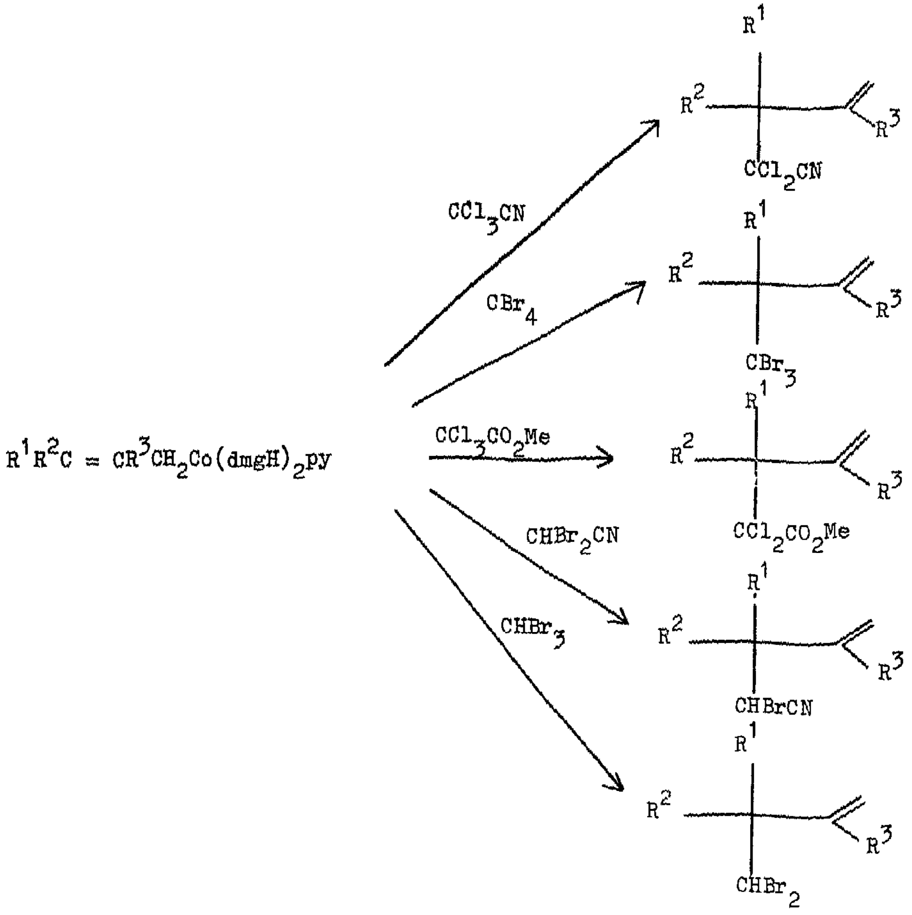
$$(R = Me,\ Et,\ Pr^n,\ Pr^i,\ CH_2Cl)$$

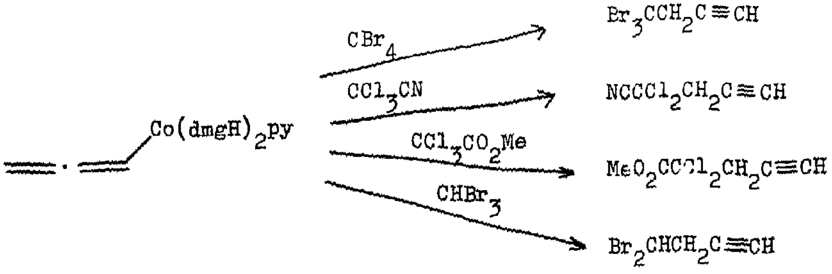
and methanol, equation (28), reveals that the mechanism proceeds via a pre-equilibrium involving the formation of a 1:1 adduct, equation (29); the rate

$$CoR(dmgH)_2(H_2O) + I_2 \rightleftharpoons CoR(dmgH)_2(H_2O)\cdot I_2 \qquad (29)$$

determining step probably consisting of an intramolecular transalkylation (ref. 64).

Allyl- and allenyl-cobaloximes have been shown to react with $CBrCl_3$ to give 4,4,4-trichlorobutene and 4,4,4-trichlorobutynes respectively as indicated below.





Other polyhalogenomethanes behave similarly. The reactions are believed to involve novel chain processes (ref. 65) and alkylcobaloximes $CoR(dmgH)_2py$ have been shown to react with other organic compounds which are considered to be good radical precursors e.g. Ph_2S_2, Ph_2Se_2 and alkylsulphonyl chlorides to give the products R-SPh, R-SePh and $R-SO_2-R^1$ (ref. 66). Allylcobaloximes have also been shown to react with ethylbromomalonate under very mild conditions to yield allyl-substituted ethylmalonates in good yield. Propargyl- and allenylcobaloximes react with $BrCH(CO_2Et)_2$ to give allenyl- and propargyl-malonic ester respectively. Similar rearrangements are observed in reactions of crotyl-, 3,3-dimethylallyl-, and cinnamyl-cobaloximes, the substitution occurring with total rearrangement of the allyl groups (ref. 66). Methylcobalamin has also been shown to react with various methyl derivatives of heavier metals e.g. Hg, Tl, Pb, Sn, Te, P, As, Sb, equation (30) (ref. 67).

$$R_nM(OH_2)^+ + MeCo \longrightarrow R_nMMe + H_2O\text{-}Co^+ \qquad (30)$$

The base catalysed hydrolysis of disulphides, equation (31), has been found to be accelerated by $CoMe(dmgH)_2(H_2O)$ and lead to the formation of $CoMe(dmgH)_2(SR)^-$

$$RSSR + OH^- \longrightarrow RS^- + RSOH \longrightarrow \text{stable products} \qquad (31)$$

This acceleration is prevented by a large excess of pyridine suggesting that disulphides coordinate to $CoMe(dmgH)_2$ at the axial ligand position although such interaction could not be detected by spectroscopic techniques (ref. 68).

Metal carbene compounds

Cobalt stabilized carbenes have been obtained by reactions of organolithium compounds as outlined in equation (32) and (33) (ref. 69).

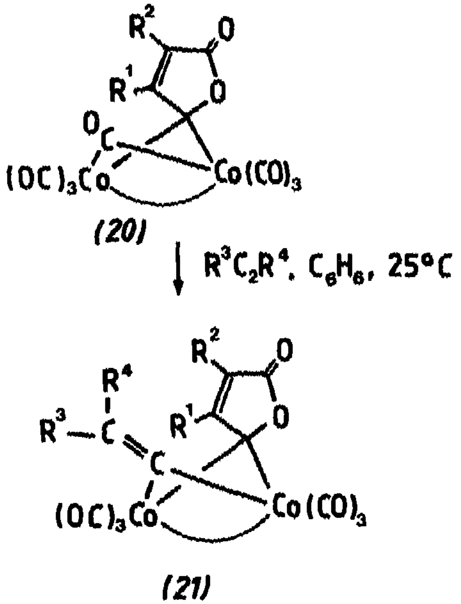
$$CoGePh_3(CO)_4 \xrightarrow{RLi} Co(RCOLi)(GePh_3)(CO)_3 \qquad (32)$$

$$Co(RCOLi)(GePh_3)(CO)_3 \xrightarrow{Et_3O^+BF_4^-} Co(RCOEt)(GePh_3)(CO)_3 \qquad (33)$$

$$(R = Me, Et, Pr^n, Bu^n, Ph)$$

A variety of complexes with bridging carbene ligands have been reported during 1979. Thus treatment of the lactone complexes (20) with mono- or dihaloacetylenes affords examples of complexes (21) which contain two different carbene bridges (ref. 70). Bridging heteromethylenecobalt complexes have been prepared by photolysis of $Co(CO)_2Cp$ with diazo compounds. Thus diazoacetates and $Co(CO)_2Cp$ afford the brown bridged methylene complexes (22) along with the green complexes (23). The triply bridged complexes (23) undergo an irreversible rearrangement in solution to give the bridged methylene complexes (22) (ref. 71). Photolysis of $N_2C(COR)(COR^1)$ in the presence of $Co(CO)_2Cp$ affords the complexes (24) which on thermolysis with $Co(CO)_2Cp$ give the complexes (25) (ref. 72).

The mass spectra of several bridged methylene complexes have been reported (ref. 73) and the electronic energy levels of $Cp(OC)Rh(\mu\text{-}CH_2)Rh(CO)Cp$ have been



(20)

(21)

$R^1 = H$, $R^2 = H, Pr^n, Bu^n$, n-pentyl, Ph

$R^3 = Cl$, $R^4 = Bu^n$
$R^3 = Br$, $R^4 = Br, Bu^n, Ph$
$R^3 = I$, $R^4 = I, Bu^n$

$$\begin{tikzcd}
& Co(CO)_2Cp + N_2CH(CO_2R) \arrow[dl, "\text{heat}"', "C_6H_6"] \arrow[dr, "h\nu,\ THF,\ < -90^\circ C"] & \\
Cp(OC)Co(\mu\text{-}CHCo_2R)Co(CO)Cp & & CpCo(\mu\text{-}CO)_2(\mu\text{-}OCORCH)CoCp
\end{tikzcd}$$

(22) (23)

described by a correlation diagram of energy levels of a CH_2 group and Cp(OC)RhRh(CO)Cp (ref. 74).

$Cp(OC)\overline{CoOC(R)C(COR^1)C}O$ (24)

$Cp(OC)Co\{\mu\text{-}C(COR)(COR^1)\}Co(CO)Cp$ (25)

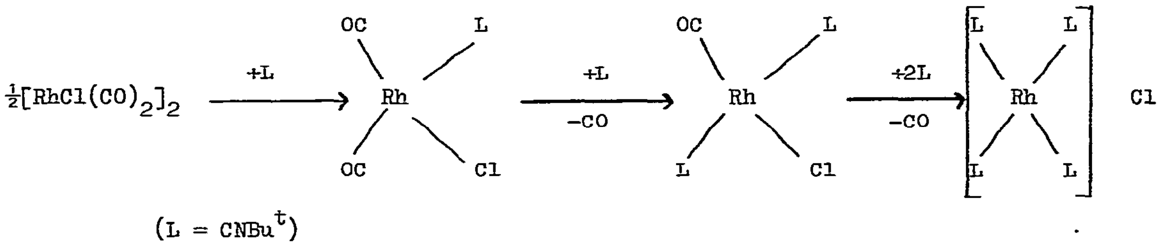
(R = MeO, EtO, Me_3CO)
(R^1 = MeO, EtO, Me_3CO, Me)

Metal isocyanide compounds

Reactions of $[Co(CNR)_5]X_2.xH_2O$ (R = aryl; X = ClO_4,BF_4) with $P(OR^1)_3$ (R^1 = alkyl, aryl) and triarylphosphines have been investigated, reduction/disubstitution is strongly favoured leading to products such as $[Co(CNR)_3\{P(OR^1)_3\}_2]X$ (ref. 75). The arsine complex $[Co(CNPh)_3(AsPh_3)_2]ClO_4$ has been obtained in a similar way (ref. 76). Photolysis of $Mn_2(CO)_{10}$ in the presence of $[Co_2(CNMe)_{10}]^{4+}$ does not give any detectable amount of the expected heterodinuclear species $[(MeNC)_5CoMn(CO)_5]^{2+}$ (ref. 77).

The complexes $[M(CNR)_4(TCNE)]X$ (M = Co(I), Rh(I); R = Me, Bu^t, $4\text{-}MeOC_6H_4$; X = ClO_4, PF_6, BPh_4; not all combinations) undergo TCNE rotation coupled with Berry pseudorotation, activation parameters have been measured by line-shape analysis of ^1H NMR spectra between -20 to 70°C. The E_a values for cobalt complexes are larger than the very low values observed for $[Co(CNR)_5]ClO_4$ which undergo Berry pseudorotation alone, suggesting that TCNE rotation is a significant contribution to the rearrangement barrier in the TCNE complexes. The E_a and $\Delta S^{\ddagger}$ values of the $[M(CNR)_4(TCNE)]X$ complexes are almost independent of steric and electronic effects of the isocyanides, but are dependent on the bulkiness of the counteranion with E_a increasing in the order $ClO_4 < PF_6 < BPh_4$ (ref. 78.).

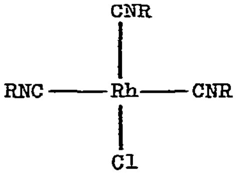
The reaction of $CNBu^t$ with $[RhCl(CO)_2]_2$ in various solvents occurs in stepwise fashion according to Scheme 1, deduced by studying the evolution of CO and



(L = $CNBu^t$)

SCHEME 1

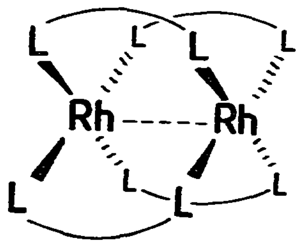
measuring the conductances and IR spectra of the solutions. The two intermediates were isolated as blue-black solids, there was no evidence for any species with composition between $RhCl(CO)(CNBu^t)_2$ and $[Rh(CNBu^t)_4]Cl$ (ref. 79). Reaction of $[RhCl(1,5\text{-}cod)]_2$ with 2,6-disubstituted phenyl isocyanides does allow isolation of the complexes (26), only (26 a) reacts with excess isocyanide to give the ionic



(26 a; R = $2,6\text{-}Me_2C_6H_3$)
(26 b; R = $2,4,6\text{-}Me_3C_6H_2$)
(26 c; R = $2,4,6\text{-}Bu^t_3C_6H_2$)

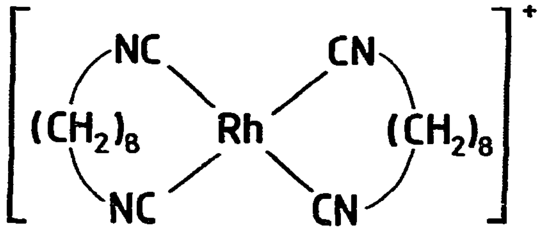
complex $[Rh(CNR)_4]Cl$, which self-associates in solution. Complex (26 c) reacts with $Bu^t_3C_6H_2NC$ in the presence of $AgPF_6$ to give $[Rh(CNR)_4]PF_6$ ($R=Bu^t_3C_6H_2$) which does not associate in solution due to the bulkiness of the isocyanide ligands. The crystal structure of (26 c) shows that the isocyanide phenyl rings are perpendicular to the RhC_3Cl plane, and that steric interference between the Bu^t groups prevents association through Rh-Rh interaction (ref. 80). The crystal structures of complexes $[Rh(CNR)_4]X$ ($R = 4\text{-}FC_6H_4$, $4\text{-}NO_2C_6H_4$; $X = Cl, ClO_4$) show that the chlorides are metal-metal bonded dimers with Rh-Rh distances of 3.207 and 3.25 Å. The perchlorates are monomeric (ref. 81). Similar dimerisation is observed in the complexes $[Rh(CNR)_4]X$ (R = Ph, vinyl, Et,Me; $X = Cl, PF_6, BF_4, ClO_4$) in solution. The crystal structures of the two complexes R = Et; X = Cl and R = vinyl, $X = ClO_4$ confirm the presence of linear chains of Rh atoms (ref. 82).

The photosensitive and deeply coloured complexes $[Rh_2(L\text{-}L)_4]X$ $\{L\text{-}L = CN(CH_2)_nNC$, n = 3-6, $1,4\text{-}(CNCH_2)_2C_6H_{10}$, $1\text{-}3\text{-}(CNCH_2)_2C_6H_3$; $X = Cl, BF_4, PF_6$ or $BPh_4\}$ are obtained by treatment of $[RhCl(1,5\text{-}cod)]_2$ or $[RhCl(CO)_2]_2$ with the diisocyanide.



$L\text{-}L = CN(CH_2)_nNC$ (n=3-6)

(27)

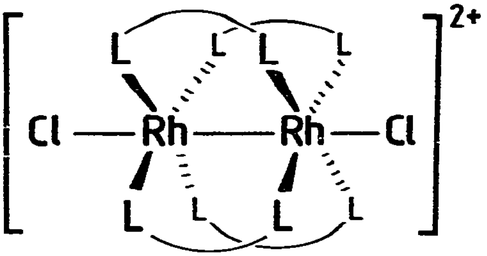


(28)

Structure (27) is assumed from spectroscopic data, when n = 3 an eclipsed conformation is expected but with longer chain lengths a staggered conformation is possible. In solution the dinuclear complexes aggregate to form oligomeric species, this tendency falls off with increasing chain length in the diisocyanide. When n = 8 the monomeric species (28) is obtained. Reaction of the rhodium diisocyanide complexes with DPM displaces two diisocyanide ligands to give trans - $[Rh_2(L\text{-}L)_2(DPM)_2]^{2+}$, substitution reactions with other phosphines also occur (ref. 83).

The position of the lowest allowed electronic transition in $[Rh_2(L\text{-}L)_4]^{2+}$ (L-L = binucleating diisocyanide) varies with the rotameric configuration of the complex. Reaction of these complexes with H_2 in acid solution yields $Rh_4H_2^{4+}$, which is a possible intermediate in the H_2 - producing photoreaction of

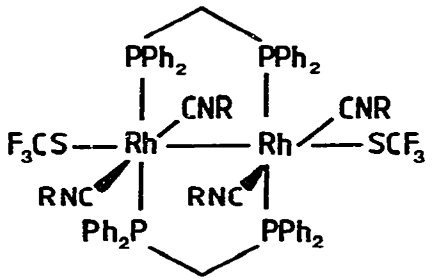
$[Rh_2(L\text{-}L)_4]^{2+}$ in aqueous HCl solution (ref. 84). The crystal structure of the complex $[Rh_2Cl_2(LL)_4]Cl_2.8H_2O$ isolated from aqueous HCl shows that it contains



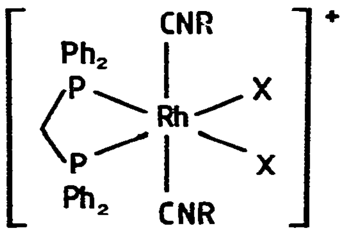
(29) $LL = CN(CH_2)_3NC$

the linear $ClRh^{II}Rh^{II}Cl^{2+}$ unit in the cation (29) (ref. 85).

A convenient new route to the diphosphine-bridged dimers $[Rh_2(CNR)_4(dppm)_2]^{2+}$ via direct reaction of the ligands with $[RhCl(1,5\text{-cod})]_2$ has been reported. The dimers react with trifluoromethyl disulphide to give rhodium(II) complexes (30), whereas rhodium(III) species (31) are obtained with $(PhS)_2$, $(PhSe)_2$ and $(C_6F_5S)_2$.

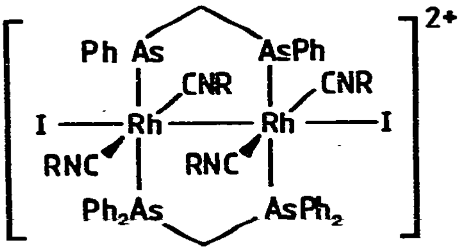


(30) (R = Me, Bu^n)



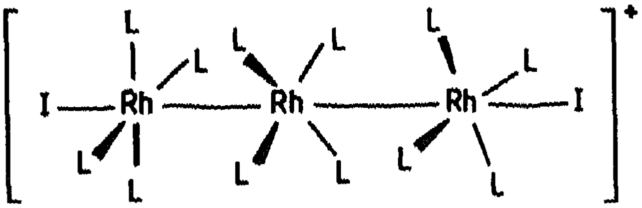
31 (R = Bu^n; X = SPh, SePh, SC_6F_5)

The corresponding diarsine-bridged dimers $[Rh_2(CNR)_4(dpam)_2]^{2+}$ are obtained by adding an isocyanide to $Rh_2Cl_2(CO)_2(dpam)_2$ and precipitation with $Na[BPh_4]$. They react with iodine to give rhodium(II) dimers (32) (ref. 86).



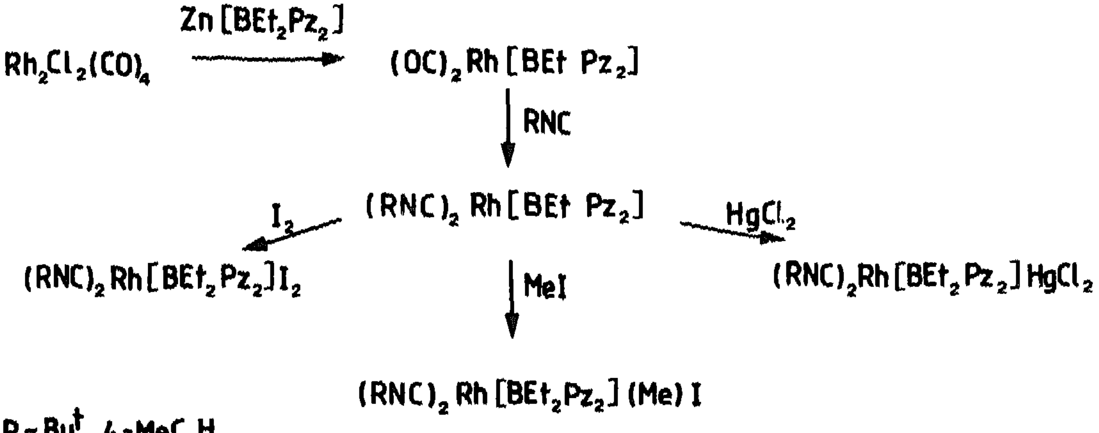
(32) (R = Bu^n, Cy)

Disulphides and diselenides react with $Rh(CNR)_4^+$ affording trans-$[Rh(X)_2(CNR)_4]^+$ ($X = SCF_3$, SPh, SC_6F_5 or SePh; R = Bu^n or C_6H_{11}) (ref. 86). Iodine and bromine are known to undergo simultaneous two-centre oxidative addition reactions to $Rh(CNR)_4^+$ forming $[X(RNC)_4RhRh(CNR)_4X]^{2+}$, the first case of three-centre oxidative addition has now been reported. Addition of 1 mol of iodine to 3 mol of $[Rh(CNCH_2Ph)_4]^+$ produces the cation (33) in 85% yield. The X-ray crystal structure of the Br_3^- salt of (33) has been determined, the Rh_3 unit is linear with Rh-Rh 2.796 Å and the four isocyanide ligands on adjacent rhodium atoms are staggered by 38°. In solution the cation (33) dissociates into the smaller fragments $[Rh_2I_2(CNR)_8]^{2+}$, $[RhI_2(CNR)_4]^+$ and $Rh(CNR)_4^+$ (ref. 87).



(33) L = CNCH Ph

Bis-substituted rhodium(I)polypyrazolylborates have been prepared and rhodium(III) derivatives obtained by oxidative addition reactions as shown in Scheme 2, (ref. 88).



$R = Bu^t$, $4\text{-}MeC_6H_4$,
or $4\text{-}MeC_6H_4SO_2CH_2$

SCHEME 2

The kinetics of oxidative addition reactions of iodine to $[Rh(CNR)_4]ClO_4$ ($R = 2,4,6\text{-}Me_3C_6H_2$ and Bu^t) (ref. 89), and to $Rh(S_2CNMe_2)(2,4,6\text{-}Me_3C_6H_2NC)_2$ (ref. 90) have been studied. Both reactions proceed via a charge transfer complex between the reactants.

Like its rhodium analogue, the complex $[Ir(CNMe)_4]Cl$ oligomerizes in solution.

The oligomers are readily cleaved by visible or UV irradiation, the monomers then readily add ligand or solvent to give 5-coordinate complexes (ref. 91). The X-ray crystal structure of $Ir_4(CO)_{11}(CNBu^t)$ has shown the complex to be the first example of an $Ir_4(CO)_{12}$ derivative containing no bridging ligands. In solution ^{13}C NMR spectra establish that carbonyl scrambling occurs through a triply bridged intermediate (refs. 92, 93).

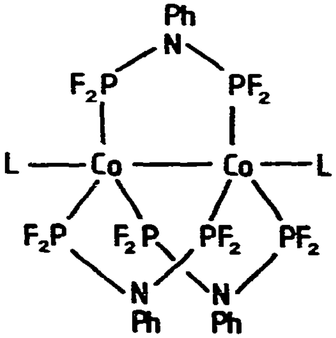
Metal carbonyl and related compounds

(a) Homonuclear carbonyl compounds

Molecular orbital techniques have been applied to various aspects of first row transition metal carbonyl chemistry. A modified extended Hückel approach has been used to predict the geometries of $[Co(CO)_4]^n$ (n =-1,0 and +1), and the unbridged forms of $Co_2(CO)_8$ (ref. 94). Using the same approach, enthalpies of dissociation for $Co_2(CO)_8$ and $CoH(CO)_4$ have been calculated (ref. 95). The interaction of Co atoms with CO and PF_3 have been studied by *ab initio* methods (ref. 96). The electronic absorption spectra of the open shell molecules $M(CO)_4$ (M = Co, Rh, Ir) have been measured and both $\sigma \rightarrow t_2(d)$ and $d \rightarrow \pi^*$ transitions observed (ref. 97). The ^{17}O and ^{13}C NMR chemical shift parameters for a number of metal carbonyl compounds including $Co_2(CO)_8$, $Co_2(CO)_6(PhC_2Ph)_2$, $PhCCo_3(CO)_9$, $Co(CO)_2Cp$ and $Rh_2Cl_2(CO)_4$ have been measured (ref. 98).

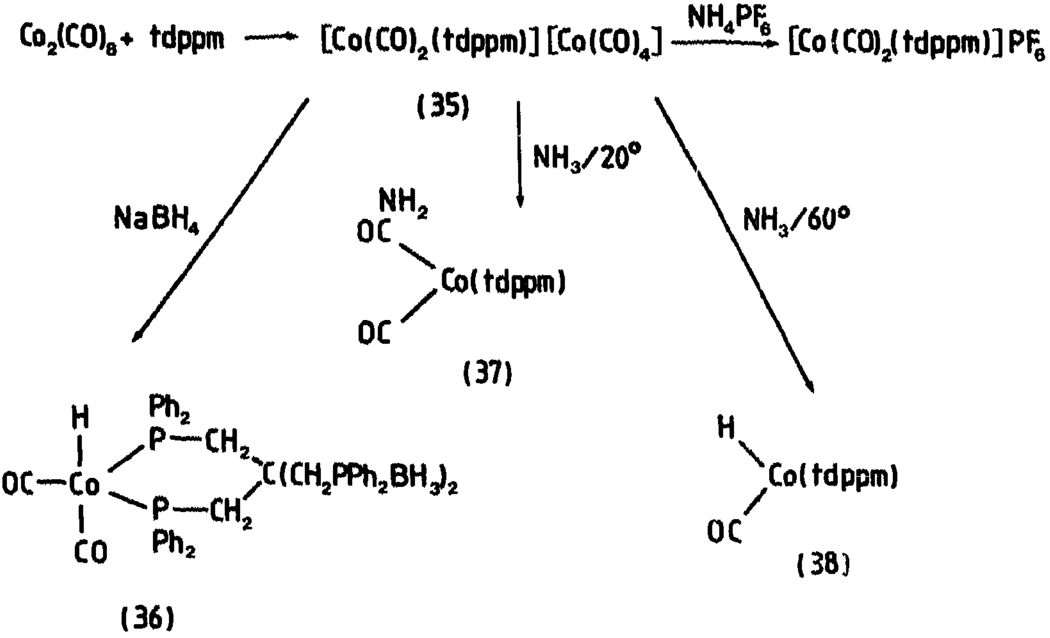
Cocondensation reactions of Co atoms with CO/O_2 mixtures at 10 - 12K give the complete series of mixed carbonyl-dioxygen complexes $Co(CO)_n(O_2)$ (n = 1-4), as well as the parent molecules $Co(CO)_n$ (n = 1-4) and $Co(O_2)_m$ (m = 1,2) (ref. 99).

Substitution reactions of $Co_2(CO)_8$ with a variety of phosphines have been studied. The complexes $Co_2(CO)_6L_2$ [L = PBu^t_3, $PHBu^t_2$, $P(SiMe_3)_3$, $P(GeMe_3)_3$, $P(SnMe_3)_3$ and $PBu^t_2(SiMe_3)$] have been obtained by direct reaction of L and $Co_2(CO)_8$ (ref. 100). The amino(difluorophosphine) $PhN(PF_2)_2$ (pnpf2) reacts with $Co_2(CO)_8$ to give $Co_2(CO)_2(pnpf2)_3$ (34; L = CO) and $Co_2(pnpf2)_5$ (34; L = monodentate pnpf2). With $Co_4(CO)_{12}$ the complex $Co_4(CO)_6(pnpf2)_3$ was isolated (ref. 101). The tetra-



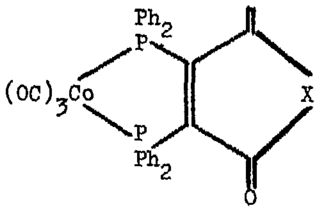
(34)

tertiary phosphine $C(CH_2PPh_2)_4$ (tdppm), which acts only as a tridentate ligand, undergoes a disproportionation reaction with $Co_2(CO)_8$ to give the salt (35), the $[Co(CO)_4]^-$ anion can be exchanged for PF_6^- using NH_4PF_6. Complex (35) reacts with $NaBH_4$ or $NaBD_4$ to give the hydridocarbonyl (36) (Scheme 3) or its deuteride. Liquid NH_3 gives the carbamoyl-carbonyl complex (37) or the hydride (38) depending on the reaction conditions (ref. 102).



Scheme 3

The unusual paramagnetic complexes (39) are obtained by reacting $Co_2(CO)_8$ with 2,3-bis(diphenylphosphine)maleic anhydride and its derivatives (PP). Formal electron counting would give cobalt one electron more than a closed shell in the



X = O,S,CH_2 or NMe (39)

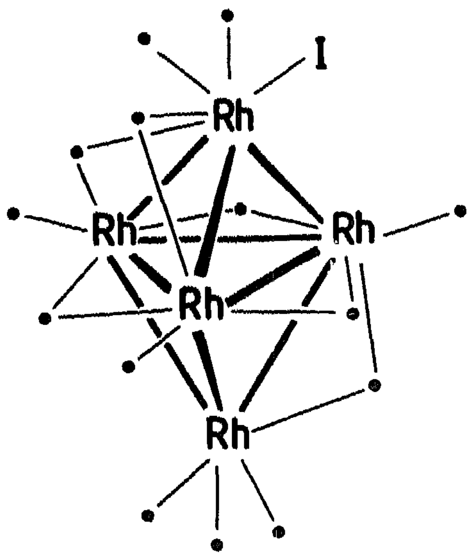
complexes (39), but ESR, IR and an X-ray crystal structure determination of (39) (X = 0) show that the unpaired electron is localized on the phosphine ligand. With iodine, complexes (39) are oxidised to the iodides $[Co(CO)_3PP]I$, and neutral complexes Co(CO)(NO)(PP) are obtained by reacting $Co(CO)_3(NO)$ with PP (ref. 103). The photocatalytic activity of the dinuclear complexes $Co_2(CO)_6L_2$ (L = PBu^n_3, $P(OPh)_3$) has been studied. Irradiation of $Co_2(CO)_6L_2$ in the presence of 1-pentene results in little net reaction, but addition of $SiHEt_3$ dramatically enhances photocatalytic activity strongly suggesting that the active catalytic species for alkene isomerization are the hydrides $CoH(CO)_3L$ rather than the 17-electron radicals $Co(CO)_3L$ (ref. 104). Kinetic studies of CO substitution reactions in the clusters $Co_4(CO)_{12-n}[P(OMe)_3]_n$ (n = 1,2) by $P(OMe)_3$ show that parallel dissociative and ligand-dependent paths operate for substitution in $Co_4(CO)_{10}$-$[P(OMe)_3]_2$, but for the n = 1 complex the reaction rate is strongly dependent on $P(OMe)_3$ concentration (ref. 105).

The $[Co(CO)_4]^-$ anion is rapidly and cleanly obtained from $Co_2(CO)_8$ by reduction with the readily available trialkylborohydrides $LiBHEt_3$, $LiBHBu^s_3$ and $KBHBu^s_3$ (ref. 106). Manganese metal in THF reduces $Co_2(CO)_8$ to $[Mn(THF)_6][Co(CO)_4]$ (ref. 107). Theoretical studies of the bonding in $Co(CO)_4^-$ and $Co(N_2)_4^-$ show that back-donation is of a similar order in both complexes and increases in the series Ni < Co < Fe for the corresponding isoelectronic complexes (ref. 108).

Electrochemical synthesis of the zerovalent complexes CoL_4, L = $P(OPr^i)_3$ (ref. 109) and L = $P(OPh)_3$ (ref. 110) has been achieved, paramagnetic susceptibility measurements are consistent with the presence of one unpaired electron. An unstable diamagnetic salt $Na[Co\{P(OPh)_3\}_4]$ could be obtained by further electrolytic reduction, and the complex CoL_4, L = $P(OPr^i)_3$ appears to form π-bonded organonitrile complexes $CoL_3(\pi\text{-}RCN)$ (R = Me, Ph) in solution. Cocondensation of Co vapour with aminodifluorophosphines give $Co_2[MeN(PF_2)_2]_5$ and $Co_2[Me_2N(PF_2)]_2$-$[MeN(PF_2)_2]_3$, the latter being obtained from a 4:1 mixture of $Me_2N(PF_2)$ and $MeN(PF_2)_2$ (ref. 111). The reaction between $Co_2(CO)_8$ and excess pyridine-2,6 dicarboxylic acid ($dipicH_2$) produces the polymeric complex $[Co(dipic)]_n$, whereas with pyridine-2-carboxylic acid (picH) the salt $[Co_2(picH)_3(pic)_3]Co(CO)_4\cdot 3H_2O$ is obtained (ref. 112).

Cocondensation of Rh and Ir atoms with CO/inert gas mixtures allows the synthesis and characterization of the complete series of binary complexes $M(CO)_n$ (M = Rh, Ir; n = 1-4). A careful analysis of the IR and UV-visible spectroscopic data using isotopically substituted CO suggests that $Rh(CO)_4$ and $Ir(CO)_4$, like $Co(CO)_4$, are not strictly tetrahedral (ref. 113). The electronic spectrum of cryochemically prepared $Rh_2(CO)_8$ has been measured and compared with that of $Co_2(CO)_8$. A $\sigma \rightarrow \sigma^*$ transition is found to be blue-shifted from that in $Co_2(CO)_8$, consistent with the increased bonding interactions of σ(d) orbitals of Rh over Co (ref. 114). A reappraisal of the matrix synthesis of $Ir_2(CO)_8$ confirms its existence in spite of an earlier error, unlike $Rh_2(CO)_8$ the iridium analogue exists as an unbridged metal-metal bonded isomer. At 200K $Ir_2(CO)_8$ decomposes to an undefined material whose IR spectrum resembles that of CO chemisorbed on supported Ir clusters (ref. 115). It has been established by electrochemical and chemical techniques that the reduction of $[Rh(diphos)_2]Cl$ occurs _via_ a one-electron transfer step to give the highly reactive complex $Rh(diphos)_2$, which is capable of abstracting a hydrogen atom from a variety of solvents giving $RhH(diphos)_2$ (ref. 116).

A new pentanuclear anion $[Rh_5(CO)_{14}I]^{2-}$ (40) has been isolated from the reaction of $Rh_4(CO)_{12}$ with NBu_4I or $AsPh_4I$ in 1:2 molar ratio, and characterized by X-ray crystallography. The anion (40) is unstable and reacts with $Rh_4(CO)_{12}$ to give the previously described $[Rh_6(CO)_{15}I]^-$ and $[Rh_7(CO)_{16}]^{2-}$ anions (ref. 117). The bidentate ligands $Ph_2P(CH_2)_nPPh_2$, n = 2 (dppe) and n = 4 (dppb), react with $Rh_6(CO)_{16}$ giving $Rh_6(CO)_{12}(dppb)_2$, $Rh_6(CO)_{15}(dppe)$ and $Rh_6(CO)_{13}(dppe)_3$. In the dppb complex both terminal and face-bridging carbonyls exchange readily with ^{13}CO at 20°C, both P atoms of dppb are believed to coordinate to adjacent Rh atoms. Under similar conditions ^{13}CO exchange reactions with the dppe complexes were very slow, the face-bridging carbonyls were not observed to exchange at all. In these complexes dppe is only monodentate, the free PPh_2 group is believed to be bound to a face-bridging carbonyl group (ref. 118).



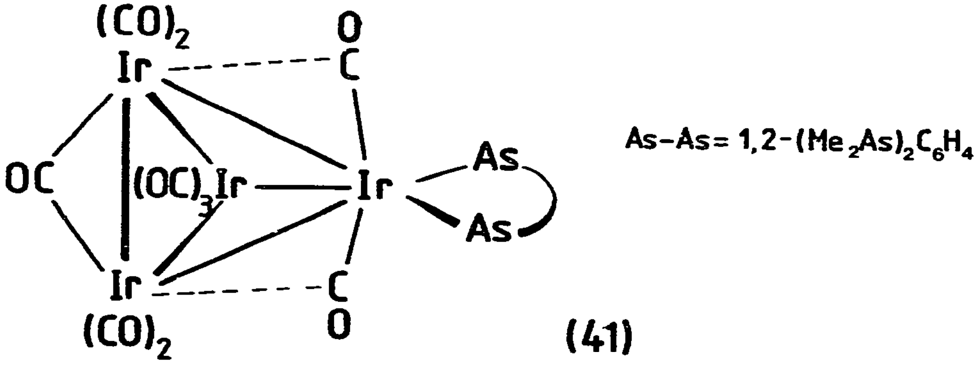
• = CO

(40)

The cluster complexes $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$ and $[Rh_{12}(CO)_{30}]^{2-}$ catalyse the

P-C bond cleavage reaction of PPh_3 to give benzene and $PhCH_2OH$, HCHO is necessary to obtain high yields of benzene (ref. 119). The behaviour of $Rh_6(CO)_{16}$ on the surface of alumina, MgO and silica-alumina has been found to be strongly dependent on the mode of impregnation and the water content of the support. Surface OH groups cause oxidation to a Rh(I) carbonyl species, from which $Rh_6(CO)_6$ can be regenerated by CO in the presence of excess water. In the absence of CO, reduction of the rhodium(I) carbonyl species by hydrogen or excess water leads to metallic Rh, which can be reversed by treatment with O_2 followed by CO. Catalytic cycles are proposed which account for the water gas shift reaction carried out with $Rh_6(CO)_{16}$ supported on the various oxides (ref. 120).

A complete assignment of the ^{13}C NMR spectrum of $[Rh_7(CO)_{16}]^{3-}$ has been achieved using specific ^{103}Rh spin-decoupling. At room temperature 3 μ_2-carbonyls exchange with 3 terminal carbonyls around the outside of the metal polyhedron, rather than by an internal rotation of the metal skeleton within the carbonyl polyhedron (ref. 121). The complex $Ir_4(CO)_{10}$(diars), (41), has been synthesized and its structure determined by X-ray diffraction. Low-temperature ^{13}C NMR studies show that three separate carbonyl exchange processes occur over different temperature ranges. For the lowest energy process, a new type of mechanism is proposed involving movement of an edge-bridging carbonyl across a triangular face to a new edge, coupled with edge-terminal exchange of two other carbonyls (ref. 122). The reaction of $LiBHEt_3$ with $Ir_4(CO)_{12}$ at 0°C results in formation of $[Ir_4(CHO)(CO)_{11}]^-$ in solution, detected by IR and 'H NMR, which decomposes smoothly to $[Ir_4H(CO)_{11}]^-$ on warming to 40°C (ref. 123).



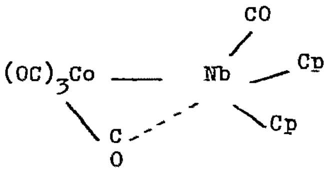
(41)

(b) Heteronuclear metal-metal bonded carbonyl compounds

Spectroscopic studies on solutions of $TlCo(CO)_4$ in a variety of solvents show that both dielectric constant and basicity of the solvent influence ion-pair formation. A direct cobalt to thallium charge-transfer band is observed in the visible region of the spectrum and IR spectra suggest that the ion-pair $Tl^+Co(CO)_4^-$

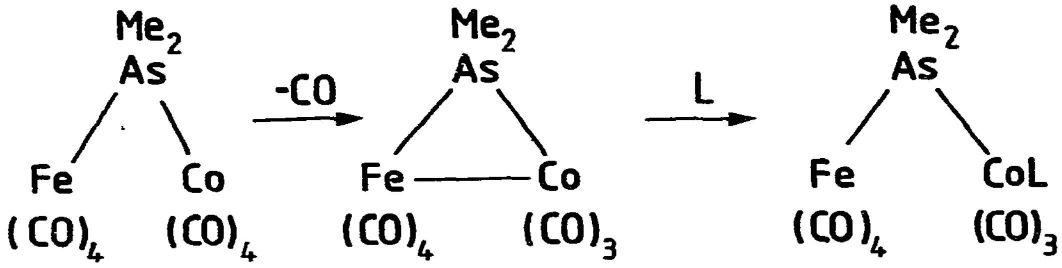
has C_{3v} symmetry (ref. 124). The unstable complex $Co(CO)_4(HgCH_2SiMe_3)$ is obtained from the reaction of $HgCl(CH_2SiMe_3)$ with $Co_2(CO)_8$ or $NaCo(CO)_4$ (ref. 125).

The ^{29}Si NMR spectrum of $Me_3SiCo(CO)_4$ has been obtained, the silicon atom shows a large downfield chemical shift relative to $(Me_3Si)_2O$ (ref. 126). The series of mixed metal-tin bonded complexes $Cl_2Sn(M)[Co(CO)_4]$ (M = $Mn(CO)_5$, $Mn(CO)_4PEt_2Ph$, $Fe(CO)_2Cp$) has been obtained by reacting Cl_3SnM with $TlCo(CO)_4$ (ref. 127). The salt $NaCo(PPh_3)_2(SnPh_3)_2(THF)_7$ has been prepared from $CoCl(PPh_3)_3$ and $NaSnPh_3$ but the analogous complex of the $SiPh_3^-$ ligand could not be obtained (ref. 128). The monomeric complexes $Me_2AsCo(CO)_{4-n}(PR_3)_n$ (R = Me, MeO) increase in stability n = o << 1 < 2. They act as Lewis bases forming arsenic-bridged complexes with metal carbonyls (ref. 129). The X-ray structures of $[\{Co(CO)_3PPh_3\}_4Sb][BPh_4].CH_2Cl_2$, (ref. 130), and of $[Co(CO)_4]_3Bi$ (ref. 131), have been determined. The geometry of the bismuth compound suggests why a tetrahedral cluster Co_3Bi is not formed. Substituted complexes $[(CO)_3(EPh_3)Co]_{3-n}$-$[(CO)_4Co]_nBi$ (n = o, E = P, As; n = 1, E = Sb) are formed from $[Co(CO)_4Bi]_3Bi$ and EPh_3 (ref. 131). A semi-bridging carbonyl group is found in the structure of the niobium-cobalt complex (42), the relevant distances are Co-C 1.792, Nb-C 2.531Å, and Co-Nb is 2.992Å (ref. 132). The reaction of chlorostannane or chlorogermane complexes of Co, Rh and Ir with heteropolyanions such as $W_{12}SiO_{40}^{4-}$ lead to the first metal-metal bonded derivatives of these anions (ref. 133).



(42)

The reactions of $MnCo(CO)_9$ with a number of perfluoromethyl compounds of the type $E_2(CF_3)_n$ (E = P, As, n = 4; E = S, Se, n = 2) and related compounds have been studied. Apart from already known mono- and binuclear compounds, the complexes $(CO)_4Mn(\mu\text{-}E(CF_3)_2)_2Co(CO)_3$ (E = P, As) are formed (ref. 134). Starting from $Me_2As[Fe(CO)_4][Co(CO)_4]$ (43) the sequence of reactions illustrated in Scheme 4 (L = PMe_3, $P(OMe)_3$) can be successively performed four times. The ligand L can also be transferred to the iron atom, 35 of the possible 44 different complexes were isolated (ref. 135) The complexes $(\eta$-dienyl$)FeCo(CO)_5L$ (dienyl = Cp, MeC_5H_4 or C_9H_7; L = tertiary phosphine or arsine) in the solid state are found to be either CO-bridged, or with nonbridged structures. In solution, many exist as equilibrium mixtures of the nonbridged isomer with several bridged tautomers, the non-bridged isomers are favoured by higher temperatures, bulky

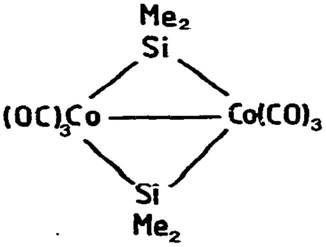


(43)

Scheme 4

ligands and for $C_9H_7 \gg MeC_5H_4 > Cp$ (ref. 136). Linear trimetallic complexes PtL_2M_2 ($M = Co(CO)_4$ or $Co(CO)_3PPh_3$; $L = Bu^tNC$ or CyNC) have been prepared (ref. 137).

Reaction of 1,1,2,2-tetramethyldisilane with $Co_2(CO)_8$ gives a complex mixture of products of which only (44) proved isolable, but a number of other products were identified spectroscopically including $HSi_2Me_4[Co(CO)_4]_2$ (ref. 138). The first example of a complex containing a diphosphide ligand symmetrically bonded to two metal atoms has been found in $Co_2(CO)_5(PPh_3)(\mu\text{-}P_2)$ (45), revealed by an X-ray structure determination. The P-P bond length of 2.019(9)Å is close to the estimated double bond length (ref. 139). The mono- and bis(triphenylphosphine) substituted derivatives of the related diarsenide complex $Co_2(CO)_6(\mu\text{-}As_2)$ have also been characterized by X-ray methods (ref. 140). ESR spectroscopy has shown that the unpaired electron in the electrochemically generated radical anions $X_2Co_2(CO)_6^{-\cdot}$ ($X = P_2$, As_2, RC_2R^1) and $R_xR^1_{6-x}C_6Co_2(CO)_4^{-\cdot}$ occupies a metal orbital which may be identified with the orientation of the bonding interaction in the 'bent' Co-Co bond model for $X_2Co_2(CO)_6$ molecules (ref. 141).



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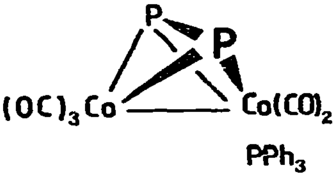
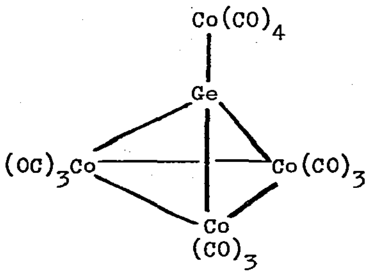


(45)

The room-temperature reaction of $Co_2(CO)_8$ with GeH_4, or of $NaCo(CO)_4$ with halogermanes, gives $Ge[Co_2(CO)_7]_2$, which loses CO at 50°C to form $GeCo_4(CO)_{13}$, (46) (ref. 142). The molecular structure of (46) has been established by X-ray crystallography (ref. 143). The principal product of the reaction between $MeGeH_3$ or $MeGeH_2Co(CO)_4$ and $Co_2(CO)_8$ is (47) (R = Me). $NaCo(CO)_4$ reacts with $MeGeX_3$ (X = Cl, Br) forming $MeGeX_2Co(CO)_4$ and $MeGeX[Co(CO)_4]_2$ (ref. 144). $GeBr_4$ and $MeGeCl_3$ also give (47) with $NaCo(CO)_4$ under mild conditions. Thermolysis of (47) at 80°C gives the germylidynetricobalt nonacarbonyl cluster $MeGeCo_3(CO)_9$ (ref. 145).



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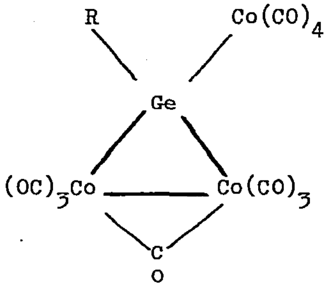


(47)

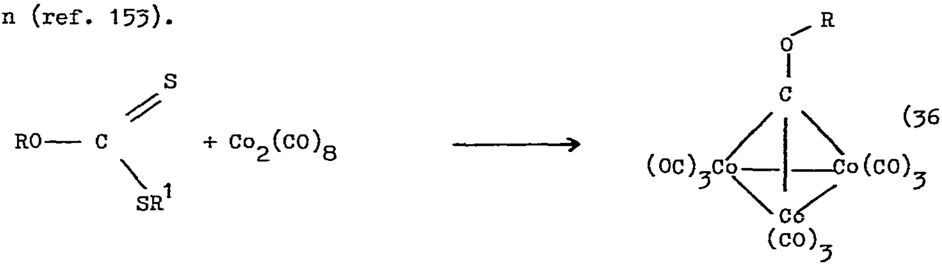
An analysis of the frontier orbitals in the tricobalt clusters $YCCo_3(CO)_9$ and related systems has been given (ref. 146). Formation of salts (48) of $[Co_3(CO)_{10}]^-$, the parent carbonyl of the tricobalt clusters, according to equilibrium (34) is found to be dependent on the cation M, cluster (48) is more stable for M = Li

$$MCo(CO)_4 + Co_2(CO)_8 \rightleftharpoons \underset{(48)}{M[Co_3(CO)_{10}]} + 2CO \qquad (34)$$

than Na (ref. 147). Reaction of (48) (M = Li) with dry HCl at -20°C in an inert atmosphere gives $HOCCo_3(CO)_9$, which decomposes at room temperature according to equation (35) (ref. 148).

$$2\ HOCCo_3(CO)_9 \longrightarrow 2CoH(CO)_4 + Co_4(CO)_{12} \qquad (35)$$

An intermediate in this reaction has been isolated and characterized by X-ray diffraction, IR and mass spectroscopy as the hydride cluster $HCo_3(CO)_9$. The molecule has D_{3h} symmetry, the hydrogen is believed to triply-bridge the three cobalt atoms. $HCo_3(CO)_9$ reacts with acetylene at room temperature to give $CH_3CCo_3(CO)_9$ (ref. 149). The X-ray crystal structure determination of $PhC(O)CCo_3(CO)_9$ does not reveal any unusual features in the ground state geometry of the molecule which could explain the ease of its thermal decarbonylation and the facile hydrogenation of the organic C=O bond (ref. 150). The action of strong acids such as H_2SO_4, HPF_6 on $RCH(OH)CCo_3(CO)_9$ results in formation of stable carbonium ion salts such as $[RCHCCo_3(CO)_9]PF_6$. It was concluded from NMR and IR studies and their reactivity towards nucleophilic reagents that the carbonium ion positive charge is delocalized onto the cobalt atoms (ref. 151). A large variety of silylmethylidynetricobalt nonacarbonyl complexes of the general type $R_nY_{3-n}SiCCo_3(CO)_9$, where R and Y are organic and inorganic substituents respectively, has been obtained by reacting a silicon hydride with $HCCo_3(CO)_9$. The range of compounds can be further extended by functional group interconversions at silicon. The compounds $X(HO)_2SiCCo_3(CO)_9$ (X = HO, Me) have been incorporated into methylsilicone polymers by cocondensation with polysiloxanes (ref. 152). Alkoxyalkylidynetricobalt nonacarbonyl clusters (49) were obtained as unexpected products from the reaction between organic xanthates and $Co_2(CO)_8$, equation (36) (R = cholesteryl, α or β-cholestanyl etc.; R^1 = Me, benzyl etc.). The clusters (49) are active catalysts for hydroformylation of olefins, but without any asymmetric induction (ref. 153).



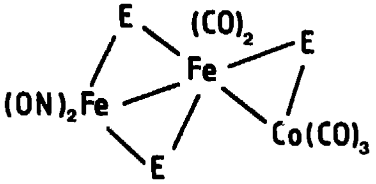
(36)

(49)

A detailed electrochemical study of Lewis base derivatives of tricobalt clusters $YCCo_3(CO)_{9-n}L_n$ (n = 1-3; L = PR_3, $P(OR)_3$ or RNC) has been made. Reduction becomes progressively more difficult, and oxidation easier, as CO is replaced by L (ref. 154). The preparation and properties of the phosphite ($P(OMe)_3$ and $P(OPh)_3$) derivatives for Y = Me, F; n = 1-3 have been described. The X-ray crystal structure of $MeCCo_3(CO)_6\{P(OMe)_3\}_3$ reveals that the CO groups are all terminal and the three phosphite ligands occupy equatorial positions on the Co_3 triangle (ref. 155). A tin analogue of the methylidyne clusters, $MeSnCo_3(CO)_9$, has been obtained from the reaction of $MeSnCl_2$ with $Co_2(CO)_8$ (ref. 156).

In an attempt to extend the size of the $RCCo_3(CO)_9$ cluster by reaction with $[Fe(CO)_4]^{2-}$, the expected pentanuclear $FeCo_3C$ clusters were not obtained but instead a new class of heterometal alkylidyne clusters $RCFeCo_2H(CO)_9$ (R = Me, Et, Ph) were obtained. Spectroscopic evidence suggests that the clusters have structures similar to the parent $RCCo_3(CO)_9$ clusters without bridging CO groups, but the location of the hydride ligand could not be deduced (ref. 157).

The reaction between $Co(CO)_3(\eta^3\text{-}C_3H_5)$ and $Co(CO)_2(NO)(PMe_2H)$ or $Co(CO)_2(PMe_2H)(\eta^3\text{-}C_3H_5)$ gave the complexes (50), (51) and (52), investigated by X-ray diffraction and NMR spectroscopic methods (ref. 158). The heteronuclear cluster



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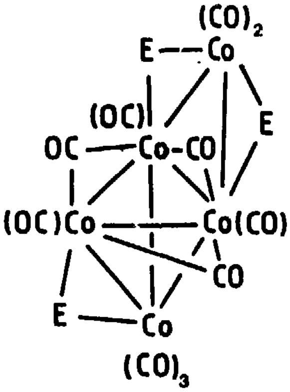

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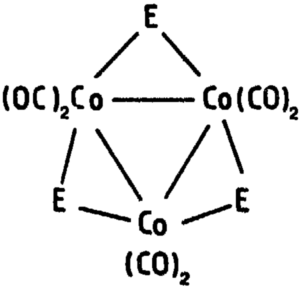
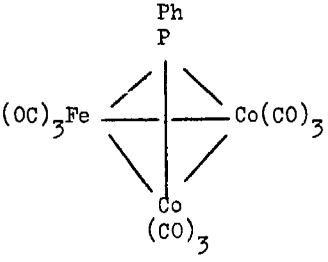


(52)

E = PMe$_2$

(53) has been prepared by the reaction of $(CO)_4FePPhH_2$ and $Co_2(CO)_8$. Related clusters (54) and the chiral complex $(PhP)CoFeMo(CO)_8Cp$ have also been obtained (ref. 159). Comparison of the X-ray crystal structures of (53) and that of the analogous cluster $(PhP)Co_3(CO)_9$ (which contains one more electron than is required by the 18-electron rule), together with the ESR spectra of the latter cluster and of the anion of (53), shows that the LUMO of (53) is almost exclusively made up of metal d-orbitals (ref. 160).



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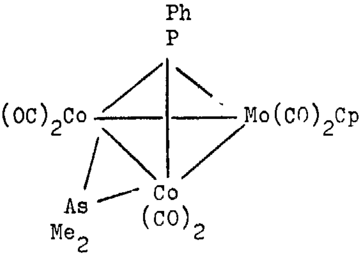
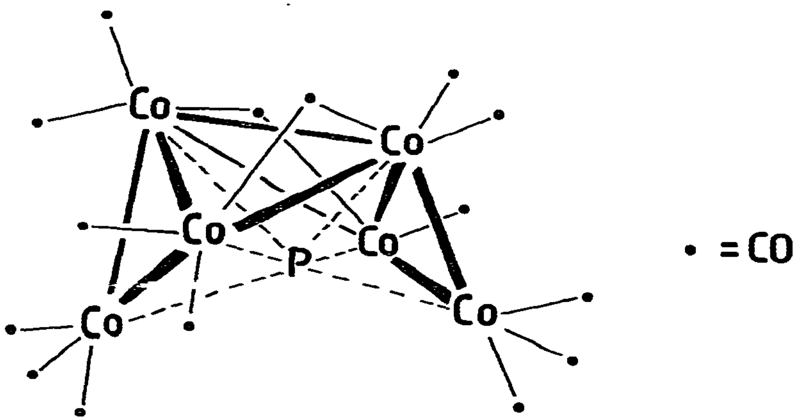


(54)

The reaction of cis - $PtCl_2(PEt_3)_2$ with $NaCo(CO)_4$ gave as a major product the mixed cluster $Pt_3Co_2(CO)_4(\mu_2\text{-}CO)_5(PEt_3)_3$, the X-ray crystal structure was determined (ref. 161). A single-crystal neutron diffraction study of [PNP]-$[Co_6H(CO)_{15}]$ shows that the hydrogen atom is located at the centre of a Co_6 octahedron. The cluster has ten terminal, one symmetrical bridging and four asymmetrically bridging CO groups. ^1H NMR evidence suggests that the H atom may easily enter and leave the Co_6 cage (ref. 162). An IR study of the cluster $Co_6C(CO)_{12}S_2$ containing 90% ^{13}C in the central cavity has allowed identification of the vibration modes involving the interstitial carbon atom (ref. 163). The first example of interstitial nitrogen in a metal carbonyl cluster has been found in the anions $[M_6N(CO)_{15}]^-$ (M = Co, Rh). The anion is formed in the reaction of $K_2[M_6(CO)_{15}]$ with $NOBF_4$, or for M = Rh, by reacting $K_3[Rh_7(CO)_{16}]$ with a 1:1 mixture of CO and NO. The crystal structure of $PPN[Co_6N(CO)_{15}]$ shows that the N atom is at the centre of a trigonal prism of cobalt atoms each with one terminal CO and all nine edges carry one bridging CO. (ref. 164). It appears that phosphorus is too large to fit inside a Co_6 cavity, as the structure of the anion $[Co_6P(CO)_{16}]^-$ (55), prepared from $NaCo(CO)_4$ and PCl_3 in THF, consists of an open array of linked cobalt atoms with the P atom occupying a 'semi-interstitial'



(55)

site (ref. 165). A single P atom is found encapsulated in the larger cavity provided by a nine-atom rhodium cluster in the anion $[Rh_9P(CO)_{21}]^{2-}$. The anion is isolated from the reaction of $Rh(CO)_2acac$ with PPh_3 in the presence of caesium benzoate, an X-ray structure determination reveals the P atom at the centre of a cubic antiprism of Rh atoms capped on one square face (ref. 166). The $[Rh_{13}H_2(CO)_{24}]^{3-}$ anion contains a polyhedron of Rh atoms forming part of a hexagonal close-packed lattice, the hydride atoms were assigned to two semi-octahedral cavities of the cluster (ref. 167). A ^{13}C variable-temperature NMR study of the $[Rh_{17}S_2(CO)_{32}]^{3-}$ cluster has been reported and a mechanism for the carbonyl scrambling processes suggested (ref. 168).

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

A comparison of the metal $2p_{3/2}$, carbon and oxygen 1s binding energies in $Co_2(CO)_8$, $CoH(CO)_4$ and related compounds of Fe and Mn, measured by XPS, leads to the conclusion that the hydrogen atoms in carbonyl hydrides are negatively charged (ref. 169). The reaction between $CoH(CO)_4$ and formaldehyde at 0°C in the presence of CO leads to stoichiometric hydroformylation giving glycolaldehyde in high yield, equation (37) (ref. 170).

$$CH_2O \; + \; CoH(CO)_4 \xrightarrow[0^oC]{CO \;\; 1atm} HOCH_2CHO \qquad (37)$$

Although PR_3 and $P(OR)_3$ stabilized cobalt hydrides are relatively inert to substitution, under irradiation by 340 nm light reaction (38) is complete within

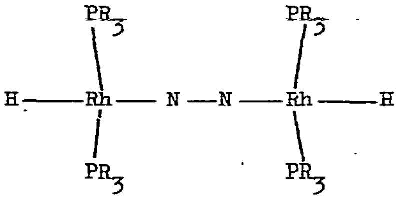
$$CoH[P(OPh)_3]_4 \; + \; L \xrightarrow{h\nu} CoH[P(OPh)_3]_3L \; + \; P(OPh)_3 \qquad (38)$$

20 min. When L = CO, prolonged irradiation leads to further substitution by CO. It is believed that the reaction involves formation of a solvated $CoH[P(OPh)_3]_3$ intermediate as the rate-determining step. (ref. 171). The crystal structure of $CoH[N(C_2H_4PPh_2)_3]$ has been reported, the Co atom is trigonal-bipyramidal with N and H axial, Co-H is 1.38(10) Å (ref. 172). The complexes $[Co(PHRR^1)_5]^{2+}$ are obtained by addition of the secondary phosphines $PHRR^1$ (RR^1 = Et_2, MePh or EtPh) to $Co(BF_4)_2.6H_2O$ and exist in red and green forms in the solid state. The red forms are five-coordinate, low-spin complexes whereas the green forms, which have C_{4v} symmetry, are probably weakly coordinated in the sixth axial position. Some reactions of the $[Co(PHRR^1)_5]^{2+}$ ions are reported, including formation of a new class of cobalt(III) hydrides, $[CoH(PHRR^1)_5]^{2+}$ (ref. 173).

An MO analysis of the oxidative addition reaction (39) has been carried out

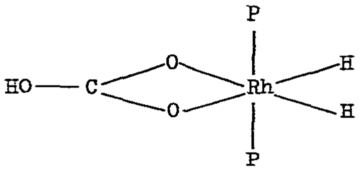
$$H_2 \; + \; RhCl(PH_3) \rightleftharpoons RhH_2Cl(PH_3)_3 \qquad (39)$$

as a model for one of the possible first steps in the catalytic hydrogenation of olefins by $RhCl(PPh_3)_3$ (ref. 174). The hydridodinitrogen complexes $RhH(N_2)(PR_3)_2$ ($R = Pr^i$, Bu^t, Cy or $R_3 = PhBu^t_2$) have been obtained either directly by reduction of $RhCl_3.3H_2O$ under N_2 in the presence of excess PR_3, or by an indirect route. The compounds lose N_2 to form $RhH(PR_3)_2$ (except $R_3 = PhBu^t_2$) and, in the case of R = Pr or Cy, the bridging-dinitrogen complex (56). The complexes $RhH(PR_3)_2$ react with H_2 to give $RhH_3(PR_3)_2$. The crystal structure of (56) ($R = Pr^i$) has been determined, the HRhNNRhH linkage is linear with N - N 1.134 Å and the dihedral angle between $RhHP_2$ planes is 55.2°(ref. 175). The rhodium(I) hydrides $RhH(Pr^i_3)_3$ and (56) (R = Cy) are active catalysts for the



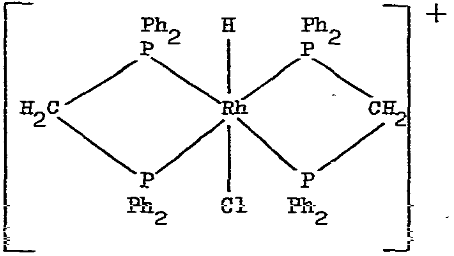
(56)

hydrogenation of nitriles to primary amines, and for the reverse reaction at higher temperatures (ref. 176). Reaction of $LiNR_2$ ($R = Me_3Si$) with $RhCl(PPh_3)_3$ gives the diamagnetic three-coordinate rhodium(III) complex $Rh(NR_2)(PPh_3)_2$, the first reported rhodium amide (ref. 177). Reaction of rhodium(I) hydride complexes $RhH(PPr^i_3)_3$, $RhH(N_2)(PPhBu^t_2)_2$ or (56) ($R = Cy$) with CO_2 in the presence of water affords the dihydro bicarbonato complexes (57) ($P = PPr^i_3$, $PPhBu^t_2$ or PCy_3). The crystal structure of (57) ($P = PPr^i_3$) has been determined. The complexes (57), and also the analogous formato complexes, react further with CO_2 to form rhodium(I) carbonyl complexes according to equation (40) for example; this reaction is the reverse of the water-gas shift reaction (ref. 178). New convenient routes to tricyclohexylphosphine (PCy_3) complexes of rhodium and iridium, including $MCl(CO)(PCy_3)_2$, $MHCl_2(PCy_3)_2$ ($M = Rh$, Ir) and the new complexes $IrH_2Cl(CO)(PCy_3)_2$, $IrHCl_2(CO)(PCy_3)_2$, have been reported (ref. 179). The $[RhCl_2(CO)_2]^-$ anion reacts with dppm to give two products depending on the dppm:Rh molar ratio. With a 1:1 ratio the binuclear "A-frame" complex $[Rh_2(\mu\text{-}Cl)(CO)_2(dppm)_2]^+$ is obtained, with a twofold excess of dppm the hydrido species (58) is the major product established by an X-ray



(57)

$$CO_2 + RhH_2(O_2COH)(PR_3)_2 \longrightarrow H_2O + Rh(CO)(O_2COH)(PR_3)_2 \qquad (40)$$



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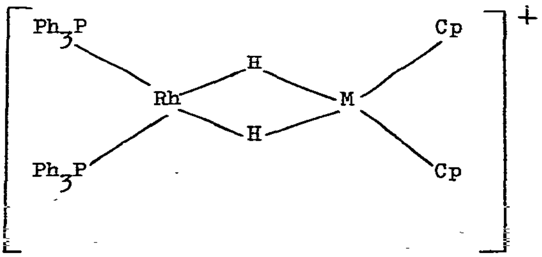
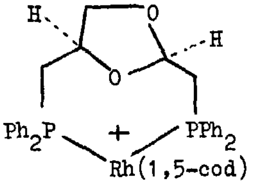


(59)

structure determination (ref. 180). The hydride-bridged mixed metal complexes (59) (M = Mo, W) have been prepared by reaction of $MH_2(Cp)_2$ with $[RhH_2(OCMe_2)_2(PPh_3)_2]^+$, the crystal structure of (59) (M = W) has been determined and ^{1}H NMR spectra of (59) in $(CD_3)_2CO$-D_2O show that H/D exchange of bridging hydride and terminal Cp hydrogen atoms occurs under mild conditions (ref. 181).

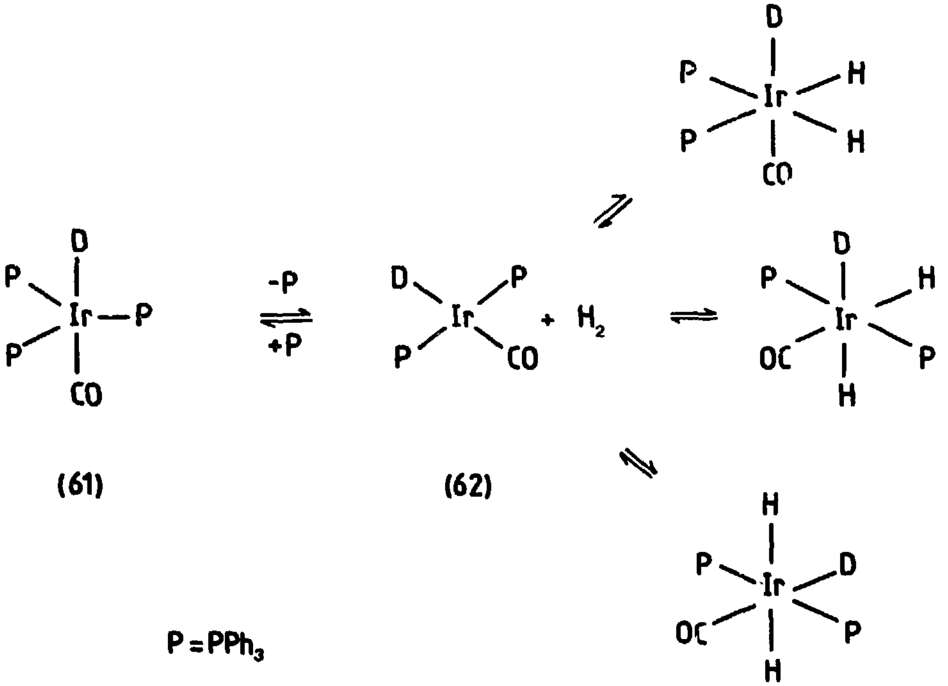
The complex (60) is an interesting hydrogenation catalyst since it effects



(60)

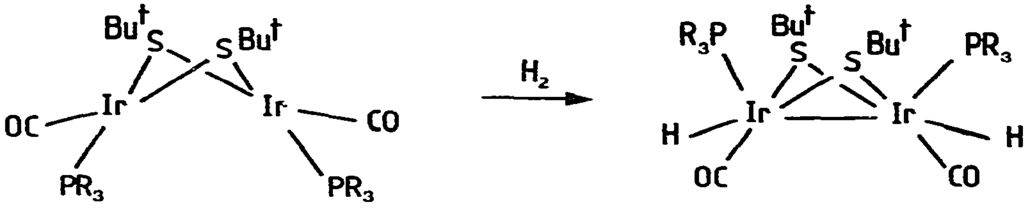
asymmetric reduction of α,β-unsaturated acids and of dehydroamino acids, particularly in the presence of NMe_3. The mechanism of hydrogenation has been deduced from ^{31}P NMR studies (ref. 182).

A study of the oxidative addition of H_2 to (61) by IR and ^{1}H NMR spectroscopy has been interpreted with the assumption that three stereochemical pathways exist for the addition of H_2 to (62), Scheme 5.



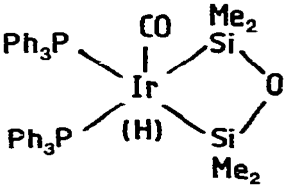
SCHEME 5

The third pathway corresponds to the first example of trans-addition of H_2 to a metal complex, if this the correct interpretation of the presence of the trans dihydride in the equilibrium mixture (ref. 183). The thiolato-bridged complexes (63) (R = Me, Ph, NMe_2 or OMe) react irreversibly with H_2 to yield $[IrH(\mu\text{-}SBu^t)(CO)(PR_3)]_2$ (64) which can be protonated giving complexes $[\{IrH(\mu\text{-}SBu^t)(CO)(PR_3)\}_2H]^+$ in which the additional proton bridges the two Ir atoms. X-ray crystal structure determinations of (63) and (64) (R = OMe) have established their geometries, the isomer of (64) examined proved to be cis-syn-endo although the trans-syn isomer is also produced in the addition (ref. 184). The crystal structure of the cyclo-metalladisiloxane (65), which catalyses the disproportionation of tetramethyldisiloxane into higher polysiloxanes, has been reported (ref. 185). New silylcobalt(III) complexes $CoH_2(SiR_3)L_3$ [R_3= F_3, MeF_2 or $(OEt)_3$; L = PPh_3] have been obtained by reacting $SiHR_3$ with CoH_3L_3 or $CoH(N_2)L_3$, their reactions with N_2, H_2, HCl and CCl_4 are described. With CO the five-coordinate complex $Co(SiF_3)(CO)_2L_2$ is formed. The silylcobalt(III) complexes act as catalysts for deuteriation, hydrosilylation and O-silylation reactions (ref. 186). The oxidative addition products of a wide range of silyl and germyl halides and related molecules with $IrX(CO)(PEt_3)_2$ (X = Cl or I) have been studied and their structures determined by ^1H and ^{31}P NMR spectroscopy. With silyl halides the major product is an adduct of type (66), (Y = H, Cl, Br, I, Me, or SiH_3), germyl halides give compounds of type (67) as major products (Y = H, Cl, Br, or I). In the addition reaction of SiH_3Q (Q = Br or I) with $IrCl(CO)(PEt_3)_2$, the product (66) has Br or I bound to Ir and Y = Cl (ref. 187).



(63)

(64)



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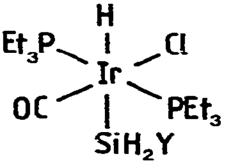

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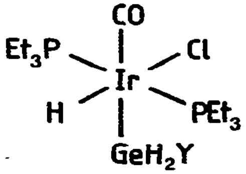
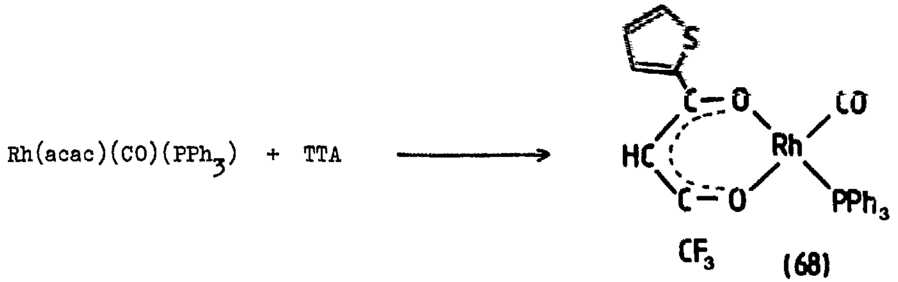


(67)

The ^{13}C NMR spectra of a wide range of rhodium carbonyl complexes have been measured, there is an approximate correlation of chemical shift with $\nu(CO)$,

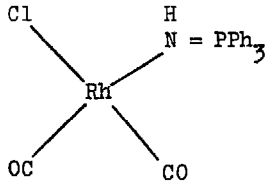
δ(^{13}C) tends to decrease with increasing ν(CO) (ref. 188). Force constant calculations for the planar complexes cis$[MX_2(CO)_2]^n$ (MX = RhCl, RhBr, IrCl, n = -1, and MX = PtCl, PtBr, n = 0) have been reported (ref. 189). Photoelectron spectra of $[RhCl(CO)_2]_2$ suggest that there is only a small net transfer of electron density from Rh to Cl and CO (ref. 190). The complex (68) obtained from reaction (41) (TTA = thenoyltrifluoroacetone) proved to be the isomer


(68)

(41)

predicted from trans effect considerations (ref. 191).

An extensive study of some fifty species of the type $RhX(CO)_2$(amine) (X = Cl or Br, amine = primary, secondary and heteroaromatic amines) by spectroscopic techniques has revealed that in the solid state two structural types occur. One form consists of a monomeric, square-planar entity, which is the only form existing in solution. A second solid state form involves an intermolecular interaction through the Rh(I) atoms leading to a one-dimensional chain structure (ref. 192). An anion-cation Rh-Rh interaction is also observed in the complexes $[Rh(CO)_3(L\text{-}L)][Rh_2Cl_2(CO)_2]$ (L-L = 2,2^1-bipyridine or 1,10-phenanthroline) (refs. 193, 194). New carbonyl complexes of the type $RhX(CO)_2$(biq), RhX(CO)(biq), (X = Cl, Br, I; biq = biquinoline), and $[Rh(CO)(biq)L_2]ClO_4$ (L = PR_3 or AsR_3) have been prepared (ref. 195). Bifunctional amine ligands such as 1,8-naphthyridine pyrazine and 1,3-di-4-pyridylpropane give bridged complexes $M_2Cl_2(CO)_4$(amine) (M = Rh, Ir) (ref. 196). Complex (69) can be prepared by the in situ alcoholysis of $Ph_3P = NSiMe_3$ in the presence of $[Rh(CO)_2Cl]_2$ (ref. 197).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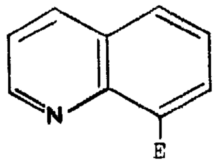

E = NH_2, PPh_2, or $AsPh_2$

(70)

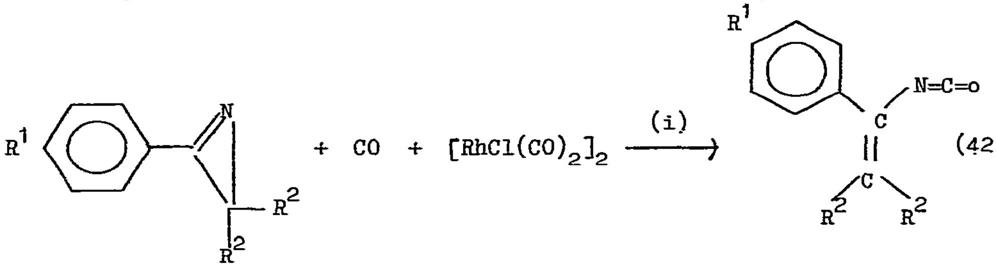
The 8-substituted quinolines (70) (E = PPh_2, N-P and E = $AsPh_2$, N-As) react with $[Rh(CO)_2Cl_2]^-$ affording the complexes $[RhCl_2(CO)(N\text{-}P)]_2$ and the N-As analogue respectively. With (70) (E = NH_2, N-N) the reaction follows a complicated sequence finally giving the rhodium(III) complex $RhCl_3(N\text{-}N)_2.H_2O$ in which one N-N ligand is only monodentate (ref. 198). A thermogravimetric study of the complex $[RhCl(CO)L_2]$ (L = 2-[2-(diphenylphosphino)ethyl]pyridine) has shown that oxidation of the phosphine L to its corresponding oxide occurs, followed by loss of CO from the complex (ref. 199).

The enthalpies of oxidative addition reactions of I_2, SO_2, $C_2(CN)_4$, $o\text{-}O_2C_6Cl_4$ and $MeO_2CC_2CO_2Me$ to the Rh and Ir complexes $MX(CO)L_2$ (X = F, Cl, Br or I; L = tertiary phosphine) have been measured by titration calorimetry and correlated with phosphine steric and electronic parameters (ref. 200).

Paramagnetic complexes $Rh(CO)_2L$, $Rh(CO)(PPh_3)L$ and $Rh(CO)(PPh_3)_2L$ have been obtained by reacting $[RhCl(CO)_2]_2$ or $RhCl(CO)(PPh_3)_2$ with sodium 3,6-di-t-butyl-1,2-benzosemiquinolate (NaL) (ref. 201). Both 1:1 and 1:2 adducts are formed between $(Ph_3P)(ArNC)Pt[C(OMe)=NAr]_2$ (Ar = p-totyl) and $Rh(CO)_2Cl$, which suggests that the two $-C(OMe)=NAr$ groups in the Pt(II) bidentate ligand have different donor abilities (ref. 202).

A correlation is observed between the binding energies of N and P atoms in the complexes $RhCl(CO)L_2$ [L = aminophosphines $Ph_{3-n}P(NRR^1)_n$ (n = 1-3)], as measured by XPS, and the selectivity for normal to branched chain aldehydes during catalyzed hydroformylation of 1-hexene (ref. 203). This same reaction has also been used to test the catalytic activity of the complexes $RhX(CO)(Ph_2PR)_2$ (R = CH_2SiMe_3, $(CH_2)_3SiMe_3$ or $CH_2(Me)Si(OSiMe_2)_3O$; X = Cl or I). The activity of the iodo derivatives varied considerably with the R = CH_2SiMe_3 complex producing an unexpectedly low linear/branched aldehyde product ratio (ref. 204). The catalytic activity of phosphinated silicone polymer supported chlorocarbonylrhodium(I) complexes has also been investigated (ref. 205).

Carbonylation reactions carried out in the presence of rhodium or iridium compounds have attracted interest. 2-Arylazirines react with CO and $[RhCl(CO)_2]_2$ under mild conditions to give the highly reactive vinyl isocyanates (71), equation (42), in good yields (ref. 206). Carbon monoxide reacts with trans-$M(N_3)(CS)(PPh_3)_2$ (M = Rh, Ir) to give trans - $M(NCS)(CO)(PPh_3)_2$ rather than



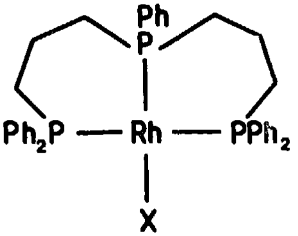
(42)

(i) C_6H_6, 1 atm CO, 5-20°C

(71)

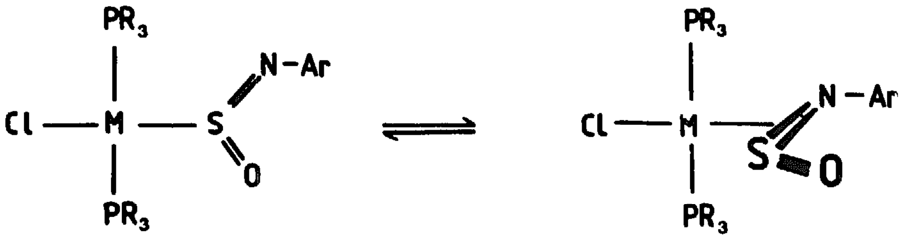
the thiocarbonyl isocyanate complex (ref. 207). A detailed mechanistic study of the carbonylation of methanol in the presence of iridium halides as catalyst precursor and methyl iodide as promoter has been made. Two principal catalytic cycles were identified, the kinetic dependencies for the reactions depend dramatically on such factors as iodide, water, methanol and Me^+ concentrations (ref. 208).

Complexes $RhCl(PMe_3)_3$ and $[Rh(PMe_3)_4]Cl$ have been obtained from $RhCl(PPh_3)_3$ by phosphine exchange and their X-ray crystal structures determined. With H_2 either complex gives $[RhH_2(PMe_3)_4]^+$ and with sodium amalgam an air-sensitive cluster $CHg_6Rh_4(PMe_3)_{12}$ was obtained (ref. 209). An extended series of $[RhX(ttp)]^{n+}$ complexes (72) (n = 0 for X = CH, Cl, N_3, NCS, CN, Me; n = 1 for X = MeCN, py, CO, PEt_3, $P(OMe)_3$) has been synthesized and the ^{31}P NMR spectra examined. From J(Rh-P) coupling constants a trans influence series emerges which is considerably different to that based on J(Pt-P) for platinum complexes.



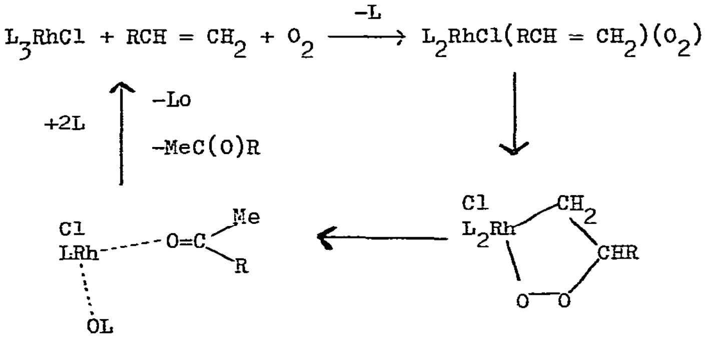
(72)

The crystal structures for X = py and PEt_3 were determined, the Rh-P bond length trans to X increases smoothly in the series Cl < py < EPt_3, in agreement with J(Rh-P) trends (ref. 210). The crystal structure of $RhCl(N_2)(PPr^i_3)_2$ has been redetermined at -160°C and in contrast to an earlier report, it is concluded that the N_2 ligand is bound end-on in both the solid state and in solution (ref. 211). The compounds $MCl(PR_3)_2(ArNSO)$ (M = Rh, Ir; R = Pr^i, Cy; Ar = Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, $2,4,6\text{-}Me_3C_6H_2$) appear to exist in two isomeric forms (73a) and (73b), in solution and in the solid state. The structure of isomer (73a)



(73a) (73b)

(M = Rh, R = Pr^i, Ar = 4-MeC_6H_4) was established by an X-ray structure determination, and the structure of the second isomer was deduced from IR, ^{31}P and ^{15}N NMR spectroscopic data. The ratio of the two isomers decreases in the order Ar = 4-Cl C_6H_4 > Ph > 4-MeC_6H_4; R = Pr^i > Cy and M = Rh > Ir, interconversion is intramolecular. Cyclometallation is observed via the ortho-carbon atom of the sulphinylaniline in (73) (M = Ir, R = Pr^i, Ar = 4-MeC_6H_4), but via PPr^i_3 when the ortho-aryl positions are blocked (ref. 212). Further evidence suggests that rhodium catalysed co-oxidation of terminal olefins and phosphines proceeds via direct oxygen transfer as in Scheme 6 (ref. 213).



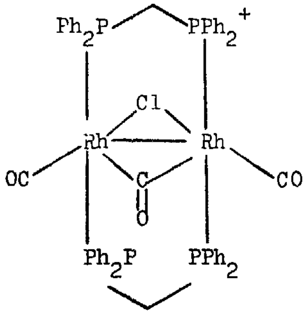
L = PPh_3, $AsPh_3$

SCHEME 6

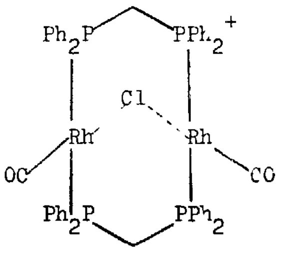
Rhodium(I) and iridium(I) complexes have proved to be useful decarbonylating reagents from organic acyl halides and aldehydes, and from transition metal carbonyl complexes. A study of the synthetic utility of $RhCl(PPh_3)_3$ for the abstraction of CO and CS from some cyclopentadienyl iron carbonyl complexes has been made, terminal ligands are found to be preferentially removed. A comparison of the decarbonylation of organic compounds by $RhCl(PPh_3)_3$ with that of metal carbonyls has also been made (ref. 214). There is evidence that the active decarbonylating agent is "$RhCl(PPh_3)_2$" formed by dissociation of a PPh_3 ligand, and the use of $[RhCl(PPh_3)_2]_2$ in MeCN has proved to be synthetically useful in the preparation of the alkyl compound $FeR(CO)_2Cp$ without complication of PPh_3 substitution. The complex $IrCl(PPh_3)_3$ will also effect decarbonylation but at a much slower rate (ref. 215). Partial decarbonylation of $Mo(CO)_6$ and $Fe(CO)_5$ by rhodium(I) complexes gives $Mo(CO)_4(PPh_3)_2$, $Mo(CO)_3$(arene), $Fe(CO)_{5-n}(PPh_3)_n$ (n = 1,2), $Fe(CO)_3$(diene). In the absence of suitable stabilizing ligands, decarbonylation goes to completion (ref. 216).

Several bis(ditertiaryphosphine) complexes of rhodium(I) have been prepared and investigated for catalytic hydrogenation activity. The complexes $RhCl(PP)_2$ (PP = $Ph_2P(CH_2)_nPPh_2$, n = 1-4, or (+)-diop) are prepared by reacting PP with $[RhCl(cyclooctene)_2]_2$, they are five coordinate with the exception of the $n = 2$ and 3 species which are ionic $[Rh(PP)_2]Cl$. Cationic species $[Rh(PP)_2]X$ (X = SbF_6, PF_6, BF_4) are prepared using AgX, and the hydrides $RhHL_2$ are obtained using borohydride. Activity for catalytic hydrogenation of methylenesuccinic acid increases with increasing phosphine chain length, the chloro complexes are less active than the cationic or hydrido species (ref. 217). Reduction of the dioxygen species $[RhCl(O_2)(PPh_3)_2]_2$ in the presence of another phosphine gives catalytically active mixtures for hydrogenation of olefins (ref. 218). There is considerable interest in attaching transition-metal homogeneous catalysts to insoluble supports. An XPS study of the Rh d-electron binding energies of $RhCl_3$ and $Rh_6(CO)_{16}$ attached to phosphine-modified silica supports has been made to determine the metal oxidation state in the catalyst. The $RhCl_3$ systems gave non-uniform catalysts of low activity, but $Rh_6(CO)_{16}$ gave complexes of general form $L_nRh^I(CO)_2$ which are active catalysts (ref. 219). A number of poly(siloxyphosphine)-rhodium(I) species have been obtained by polymerizing the soluble (chlorosilyl)phosphine complexes $L_2RhCl(CO)$, L_3RhCl, $L_4Rh_2Cl_2$ ($L = Cl_3Si(CH_2)_2PPh_2$) and $\{Cl_3Si(CH_2)_8PPh_2\}_3RhCl$. Other soluble siloxyphosphine complexes have been prepared as model systems for their polymeric counterparts (ref. 220). The rate of homogeneous hydrogenation of ethyl acrylate with the catalyst $IrCl(CO)(PPr^i_3)_2$ is much enhanced by irradiation with monochromatic light ($\lambda < 407$ nm), it is the hydrido-complex which is photochemically activated (ref. 221).

The full details of the preparation, crystal structures and reactions of the "A-frame" complex (74a) and the open-site complex (74b) formed by reversible loss of CO, described in preliminary form last year, have now appeared (ref. 222 - 224). The corresponding Ir complex to (74a) reacts with CO and $NaBPh_4$ to give

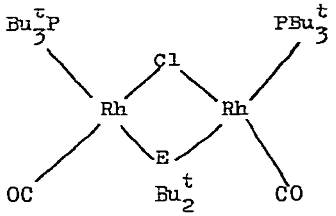


(74a)



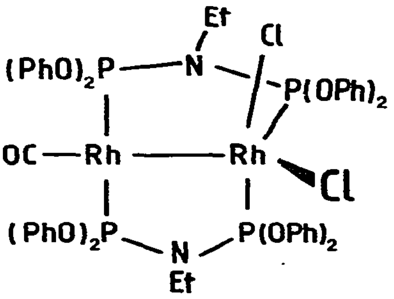
(74b)

$[Ir_2(CO)_2(\mu\text{-}CO)_2Cl(dppm)_2]^+$. The complex (74b) as its $[RhCl_2(CO)_2]^-$ salt is also obtained by the reaction of 4 moles of dppm with 3 moles of $Rh_2Cl_2(CO)_4$, the product was originally incorrectly formulated as $dppm[Rh(CO)_2Cl]_2$. The arsenic analogue dpam reacts similarly, the reaction of $Rh_2Cl_2(CO)_2(dpam)_2$ with $Rh_2Cl_2(CO)_4$ proceeds by halide abstraction to give $[Rh_2(\mu\text{-}Cl)(CO)_2(dam)_2]^+$ $[RhCl_2(CO)_2]^-$(ref. 225). The complexes (75) are obtained by reacting $Rh_2(\mu\text{-}Cl)_2\text{-}(CO)_2(PBu^t_3)_2$ with $EBu^t_2(SiMe_3)$ (E =P or As) (ref. 226). The mixed valence dirhodium complex (76) has been isolated from the reaction between $(PhO)_2PN(Et)P(OPh)_2$



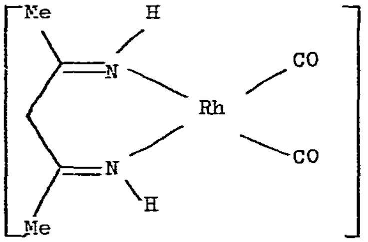
E = P or As

(75)



(76)

and $Rh_2Cl_2(CO)_4$, and characterized by an X-ray crystal structure determination, the distance between the Rh(II) and Rh(0) atoms is 2.66 Å (ref. 227). The crystal structure of the gold-coloured complex (77) obtained from the reaction of $Rh_2Cl_2(CO)_4$ with 2,4-pentanediiminium tetrafluoroborate shows that the $[Rh(C_5H_{10}N_2)(CO)_2]^+$ cations form weak dimers (Rh–Rh = 3.271 Å) which are stacked to form a linear Rh-Rh chain (Rh-Rh between dimers = 3.418 Å) (ref. 228).



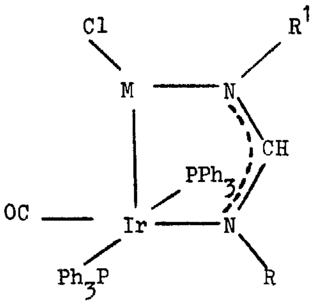
(77)

The reaction between $IrCl(CO)_3$ and PBu^t_3 gives either cis-$IrCl(CO)_2(PBu^t_3)$ or trans-$IrCl(CO)(PBu^t_3)_2$ depending on the proportions of ligand to metal complex, the crystal structure of the cis dicarbonyl was determined (ref. 229). The optically active bisphosphine $Ph_2PCH_2CH(OCMe_2O)CHCH_2PPh_2$ (diop) reacts with $Ir_2Cl_2(1,5\text{-cod})_2$ in the presence of CO to give $[Ir_2(CO)_2(diop)_3]^{2+}$, $[Ir_2(CO)_4(diop)_3]^{2+}$, $[IrCl(CO)(diop)]_2$ or $IrCl(CO)(diop)_2$ (ref. 230). Enthalpies of adduct formation between the metal lone pair in $IrCl(CO)(PPh_3)_2$ with SO_2, and of the hydrogen-bonding interaction of CF_3CH_2OH and the iridium complex, have been measured (ref. 231). The coordination behaviour of CO_2 towards a number of four- and five-coordinate Ir(I) and Ir(III) complexes has been investigated. Only the four-coordinate complexes $Ir(OH)(CO)(PPh_3)_2$, $IrCl(PMe_3)_3$-(cyclooctene) and $IrCl(L\text{-}L)_2$ (L-L = dmpe or depe) gave CO_2 complexes (ref. 232).

The influence of ancillary ligands on the stability of iridium-dinitrogen complexes prepared by reaction (43) has been examined for a wide range of anions

$$IrX(CO)(PR_3)_2 \; + \; R'N_3 \longrightarrow \underset{(78)}{IrX(N_2)(PR_3)_2} \; + \; R'NCO \qquad (43)$$

X and tertiary phosphines, some $AsPh_3$ complexes were also included. New complexes (78) isolated included R = Ph, X = F and NCO, and the first arsine-nitrogen complex $Ir(NCO)(N_2)(AsPh_3)_2$, the cyanate ion appeared to give the most stable dinitrogen complexes (ref. 233). The complexes (79) are obtained by the reaction between $IrCl(CO)(PPh_3)_2$ and $[M(RNC(H)NR^1)]_n$, corresponding rhodium

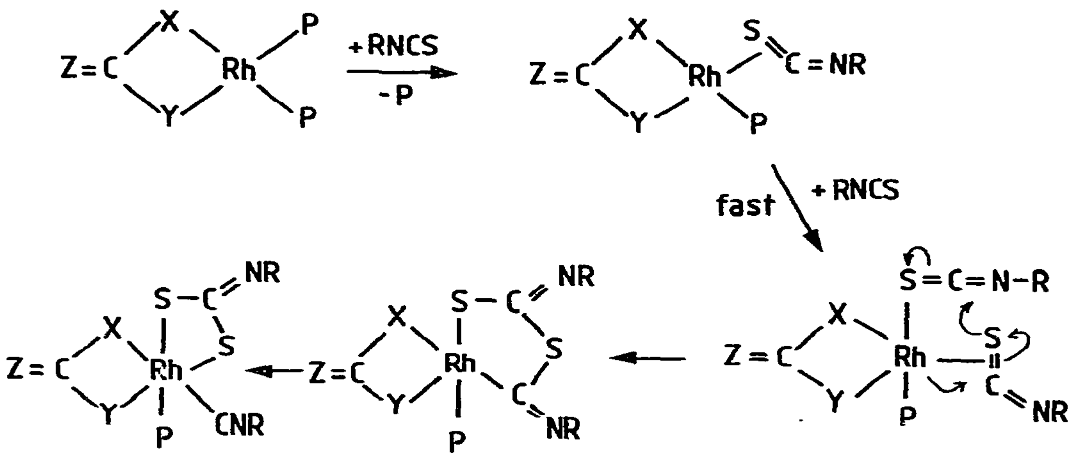


M = Cu, Ag
R = Me, Et, Pr^i, Bu^t, Cy
R^1 = p-tolyl

(79)

complexes could not be isolated. Reaction of (79) (M = Ag) with CO gives products believed to contain an acylformamidino group (ref. 234) The crystal structure of the dimethylthiocarboxamido complex of iridium(III), $[Ir(C(S)NMe_2)(S_2CNMe_2)(CO)(PPh_3)]PF_6$ has been reported (ref. 235).

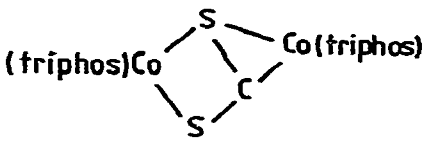
The reaction of isothiocyanates with rhodium(I) complexes of the type $Rh[X\text{-}C(Z)\text{-}Y](PPh_3)_2$ (X,Y,Z = N,P or S) leads to the formation of dithiocarbonimidato complexes (80), a three-step mechanism is proposed (Scheme 7). Complexes (80) react with PPh_3 resulting in $Rh[X\text{-}C(Z)\text{-}Y](RNC)(PPh_3)$ which readily oxygenates to $[Rh[X\text{-}C(Z)\text{-}Y](RNC)(PPh_3)(O_2)$ (ref. 236). Two new types of bridging CS_2 interaction have been found in the crystal structures of the triphos cobalt complex (81) (ref. 237), and the dinuclear complex (82) (ref. 238). Although physicochemical properties of individual SO_2 complexes have not been a reliable guide to the type of coordination geometry of the SO_2 ligand, certain combinations of properties have been found to be diagnostic of specific geometries and the properties of two new complexes $Ir(SPh)(CO)(PPh_3)_2(SO_2)$ and $[RhCl(PPh_3)_2(SO_2)]_2$ have been related to the new criteria (ref. 239). The first di(μ-S)-bridge between two metal atoms was discovered by crystal structure determination of complex (83) obtained by reacting the tetrathiolene $C_{10}H_{14}S_4$ with $IrBr(CO)(PPh_3)_2$ (ref. 240). The reactions of the cyclic disulphides (84), (85) and hexachloronaphthalene-1,8-disulphide with $RhCl(PPh_3)_3$ result in oxidative addition of the

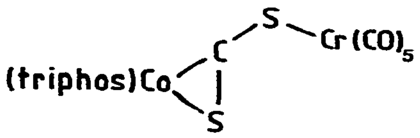


(80)

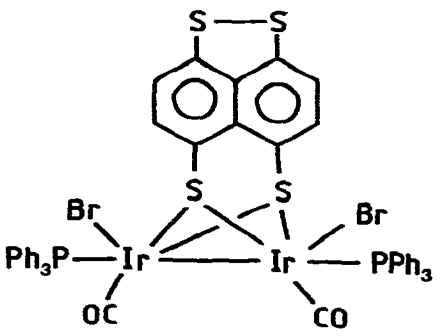
$P = PPh_3$; R = Ph, Me; X,Y,Z = N, P or S

SCHEME 7

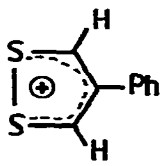




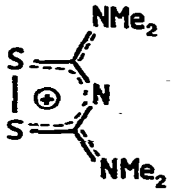
(81) triphos = $MeC(CH_2PPh_2)_3$ (82)



(83)



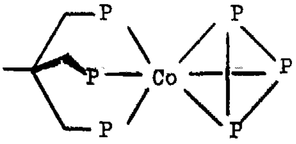
(84)



(85)

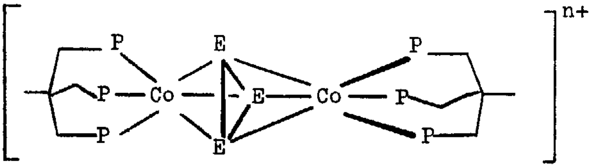
-S-S- bond to the metal atom (ref. 241).

The cyclotriphosphorus complex (86) possesses Lewis base properties due to



(86)

the P atoms of the μ_3-P_3 unit, with $Cr(CO)_6$ the complexes (triphos)Co(μ_3-P_3)–$[Cr(CO)_5]_n$ were obtained for n = 1 or 2 but not 3 (ref. 242). The corresponding Rh and Ir complexes to (86) have been obtained by reacting P_4 with $[RhCl(C_2H_4)_2]_2$ or $IrCl(CO)(PPh_3)_2$ (ref. 243). The double sandwich complexes (87) are obtained



E = P, As
n = 1,2

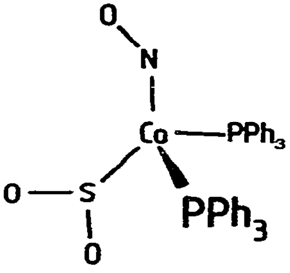
(87)

by reacting cobalt tetrafluoroborate with P_4 or As_4 in the presence of triphos. The corresponding Ni_2 and mixed CoNi complexes were also prepared and their magnetic properties measured (ref. 244). The redox behaviour of the series of complexes (87) has also been reported (ref. 245).

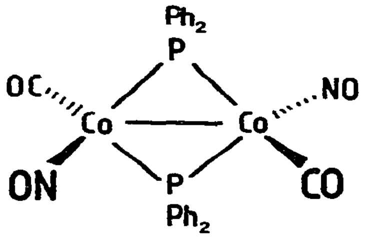
Metal nitrosyl and aryldiazo compounds

A general review of the reactions of nitric oxide coordinated to transition metals has appeared (ref. 246).

The complexes Co(S-S)(N-N)(NO) (S-S = maleonitriledithiol; N-N = azomethines of biacetyl with $PhNH_2$, p-toluidine, p-anisidine and 4-$ClC_6F_4NH_2$) have been prepared and characterized by IR, ESR, ESCA and magnetic measurements (ref. 247). The crystal structure of the complex (88) contains a sulphur coordinated SO_2 group and linear nitrosyl group (M-N-O angle is 169°), in contrast to the rhodium analogue which contains an η^2-SO_2 group and a bent nitrosyl group (ref. 248). The crystal structures of NO and NO_2 complexes of partially Co(II)-exchanged zeolite A have been determined. The NO complex contains strongly bent Co(III)-NO^- units (angle = 141°), in the NO_2 complex the Co(II)-NO_2 moiety is planar (ref. 249). The molecular structure of (89) has been determined by X-ray crystallography as part of the series $[L_2MPPh_2]_2$, (L_2M = $(NO)_2Fe$, (CO)(NO)Co and $(CO)_2Ni$), the M-M bond lengths are 2.70, 2.60 and 2.51 Å respectively (ref. 250)



(88)



(89)

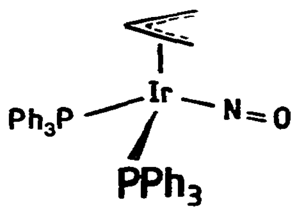
A method for predicting ν(CO) in a wide range of $M(CO)_xL_y$ and substituted systems, including derivatives of $Co(CO)_3(NO)$, has been reported (ref. 251). In the isoelectronic series of nitrosyl carbonyl compounds $M(CO)_n(NO)_{4-n}$ (M = Ni, Co, Fe, Mn, Cr; n = 4,3,2,1,0), XPS measurements of core binding energies indicate that NO is a much stronger π-acceptor than CO (ref. 252).

The complexes $M(NO)(PPh_3)_3$ (M = Co, Rh) readily undergo intermolecular transfer reactions of the nitrosyl ligand to other Co and Ni phosphine halide complexes. With trityl and silver perchlorates, the species $[Rh(PPh_3)_3(Me_2CO)]^+$ and $[Rh(NO)_2(PPh_3)_2]^+$ were obtained from $Rh(NO)(PPh_3)_3$ (ref. 253). Reaction (44) (saloph = N,N^1-bisalicylidene-o-phenylenediamino) represents the first

$$Co(saloph)(py)(NO_2) + PPh_3 \longrightarrow Co(saloph)(NO) + Ph_3PO + py \qquad (44)$$

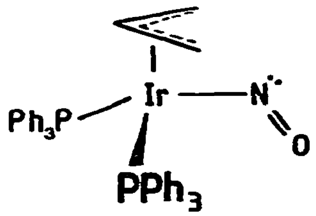
example of an oxygen transfer reaction where the metal remains at a constant formal oxidation state (ref. 254). Nitrosyl tribromide reacts with $RhCl(CO)(EPh_3)_2$ (E = P, As) to give $RhBr_2(CO)(NO)(EPh_3)_2$, a number of reactions with other Rh(I) and Rh(III) compounds are also reported (ref. 255).

The two isomers of the complex cation $[Ir(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$, (90) and (91), have been isolated as their crystalline PF_6^- and BF_4^- salts respectively,



(90)

$\rightleftharpoons$



(91)

ν(NO) values are 1763 cm^{-1} for (90) and 1631 cm^{-1} for (91). In solution the two IR frequencies are present with equal intensity suggesting that the two forms are in equilibrium. The crystal structure of (91) confirms the formulation shown, angle Ir - N - O is 129°. Variable temperature ^1H NMR spectra show that other equilibrium processes involving rotation and $\eta^3 \rightleftharpoons \eta^1$ transformations of the allyl group also occur with different activation energies. Both (90) and the corresponding Rh complex react rapidly with CO to give acrolein oxime, equation (45) (ref. 256). The complexes $Ir(NO)(2\text{-}ap)(PPh_3)$ and $[Ir(2\text{-}ap)(PPh_3)_3]$

$$[M(NO)(C_3H_5)(PPh_3)_2]^+ \xrightarrow{CO} [M(CO)_3(PPh_3)_2]^+ + CH_2{=}CHCH{=}NOH \qquad (45)$$

have been obtained by reacting $[Ir(NO)(MeCN)_2(PPh_3)_2]^{2+}$ with 2-aminophenols (2-ap) (ref. 257). Extended Hückel MO calculations have been made for the complex $[M(NO)_2(PH_3)_2]^+$ and a related Pt complex (ref. 258).

The triazenido complexes $M(ArN_3Ar)(CO)(PPh_3)_2$ (M = Rh, Ir; Ar = 4-MeC_6H_4, 4-FC_6H_4) readily react with aryl diazonium cations according to equations (46) and (47).

$$Ir(ArN_3Ar)(CO)(PPh_3) + [ArN_2]BF_4 \longrightarrow$$

$$Ir(ArN_3Ar)(CO)(PPh_3)_2(ArN_2)][BF_4] \qquad (46)$$

(92)

$$Rh(ArN_3Ar)(CO)(PPh_3) + [ArN_2]BF_4 \longrightarrow$$

$$[Rh(OCN(Ar)N{=}NAr)(N_2Ar)(PPh_3)_2][BF_4] \qquad (47)$$

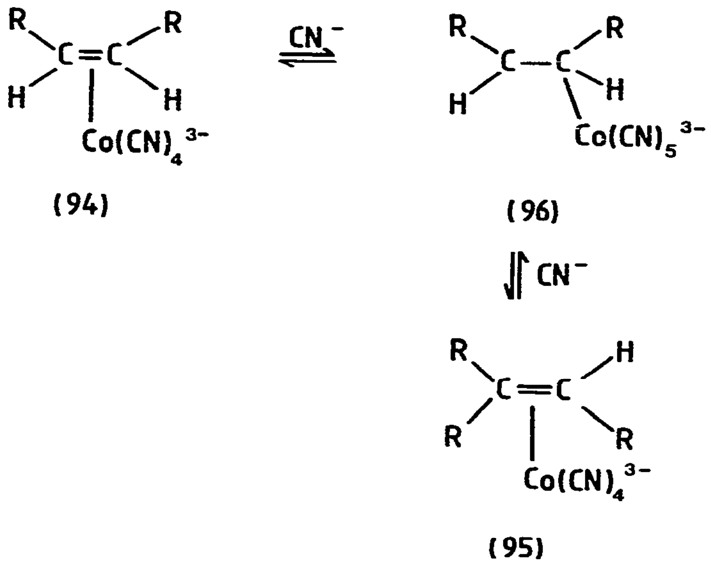
(93)

Compound (92) is believed to contain a doubly bent Ir - N = N - Ar aryl diazonium linkage, compound (93) possibly contains a bidentate acyltriazenido ligand formed by insertion of CO into an Rh-N bond of the triazenido ligand (ref. 259).

Metal alkene compounds

The bonding, conformational preferences, and rotational barriers in polyene-ML_2, polyene-ML_4 (ref. 260) and ethylene-ML_{2-5} (ref. 261) complexes have been analysed and a review which contains data on binary cobalt-ethylene complexes has been published (ref. 262).

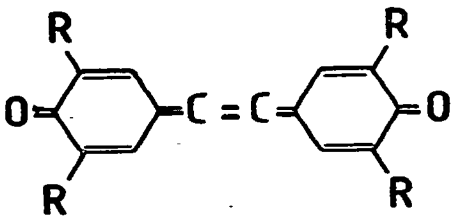
Clear NMR evidence has been obtained for the direct formation of pi- complexes of maleates and fumarates with $Co(CN)_4^{3-}$. The observed isomerization of (94)



to (95) is considered to occur via the cobalt-carbon bonded intermediate (96) (ref. 263). The interaction of styrene with $Co(N_2)(PPh_3)_3$, $CoH(N_2)(PPh_3)_3$ and $CoH_3(PPh_3)_3$ yields mono and dinuclear complexes which have been identified by ESR spectroscopy. A paramagnetic complex $Co(styrene)_2(PPh_3)$ is one of the intermediates in the catalytic hydrogenation of styrene (ref. 264) and π-olefin complexes of cobalt(II) are claimed to be formed upon reaction of $Et_2NCH_2CMe = CHCH_2NEt_2$ or $Me_2C = CHCH_2\overline{N(C}H_2)_5$ with $CoCl_2$ (ref. 265).

The reaction of CS_2 with cobalt(II) tetrafluoroborate, $NaBPh_4$ and triphos, where triphos is $MeC(CH_2PPh_2)_3$, affords the dinuclear complex $[(triphos)CoCS_2Co(triphos)][BPh_4]_2$. In the complex cation the CS_2 molecule is π-bonded to one cobalt via a C=S bond and bonds to the other cobalt via its two sulphur atoms (ref. 266).

Ethylene displaces methyl cyanide from the complex $RhCl(MeCN)(PPh_3)_2$ to give $RhCl(C_2H_4)(PPh_3)_2$ and the kinetics of this reaction have been studied (ref. 267). The reactions of the diquinoethylenes (dqe) (97) with $RhCl(PPh_3)_3$ gives the



(R = Bu^t, Pr^i)

(97)

complexes trans - $RhCl(dqe)(PPh_3)_2$ in which the central double bond of the cumulene system of (97) is coordinated to the rhodium. Treatment of $Rh(acac)(C_2H_4)_2$ with dqe gives the complexes $Rh(acac)(C_2H_4)(dqe)$ (ref. 268).

Treatment of $Rh_2Cl_2(C_2H_4)_4$ with the thallium Schiff-base derivatives $TlOC_6H_4CH = NR$ (R = p-tol,Me) affords the salicylaldimino complexes (98).

$$\mathrm{Rh(OC_6H_4CH = NR)(C_2H_4)_2} \qquad (98)$$

Reactions of these complexes with tertiary phosphines and arsines gives the complexes $Rh(OC_6H_4CH = NR)(C_2H_4)L$, ($L = PPh_3$, $AsPh_3$; R = Me, p-tol) and $Rh(OC_6H_4CH = NR)L_2$, ($L = PPh_3$, $PMePh_2$; R = Me). Certain ditertiary-phosphines and -arsines react with (98) to give $Rh(OC_6H_4CH = NR)L_2$ ($L_2 = Ph_2PCH_2CH_2PPh_2$, cis - $Ph_2AsCH = CHAsPh_2$, cis - $Ph_2PCH = CHPPh_2$; R = p-tol, Me). The complexes $Rh(OC_6H_4CH = NR)L_2$ react with methyl iodide to give $Rh(OC_6H_4CH = NR)IMeL_2$ (R = Me; $L = PPh_3$, $PMePh_2$) and chloroform reacts with $Rh(OC_6H_4CH = NMe)(PPh_3)_2$ to give $Rh(OC_6H_4CH = NMe)Cl_2(PPh_3)_2$ (ref. 269).

The bis(ethylene) cobalt complex $Co(C_2H_4)_2(etmcp)$, (etmcp is ethyltetramethylcyclopentadienyl) has been obtained by sodium-amalgam reduction of $Co_2Cl_2(\mu\text{-}Cl)_2(etmcp)_2$ in the presence of ethylene. The complexes Co(butadiene)(etmcp) and Co(cod)(etmcp) have also been described (ref. 270).

Electrochemical and NMR data have shown that cyclooctatetraene can bind to cobalt either as a 1,3-diene or 1,5-diene in the compound Co(cot)Cp (cot = cyclooctatetraene) in an equilibrium mixture and that the thermodynamically favoured 1,5-complex rapidly and quantitatively isomerizes to the 1,3-complex upon one electron reduction.

$$\begin{tikzcd}
\mathrm{Co(1,3\text{-}cot)Cp} \arrow[r, shift left] \arrow[d, shift left, "e^-(-1.8V)"] & \mathrm{Co(1,5\text{-}cot)Cp} \arrow[l, shift left] \arrow[d, "e^-(-2.0V)"] \\
\mathrm{Co(1,3\text{-}cot)Cp^-} \arrow[u, shift left] & \mathrm{Co(1,5\text{-}cot)Cp} \arrow[l]
\end{tikzcd}$$

This appears to be first example of a reversible electrochemical isomerization of a metal-hydrocarbon bond (ref. 271). Two new cyclononatetraene cobalt complexes $Co(C_9H_{10})Cp$ have been shown to contain the cyclononatetraene ligand coordinated in a (3-6-η)- and in a (1-2:5-6-η) mode. The (3-6-η)- complex rearranges at elevated temperatures to the (1-2:5-6-η)- complex and this latter complex can be protonated by stronge acids and the uncomplexed double bonds can be hydrogenated (ref. 272).

Ethylene is readily displaced from $Rh(C_2H_4)_2(indenyl)$ by carbon monoxide, fluorophosphines and also by more basic phosphines to give the complexes RhL_2(indenyl). Unhindered dienes also displace ethylene from $Rh(C_2H_4)_2$(indenyl) and mixed complexes $RhLL^1$(indenyl) (L,L^1 = CO, phosphine) have also been obtained. The barrier to ethylene rotation in $Rh(C_2H_4)_2$(indenyl) is lower than that in $Rh(C_2H_4)_2Cp$ (ref. 273). A determination of the enthalpies of reactions of various complexes of the type M(acac)$(olefin)_2$ with 1,5-cod, equation (48), reveals that pi-back bonding is slightly more important in the

$$M(acac)(olefin)_2 + 1{,}5\text{-cod} \rightarrow M(acac)(1{,}5\text{-cod}) + 2\ olefin \qquad (48)$$

(M = Rh, Ir; olefin = C_2H_4, propene, vinyl chloride, vinyl acetate, methacrylate, styrene)

iridium-olefin bond than in the rhodium-olefin bond (ref. 274).

Although the insertion of ethylene into a metal hydride bond is considered to proceed via an ethylene-metal-hydride intermediate, equation (49), very few examples of stable ethylenehydridometal complexes are known. However, it has

$$MHL_n + C_2H_4 \rightleftharpoons MH(C_2H_4)L_n \rightleftharpoons MEtL_n \qquad (49)$$

now been shown that treatment of the complexes (99) with HBF_4 affords the hydrides (100), equation (50) and that the temperature dependence of the NMR

$$RhL(PMe_3)Cp \;+\; HBF_4 \rightarrow [RhH(L)(PMe_3)Cp]BF_4 \qquad (50)$$

(L = CO, C_2H_4)

(99) (100)

spectrum of (100; L = C_2H_4) indicates that an equilibrium is set up between the ethylenehydrido- (101) and ethyl complex (102), equation (51). Treatment of

$$RhH(C_2H_4)(PMe_3)Cp^+ \rightleftharpoons RhEt(PMe_3)_3Cp^+ \qquad (51)$$

(101) (102)

$[RhH(C_2H_4)(PMe_3)Cp]BF_4$ with ethylene affords $[RhEt(C_2H_4)(PMe_3)Cp]BF_4$ and reaction of (100; L = C_2H_4) with NaCl, NaBr or NaI affords the neutral complexes RhEtX(PMe_3)Cp, equation (52). However, with NaF a deprotonation reaction occurs, equation (53) (ref. 275). The reaction of $[RhEt(PMe_3)_2Cp]PF_6$ with $Ph_3C.PF_6$ in nitromethane at room temperature affords the dicationic salt

$$[RhH(C_2H_4)(PMe_3)Cp]BF_4 \quad + \quad NaX \rightarrow RhEtX(PMe_3)Cp \quad + \quad NaBF_4 \tag{52}$$

$$(X = Cl,\ Br,\ I)$$

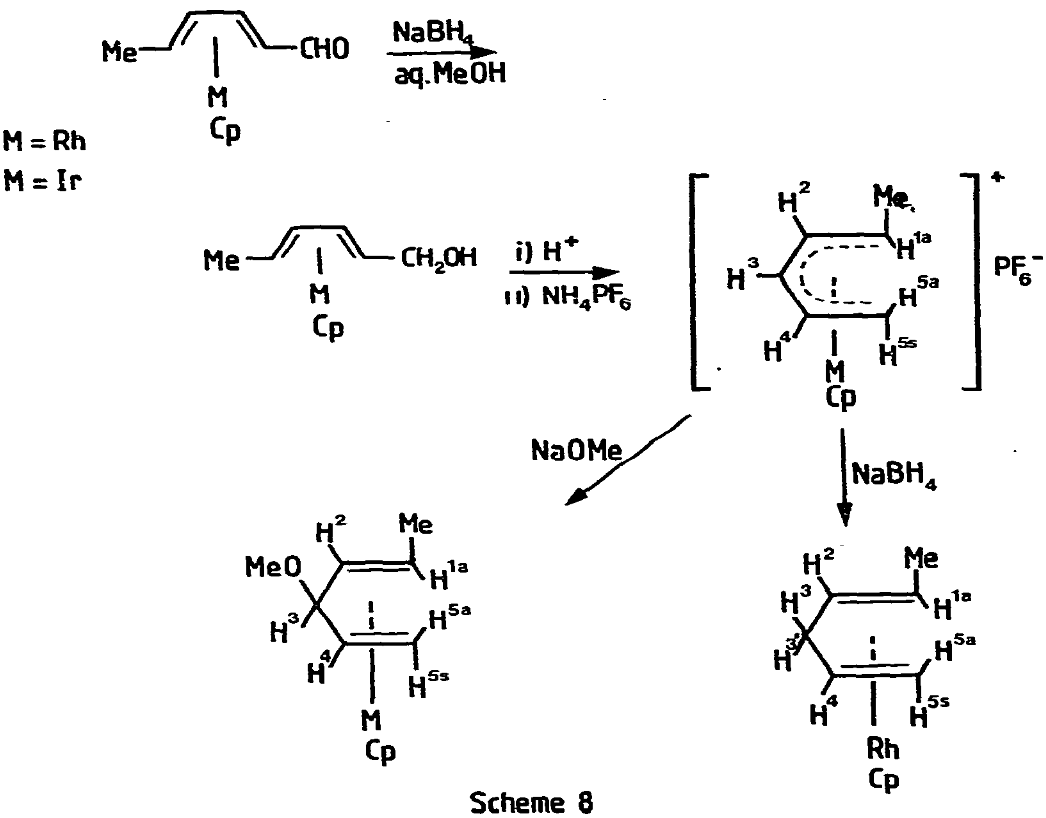
$$[RhH(C_2H_4)(PMe_3)Cp]BF_4 \quad + \quad NaF \rightarrow Rh(C_2H_4)(PMe_3)Cp \quad + \quad HF \quad + \quad NaBF_4 \tag{53}$$

$[Rh(C_2H_4)(PMe_3)_2Cp][PF_6]_2$. This salt reacts with nucleophiles such as tertiary amines or phosphines, N, to form complexes of the type $[Rh(C_2H_4N)(PMe_3)_2Cp]^{2+}$, equation (54). With $P(OMe)_3$ two products are formed, $[Rh\{C_2H_4P(OMe)_3\}(PMe_3)_2Cp]^{2+}$ and $[Rh\{C_2H_4P(O)(OMe)_2\}(PMe_3)_2Cp]^+$. Anionic nucleophiles e.g. KSCN also attack the coordinated ethylene but the products are more labile. Thus KSCN and $[Rh(C_2H_4)(PMe_3)_2Cp][BF_4]_2$ give $[Rh(C_2H_4SCN)(PMe_3)_2Cp][BF_4]$ but on warming in nitromethane the product slowly loses ethylene to give either $[RhNCS(PMe_3)_2Cp]^+$ or $[RhSCN(PMe_3)_2Cp]^+$. In general it appears that at low temperatures the preferred reaction is nucleophilic addition of the anion e.g. with SCN^-, I^-, but at higher temperatures the cations $[RhX(PMe_3)_2Cp]^+$ (X = SCN, I) are formed, either by direct displacement of ethylene or by a beta-elimination route (ref. 276).

$$[Rh(C_2H_4)(PMe_3)_2Cp]^{2+} \quad + \quad N \rightarrow [Rh(C_2H_4N)(PMe_3)_2Cp]^{2+} \tag{54}$$

A stopped-flow investigation of the reversible addition of triphenylphosphine to the cation $[Co(C_8H_{11})Cp]^+$ has been reported. Comparison of this result with previous studies shows that the general reactivity of various cations towards nucleophiles decreases in the order $[Co(C_7H_9)Cp]^+ > [Fe(CO)_3(C_6H_7)]^+ > [Fe(CO)_3(2\text{-}MeOC_6H_6)]^+ > [Cr(CO)_3(C_7H_7)]^+ > [Co(C_8H_{11})Cp]^+ > [Fe(CO)_3(C_7H_9)]^+$ (ref. 277). Protonation of the hex-2,4-dien-1-ol iridium complex, Scheme 8, affords a novel open chain pentadienyl complex. This complex and the corresponding rhodium cation undergo nucleophilic attack by methoxide ion at the central 3-position of the dienyl group to give 1,4-diene complexes. In pentadienyltricarbonyliron cations nucleophilic attack occurs at the terminal positions of the dienyl group (ref. 278). Complexes of the type IrH(1,5-cod)(diene) (diene = cyclohexa-1,3-diene, 2-methylcyclohexa-1,3-diene, 5-ethylcyclohexa-1,3-diene, cyclohepta-1,3-diene) have been obtained by reaction of $Ir_2Cl_2(1,5\text{-}cod)_2$ with Pr^iMgBr in the presence of cyclic dienes. The cyclohexa-1,3-diene complex $IrH(1,3\text{-}chd)_2$, equation (55), can similarly be prepared.

$$IrCl_3 + 1,3\text{-}chd \xrightarrow{Pr^iMgBr} IrH(1,3\text{-}chd)_2 \tag{55}$$



Scheme 8

At room temperature solutions of these hydrido complexes exhibit dynamic H-addition-elimination equilibria of the type:

$$\mathrm{IrH}(\eta^4\text{-diene})(1,5\text{-cod}) \rightleftharpoons \mathrm{Ir}(\eta^3\text{-enyl})(1,5\text{-cod})$$

$$\mathrm{IrH}(\eta^4\text{-}1,3\text{-chd})_2 \rightleftharpoons \mathrm{Ir}(\eta^3\text{-}C_6H_9)(\eta^4\text{-}1,3\text{-chd})$$

the hydrogen atom at the iridium being transferred to the endo positions of the diene ligands. The pure hydrido complexes only exist in solution at low temperatures (ref. 279).

The complexes Rh_2Cl_2(diene)$_2$ (diene = 1,5-cod, nbd) are known to readily undergo bridge splitting reactions with donor ligands. Thus with pyridine the complexes RhCl(py)diene are formed (ref. 280). It is also well established that tertiary phosphines react in a similar manner. However, in contrast, $P(OPh)_3$ in benzene solution has been shown to preferentially displace the diene

:oups to afford successively $Rh_2X_2L_2$(diene), $Rh_2X_2L_4$ and $RhXL_3$, L = $P(OPh)_3$. ; has now been reported that the ditertiary phosphite $(PhO)_2PN(Et)P(OPh)_2$, :dp, behaves similarly to triphenylphosphite. Carbon monoxide reacts reversibly ıth $[Rh(etdp)_2]^+$ and $[Rh(etdp)(1.5\text{-cod})]^+$ to give $[RhCO(etdp)_2]^+$ and ɘhCO(etdp)(1,5-cod)$]^+$ respectively. The cation $[Rh(etdp)_2]^+$ oxidatively adds 3r and Br_2 although the product *trans*-$[RhHBr(etdp)_2]^+$ gives $[Rh(etdp)_2]^+$ in ›lution (ref. 281). The reaction of trimethylphosphite with $Rh_2Cl_2(1,5\text{-cod})_2$ ı benzene solution results in simultaneous bridge cleavage and olefin displace- ɜnt and the reaction has been studied quantitatively by spectroscopic titrations ıd thermodynamic data for product formation have been determined. The reaction ˋ $P(OMe)_3$ with $Rh_2Cl_2(CO)_4$ in benzene is different in that some carbon monoxide ɜmains coordinated to the rhodium giving $Rh(CO)L_4^+$ where L is $P(OMe)_3$ (ref. 282). ıe reactions of the triphenylphosphite complexes $Rh_2Cl_2L_2$(diene), $Rh_2Cl_2L_4$, ıd $RhClL_3$, where L is $P(OPh)_3$, with arenes yields the cationic complexes ıL$_2$(arene)$^+$ and with nitrogen donor ligands, N, complexes of the type $RhN_mL_n{}^+$ I = py, substituted pyridines, bipy, dinitriles, n = 3,2, m = 1,2) have been ›tained (ref. 283).

When the reactions of tertiary phosphines with $Rh_2Cl_2(\text{diene})_2$ are carried ıt in polar media the complexes RhCl(phosphine)(diene) react further with the ıosphine to give the cations $[Rh(PR_3)_2(\text{diene})]^+$. It seems likely that these ›actions proceed through five coordinate intermediates and such complexes ıX$(PR_3)_2$(nbd) (R = *p*-ClC_6H_4) have been isolated. Similar five coordinate ›mplexes using $Rh_2Cl_2(1,5\text{-cod})_2$ could not be isolated, the lower π-acidity of 5-cod, as compared to nbd, decreasing the stability of the pentacoordinate ›mplex. Molecular hydrogen reacts with $RhX(PR_3)_2$(nbd) to give $RhH_2X(PR_3)_2$ and e hydride chloride complex shows catalytic activity in the hydrogenation of clic and terminal alkenes. The complexes $RhX(PR_3)_2$(nbd) react with carbon monoxide give $RhX(CO)(PR_3)_2$ (ref. 284). The complexes $[RhN_2(1,5\text{-cod})]ClO_4$ (N = nodentate nitrile, N_2 = bidentate nitrile) and $[RhN(PR_3)(1,5\text{-cod})]A$ (A = BF_4, O_4, R = *p*-FC_6H_4, Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) have also been prepared and they act with molecular hydrogen to form species that act as hydrogenation catalysts ›ef. 285). A variety of cationic complexes of the type $[RhL_2(\text{diene})_2]ClO_4$ ı = Ph_3As, Ph_3Sb; diene = 1,5-cod, nbd) and $[RhN_2(nbd)]ClO_4$ (N = quinoline, oquinoline, pyridine, 2-ethylpyridine; N_2 = tetramethylethylenediamine, 2-diphenylethylenediamine, bipy, 1,10-phen) have been described (ref. 287) and me reactions of these complexes are illustrated in equations (56) – (59). e ability of some of these complexes to act as hydrogenation catalysts has en examined.

$$Rh(AsPh_3)_2(\text{diene})]ClO_4 + CO \rightarrow [RhCO(AsPh_3)_2(\text{diene})]ClO_4 \qquad (56)$$

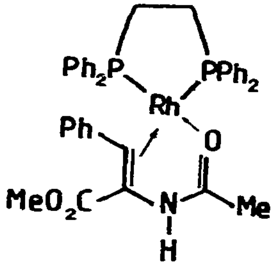
$$[Rh(SbPh_3)_2(diene)]ClO_4 + 2CO \rightarrow diene + [Rh(CO)_2(SbPh_3)_2]ClO_4 \qquad (57)$$

$$[Rhpy_2(nbd)]ClO_4 + 2PPh_3 \rightarrow 2py + [Rh(PPh_3)_2(nbd)]ClO_4 \qquad (58)$$

$$[Rhpy_2(nbd)]ClO_4 + PPh_3 \rightarrow py + [Rh(PPh_3)(py)(nbd)]ClO_4 \qquad (59)$$

The reaction of $Rh_2Cl_2(1,5\text{-cod})_2$ with $Pd(PPr^i_3)_2$ has been shown to give $RhCl(PPr^i_3)(1,5\text{-cod})$ possibly via a bridged intermediate (ref. 288).

The catalytic asymmetric hydrogenation of prochiral olefins by rhodium(I) complexes of chiral tertiary phosphines continues to be an active area of research. High optical yields have been attained with α-amidocinnamic acid derivatives as substrates, e.g. methyl(Z)-α-acetamidocinnamate (MAC) with Rh(I) catalysts containing chiral diphosphines, and a crystal structure of a hydrogenation intermediate $[Rh(diphos)(MAC)]^+$ (103) has been reported. The substrate is bound through the amide oxygen in addition to the η^2 C=C bond, which is considered to contribute to the stereoselectivity exhibited by the chiral catalysts (ref. 289). Studies of the catalytic asymmetric hydrogenation of itaconic acid and some of its derivatives and homologues with a rhodium(I) chiral diphosphine system have shown that the major limitation to efficient asymmetric hydrogenation is the ability of the substrate to form a bidentate complex in the transition state (ref. 290).



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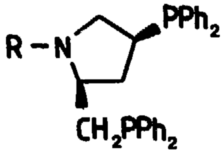
^{31}P NMR studies have been used to determine the nature of the olefin hydrogenation catalyst species present in solution on treating $Rh_2Cl_2(C_2H_4)_4$ with chelating diphosphines and on treating the complexes $Rh(diphosphine)(nbd)^+$ with molecular hydrogen. *An investigation of the reactions of* $RhCl(Ph_2PCH_2CH_2CH_2PPh_2)_2$ with H_2, HCl and O_2 has also been reported (ref. 291).

Chiral pyrrolidinephosphine-rhodium catalysts of the type $[Rh(1,5\text{-cod})L_2]ClO_4$ (L_2 = FPPM, BPPM, PPPM, PPM as shown below] have been shown to be useful catalysts



FPPM, R = CHO
BPPM, R = CO$_2$Bu^t
PPPM, R = COBu
PPM, R = H

for the syntheses of chiral <u>alpha</u>-amino acids, salsolidine, <u>alpha</u>-hydroxy esters R-(-)-pantolactone, <u>beta</u>-amino acids, <u>alpha</u>-methylsuccinic acid <u>beta</u>-methylaspartic acid and <u>beta</u>-substituted butyrolactone. ^{31}P NMR studies of the complexes Rh(1,5-cod)L$_2$$^+$ (L$_2$ = FPPM, BPPM, PPPM) have shown that they have planar four coordinate structures but that Rh(1,5-cod)(PPM)$^+$ has a trigonal bipyramidal five-coordinated structure (ref. 292) and ^{31}P NMR studies have provided evidence for the regioselective coordination of prochiral olefinic substrates with rhodium(I) complexes of pyrrolidinodiphosphines, and suggest a mechanism for chiral recognition of enantiofaces (ref. 293). Some aspects of the chemistry and catalytic properties of cationic rhodium phosphine complexes have been studied and it is clear that the chemistry of cationic complexes containing chelating diphosphine ligands is different from that of the corresponding complexes of monodentate phosphine ligands (ref. 294).

Bis(2-diphenylphosphinoethyl)amine has been converted to a wide variety of water-soluble diphosphines and the catalytic activity of several rhodium complexes of these new ligands has been surveyed (ref. 295).

Triphenylphosphine and the positively charged phosphonium phosphine ligand Ph$_2$PCH$_2$CH$_2$P$^+$BzPh$_2$ react with Rh$_2$Cl$_2$(1,5-cod)$_2$ to give mixed-ligand cationic analogues of Wilkinson-type complexes. The presence of the positive charge on the phosphine ligand allows the complexes to be electrostatically bound between the negatively charged sheets of the swelling layer-lattice silicate mineral hectorite. The activity of the intercalated hydrogenation catalyst is about twice that of the homogenous catalyst in methanol. The complex [RhCl(Ph$_2$PCH$_2$CH$_2$PBzPh$_2$)(1,5-cod)]BF$_4$ has also boen isolated (ref. 296). Other cationic complexes of the type [RhL$_2$(1,5-cod)]ClO$_4$, L$_2$ = RNCH$_2$CH(PPh$_2$)CH$_2$CHCH$_2$Ph (ref. 292) and L$_2$ = OCH(CH$_2$PPh$_2$)OCH(CH$_2$PPh$_2$)CH$_2$ (ref. 297) have been described and their use as olefin hydrogenation catalysts examined. Some rhodium carboxylate complexes of the type Rh$_2$(OCOR)$_2$(1,5-cod)$_2$ have also been prepared and have been treated with tertiary phosphines to give catalysts for olefin hydrogenation (ref. 298). The complexes [RhL$_2$(diene)]$^+$ (L = mono- or -bi-dentate tertiary phosphine, diene = 1,5-cod, nbd) have been shown to catalyze hydrogen transfer from isopropanol to various ketones such as cyclohexanone, 4-t-butylcyclohexanone and acetophenone (ref. 299).

Metal-to-ligand charge transfer spectra of the complexes $Rh_2Cl_2(CO)_4$, $Rh_2Cl_2(1,5\text{-cod})_2$, $Rh_2Cl_2(nbd)_2$, and $Ir_2Cl_2(1,5\text{-cod})_2$ in dichloromethane solution have been obtained (ref. 300).

The reaction of molecular hydrogen with the complexes $[IrL_2(1,5\text{-cod})]PF_6$, where L is a tertiary phosphine, or the reaction of 1,5-cod with a hydrido complex provides two isomeric series of dihydrido-diene complex cations <u>cis</u>- and <u>cis</u>, <u>trans</u>-$[IrH_2(1,5\text{-cod})L_2]PF_6$, equations (60) and (61). The complexes

$$[IrL_2(cod)]PF_6 \overset{H_2}{\rightleftharpoons} \underline{cis}\text{-}[IrH_2L_2(cod)]PF_6 \tag{60}$$

$$[IrH_2(Me_2CO)_2L_2] + cod \rightarrow \underline{cis},\ \underline{trans}\text{-}[IrH_2L_2(cod)]PF_6 \tag{61}$$

are important intermediates in the catalytic hydrogenation of 1,5-cod by $[IrL_2(1,5\text{-cod})]PF_6$. The <u>cis</u>-isomers transfer hydrogen to the coordinated cyclo-octa-1,5-diene much more rapidly than the <u>cis</u>, <u>trans</u> isomers, hydrogen transfer to the olefin appearing to require a coplanar Ir(C=C)H arrangement. Molecular hydrogen reacts with $[Ir(1,5\text{-cod})_2]^+$ at -80°C to give $[IrH_2(1,5\text{-cod})_2]^+$ and it is apparent that electron-withdrawing substituents do not deactivate the iridium centre towards oxidative addition (ref. 301). The complexes $[IrL_n(1,5\text{-cod})]PF_6$ ($n = 2$, L = PPh_3, $PMePh_2$; $n = 3$, L = PMe_2Ph also oxidatively add hydrogen halides to give $[IrHX(1,5\text{-cod})L_2]PF_6$ (L = PMe_2Ph, $PMePh_2$) or $IrHX_2(1,5\text{-cod})(PPh_3)$. The iridium(I) intermediates, $IrXL_2(1,5\text{-cod})$ (L = $PMePh_2$, X = Br, I) can be isolated from the reaction mixtures at 0°C and are also formed upon treatment of $[IrL_2(1,5\text{-cod})PF_6$ with KX (L = PPh_3, X = Cl; L = $PMePh_2$, X = Cl, Br, I). Protonation of these intermediates occurs as indicated in equations (62) and (63). The hydride $IrHI_2(PPh_3)(1,5\text{-cod})$ is also formed upon

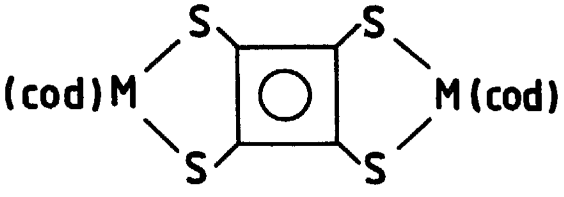
$$IrXL_2(1,5\text{-cod}) + HPF_6 \rightarrow [IrHXL_2(1,5\text{-cod})]PF_6 \tag{62}$$
$$(L = PMePh_2,\ X = Cl,\ Br,\ I)$$

$$2IrCl(PPh_3)_2(1,5\text{-cod}) + HPF_6 \xrightarrow{-60^{\circ}C} IrHCl_2(PPh_3)(1,5\text{-cod}) + [Ir(PPh_3)_2(1,5\text{-cod})]PF_6 + PPh_3 \tag{63}$$

reaction of $[IrHI_2(PPh_3)_2(1,5\text{-cod})]PF_6$ with iodine in dichloromethane (ref. 302).

An organometallic cluster $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$, which illustrates steps in the dehydrogenation of cylo-octa-1,5-diene by a metal cluster, has been obtained as a minor product from the reaction of $Ir_4(CO)_{12}$ with cyclo-octa-1,5-diene (ref. 303).

Displacement of chloride from the complexes $M_2Cl_2(1,5\text{-cod})_2$ (M = Rh, Ir) by the tetrathiosquarate dianion has been reported. Thus treatment of $M_2Cl_2(1,5\text{-}cod)_2$ (M = Rh, Ir) with $C_4S_4K_2.H_2O$ affords the complexes (104) (ref. 304). The organometallic alpha-diimines RN = $CR^1C(Me)$ = NR", R^1 = trans - $PdCl(PPh_3)_2$, also react with $Rh_2Cl_2(1,5\text{-}cod)_2$, equation (64) to afford the binuclear complexes (105). The reactions of the alpha-diimines RN = $CR^1C(Me)$ = NR", R' = PdCl(diphos) or $Rh(S_2CNMe_2)(PPh_3)$, with $Rh_2Cl_2(1,5\text{-}cod)$ have also been reported. In all the binuclear complexes isolated the 1,5-cod ligands are readily displaced by carbon monoxide to give the corresponding dicarbonyl complexes. The reactions of the diimines RN = $C(R^1)C(Me)$ = NR", DAB, with $Rh_2Cl_2(CO)_4$ afford trinuclear complexes $Rh_2Cl_2(CO)_4(DAB)$ in which the diazabutadiene group acts as a bridging ligands (ref. 305).



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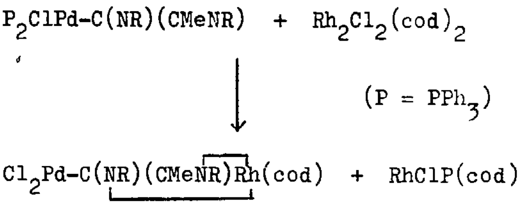


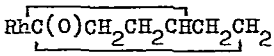
$$\mathrm{P_2ClPd\text{-}C(NR)(CMeNR)} + \mathrm{Rh_2Cl_2(cod)_2} \xrightarrow{(\mathrm{P} = \mathrm{PPh_3})} \mathrm{Cl_2Pd\text{-}C(NR)(CMeNR)Rh(cod)} + \mathrm{RhClP(cod)} \qquad (64)$$

(105)

Several dinuclear arsenic bridged carbonyl complexes with Fe-Fe, Mn-Co, and Fe-Co bonds catalyze the dimerization of norbornadiene and the X-ray crystal structure of one of these $(OC)_4Fe\text{-}AsMe_2\text{-}Co(CO)_2(nbd)$ has been determined (ref. 306). Studies on the dimerization of 7-methylnorbornadiene by $Co_2(CO)_4(nbd)_2$-$BF_3.OEt_2$ or $Co_2(CO)_4(nbd)_2$-I_2 catalyst systems suggest that a π-complex multicentre process is not important and that a metal-catalyzed cationic polymerization of norbornadiene is involved the catalyst system having the ability to align two dimerizing nbd molecules to give Binor-S (ref. 307).

Various rhodium catalyzed rearrangements of strained-ring organic compounds have been reported during the present year.

Thus $Rh_2(OAc)_2(nbd)_2$, the crystal structure of which has been determined (ref. 308), catalyzes the isomerization of quadricyclane to norbornadiene and two endo bis(norbornadienes) (ref. 309). The rearrangement of bicyclo[2.2.0] hexane to cyclohexane is catalyzed by $Rh_2Cl_2(1,5\text{-cod})_2$. The stoichiometric reaction of bicyclo[2.2.0]hexane with $Rh_2Cl_2(CO)_4$ yields an acyl oxidative addition product (106) which upon treatment with triphenylphosphine yields



$$RhC(O)CH_2CH_2CHCH_2CH_2(Cl)(CO) \qquad (106)$$

3-cyclohexane-1-carboxaldehyde. No 7-norbornanone could be detected in the products and this contrasts with the corresponding reaction of the cubane adduct which yields homocubanone (ref. 310).

The octamethylene chains in di-[8](1,4)-7-oxanorbornadienerhodium chloride have been shown to exhibit dynamic processes which involve a swinging of the octano bridge over the ether-oxygen atom, a conformational change within the octano bridge, a rotation of the 7-oxanorbornadiene ligands around the rhodium-oxygen axes and an exchange of free and coordinated 7-oxanorbornadiene (ref. 311).

A series of papers on the preparations, X-ray structures and ^{13}C NMR spectra of rhodium(I) and -(III) and iridium(I) and -(III) complexes containing chelating unsaturated tertiary phosphines and arsines have appeared. Thus the olefin complexes $RhCl_3(BDPH)$, $RhClBr_2(BDPH)$, $IrCl_3(BDPH)$, $IrClBr_2(BDPH)$, $IrMeClI(BDPH)$, $IrHCl_2(BDPH)$ and $IrHBr_2(BDPH)$, where BDPH is $Ph_2PCH_2CH_2CH = CHCH_2CH_2PPh_2$, have been obtained by oxidative-addition reactions of the complexes RhCl(BDPH) and IrCl(BDPH) (ref. 312). An X-ray study of IrCl(BDPH) shows that the complex is square planar with trans phosphorus atoms and with the coordinated C=C bond lying essentially perpendicular to the $IrClP_2$ plane. In $IrH_2Cl(BDPH)$ the geometry is octahedral with Cl and olefin ligands each trans to hydride ligands. The Ir-C distances are much longer than those in IrCl(BDPH) and the C=C bond length in $IrH_2Cl(BDPH)$ is approximately the same as that in free ethylene. It would seem that there is little back-bonding in this iridium(III)-olefin bond (ref. 313) and a similar result is found for $IrCl_3(BDPH)$ (ref. 312). A ^{13}C NMR analysis of the square planar complexes RhX(BDPH), X = Cl or Br, RhCl(BDAH), where BDAH is $Ph_2AsCH_2CH_2CH = CHCH_2CH_2AsPh_2$, the trigonal-bipyramidal complexes $RhX(DBP)_2$, X = Cl or Br, RhX(CO)(DBP), X = Cl, Br or I, IrX(CO)(DBP), X = Cl, Br, or I, where DBP is $PhP(CH_2CH_2CH = CH_2)_2$, RhX(TBP), X = Cl, Br, or I, IrCl(TBP), where TBP is $P(CH_2CH_2CH = CH_2)_3$, and the octahedral complexes RhXYCl(BDPH), XY = Cl_2 or Br_2 and IrXYCl(BDPH), XY= Cl_2, H_2, or HCl have been reported. In general it is apparent that the ^{13}C NMR parameters of the complexes reflect the relative amount of electron density at the metal centre available for back-bonding (ref. 314).

Metal alkyne compounds

The reaction of $Co_2(CO)_6(PhC{\equiv}CPh)$ with 1,1,1-tris(diphenylphosphinomethyl) ethane, triphos under UV irradiation affords $Co_2(CO)_4(triphos)(PhC{\equiv}CPh)$. An X-ray structural study of this molecule shows that the triphos behaves as a bidentate ligand, displacing two carbonyl groups both on the same cobalt atom (ref. 315).

The reaction of 15-$PhC{\equiv}C$- substituted benzo-15-crown-5 ether, $PhC{\equiv}CR$ with $Co_2(CO)_8$ gives $Co_2(CO)_6(PhC{\equiv}CR)$ and a complex of phenyl 3,4-dimethoxyphenylacetylene, $Co_2(CO)_6PhC{\equiv}CC_6H_3(OMe)_2$ has also been prepared. The former complex provides an example of an acetylene cobalt carbonyl complex containing a crown ether group which should combine the properties of a transition metal compound and a crown ether within the same molecule (ref. 316). The reaction of hex-3-yne with a mixture of $Fe(CO)_5$ and $Co_2(CO)_8$ proceeds as outlined below:

$$Fe(CO)_5 \; + \; Co_2(CO)_8 \; + \; EtC{\equiv}CEt$$

$$\downarrow$$

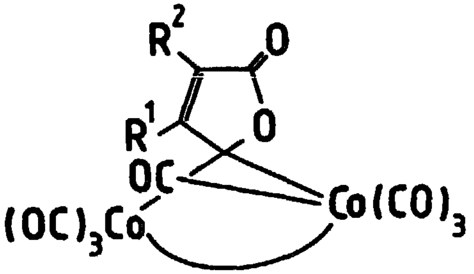
$$\underset{70\%}{Co_2(CO)_6(C_2Et_2)} \; + \; \underset{5\%}{Co_4(CO)_{10}(C_2Et_2)}$$

$$+ \; \underset{7\%}{Co_2(CO)_6\{EtC{\equiv}CH(OH)Me\}} \; + \; \underset{2\%}{Co_2(CO)_6(EtC{\equiv}CAC)}$$

$$+ \; \underset{1\%}{FeCo_2(CO)_7(C_2Et_2)_2} \; ?$$

Activation of one of the methylene groups alpha to the triple bond was also observed in the reaction of oct-4-yne with $Fe(CO)_5$ and $Co_2(CO)_8$ (ref. 317).

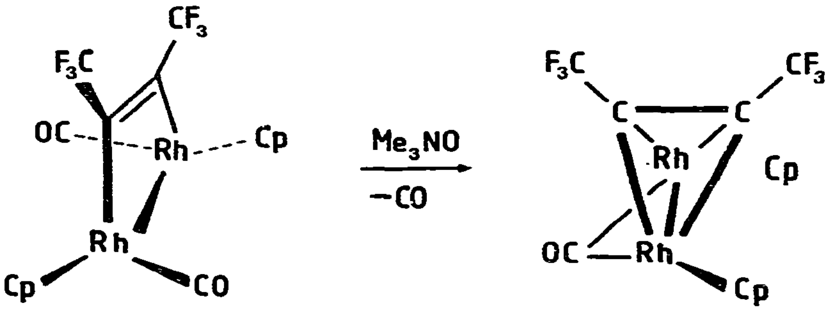
It is known that acetylenes can be carbonylated in the presence of catalytic amounts of $Co_2(CO)_8$ in polar solvents to give bifurandiones or with stoichiometric amounts of $Co_2(CO)_8$ to give lactone complexes $Co_2(CO)_7(C_4O_2R^1R^2)$ (107).



(107)

These lactone complexes have now been obtained with internal acetylenes and it has been found that the reaction is regiospecific. Further it appears that in the products derived from asymmetric internal acetylenes the 2-position of the lactone ring is occupied by the sp carbon atom of the acetylene with the higher value of the ^{13}C NMR chemical shift (ref. 318).

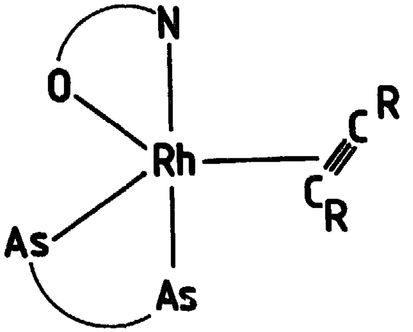
The reaction of trans-$Rh_2(CO)_2(C_4F_6)Cp_2$ (108) with Me_3NO results in decarbonylation of the complex and conversion of a two-electron into a four-electron donating acetylene ligand. The resulting complex (109) forms adducts with CO, $AsPh_3$, $P(OMe)_3$, $PMePh_2$, $Ph_2PCH_2CH_2PPh_2$, SO_2, Me_2SO and Bu^tNC and reactions of (109) with C_2R_2 (R = Me, CF_3, Ph) give the bridging metallodiene complexes $Rh_2\{C_4(CF_3)_2R_2\}Cp_2$ and the bridging metallodienone complexes $Rh_2\{C_4(CF_3)_2R_2CO\}Cp_2$ as major products. Treatment of (109) with molecular hydrogen at 20°C and 1 atm gives a variety of products e.g. $CF_3CH_2CH_2CF_3$, $Rh_3(CO)(C_4F_6)Cp_3$, $Rh_3(CO)_3Cp_3$, $Rh_4(CO)_2Cp_4$ and multinculear hydrido-rhodium species. It is also noteworthy that whereas trans-$Rh_2(CO)_2(C_4F_6)Cp_2$ (108) is fluxional, the terminal ^{13}CO ligands giving equivalent coupling to both ^{103}Rh nuclei at room temperature but to only one at -40°C, the cis-isomer is not fluxional (ref. 319).



(108) (109)

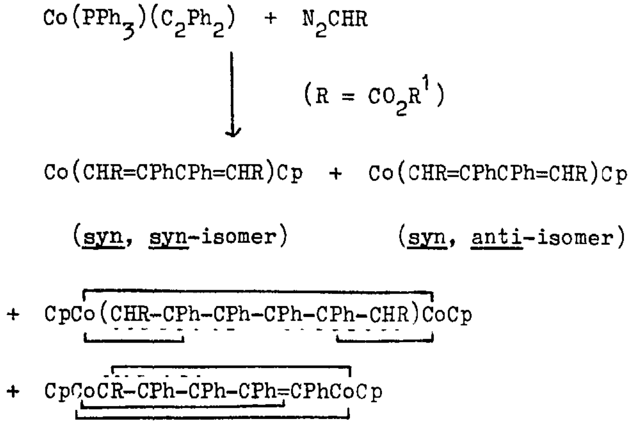
The complex (110) which is formed by the reaction of hexafluorobut-2-yne with Rh(Sal=N-p-tol)($Ph_2AsCH_2CH_2AsPh_2$), where Sal = N-p-tol is N-p-tolysalicylaldimine, exhibits acetylene rotation at higher temperatures but at low temperatures the CF_3 groups are non-equivalent suggesting the structure (110) (ref. 269).

Studies on the reactions of alkyl diazoacetates, which are potential carbene precursors, with $Co(PPh_3)(C_2Ph_2)Cp$, equation (65), reveal that the addition of alkoxycarbonylcarbenes to this cobalt-acetylene complex is analogous to that of isocyanides. The reactions are considered to proceed via an intermediate cobaltacyclobutene $\overline{Co(CHRCPh=C}Ph)Cp$ (ref. 320).



(R = CF_3)

(110)



$Co(PPh_3)(C_2Ph_2)$ + N_2CHR

$\downarrow$ (R = CO_2R^1)

Co(CHR=CPhCPh=CHR)Cp + Co(CHR=CPhCPh=CHR)Cp

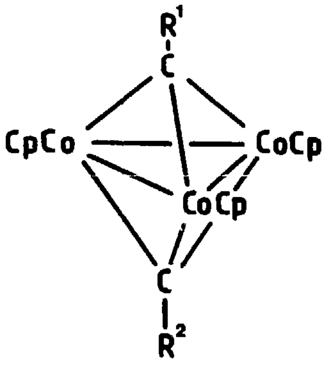
(*syn*, *syn*-isomer) (*syn*, *anti*-isomer)

+ CpCo(CHR-CPh-CPh-CPh-CPh-CHR)CoCp

+ CpCoCR-CPh-CPh-CPh=CPhCoCp (65)

The ^{17}O and ^{13}C NMR spectra of the acetylene compounds, $Co_2(CO)_6(C_2R_2)$ (R = CH_2OH, CO_2Me) have been reported (ref. 321).

The reaction of $Me_3SiC{\equiv}CSiMe_3$ with $Co(CO)_2Cp$ at 137°C affords a mixture of $(Me_3Si)_2C{=}C{=}C{=}C(SiMe_3)_2$, $Co\{C_4(SiMe_3)_4\}Cp$, $Co\{C_4(SiMe_3)_3(C_2SiMe_3)\}Cp$ and the novel trinuclear transition metal cluster (111, R^1 = $SiMe_3$, R^2 = C_2SiMe_3) which is capped by two triply bridging carbyne ligands (ref. 322). Thermolysis of



(111)

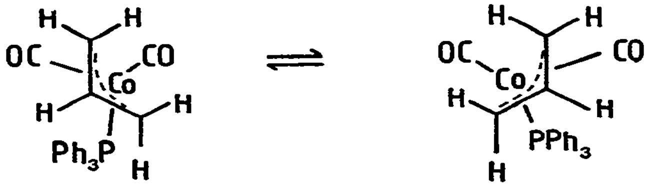
R^1 = Me_3Si, R^2 = $Me_3SiC{\equiv}C$
R^1 , R^2 = Ph
R^1 = Ph, R^2 = CO_2Me
R^1 = Me, R^2 = CN
R^1 = Me, R^2 = CO_2Me

acetylenecobalt complexes of the type $Co(PPh_3)(R^1C{\equiv}CR^2)Cp$ also give complexes of the type (111) (ref. 323).

Other reactions of acetylenes with cyclopentadienyl complexes of the type ML_2Cp (M = Co, Rh, Ir; L = donor ligand) are discussed in the section on metal cyclopentadienyl and arene compounds.

Metal allyl compounds

An X-ray structure analysis of the complex $Co(CO)_2(PPh_3)(C_3H_5)$ reveals that the cobalt atom has a distorted square pyramidal coordination with a formally bidentate allyl ligand, one carbonyl ligand, and a phosphine ligand occupying the basal position. Furthermore it is apparent that at temperatures down to 135 K there is a fluxional equilibrium with the allyl ligand oscillating between two enantriomeric positions as indicated below (ref. 324).



Some 16-electron allyl complexes of the type Rh(allyl)(1,5-cod), (allyl = 1-methylallyl, 1,2-dimethylallyl, 1,3-dimethylallyl, 1,1,2-trimethylallyl) have been obtained by the reaction of $Rh_2Cl_2(1,5\text{-cod})_2$ with Pr^iMgBr in the presence of the acyclic conjugated dienes buta-1,3-diene, isoprene, cis- or trans-penta-1,3-diene, and 2,3-dimethylbuta-1,3-diene respectively. The complex formation is regio- and stereoselective and only one isomer is produced in each reaction (ref. 325). A variety of allyl complexes of rhodium and iridium have also been obtained via reactions of appropriate complexes with allylmercury halides $HgX(C_3H_4R)$ as outlined in the equations (66) - (69) (ref. 326).

$$Na_3RhCl_6 + HgCl(C_3H_5) \xrightarrow{MeOH,H_2O} Rh_2Cl_2(C_3H_5)_4 \qquad (66)$$

$$RhCl_3.3H_2O + HgCl(C_3H_5) + TlCp \longrightarrow RhCl(C_3H_5)Cp \qquad (67)$$

$$IrI_2Cp + HgCl(C_4H_7) \longrightarrow IrHgC_9H_{12}Cl_2I_2 \qquad (68)$$

$$IrHgC_9H_{12}Cl_2I_2 \xrightarrow[Na_2S_2O_3]{Me_2CO} Hg + IrI(C_4H_7)Cp + IrCl(C_4H_7)Cp \qquad (69)$$

The reactions of $Rh(C_3H_5)(1,5\text{-cod})$ with phosphites and phosphines give a series of quasi-four-coordinate and five-coordinate complexes of the type $Rh(C_3H_5)L_2$ and $Rh(C_3H_5)L_3$. These complexes readily react with molecular hydrogen at 20°C to form initially propene and rhodium hydrides of the type $RhHL_4$, RhH_3L_3, $[RhHL_2]_x$, and an unidentified hydride. The polynuclear hydrides $[RhHL_2]_3$, L is $P(OMe)_3$ or $P(OEt)_3$ and $[RhHL_2]_2$, L is $P(OPr^i)_3$, were fully identified. The stabilities of the phosphine analogues were substantially lower. These hydrides are very active catalyst precursors for olefin and acetylene hydrogenations. The dimer $[RhHL_2]_2$, L is $P(OPr^i)_3$, is a catalyst for arene hydrogenations. In the reactions of $[RhH(\text{phosphite})_2]_n$ with molecular hydrogen, there was no detectable cluster fragmentation. In the case of the dimer and the trimer the fluxional intermediates $HL_2RhH_3RhL_2$ and $Rh_3H_5L_6$ respectively were identified (ref. 327).

Although the reactions of alkyl halides with <u>trans</u>-$IrX(CO)L_2$ commonly give products in which the alkyl and added halogen groups are <u>trans</u> to each other, it is known that the oxidative addition of allylic halides to <u>trans</u>-$IrCl(CO)(PMe_2Ph)_2$ occurs in a <u>cis</u> manner and that the phosphine ligands are also <u>cis</u> to each other in the product, equation (70). Studies on this reaction in benzene solution show that the reaction probably proceeds via a <u>pi</u>-allyl complex which reacts with anions to give a <u>sigma</u> bonded allyl <u>cis</u> to the added anion. Thus both <u>alpha</u>-methylallyl and crotyl chlorides give the same complexes. However, in methanol the <u>pi</u>-allyl complex is not an intermediate since these allyl chlorides gives different products, the iridium bonding predominantly to the carbon atom which was bonded to chloride (ref. 328). Phenylcyclopropane has been shown to react with <u>trans</u>-$IrCl(N_2)(PPh_3)_2$ to give $IrHCl(C_3H_4Ph)(PPh_3)_2$ and this complex is also formed from reactions using allylbenzene or <u>trans</u>-PhCH = CHMe. Allylbenzene also reacts with $Ir_2Cl_2(C_8H_{14})_4$ in the presence of a donor ligand L to give $IrHCl(C_3H_4Ph)L_2$ where L is PPh_3, $P(\underline{p}\text{-tol})_3$, $AsPh_3$, $As(\underline{p}\text{-tol})_3$, or $SbPh_3$. Some reactions of the complexes are given in equations (71) and (72). Treatment of the $IrHCl_2(PPh_3)_2$ mixture obtained in equation (72) with CO yields

$$\underline{\text{trans}}\text{-}IrCl(CO)L_2 \quad + \quad \text{allyl}X \rightarrow IrClX(\text{allyl})L_2 \tag{70}$$

(allyl is $CH_2 = CR\text{-}CH_2$, R = H,Cl,Me; X = Cl, Br; L = PMe_2Ph)

$$IrHCl(C_3H_4Ph(PPh_3)_2 \quad + \quad L \rightarrow IrCl(L)(PPh_3)_2 \quad + \quad PhCH = CHMe \tag{71}$$

(L = CO or PF_3)

$$\mathrm{IrHCl(C_3H_4Ph)(PPh_3)_2 + HCl \rightarrow \alpha\text{-}IrHCl_2(PPh_3)_2 + PhCH = CHMe + \beta\text{-}IrHCl_2(PPh_3)_2 + PhCH_2CH = CH_2} \quad (72)$$

a new isomer of $\mathrm{IrHCl_2(CO)(PPh_3)_2}$. The complex $\mathrm{IrHCl(C_3H_4Ph)(PPh_3)_2}$ adopts a structure in which the pi-allyl occupies two coordination sites, the phosphine ligands are mutally cis, and the hydrido and chloro ligands are trans (ref. 329).

The reaction of tetrafluoroethylene with $\mathrm{Co(CO)_2(PMe_2Ph)(C_3H_5)}$ affords $\mathrm{\overline{Co(CF_2CF_2CH_2CH}{=}CH_2)(CO)_2(PMe_2Ph)}$ and the complexes $\mathrm{Co(CO)_2L(allyl)}$, allyl $= \mathrm{C_3H_5}$, $\mathrm{L = P(OMe)_3}$ and allyl = 1-syn-$\mathrm{PhC_3H_4}$, L = CO afford analogous products with $\mathrm{C_2F_4}$. Some reactions of hexafluoropropene and octafluorobut-2-ene are given in equations (73) and (74). The structure of the complex $\mathrm{\overline{Co\{CF(CF_3)CF(CF_3)CH_2CH}{=}CH_2\}(CO)_2P(OMe)_3}$ is essentially trigonal bipyramidal

$$\mathrm{Co(CO)_2L(2\text{-}MeC_3H_4) + C_3F_6 \rightarrow \overline{Co\{CF(CF_3)CF_2CH_2CMe}{=}CH_2\}(CO)_2L} \quad (73)$$

$\mathrm{L = P(OMe)_3}$

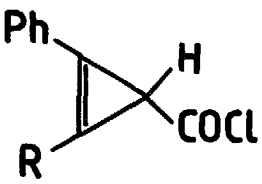
$$\mathrm{Co(CO)_3(C_3H_5) + CF_3CF = CFCF_3 \rightarrow \overline{Co\{CF(CF_3)CF(CF_3)CH_2CH} = CH_2\}(CO)_3} \quad (74)$$

with the phosphite ligand and fluoroalkyl group occupying the apical positions. The reaction of $\mathrm{Co(CO)_3(C_3H_5)}$ with chlorotrifluoroethylene leads to an unusual cyclization reaction to afford $\mathrm{Co(CO)_2(\overline{CH{=}CH{=}CFCF_2CH_2})}$. The allyl complexes $\mathrm{Co(CO)_3(2\text{-}MeC_3H_4)}$ and $\mathrm{Co(CO)_3(1\text{-}MeC_3H_4)}$ behave similarly (ref. 330).

Metal cyclopropenyl and cyclobutadiene compounds

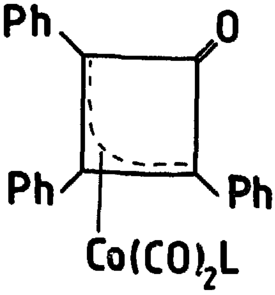
The reaction of $\mathrm{Ph_3C_3{}^+BF_4{}^-}$ with $\mathrm{Co_2(CO)_8}$ affords the η^3-triphenylcyclopropenyl complex, $\mathrm{Co(CO)_3(C_3Ph_3)}$. Synthesis of this complex completes the cobaltatetrahedrane family, $\mathrm{Co_2C_2R_2(CO)_6}$ $\mathrm{Co_3CR(CO)_9}$, and $\mathrm{Co_4(CO)_{12}}$. The complex $\mathrm{Co(CO)_3(C_3Ph_3)}$ is a yellow air-stable solid (ref. 331).

Treatment of (112; R = Ph) with $\mathrm{NaCo(CO)_3L}$ (L = CO, $\mathrm{PPh_3}$, $\mathrm{PMePh_2}$, $\mathrm{PMe_2Ph}$, $\mathrm{PEt_3}$) in THF affords the cyclobutenonyl complexes (113) in good yield, the reactions proceeding via intermediate acyl species e.g. $\mathrm{Co(CO\overline{CHCPh{=}C}Ph)(CO)_3PEt_3}$. In benzene solution the complex (113; L = CO) is in equilibrium with the novel dimer (114). The IR spectra of the complexes (113) are also of interest since it is apparent that the stretching frequency of the ring carbonyl group is dependent upon the nature of the ligand L. Thus an increase in the donor ability of L lowers the C=O stretching frequency and increases the contribution of the canonical form (115) (ref. 332). Further studies have demonstrated the



R = Ph
R = $\underline{p}$-$MeOC_6H_4$
R = Me

(112)



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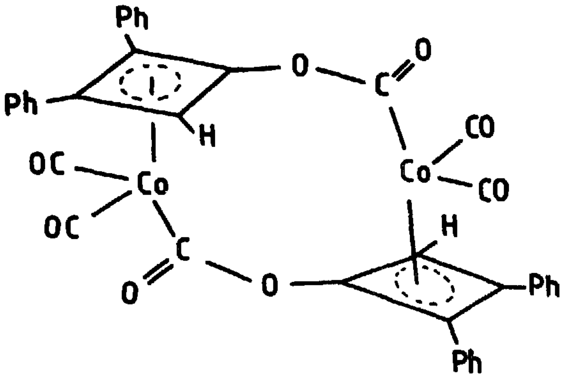

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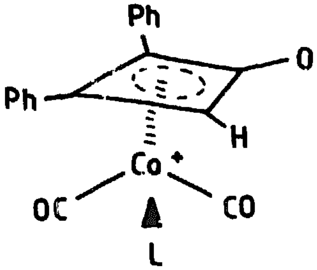


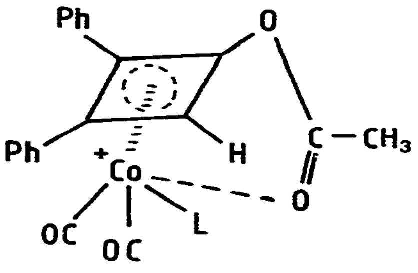
(115)

nucleophilicity of the ketone oxygen, equations (75) and (76). Treatment of

$$Co^+(CO)_2L(C_4Ph_2HO^-) \; + \; Me_3O^+PF_6^- \rightarrow [Co(CO)_2L\{C_4Ph_2H(OMe)\}]PF_6 \qquad (75)$$

$$Co^+(CO)_2L(C_4Ph_2HO^-) \; + \; Et_3O^+BF_4^- \rightarrow [Co(CO)_2L\{C_4Ph_2H(OEt)\}]BF_4 \qquad (76)$$

(115) with $PhCO^+SbF_6^-$ and $MeCO^+BF_4^-$ affords acyloxy complexes but they are significantly less stable than their alkoxy analogues and seem to regenerate the starting cyclobutenonyl complexes on standing in solution. These complexes may exhibit interactions of the type indicated in (116). The cationic complexes produced in equations (75) and (76) are air-stable crystalline solids.



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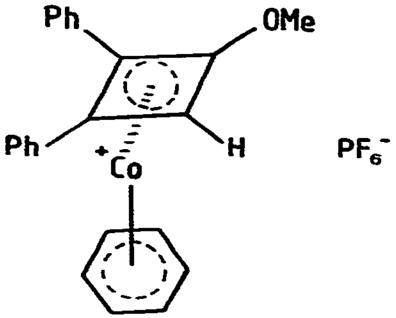
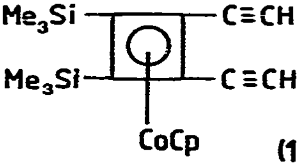


(117)

However, the carbonyl ligands in $[Co(CO)_3\{C_4Ph_2H(OMe)\}]PF_6$ are labile and on warming a benzene solution the cationic sandwich complex (117) is produced (ref. 333).

Pyrolysis of the complexes (118) - (121) gives varying amounts of the other



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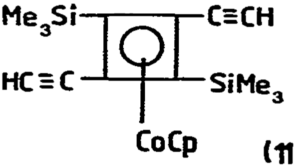

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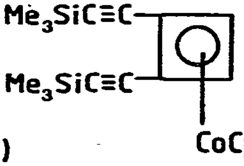

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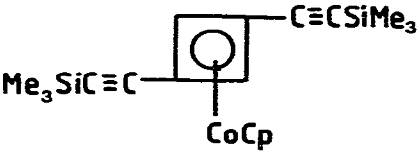
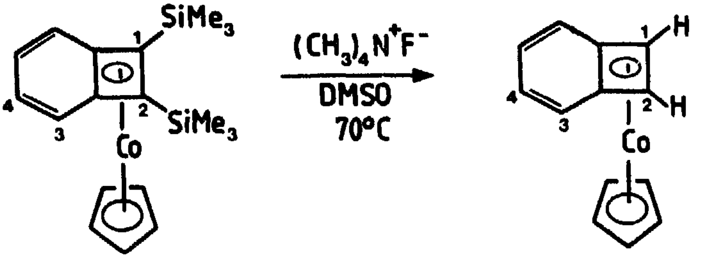


(121)

isomers together with $Me_3SiC{\equiv}CC{\equiv}CH$ and $Me_3Si(C{\equiv}C)_3SiMe_3$. These results are clearly related to the role of metal-cyclobutadiene complexes in alkyne metathesis. The free energies of activation for the decomposition of these complexes are in the range 47-50 kcal/mol and are considerably lower than the CpCo bond strength of 64 kcal/mol (ref. 334).

The reaction of 1,8-bis(trimethylsilyl)-cis,cis-octa-3,5-diene-1,7-diyne with $Co(CO)_2Cp$ affords the benzocyclobutadiene complex (112) which on treatment with fluoride affords the first known benzocyclobutadiene sandwich complex (123) The reactions of symmetrical and unsymmetrical acetylenes with $Co(CO)_2Cp$ are



(122) (123)

known to produce a variety of cyclobutadiene and cyclopentadienone complexes. Thus the reactions of both phenyl-1-naphthylacetylene and phenyl-2-naphthylacetylene with $Co(CO)_2Cp$ have been shown to produce all four possible cyclobutadiene-cobalt derivatives and all six possible cyclopentadienone cobalt derivatives. The structure of one of these complexes, $Co\{(1,3\text{-}Np)_2(2,4\text{-}Ph)_2C_4\}Cp$ (Np = naphthyl) has been established by an X-ray study (ref. 336). X-ray studies have also been reported for the complexes $Co(C_4Ph_4)(C_5H_4SiMe_3)$ (ref. 337) and $Co\{(1,3\text{-}Mes)_2(2,4\text{-}Ph)_2C_4\}Cp$ (Mes = mesityl) (ref. 63) and NMR studies indicate the presence of restricted rotation about mesityl-cyclobutadiene bonds in the latter complex (ref. 338).

Metal cyclopentadienyl and arene compounds

The chemistry of cobaltocene, cobalticinium salts and other cobalt sandwich compounds has been reviewed (ref. 339). The heats of formation of cobaltocene (205 ± 4 kJ/mol) and $Co(CO)_2Cp$ (-169 ± 10 kJ/mol) have been determined by static-bomb calorimetry (ref. 340) and the magnetic circular dichroism spectrum of cobaltocene has been reported (ref. 341).

The acidity constant, $\underline{K}_a$, has been determined spectrophotometrically for a number of substituted hydroxycobalticinium and hydroxyrhodicinium salts. Increasing the electronegativity of the substituent increases the acidity but the acidity is reduced on replacing cobalt(III) by rhodium(III) or by the replacement of a cyclopentadienyl group by a pentamethylcyclopentadienyl group (ref. 342).

The electrochemical reduction of $RhCp_2^+$ has been shown to occur in two separate one-electron processes to give reactive rhodium(II) and rhodium(I) complexes. $RhCp_2$ has a lifetime of about 2 seconds at room temperature but it can be stabilized by carrying out the electrolysis at low temperatures. $RhCp_2$ decomposes by dimerizing to give Rh_2Cp_4 which can be isolated in good yield by electrolysis of $RhCp_2^+$ solutions. Evidence has also been obtained for the transient existence of $RhCp_2^-$ (ref. 343). Deuterium labelling experiments establish that protonation of the anion $CoCp_2^-$ involves exo addition at the ligand and does not involve a metal hydride intermediate (ref. 344).

1,1^1-Dimethylcobaltocene has been shown to react with 2-cyanoazopropane and 2-bromo-2-phenylpropane to give isomerically pure (methylcyclopentadienyl) (2-methyl-5-*exo*-alkylcyclopentadiene)cobalt complexes. In the reaction with 2-bromo-2-phenylpropane, 2,3-dimethyl-2,3-diphenylbutane was obtained as a by-product supporting a radical mechanism for this type of reaction (ref. 345).

Some ethyltetramethylcyclopentadienyl (etmcp) complexes of cobalt $Co_2Cl_2(\mu\text{-}Cl)_2(etmcp)_2$ and $Co_3Cl_6(etmcp)_2$ have been prepared by reaction of $Sn(etmcp)Bu^n{}_3$ with $CoCl_2$. From these complexes many cobalt complexes containing the etmcp ligand have been prepared. These include $[(etmcp)Co(\mu\text{-}Cl)_3Co(etmcp)]FeCl_4$, $CoCl_2(PPh_3)(etmcp)$, $[CoCl(diphos)(etmcp)]PF_6$, $[CoL_3(etmcp)]PF_6$ $\{L = NH_3$, MeCN, $CH_2 = CHCN$; $L_3 = (MeCN)_2(Me_2C{=}NH$, benzene, toluene$\}$, and $CoL_2(etmcp)$ (L = ethylene; L_2 = butadiene, 1,5-cod) (ref. 270).

Treatment of $CoCl_2(PPh_3)_2$ with TlCp affords the cobalt(II) complex $CoCl(PPh_3)Cp$ which reacts with $Ag(RN_3R)$ or $Cu(RN_3R)$ to give the low-spin triazenido complexes $Co(RN_3R)(PPh_3)Cp$ (R = *p*-MeC_6H_4, *p*-ClC_6H_4, 3,5-$Cl_2C_6H_3$). These complexes provide some rare examples of paramagnetic monocyclopentadienyl transition metal complexes (ref. 346). Some cobalt(III) complexes $[Co(RN_3R)(LCp]PF_6$, where L is PEt_3, PPh_3, $P(OMe)_3$, or $P(OPh)_3$ have been obtained by the reactions outlined in equations (77) and (78).

$$CoI_2LCp + Ag(RN_3R) \rightarrow [Co(RN_3R)LCp]I \qquad (77)$$

$$[Co(RN_3R)LCp]I + TlPF_6 \rightarrow TlI + [Co(RN_3R)LCp]PF_6 \qquad (78)$$

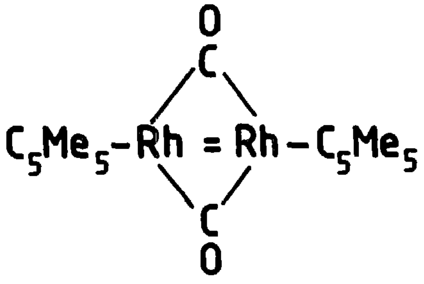
The carbonyl complex, L = CO, could not be prepared but the carbonyl inserted product $\overline{Co(CONRNN}R)ICp$ was isolated. In the reaction of $CoI_2(PPh_3)Cp$ with $Ag(RN_3R)$ the novel triphenylphosphonium cyclopentadienylide complex, $[Co(C_5H_4PPh_3)Cp][PF_6]_2$ was isolated as a side product (ref. 347).

Treatment of $Na[Co\{P(O)(OEt)_2\}_3Cp]$ with the salts MX (M = Li, K, Ag, NH_4, NMe_4) affords the salts $M[Co\{P(O)(OEt)_2\}_3Cp]$. The air-stable diamagnetic anion, $[Co\{P(O)(OEt)_2\}_3Cp]^-$ reacts as a tridentate chelating ligand with all main Group (III) elements. Using $NaBPh_4$ the cage-like cationic complex $[PhBCo\{P(O)(OEt)_2\}_3Cp]^+$ is obtained and with Al, Ga, In, Tl, (M), the trinuclear sandwich compounds $M[Co\{P(O)(OEt)_2\}_3Cp]_2^+$ are formed which contain MO_6 octahedra (ref. 348). The trinuclear complexes $Co[Co\{P(O)(OEt)_2\}_3Cp]_2$ and $M[Co\{P(O)(OEt)_2\}Cp]_2$ (M = Mg, Ca, Sr, Ba, Pb, Mn, Co, Ni, Cu, Zn, Cd, Hg) have been studied by X-ray diffraction and the structures of the complexes M = Co, R = Me and M= Cu, R = Et have been determined. Solid-solid phase transitions occur in the range 160-230 K and are best discussed in terms of order-disorder transitions(ref. 349). The electrochemistry of the complexes $M[Co\{P(O)(OEt)_2\}_3]_2$ (M = Co, Fe, Hg, Cu) has been investigated. The cobalt complex, M = Co, is difficult to oxidise but the resulting cobalt(III) complex is surprisingly inert (ref. 350).

The gas-phase electron diffraction structure of $Co(CO)_2Cp$ has been studied and it is found that the extended $Co(CO)_2$ plane passes through a ring carbon atom (ref. 351). The crystal structure of the complex $[Co(CO)_2(C_5H_4PPh_3)]Co(CO)_4$ has been determined. A square-planar coordination about the cobalt in the cation is observed (ref. 352). Polymer supported cyclopentadienyldicarbonylcobalt and -rhodium have been reported and their catalytic behaviour has been examined. The cobalt system can act as an immobilized, homogeneous, Fischer-Tropsch catalyst (ref. 352). The rhodium system was effective in the hydrogenation of olefins, aldehydes and ketones, isomerization of olefins, disproportionation of cyclohexene and cyclohexa-1,4-diene, cyclotrimerization of ethylpropiolate and hydroformylation of pent-l-ene and hex-l-ene (ref. 354).

Photolysis of $Co(CO)_2(C_5Me_5)$ affords the ethylidyne cluster $Co_3CMe(CO)_4(C_5Me_5)$, which can also be obtained by reaction of C_5Me_5H with $Co_3CMe(CO)_9$. The structure consists of a triangular pyramid with two $Co(C_5Me_5)$ groups and one $Co(CO)_3$ group in the base and CMe at the apex. The basal edge between the two $Co(C_5Me_5)$ groups has a bridging CO group (ref. 355).

Upon heating $Rh(CO)_2(C_5Me_5)$ for one hour at 80-85°C under a pressure of 10-20mm Hg the dark-blue complex $Rh_2(\mu_2\text{-}CO)_2(C_5Me_5)_2$ (124) is formed which is formulated with a rhodium-rhodium double bond. Treatment of the complex with CO affords about 30% of $Rh(CO)_2(C_5Me_5)$ (ref. 356). Single crystal X-ray studies on the corresponding cobalt compound $Co_2(CO)_2(C_5Me_5)_2$ establish the presence of a multiple cobalt-cobalt bond (ref. 357, 358). Structural studies on the monoanion $[Co_2(\mu_2\text{-}CO)_2(C_5Me_5)]^-$ also show that there is a decrease of 0.034 Å between the Co-Co bond length of 2.372(1) Å in the monoanion (assumed bond order



(124)

1.5) and that of 2.383(2) Å in its oxidized neutral dimer (assumed bond order 2). This contraction of bond length is consistent with the removal of the unpaired electron from an MO of the monoanion which is primarily composed of out-of-plane antibonding $d\pi^*$ dimetal character (ref. 358). The reaction of the neutral $Co_2(\mu_2\text{-}CO)_2(C_5Me_5)_2$ with $Co_2(CO)_8$ affords a new type of tetrahedral metal cluster $Co_4(CO)_4(\mu_2\text{-}CO)(\mu_3\text{-}CO)_2(C_5Me_5)_2$ which can be envisaged as resulting from the insertion of a $Co_2(CO)_4(\mu_2\text{-}CO)$ fragment across the cobalt-cobalt double bond of $Co_2(\mu_2\text{-}CO)_2(C_5Me_5)$. The cluster can also be obtained by oxidation of the monoanion $[Co_2(\mu_2\text{-}CO)_2(C_5Me_5)_2]^-$ with toluene-*p*-sulphonic acid in the presence of $NaCo(CO)_4$ (ref. 359).

Exposure of frozen solutions of $Co(CO)_2Cp$ to ^{60}Co gamma rays produces the anion $[Co(CO)_2Cp]^-$ (ref. 360) which has previously been observed by gas-phase ion cyclotron resonance spectroscopy. The anion $[Co(CO)_2Cp]^-$ is involved in the formation of $[Co_2(\mu_2\text{-}CO)_2Cp_2]^-$ which results from the sodium-amalgam reduction of $Co(CO)_2Cp$. The reductions of various substituted cyclopentadienyl dicarbonyl cobalt complexes, $Co(CO)_2(C_5Me_5)$, $Co(CO)_2(C_5H_4R)$ ($R = SiMe_3$, $SiMePh_2$, CO_2Me, CH_2CO_2Me) have been carried out. These reactions lead to the anions $[Co_2(\mu_2\text{-}CO)_2(C_5H_4R)_2]$ together with ring loss products but only with the complex $Co(CO)_2(C_5H_4CO_2Me)$ does the ring loss product predominate. ESR and IR studies on the radical anions reveal variations in spin density on the cobalt over the series and a reduction mechanism has been proposed (ref. 361).

Treatment of the radical anion $[Co_2(\mu_2\text{-}CO)_2Cp_2]^{\dot{-}}$ with MeI is known to give the dinuclear dialkyl $Co_2Me_2(\mu_2\text{-}CO)_2Cp_2$. Studies on the carbonylation of the complexes $Co_2R_2(\mu_2\text{-}CO)_2Cp_2$ (R = Me, Et) show that these complexes afford ketones via dinuclear diacyl complexes $Co_2(COR)_2(\mu_2\text{-}CO)_2Cp_2$. In this reaction a cobalt(II) acyl complex Co(COR)(CO)Cp is an important species. This cobalt(II) complex givesthe diacyl $Co_2(COR)_2(\mu_2\text{-}CO)_2Cp$ and also acts as an alkyl transfer reagent, equation (79) to afford the ketone, equation (80) (ref. 362).

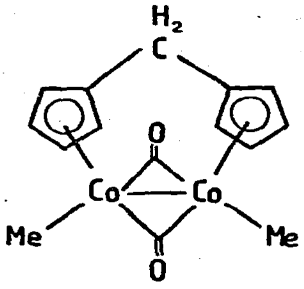
$$2Co(COMe)(CO)Cp \rightarrow Co(CO)_2Cp + CoMe(COMe)(CO)Cp \tag{79}$$

$$CoMe(COMe)(CO)Cp + CO \rightarrow Co(CO)_2Cp + Me_2CO \tag{80}$$

Reactions of the bridged dinuclear dialkylcobalt complex (125) with carbon monoxide and PPh_3, equations (81) and (82) have provided evidence for competing

$$(125) + CO \rightarrow Me_2CO + (OC)_2Co(C_5H_4CH_2C_5H_4)Co(CO)_2 \tag{81}$$

$$(125) + PPh_3 \rightarrow (Ph_3P)Me_2Co(C_5H_4CH_2C_5H_4)Co(CO)_2 \tag{82}$$



(125)

inter- and intramolecular metal to metal methyl transfer (ref. 363).

Complexes of the type CoL_2Cp (L = two-electron donor ligand) are known to undergo oxidative-addition reactions with a variety of molecules and new examples of this reaction type have been reported during 1979. The complex $Co(CO)(PMe_3)Cp$ has been shown to react with alkyl halides to give acyl complexes $Co(COR)(I)(PMe_3)Cp$ (R = Me, Et). The complex $[CoMe(CO)(PMe_3)Cp]I$ is an intermediate in the formation of the acetyl complex and in solutions of polar solvents the two complexes are in equilibrium. The methyl complex $[CoMe(CO)(PMe_3)Cp]PF_6$ is stable but it reacts with PPh_3 to give an acyl complex, equation (83), which is also in equilibrium with the methyl complex, equation (84). Treatment of $Co(CO)(PMe_3)Cp$ with acyl halides affords the acyl complexes

$$[CoMe(CO)(PMe_3)Cp]PF_6 + PPh_3 \rightarrow [CoAc(PMe_3)(PPh_3)Cp]PF_6 \qquad (83)$$

$$[CoAc(PMe_3)(PPh_3)Cp]PF_6 \rightleftharpoons [CoMe(CO)(PMe_3)Cp]PF_6 + PPh_3 \qquad (84)$$

$[Co(COR)(CO)(PMe_3)Cp]^+$ (R = Me, Et, Ph) but they do not appear to form alkyl complexes under mild conditions (ref. 364). The complexes $Co(CO)_2Cp$ and $Co(CO)(PR_3)Cp$ react with allyl halides to form allyl complexes e.g. equations (85) - (87). The complex $CoI(2\text{-}MeC_3H_4)Cp$ reacts with donor ligands such as

$$Co(CO)_2Cp + MeCH{=}CHCH_2Br \rightarrow [Co(CO)(1\text{-}MeC_3H_4)Cp]I \qquad (85)$$

$$Co(CO)_2Cp + CH_2{=}CMeCH_2I \rightarrow CoI(2\text{-}MeC_3H_4)Cp \qquad (86)$$

$$Co(CO)(PMe_3)Cp + C_3H_5Br \rightarrow [Co(PMe_3)(C_3H_5)]Br \qquad (87)$$

L = CO, PMe_3, py and NH_3 to give the cations $[CoL(2\text{-}Me\text{-}C_3H_4)Cp]^+$. Attempts to convert these cationic allyl complexes to cobaltacyclobutane complexes by the addition of H^- or Me^- have not been successful (ref. 365). Treatment of the complex $CoI_2(CO)Cp$, which is formed by the reaction of $Co(CO)_2Cp$ with I_2, with PMe_3 affords cationic complexes, equation (88) (ref. 365, 366). The reaction

$$CoI_2(CO)Cp \quad + \quad PMe_3 \rightarrow [CoI(PMe_3)_2Cp]I \quad + \quad [Co(PMe_3)_3Cp]\ I_2 \tag{88}$$

of MeLi with $[Co(PMe_3)_3Cp]^{2+}$ affords $[CoMe_2(PMe_3)Cp]$. Interestingly the reaction of Pr^iMgBr with $CoI_2(PMe_2Ph)Cp$ followed by addition of aqueous NH_4PF_6 gives the hydride $[CoH(PMe_2Ph)_2Cp]PF_6$ (ref. 365). The carbonylation of $[CoI(PMe_3)_2Cp]I$ in the presence of silver ion affords the cationic complexes $[Co(CO)(PMe_3)_2Cp]X_2$ (X = BF_4, PF_6). The carbonyl group in these dicationic species undergoes nucleophilic attack by alcohols, amines and ammonia to afford complex cations of the type $[Co(CXR)(PMe_3)_2Cp]^+$ (X = O, R = Me, Et; X = NH, R = H, Me, Et, Bz). The carbonyl group of the dication is displaced by donor solvents to give either $[CoL(PMe_3)_2Cp]^{2+}$ (L = MeCN) or $[Co(PMe_3)_3Cp]^{2+}$ (L = DMF, DMSO, $MeNO_2$). Treatment of the alkoxycarbonyl and carbamoyl complexes with fluoroboric acid regenerates the dicationic carbonyl complex (ref. 366).

Treatment of $CoI_2(CO)Cp$ with $Na_2[S_2C_2(CN)_2]$ is known to form the 16 electron monomer $Co\{S_2C_2(CN)_2\}Cp$. This complex has now been shown to form air-stable crystalline adducts with tertiary phosphines and phosphites. The phosphite compounds exhibit long range ^{31}P – ^1H spin-spin coupling interactions with the hydrogen atoms of the cyclopentadienyl ligand. This effect is not observed in the tertiary phosphine complexes and may be due to a shorter Co–P bond length in the tertiary phosphite complexes (ref. 367).

The thiocarbonyl complexes, $M(CS)(PPh_3)Cp$ (M = Rh, Ir) have been prepared from trans-$MCl(CS)(PPh_3)_2$ and NaCp. These complexes undergo oxidative reactions with halogens, e.g. equations (89) - (91) the cationic iridium(III) complexes

$$Rh(CS)(PPh_3)Cp \quad + \quad X_2 \xrightarrow{77K} [RhX(CS)(PPh_3)Cp]X \qquad (X = Cl,\ Br,\ I) \tag{89}$$

$$[RhX(CS)(PPh_3)Cp]X \xrightarrow{RT} RhX_2(PPh_3)Cp \tag{90}$$

$$Ir(CS)(PPh_3)Cp \quad + \quad X_2 \xrightarrow{RT} [IrX(CS)(PPh_3)Cp]X \tag{91}$$

being more stable than the corresponding rhodium(III) complexes. Reactions with dry HCl proceed as indicated in equations (92) and (93) and treatment of the

$$Rh(CS)(PPh_3)Cp \quad + \quad HCl \rightarrow RhCl(CS)(PPh_3) \tag{92}$$

$$Ir(CS)(PPh_3)Cp + HCl \rightarrow [IrH(CS)(PPh_3)Cp]Cl \qquad (93)$$

complexes with MeI afford the thiocarbene complexes $[M\{CMe(SMe)\}(I)(PPh_3)Cp]I$. Reaction of $RhCl(CS)(PPh_3)_2$ with MeI affords $Rh\{CMe(SMe)\}ClI_2(PPh_3)_2$ while $IrCl(CS)(PPh_3)_2$ and MeI give $IrMeClI(CS)(PPh_3)_2$. A similar reaction occurs upon treatment of $Ir(CS)(PPh_3)Cp$ with $ClCH_2CN$ to give $[Ir(CH_2CN)(CS)(PPh_3)Cp]Cl$. The reaction of mercury(II) chloride with $M(CS)(PPh_3)Cp$ affords the metal donor-metal acceptor adducts $Cp(PPh_3)(CS)M \rightarrow HgCl_2$ (ref. 368).

The cobalt atom in the complex $Co(PMe_3)_2Cp$ is quite basic and this complex reacts with equimolar amounts of $ZnCl_2$ and PMe_3 to give the complex $Cp(PMe_3)_2CoZnCl_2(PMe_3)$. Reaction of $Co(PMe_3)_2$ with $ZnCl_2$ and PPh_3 gives a mixture of $ZnCl_2(PPh_3)_2$ and $Cp(PMe_3)_2CoZnCl_2$. The cobalt-zinc bond in $Cp(PMe_3)_2CoZnCl_2(PMe_3)$ is cleaved by reaction with PMe_3 to give $Co(PMe_3)_2Cp$ and $ZnCl_2(PMe_3)_2$. These reactions give an indication of the basicity of the cobalt atom in $Co(PMe_3)_2Cp$ and other reactions of this complex are given in equations (94) - (97). Mercury(II) chloride reacts with $Co(PMe_3)_2Cp$ to form the 1:1 and 1:2 adducts, $Cp(PMe_3)_2CoHgCl_2$ and $Cp(PMe_3)_2Co(HgCl_2)_2$ respectively (ref. 369).

$$Co(PMe_3)_2Cp + Cu_2Cl_2(PMe_3)_4 \rightarrow Cp(PMe_3)_2CoCuCl(PMe_3)_2 \qquad (94)$$

$$Co(PMe_3)_2Cp + R_3SnCl \rightarrow Cp(PMe_3)_2CoSnClR_3 \quad (R = Cl, Me, Ph) \qquad (95)$$

$$Cp(PMe_3)_2CoSnClR_3 + SnCl_4 \rightarrow Cp(PMe_3)_2CoSnR_3{}^+ \qquad (96)$$

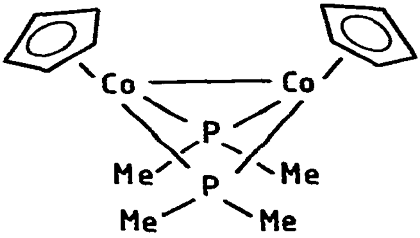
$$[Cp(PMe_3)_2CoSnMe_3]PF_6 + SnCl_4 \rightarrow [Cp(PMe_3)_2CoSnCl_3]PF_6 \qquad (97)$$

The rhodium atom in $Rh(PMe_3)_2Cp$, which is prepared as indicated in equations (98) and (99), is also a strong base. It reacts with a variety of electrophiles Y^+ to give the cations $[RhY(PMe_3)_2Cp]^+$ (Y = H, Me, Et, Ac, COPh, COC_6H_4OMe-*p*, $GeMe_3$, $SnMe_3$, Br, Cl, I). Treatment of $Rh(PMe_3)_2Cp$ with $CF_3SO_3SiMe_3$ affords $[RhH(PMe_3)_2(C_5H_4SiMe_3)]^+$ together with $[RhH(PMe_3)_2Cp]^+$. Reduction of the former complex with NaH gives $Rh(PMe_3)_2(C_5H_4SiMe_3)$ (ref. 370). The crystal structure of $[RhH(PPh_3)_2C_5Me_5]PF_6$ shows that the observed distortions in the C_5Me_5 ring may be attributed to the large *trans*-influence of the hydrido ligand (ref. 371).

$$Rh_2Cl_2(cod)_2 + PMe_3 \rightarrow Rh(PMe_3)_4Cl \qquad (98)$$

$$Rh(PMe_3)_4Cl + TlCp \rightarrow Rh(PMe_3)_2Cp \qquad (99)$$

Attempts to obtain $Co(PMe_2H)_2Cp$ by reaction of $CoCp_2$ with PMe_2H lead to the dinuclear complex (126) and an attempt to obtain $Co(PMe_3)(PMe_2H)Cp$ by reaction



(126)

of PMe_2H with $Cp(PMe_3)Co(\mu_2\text{-}CO)_2Mn(CO)(C_5H_4Me)$ also leads to (126) as does the reaction of PMe_2H with $Co(PMe_3)_2Cp$. The Co-Co bond of (126) should exhibit nucleophilic character since the <u>sigma</u> electron pair of the Co-Co bond occupies the HOMO of this molecule. In agreement with this (126) readily reacts with trifluoroacetic acid to give the cationic hydride $[CpCo(\mu\text{-}H)(\mu\text{-}PMe_2)_2CoCp]^+$. This cation (a 34-valence electron system) has a triple-decker-like structure and like the 34-electron complex $[Ni_2Cp_3]^+$ reacts with Lewis bases L to give the complexes $[Cp(L)Co(\mu\text{-}PMe_2)CoHCp]^+$ where L is either PMe_3 or $P(OMe)_3$. No addition takes place on reaction with anionic bases such as H^- or Me^-. These reactions give the dinuclear complex (126) (ref. 372).

The reaction of $Co(PMe_3)_2Cp$ with CSSe at -20°C gives a mixture of $Co(CS)(PMe_3)Cp$ and $Co(CSSe)(PMe_3)Cp$ which on treatment with PPh_3 affords the thiocarbonyl complex quantitatively, equation (100). A rhodium complex can be similarly

$$Co(CSSe)(PMe_3)Cp \ + \ PPh_3 \rightarrow Ph_3PSe \ + \ CoCS(PMe_3)Cp \qquad (100)$$

prepared, equations (101) and (102) (ref. 373). Treatment of $Co(CS_2)(PMe_3)Cp$

$$Rh(C_2H_4)(PMe_3)Cp \ + \ CSSe \rightarrow Rh(CSSe)(PMe_3)Cp \qquad (101)$$

$$Rh(CSSe)(PMe_3)Cp \ + \ PPh_3 \rightarrow Ph_3PSe \ + \ RhCS(PMe_3)Cp \qquad (102)$$

with $Cp(PMe_3)Co(\mu_2\text{-}CO)_2Mn(CO)(C_5H_4Me)$ gives the trinuclear complex $Co_3(\mu_3\text{-}S)(\mu_3\text{-}CS)Cp_3$ The sulphur atom of the CS bridging group is the site of maximum nucleophilicity of this complex, reacting with MeI, EtI and $Cr(THF)CO)_5$, e.g. equation (103) (ref. 374).

$$Co_3(\mu_3\text{-}S)(\mu_3\text{-}CS)Cp_3 + RI \rightarrow [Co_3(\mu_3\text{-}SR)(\mu_3\text{-}CS)Cp_3]I \quad (R = Me,\ Et) \qquad (103)$$

The reaction of ethylene with $CoMe_2(PPh_3)Cp$ gives methane and propene as products, equation (104), and a labelling study demonstrates that insertion of

$$CoMe_2(PPh_3)Cp \; + \; C_2H_4 \rightarrow Co(C_2H_4)(PPh_3)Cp \; + \; CH_4 + C_3H_6 \qquad (104)$$

ethylene into a cobalt-methyl bond rather than alpha-elimination from a cobalt-methyl bond is the critical step in the reaction mechanism (ref. 375). The reaction of $Me_2\overline{SiCH{=}CHBPhCH{=}CH}$ with $Co(CO)_2Cp$ give the diene complex $Co(Me_2\overline{SiCH{=}CHBPhCH{=}CH})Cp$ which upon acetylation with $MeCOCl/AlCl_3$ and subsequent hydrolysis affords the ring opened complex $Co(CH_2{=}CHSiMe_2CH{=}CHAc)Cp$ (ref. 376). The electrochemical oxidation of $Co(\underline{exo}\text{-}C_5H_5CO_2Me)Cp$ gives the substituted cobalticinium salt (ref. 377).

Various studies on the formation and chemistry of cobalt and rhodium metallacycles containing a cyclopentadienyl ligand have appeared. Previous experiments have indicated that, in the reaction of $RhI_2(PPh_3)(C_5Me_5)$ with either $BrMg(CH_2)_4MgBr$ or $Mg(CH_2)_4$ which gives a mixture $Rh(C_2H_4)(PPh_3)(C_5Me_5)$ and $\overline{Rh(CH_2CH_2CH_2CH_2})(PPh_3)(C_5Me_5)$, the latter rhodacycle could be a precursor of the ethylene complex as a result of a carbon-carbon bond cleavage reaction. However, further studies have now shown that the formation of $Rh(C_2H_4)(PPh_3)Cp$ is a consequence of a facile diethyl ether C-O cleavage by organomagnesium compounds (ref. 378).

Several cobaltacyclopentadiene complexes $\overline{Co(CR{=}CRCR{=}CR})(PPh_3)Cp$ have been shown to react with olefins (ethylene, propene, styrene, methyl acrylate, dimethyl maleate) to give the corresponding cyclohexadienes and/or intermediate cyclohexadiene metal complexes depending upon the reactants and reaction conditions, e.g. equation (105). The cyclohexadiene complexes liberate the free

$$\overline{Co(C_4Ph_4})(PPh_3)Cp + C_3H_6 \rightarrow PPh_3 + Co(\overline{CPh{=}CPhCH_2CHMeCPh{=}CPh})Cp \qquad (105)$$

cyclohexadienes upon treatment with cerium(IV). The first step of the reaction of the olefin with the cobaltacyclopentadiene complex is displacement of PPh_3 by olefin. The cycloaddition reaction then takes place between two coordinated ligands (ref. 370). The complexes Co(acetylene)$(PPh_3)Cp$, acetylene = DMAD or $PhC{\equiv}CCO_2Me$, react with 1,2-disubstituted olefins to give metallacyclopentene complexes $\overline{Co(CR^1{=}CR^2CHR^3CHR^4})(PPh_3)Cp$, intermediate olefin-acetylene complexes being involved in these reaction. The reactions of Co(acetylene)$(PPh_3)Cp$ with monosubstituted olefins gives cobalt diene complexes via cobaltcyclopentene intermediates. Reactions of acetylenes with cobaltacyclopentenes yield cobalt-cyclohexadiene complexes (ref. 380). Diene complexes $Co(CHR^1{=}CR^2CR^2{=}CR^1R)(PPh_3)Cp$ or highly substituted butadiene derivatives $CHR^1{=}CR^2CR^2{=}CR^1R$ are formed upon treatment of the cobaltacyclopentadiene complexes $\overline{Co(CR^1{=}CR^2CR^2{=}CR^1})(PPh_3)Cp$

(R^1, R^2 = Me, Ph, CO_2Me) with the compounds RH (RH = Et_3SiH, thiocresol, dimethyl- and ethylene-thiourea, pyrrole, thiophene) (ref. 381). Cobaltacyclopentadiene complexes have also been shown to react with isocyanides to give iminocyclopentadiene complexes which can be protonated or alkylated to give some substituted cobalticinium salts, equation (106) and (107) (ref. 382).

$$\overline{\mathrm{Co(CPh{=}CRCR{=}CPh})}\mathrm{(PPh_3)Cp} + \mathrm{R^1NC} \rightarrow \mathrm{Co(C_4Ph_2R_2CNR^1)Cp} \tag{106}$$

$$\mathrm{Co(C_4Ph_2R_2CNR^1)Cp} + \mathrm{MeI} \rightarrow \mathrm{[Co(C_5Ph_2R_2NR^1Me)Cp]I} \tag{107}$$

(R = Ph, Me, CO_2Me; R^1 = Bu^t, p-tol, 2,6-xylyl)

The reaction of $Ir(CO)(PPh_3)Cp$ with $C_6F_5C{\equiv}CC_6F_5$ has been investigated in detail. The metallacyclic complex $\overline{\mathrm{Ir(CR{=}CRCR{=}C}}\mathrm{R)(PPh_3)Cp}$ (R = C_6F_5) is formed in low yield and a variety of highly fluorinated organic products are also obtained including hexakis(pentafluorophenyl)benzene, trans-1,2-bis(pentafluorophenyl)ethylene and 1,2,3,4-tetrakis(pentafluorophenyl)naphthalene (ref. 383, 384).

A series of papers on pentamethylcyclopentadienyl complexes has appeared during the year including a review on pentamethylcyclopentadienyl catalysts for olefin and arene hydrogenation (ref. 385). Metathesis reactions of $Rh_2Cl_4(C_5Me_5)_4$, {the crystal structures of $Rh_2I_4(C_5Me_5)_2.2PhMe$ (ref. 386) and $Ir_2X_4(C_5Me_5)_2$ (X = Br, I) (ref. 387) have been determined}, with NaZ give $Rh_2Z_4(C_5Me_5)_2$ (Z = N_3, NCO, SCN). Some reactions of the azido complex are given in equations (108) – (115).

$$\mathrm{Rh_2(N_3)_4(C_5Me_5)_2} + \mathrm{L} \rightarrow \mathrm{Rh(N_3)_2L(C_5Me_5)} \tag{108}$$

L = R_3P, $(RO)_3P$, R_3As, RNC, py, $RNHNH_2$

$$\mathrm{Rh_2(N_3)_4(C_5Me_5)_2} + \mathrm{phen} \rightarrow \mathrm{[Rh(N_3)(phen)(C_5Me_5)]N_3} \tag{109}$$

$$\mathrm{Rh_2(N_3)_4(C_5Me_5)} + \mathrm{CO} \rightarrow \mathrm{Rh_2(NCO)_3(N_3)(C_5Me_5)_2} \tag{110}$$

$$\mathrm{Rh_2(NCO)_3(N_3)(C_5Me_5)_2} + \mathrm{CO} \rightarrow \mathrm{Rh_2(NCO)_4(C_5Me_5)_2} \tag{111}$$

$$\mathrm{Rh(N_3)_2(PPh_3)(C_5Me_5)} + \mathrm{CS_2} \rightarrow \mathrm{[Rh(N_3CS_2)_2(C_5Me_5)]_n} \tag{112}$$

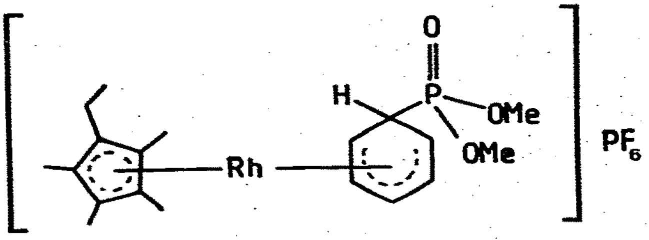
$$\mathrm{[Rh(N_3CS_2)_2(C_5Me_5)]_n} \rightarrow \mathrm{Rh_2(SCN)_4(C_5Me_5)_2} \tag{113}$$

$$\mathrm{Rh_2(N_3)_4(C_5Me_5)_2} + \mathrm{C_4F_6} \rightarrow \mathrm{Rh_2\{N_3C_2(CF_3)_2\}_2(N_3)_2(C_5Me_5)_2} \tag{114}$$

$$Rh_2(N_3)_4(C_5Me_5)_2 \ + \ CF_3CN \rightarrow Rh_2(N_4CCF_3)_3(N_3)(C_5Me_5)_2 \qquad (115)$$

From these studies it is apparent that terminal azide ligands are very much more reactive than bridging ones. Reaction of $Rh_2Cl_4(C_5Me_5)_2$ with $NaNO_2$ or KNO_2 gives $M[Rh(NO_2)_3(C_5Me_5)]$ (M = Na, K) which on treatment with PPh_3 gives $Rh(NO_2)_2(PPh_3)(C_5Me_5)$. Reaction of $Rh_2(N_3)_4(C_5Me_5)_2$ with N_2O_4 gives $Rh(NO_3)_2(C_5Me_5)$ (ref. 388). The reaction of $Rh_2Cl_4(C_5Me_5)_2$ with N_2H_4 eventually leads to $[Rh(N_2H_4)_3(C_5Me_5)]Cl_2$ and analogous ammine complexes $[Rh(NH_3)_3(C_5Me_5)]^{2+}$ can be obtained. The adducts $RhX_2(NH_2NR^1R^2)(C_5Me_5)$ are formed by reaction of $Rh_2X_4(C_5Me_5)_2$ with $NH_2NR^1R^2$ ($R^1 = R^2$ = Me, X = Cl, Br, I; R^1 = H, R^2 = Ph, C_6F_5, *p*-tol, X = Cl; R^1 = Me, R^2 = Ph, X = Cl). The bis complexes $[RhCl(NH_2NHR)_2(C_5Me_5)]PF_6$ (R = Ph, *p*-tol) can also be obtained. All these complexes are labile and lose the hydrazine readily (ref. 389). Treatment of $M_2Cl_4(C_5Me_5)_2$ with $Na[R^1COCHCOR^2]$ gives the β-diketonato complexes $MX(R^1COCHCOR^2)(C_5Me_5)$ (M = Rh, X = Cl, $R^1 = R^2$ = Me, $R^1 = R^2 = CF_3$, R^1 = Me, $R^2 = Pr^n$, R^1 = Me, R^2 = OEt, R^1 = Me, $R^2 = CF_3$; M = Rh, $R^1 = R^2$ = Me, X = Br, I, N_3, OAc; M = Ir, X = Cl, $R^1 = R^2$ = Me, $R^1 = R^2 = CF_3$). Iridium forms a stable complex $Ir(acac)_2(C_5Me_5)$ which contains both oxygen and carbon bonded acac. No exchange between these bonding modes is detectable on the NMR time scale. The complex $[Rh_2(acac)_2(C_5Me_5)_2][BF_4]_2$ contains two bridging acac ligands oxygen bound to one rhodium and carbon bonded to the other. The C_5Me_5 ring in the complex is distorted towards an ene-enyl structure. Some triazenido complexes $RhCl(PhNCMeNPh)(C_5Me_5)$ have also been prepared as have the complexes $Rh_2(N_3)_4(RNHN{=}NR)(C_5Me_5)$ and the cationic allyl complexes $[RhL(1\text{-}MeC_3H_4)(C_5Me_5)]PF_6$, L = MeCN, $P(OMe)_3$, PPh_3, NH_2Et (ref. 390).

Some blue five coordinate rhodium(III) catechol complexes $[Rh(4\text{-}XC_6H_3O_2)].H_2O$ (X = H, Cl, Me, Bu^t)are formed upon reaction of $Rh_2Cl_4(C_5Me_5)_2$ with 4-substituted catechols in the presence of aqueous base. These complexes form adducts with phosphines and the complexes $Rh\{$*o*-$C_6H_4(NH)Y\}(C_5Me_5)$ (Y = O, NH) have also been reported (ref. 391). Resorcinol and hydroquinone, $C_6H_4(OH)_2$, displace acetonitrile from $[Rh(MeCN)_3(C_5Me_5)][PF_6]_2$ to give three different types of complexes $[Rh_2(HOC_6H_4O...H...OC_6H_4OH)(C_5Me_5)_2][PF_6]_3$, $[Rh(...OC_6H_4OH)(C_5Me_5)]_n[PF_6]_n$, and $[Rh(...H...OC_6H_4O...H...OC_6H_4O...)(C_5Me_5)]_n$ depending on the amount of base present and on the ratio of diol to acetonitrile complex. In the first two complexes spectroscopic data indicate that the $C_6H_4O_2$ ligands are *pi*-bonded to the rhodium and that in the third complex one $C_6H_4O_2$ ligand is *pi*-bonded and the other hydrogen bonded to it. The complexes are rather insoluble in organic solvents but dissolve in water with breakdown of the hydrogen-bonding interaction between the complexed diols (ref. 392). The cationic benzene complex $[Rh(C_6H_6)(C_5Me_4Et)][PF_6]_2$ undergoes attack by trimethylphosphite to give (127) (ref. 393).



(127)

The green tetranuclear dication $[Rh_4H_4(C_5Me_5)_4]^{2+}$ results from the reaction of hydrogen with $[Rh_2(\mu\text{-}OH)_3(C_5Me_5)_2]Cl.4H_2O$ in water (ref. 394).

Treatment of $[CoI_2(C_5Me_5)]_n$ with a donor ligand L affords the complexes $CoI_2L(C_5Me_5)$, where L = PMe_2Ph, $P(OPh)_3$ or Bu^tNC, and $CoIL_2(C_5Me_5)$, where L = Bu^tNC. The complexes $[Co(solvent)_n(C_5Me_5)]X_2$ (solvent = MeCN, $\underline{n}$ = 3, X = PF_6; solvent = Me_2CO, $\underline{n}$ believed to be 3) have also been prepared and some reactions of the complexes are given in equations (116) - (121). The benzene complex

$$[Co(MeCN)_3(C_5Me_5)]^{2+} + L \rightarrow [CoL_3(C_5Me_5)]^{2+} \tag{116}$$

$$L = P(OMe)_3,\quad P(OEt)_3,\quad py,\quad Bu^tNC$$

$$[Co(MeCN)_3(C_5Me_5)]^{2+} + L \rightarrow [Co(MeCN)_2L(C_5Me_5)]^{2+} \tag{117}$$

$$L = PMe_2Ph,\quad P(OPh)_3,\quad PPh_3$$

$$[Co(MeCN)_3(C_5Me_5)]^{2+} + phen + MeCN \rightarrow [Co(phen)(MeCN)(C_5Me_5)]^{2+} \tag{118}$$

$$[Co(MeCN)_3(C_5Me_5)]^{2+} + xs\ phen \rightarrow [Co(phen)_3]^{2+} \tag{119}$$

$$CoI_2(CO)(C_5Me_5) + AgPF_6 + Me_2SO \rightarrow [Co(Me_2SO)_n][PF_6]_2 \tag{120}$$

$$[Co(Me_2CO)_3(C_5Me_5)]^{2+} + indole \rightarrow [Co(indole)(C_5Me_5)]^{2+} \tag{121}$$

$[Co(C_6H_6)(C_5Me_5)][BF_4]_2$ can be obtained by the reaction of $Co(1,3\text{-}chd)(C_5Me_5)$ with $Ph_3C^+BF_4^-$. The cyclopentadienyl complex $[Co(C_6H_6)Cp][BF_4]_2$ undergoes arene exchange with mesitylene and hexamethylbenzene and forms charge-transfer complexes with methyl substituted benzene in solution. The preparation and reactions of a duroquinone complex are given in equations (122) - (124) (ref.

$$Co(CO)_2(C_5Me_4R) \; + \; C_6Me_4O_2 \; \rightarrow Co(C_6Me_4O_2)(C_5Me_4R) \qquad (122)$$

$$(R = Me, Et)$$

$$Co(C_6Me_4O_2)(C_5Me_5) \; + \; HBF_4 \; \rightarrow [Co\{C_6Me_4(OH)_2\}(C_5Me_5)]^{2+} \qquad (123)$$

$$Co(C_6Me_4O_2)(C_5Me_5) \; + \; MeI/AgPF_6 \; \rightarrow [Co\{C_6Me_4O(OMe)\}(C_5Me_5)]PF_6 \qquad (124)$$

395, 396).

Review articles on the synthesis, structures and chemical properties of Group VIII arene complexes (ref. 397), catalytic hydrogenation of aromatic hydrocarbons (ref. 398), arene transition metal chemistry (ref. 399) and iridium compounds in catalysis (ref. 400) contain information on the cobalt triad.

The X-ray photoelectron spectra of the bis(fulvalene)dicobalt complexes $Co_2(C_{10}H_8)_2$ and $[Co_2(C_{10}H_8)_2]PF_6$ have been reported (ref. 401).

Metalla-borane and -carbaborane compounds

The reactions of cobaltocene with dihalomethyl- and dihalophenylboranes to give cobalt complexes of 1-methylborinate and 1-phenylborinate ions have been extended to other alkyl- and aryldihaloboranes e.g. equations (125) - (129). The complex $Co(C_5H_6BMes)Cp$ is stable towards heat and oxidation and no

$$CoCp_2 \; + \; PhCH_2BBr_2 \; \rightarrow Co(C_5H_5BCH_2Ph)Cp \qquad (125)$$

$$Co(C_5H_5BCH_2Ph)Cp \; + \xrightarrow[CoCp_2]{PhCH_2BBr_2} Co(C_5H_5BCH_2Ph)_2 \qquad (126)$$

$$CoCp_2 \; + \; MesBCl_2 \; \rightarrow [Co(C_5H_5BMes)Cp]Cl \qquad (127)$$

$$[Co(C_5H_5BMes)Cp]Cl \xrightarrow[FeCl_3.6H_2O]{CoCp_2} Co(C_5H_5BMes)Cp \qquad (128)$$

$$[Co(C_5H_5BMes)Cp]Cl \; + \; H^- \; \rightarrow Co(C_5H_6BMes)Cp \qquad (Mes = mesityl) \qquad (129)$$

decomposition was observed upon exposing it to air for two days. The reaction of $CoCp_2$ with $C_6F_5BCl_2$ gave only decomposition products and the desired boranaphthalene anion complexes were not formed upon treatment of bis(indenyl)-cobalt with $PhBCl_2$ or $MeBCl_2$. These reactions gave the bis(indenyl)cobalt-icenium cation and decomposition products (ref. 345).

The complex $Co(Me_2\overline{SiCH{=}CHBPhCH{=}CH})Cp$ undergoes acetylation with $MeCOCl/AlCl_3$ to give the ring-opened complex $Co(CH_2{=}CHSiMe_2CH{=}CHCOMe)Cp$ (ref. 376).

The chemistry of metal-boron cage and cluster complexes continues to attract much interest and a review of metal sandwich complexes of cyclic planar and pyramidal ligands containing boron has been published (ref. 402).

An extensive series of air-stable crystalline cobaltaboranes are known to be formed from the reaction of $CoCl_2$, $B_5H_8^-$ and Cp^- in cold THF. X-ray structure determinations on several of these complexes have been previously published and the crystal structure of the violet six-vertex complex $1,2\text{-}Cp_2Co_2B_4H_6$ has now been reported. The structure consists of an octahedral Co_2B_4 cage with the cobalt atoms occupying adjacent vertices and each cobalt atom coordinated to a cyclopentadienyl ring. Two crystallographic equivalent hydrogen atoms occupy face-bridging positions over the centres of the two Co_2B triangular faces (ref. 403). The crystal structure of the metallaboron cage complex $Cp_4Co_4B_4H_4$ has also been reported. The Co_4B_4 cluster has only 16 skeletal electrons instead of the expected 18 which would normally be expected for an eight-vertex closo polyhedron (ref. 404).

The direct reaction of pentaborane(9) with $Co(CO)_2Cp$ affords $1\text{-}CpCoB_5H_9$ and $2\text{-}CpCoB_9H_{13}$. The sandwich complex $1\text{-}CpCoB_5H_9$ is isolectronic with ferrocene and exhibits a dynamic behaviour which suggests that it is a structural analogue of hexaborane(10) (ref. 405).

Deprotonation of the <u>nido</u> complex $1,2,3\text{-}CpCoC_2B_3H_7$ and exposure of the resulting anion to air results in an oxidative fusion reaction to generate a series of metallacarboranes, equation (130). However, when the C,C^1-dimethyl

$$\begin{tikzcd}
CpCoC_2B_3H_7 \arrow[r, "OEt^-"] & CpCoC_2B_3H_6^- \arrow[d, "OEt^-"] \\
Cp_2Co_2C_4B_6H_{10} \quad + & CpCoC_4B_7H_{11} \quad + \quad 1,7,2,3\text{-}Cp_2Co_2C_2B_3H_5
\end{tikzcd} \qquad (130)$$

(3 - isomers)

complex $1,2,3\text{-}CpCoMe_2C_2B_3H_5$ is treated in a similar fashion the only tetracarbon metallacarborane formed is a single isomer of $Cp_2Co_2Me_4C_4B_6H_6$. X-ray studies show that the structure of this isomer consists of two pentagonal-pyramidal $CpCoMe_2C_2B_3H_3$ units which are partially fused together along their C_2B_3 faces. The structure resembles a severely distorted icosahedron with a large opening on one side (ref. 406).

The reaction of $Me_4C_4B_8H_8$ with $Co(CO)_2Cp$, equation (131), produces some new <u>nido</u>-metallacarboranes containing four skeletal carbon atoms. The same CoC_4B_7

$$\begin{tikzcd} \mathrm{Co(CO)_2Cp} + \mathrm{Me_4C_4B_8H_8} \arrow[d, "UV"] \\ \mathrm{CpCoMe_4C_4B_6H_6} + \mathrm{CpCoMe_4C_4B_7H_7} \end{tikzcd} \qquad (131)$$

isomer I (6%)
isomer II (6%)

isomer I (10%)

isomer is obtained from the closo, nido-$(Me_2C_2B_4H_4)Co(Me_2C_2B_3H_5)^-$ ion by oxidative fusion of the ligands followed by reaction with $CoCl_2$, NaCp and dioxygen and a second CoC_4B_7 isomer can be obtained from the dianion $Me_4C_4B_8H_8^{2-}$, equation (132). A third isomer can be obtained on rearrangement of $CpCoMe_4C_4B_7H_7$

$$\begin{tikzcd} \mathrm{Me_4C_4B_8H_8^{2-}} \arrow[d, "\text{(i) } CoCl_2 + NaCp", "\text{(ii) } HCl"'] \\ \mathrm{CpCoMe_4C_4B_8H_8} + \mathrm{CpCoMe_4C_4B_7H_7} + \mathrm{CpCo(C_5H_4)^+\ Me_4C_4B_8H_8^-} \end{tikzcd} \qquad (132)$$

Isomer II

(isomer I) at 140°C (ref. 407). The structure of the 12-vertex arachno carborane $CpCo(C_5H_4)^+\ Me_4C_4B_8H_8^-$, equation (132), an analogue of $B_{12}H_{12}^{6-}$ and $C_2B_{10}H_{12}^{4-}$, has been determined (ref. 408). The thermal reaction of $Co(CO)_2Cp$ with a mixture of $(2,4-C_2B_5H_6)_2$ isomers affords a number of multimetal complexes including six complexes of formula $Cp_2Co_2B_{10}H_{12}$. They consist of a 1,8,5,6-$Cp_2Co_2C_2B_5H_6$-fragment bound to an unmetalated $C_2B_5H_6$-cage, the compounds differing in the points of attachment of the two cages. Several isomers of the complexes $Me_2C_2B_4H_5$-$Me_2C_2B_3H_4CoCp$ and the coupled metallacarborane 4,5'-$(Me_2C_2B_4H_3CoCp)_2$ have also been described (ref. 409).

The closo 11-atom molecule $CpCoB_9H_9CNMe_3$ is formed upon reaction of $B_9H_{11}CNMe_3$ with NaH followed by treatment with NaCp and $CoCl_2$. The complex is fluxional at +70°C and thermal degradation gives $B_9H_9CNMe_3$ (ref. 410).

The reaction of the anion $Me_4C_2B_2SMn(CO)_3^-$ with $CoCl_2$ affords the 43 valence electron, paramagnetic, triple decker complex $(CO)_3MnMe_4C_2B_2SCoMe_4C_2B_2SMn(CO)_3$. The tetra-decker sandwich complex $Me_4C_2B_2SCoMe_4C_2B_2SFeMe_4C_2B_2SCoMe_4C_2B_2S$ is formed by the action of NaCp on $Me_4C_2B_2SCoMe_4C_2B_2SCoMe_4C_2B_2S$ followed by addition of $FeCl_2$ (ref. 411).

When *trans*-$IrCl(CO)(PPh_3)_2$ is treated with KB_5H_8 the iridium atom is incorporated into the pentaborane cluster to form a metalla-*nido*-hexaborane structure, $(Ph_3P)_2(CO)IrB_5H_8$. The coordination number of the iridium is seven and the geometry is a distorted monocapped trigonal prism (ref. 412). The reactions of $Ir(diphos)_2^+$ and $Ir(CO)(diphos)_2^+$ with $B_{10}H_{14}$, $B_{10}H_{13}Cl$-6 and $B_{10}H_{13}^-$ afford a number of ionic complexes, equation (133) and (134) (ref. 413). Treatment of trans-$IrY(CO)(PPh_3)_2$, Y is 7-Ph-1,7-$B_{10}C_2H_{10}$, with the nitriles RCN (R = Me, Ph) afford the neutral complexes $IrY(CO)RCN(PPh_3)$. Some reactions of the complexes

$$[Ir(diphos)_2]Cl \;+\; B_{10}H_{13}X \rightarrow [IrHCl(diphos)_2]B_{10}H_{12}X \qquad (X = H,\ 6\text{-}Cl) \tag{133}$$

$$[Ir(CO)(diphos)_2]Cl \;+\; B_{10}H_{13}^- \xrightarrow{MeOH} [Ir(CO)(diphos)_2]B_{10}H_{13} \;+\; [IrH_2(diphos)_2]B_9H_{14} \tag{134}$$

are given in equations (135) and (136) (ref. 414).

$$IrY(CO)(MeCN)(PPh_3) \;+\; CO \rightarrow IrY(CO)_3(PPh_3) \tag{135}$$

$$IrY(CO)(MeCN)(PPh_3) \;+\; H_2 \rightarrow IrYH_2(CO)(MeCN)(PPh_3) \tag{136}$$

A red air-stable complex 3-(PPh_3)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$ is formed upon reaction of nitric acid in dichloromethane or NO_2-N_2O_4 in benzene with 3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$. The nitrato group is bound to the rhodium in a symmetrical bidentate fashion. Some reactions of the complex are given in equations (137) - (140) (ref. 415).

$$XRh(NO_3)(PPh_3) \xrightarrow[HCl]{CO} XRhCl(CO)(PPh_3) \tag{137}$$

$$XRhCl(CO)(PPh_3) \;+\; PPh_3 \rightarrow XRhCl(PPh_3)_2 \tag{138}$$

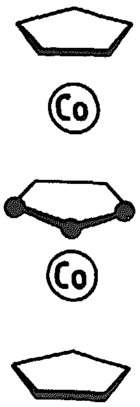
$$XRh(NO_3)(PPh_3) \;+\; PPh_3 \rightarrow XRh(NO_3)(PPh_3)_2 \tag{139}$$

$$XRh(NO_3)(PPh_3)_2 \;+\; H_2 \rightarrow XRhH(PPh_3)_2 \qquad (X = C_2B_9H_{11}) \tag{140}$$

The reaction of 3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ with sulphuric gives $(Ph_3P)_2(HSO_4)RhC_2B_9H_{11}$. This complex reacts readily with H_2 to regenerate the starting material and it also reacts rapidly with ethanol or propanol to produce 3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ and acetaldehyde or propionaldehyde respectively (ref. 416). The structures of the complexes 3,3-$(PPh_3)_2$-4-C_5H_5N-3,1,2-

$RhC_2B_9H_{10}$ and its carbonyl derivative $3\text{-}PPh_3\text{-}3\text{-}CO\text{-}4\text{-}C_5H_5N\text{-}3,1,2\text{-}RhC_2B_9H_{10}$, which are catalysts for the hydroformylation reaction, have been determined (ref. 417).

The electrochemical reduction of $Rh(C_2B_9H_{11})_2^-$ has been studied (ref. 343) and it has also been found that the reduction mechanisms of $CoCp_2^+$, $CpCoC_2B_9H_{11}$ and $CpCoC_2B_9H_8Br_3$ in the presence of added acids are similar, protonation occurring at the cyclopentadienyl ligand rather than at the dicarbollide to give $C_5H_6CoC_2B_9H_{11}^-$ and $C_5H_6CoC_2B_9H_8Br_3^-$ (ref. 344). The electrochemistry of $1,7,2,3\text{-}Cp_2Co_2C_2B_3H_5$, (128), $1,7,2,4\text{-}Cp_2Co_2C_2B_3H_5$, (129), $1,2,3\text{-}CpCoC_2B_4H_6$, (130), and $1,2,4\text{-}CpCoC_2B_4H_6$, (131) have been examined (ref. 418).



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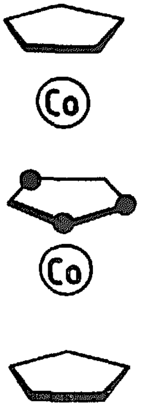

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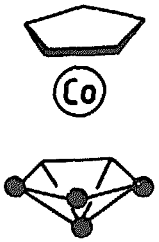

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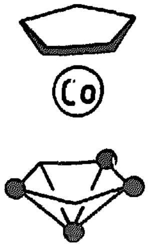

(131)

● = BH

Hydrogen-deuterium exchange of the dicarbollyl hydrogens in cyclopentadienyl-3-1,2-dicarbollylcobalt has been found to be 100 times faster than that of the cyclopentadienyl hydrogens (ref. 419) and ^{59}Co NQR spectra of derivatives of this system have been reported (ref. 420). The reaction of cyclopentadienyl-3-1,2-dicarbollylcobalt with $Tl(OCOCF_3)_3$ gives 8-(trifluoroacetyoxy)-cyclopentadienyl-3-1,2-dicarbollylcobalt and 8-(hydroxy)-cyclopentadienyl-3-1,2-dicarbolly cobalt (ref. 421).

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