COBALT, RHODIUM AND IRIDIUM

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ABBREVIATIONS

acac	acetylacetonato
ACEN	bis(acetylacetone)ethylenediaminato
azbH	azobenzene
bipy	bipyridine
CHT	cycloheptatriene
Cp	cyclopentadienyl
Cy	cyclohexyl
DBM	1,3-diphenylpropane-1,3-dionato
diphos	$Ph_2PCH_2CH_2PPh_2$
DME	dimethoxyethane
DMF	dimethylformamide
DMG	dimethylglyoxime
DMPE	dimethylphenanthroline
DMSO	dimethylsulfoxide
edas	1,2-bis(dimethylarsino)ethylene
ffars	bis(dimethylarsine)-*n*-fluorocyclobutene
ffos	bis(dimethylphosphine)-*n*-fluorocyclobutene
NBD	norbornadiene
o-phen	*o*-phenanthroline
Py	pyridine
Sal=NR	salicylaldimine (R = alkyl, aryl)
SP	styryldiphenylphosphine
TCNE	tetracyanoethylene
TDPME	tris(diphenylphosphinomethyl)ethane
THF	tetrahydrofuran
TTAS	bis(*o*-dimethylarsinophenyl)methylarsine

A new series of vitamin B_{12} coenzyme model compounds have been prepared starting with the high-spin Co^{II} chelate of the pentadentate Schiff-base ligand derived from salicylaldehyde and bis(3,3′-aminopropyl)amine (SALDPT). Reduction of this complex with $NaBH_4$ in the presence of an alkyl halide affords σ-bonded alkyl derivatives RCo(SALDPT)[1]. Cobalt(II) complexes containing the macrocyclic Schiff-bases SALOPH, NAPSALEN and NAPSALOPH have been prepared, and are reported as being low-spin; acyl–cobalt(III) derivatives were also obtained[2].

Alkyl-transfer reactions between cobalt ions are relevant to biochemical behaviour of cobalamines, and several systems exhibiting this property have been studied. Thus dissolution in dimethylsulphoxide of the Schiff-base complexes Co(TFEN) and MeCo(ACEN) leads to electron transfer accompanied by transfer of the methyl group[3].

$$Co^{II}(TFEN) + MeCo^{III}(ACEN) \rightleftharpoons Co^{II}(ACEN) + MeCo^{III}(TFEN)$$

The dimethyl derivative of 1,3-bis(biacetylmonoxineimino)propane–cobalt(III) behaves as a methylating agent, and several methyl–cobalt derivatives have been prepared from Co^{III} complexes by the transfer of a methyl carbanion[4]. The transfer of alkyl groups from Co to Co or from Co to Rh is proposed to involve a bimolecular nucleophilic displacement of one metal ion by the other[5]. The equilibrium position of the reactions:

$$\mathrm{R(Co)} + \mathrm{(Co)}^{-*} \rightleftharpoons \mathrm{R(Co)}^{*} + \mathrm{(Co)}^{-}$$

$$\mathrm{R(Co)} = \mathrm{RCo^{III}(DMG)_2Py};$$

$$\mathrm{(Co)}^{*-} = \mathrm{bis(cyclohexanedionedioximinato)Co^{I}Py}$$

is dependent on the nature of the alkyl group (R). The equilibrium position of:

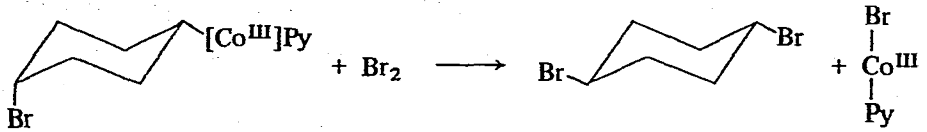
$$\mathrm{R(Co)} + \mathrm{(Rh)}^{-} \rightleftharpoons \mathrm{R(Rh)} + \mathrm{(Co)}^{-}$$

is a direct measure of the relative basicity of the two metal ions towards saturated carbon.

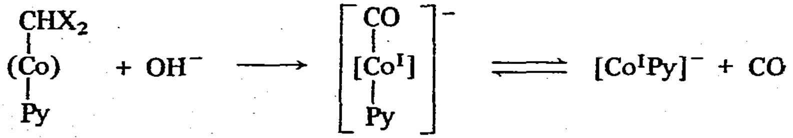
Electrophilic cleavage of alkyl-cobalamins and -cobaloximes by mercuric salts has been demonstrated[6]:

$$\mathrm{RCo^{I}} + \mathrm{Hg(OAc)_2} \rightarrow \mathrm{Co^{III}} + \mathrm{RHgOAc} + \mathrm{OAc^{-}}$$

and it was suggested that the reaction involved inversion of configuration at the carbon centre of the alkyl group. Cleavage of carbon–cobalt σ-bonds in cobaloximes by halogens has been shown to proceed via inversion at carbon[7].



Whereas, unsubstituted alkylcobaloximes are resistant to attack by hydroxide anions, halomethyl derivatives are susceptible to both OH^- and OMe^-, resulting in fission of the carbon–cobalt bond[8]:



$$\begin{matrix}\mathrm{CHX_2}\\ |\\ \mathrm{(Co)}\\ |\\ \mathrm{Py}\end{matrix} + \mathrm{OH^-} \longrightarrow \left[\begin{matrix}\mathrm{CO}\\ |\\ \mathrm{[Co^{I}]}\\ |\\ \mathrm{Py}\end{matrix}\right]^{-} \rightleftharpoons \mathrm{[Co^{I}Py]^{-}} + \mathrm{CO}$$

Methylcobaloxime has been found to add CO, MeNC, or MeCN forming species of the type $\mathrm{MeCo(DMG)_2L}$. The infrared stretching frequencies ν(CO) and ν(CN) indicate substantial (Co–L) π-bonding[9].

Reaction of $[\mathrm{Co^{I}(DMG)_2Py}]^-$ with *cis*- and *trans*-β-bromostyrene leads to β-styrylcobalt derivatives by direct substitution and with retention of configuration[10]. The cobalt anion is regarded as an extreme case of a soft nucleophile and as such, little or no contribution to the reaction from an elimination–addition mechanism would be expected.

In the presence of $[\mathrm{PdCl_4}]^{2-}$, alkylation or arylation of olefins has been obtained with cobaloxime derivatives $[\mathrm{MeCo^{I}Py}]$ and $[\mathrm{PhCo^{I}Py}]$[11]. The proposed mechanism involves initial formation of a carbon–palladium σ-bonded complex, which then reacts with the olefin.

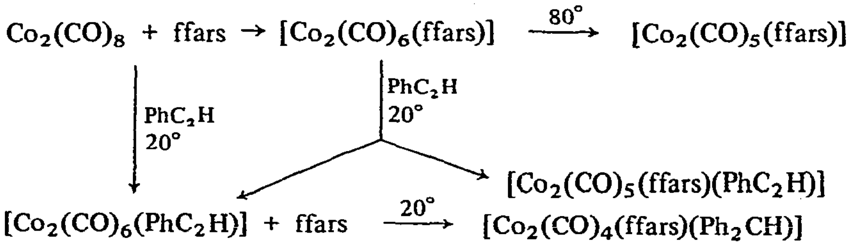
Reaction of the dicarbollide ion $[\mathrm{C_2B_{10}H_{12}}]^{2-}$ (formed from the *closo*-compound $\mathrm{C_2B_{10}H_{12}}$ and sodium) with $\mathrm{CoCl_2}$ and $\mathrm{NaC_5H_5}$ yields a mixture of products, the main component of which is $[Co(7,8\text{-}C_2B_{10}H_{12})\text{-}\pi\text{-}C_5H_5]$. This is believed to contain a 13-atom polyhedron. This compound undergoes a thermal polytopal rearrangement in refluxing hexane[12]. Treatment of 1,6-*closo*-$C_2B_8H_{10}$ with sodium naphthalenide followed by excess NaC_5H_5 and $CoCl_2$ in tetrahydrofuran afforded a reaction mixture containing 38% of the purple complex $[Co(C_2B_8H_{10})\text{-}\pi\text{-}C_5H_5]$; an 11-atom polyhedral system. This method of forming polyhedral metallocarboranes has been termed a "polyhedral expansion reaction". Reaction of 1,6-*closo*-$C_2B_8H_{10}$ with sodium and $CoCl_2$ and a catalytic quantity of naphthalene at $-78°$ in tetrahydrofuran gave the green anion $[Co(C_2B_8H_{10})_2]^-$ isolated as a caesium salt. Electronic and NMR spectra indicate the structure of $[C_2B_8H_{10}]^{2-}$ to be the same in both complexes[13]. A crystal structure determination of the complex $[Co(C_2B_9H_{10})_2S_2CH]$ has been reported[14].

Polarographic and cyclic voltammetric evidence is presented for the existence of low oxidation states in some cobalt and nickel dicarbollide complexes. Thus species $[Co\{\pi\text{-}(3)\text{-}1,2,C_2B_9H_{11}\}\text{-}\pi\text{-}C_5H_5]$, $[Co\{\pi\text{-}(3)\text{-}1,7\text{-}C_2B_9H_{11}\}_2]^-$, and $[Co_2(C_2B_8H_{10})\text{-}(C_2B_9H_{11})_2]^{2-}$ all contain cobalt in a formal (1+) oxidation state, whereas, $[Co\{\pi\text{-}(3)\text{-}1,2\text{-}C_2B_9H_{11}\}_2]$ has the cobalt in the (3+) oxidation state[15].

Reaction of cobaltocene with organoboron dihalides ($RBBr_2$) or boron trihalides affords paramagnetic borabenzene complexes of cobalt[16].

Cobalt carbonyl ($Co_2(CO)_8$) has been observed to react with certain fluorocarbon-bridged ditertiary arsines and phosphines (L) to give the species $Co_2(CO)_6L$ (where L = ffars, $f_4$fos, $f_6$fos, $f_8$fos)[17]. The complexes possess either structure A (L = ffars, $f_4$fos) or B ($L = Me_2AsC(CF_3){=}C(CF_3)AsMe_2$, $Me_2AsCF(CF_3)CF_2AsMe_2$).

Unlike $Co_2(CO)_8$, the bridged structure is retained in solution. It is suggested that the As–As distance (ligand "bite") may be the controlling factor in determining the preferred conformation. Treatment of $[Co_2(CO)_6(\text{ffars})]$ with $PhC{\equiv}CH$ resulted in the replacement of the bridging carbonyl ligands by the acetylene.



The reaction between $[MeCCo_3(CO)_9]$ and ffars yields $[MeCCo_3(CO)_7(\text{ffars})]$ with the arsenic ligand believed to be bridging two cobalt atoms. Similar treatment of $[CF_3CCo_3(CO)_9]$ produces a small amount of $[Co_4(CO)_8(\text{ffars})_2]$; the fate of the ($CF_3C$) group being unknown[17].

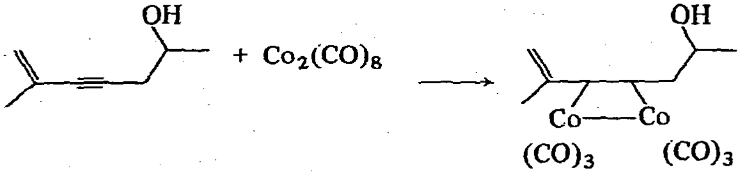
Reaction of alkynes with $Co_2(CO)_8$ has afforded a wide variety of products, whereas, the corresponding reaction of phosphines or phosphites gives straight forward substitution products. The reaction of $Co_2(CO)_8$ and $Ph_2MC{\equiv}CR$ (M = P, R = H, Me, CMe_3, CF_3, or M = As, R = CF_3) has been found to give only complexes of the type $[Co_4(CO)_{10}\text{-}(Ph_2MC{\equiv}CR)_2]$ as dark red crystals[18]. The phosphites (L), $P(OMe)_3$ and $P(OPh)_3$, readily displace carbon monoxide from these complexes to give $[Co_4(CO)_8(Ph_2PC{\equiv}CR)_2L_2]$.

An X-ray study of $[Co_4(CO)_{10}(Ph_2PC{\equiv}CCF_3)_2]$ shows that each acetylenic linkage bridges two cobalt atoms and the phosphorus atoms each donate to a $Co(CO)_2$ group.

The reaction of $Co_2(CO)_8$ with Group IVB substituted acetylene RC_2R ($Me_3SnC_2SnMe_3$, $Me_3SnC_2CMe_3$, Me_3SnC_2H, $Me_3GeC_2GeMe_3$, $Me_3GeC_2SiMe_3$ and $Me_3SnC_2SiMe_3$) affords the corresponding $[Co_2(CO)_6RC_2R]$ complexes[19], as air-stable purple-black solids. Acylation of $[Co_2(CO)_6(Me_3SnC_2H)]$ and $[Co_2(CO)_6(Me_3SnC_2CMe_3)]$ with $MeCOCl/AlCl_3$ gave $[Co_2(CO)_6(MeCOC_2H)]$ and $[Co_2(CO)_6(MeCOC_2CMe_3)]$ respectively.

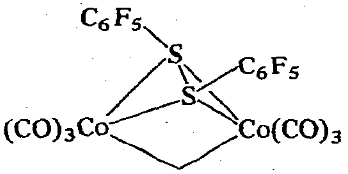
The treatment of $[Co_2(CO)_6(RC_2H)]$ ($R = H, Ph$) with excess bicyclo-[2.2.1]heptadiene in inert solvents (dimethoxyethane or isooctane) gives $[Co(CO)_2\pi\text{-}C_5H_5]$ as the major product; the cyclopentadienyl group probably resulting from a retro-Diels–Alder reaction[20]. When the reaction was conducted in an aromatic hydrocarbon (C_6H_6 or C_6H_5Me) the major product was found to be $[Co_4(CO)_9(\text{arene})]$. The same complex is obtained by warming $[Co_4(CO)_{12}]$ with the respective arene.

The readiness with which an acetylenic group will coordinate to a $Co_2(CO)_6$ moiety has been used as the basis of a method of protecting an alkyne group in an organic compound. For example, after coordination the olefinic linkage can react selectively[20a].



The protecting group can be readily removed by oxidation with ferric ion.

The reaction of equimolar quantities of $Co_2(CO)_8$ and $C_6F_5SSC_6F_5$ in hexane at room temperature affords air-stable black crystals of $[Co_2(CO)_6(C_6F_5SSC_6F_5)]$[21]. Comparison of infrared spectra suggests an analogous structure to that found for the acetylenic complexes $[Co_2(CO)_6RC_2R]$, involving a disulphide bridge:



Formation of a similar compound was observed with $C_6Cl_5SSC_6Cl_5$, but C_6F_5SH gave a mixture of the above type of complex and a species formulated as $[Co_3(CO)_6(S)(SC_6F_5)]$.

Previous investigations of methylidyne-$Co_3(CO)_9$ systems have demonstrated the ability of a wide range of organomercurials to alkylate $[HCCo_3(CO)_9]$ at carbon to give $[RCCo_3(CO)_9]$. However, reaction of halomethylmercury compounds proceeds differently[22]:

$$[HCCo_3(CO)_9] + Hg(CH_2I)_2 \xrightarrow{CO} [MeCCo_3(CO)_9]$$
$$DCCo_3(CO)_9 + Hg(CH_2Br)_2 \longrightarrow [CH_2DCo_3(CO)_9]$$

No incorporation of halide was observed in the final products. These reactions may be formally considered as involving the insertion of a carbene (CH_2) into the C–H bond, but a more complicated process is probable, since metallic mercury is a bi-product. Phenyl-(trihalomethyl)mercurials, which readily release dihalocarbenes on heating, did not exhibit the methylation reaction with $[HCCo_3(CO)_9]$. Thus, $PhHgCCl_2Br$ gave $[PhCCo_3(CO)_9]$ only, as did $PhHgCBr_3$ and $PhHgCF_3$. In each case a strong preference is shown for transfer of the phenyl groups.

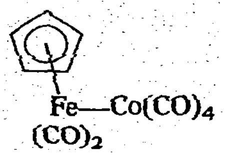
Dehalogenation of the species $[XCCo_3(CO)_9]$ (X = Cl, Br) in arenes at temperatures above 90° afford the compounds $[Co_8(CO)_{24}C_6]$, $[Co_5(CO)_{15}C_3H]$ and $[Co_6(CO)_{18}C_4]$, the latter being the main product even at higher temperatures where $[Co_8(CO)_{24}C_6]$ is formed preferentially to $[Co_5(CO)_{15}C_3H]$[23]. Spectral data indicate that each of these complexes is effectively a $Co_3(CO)_9C$ unit with various acetylene residues linked to the apical carbon atom. The crystal structure of the complex $[Co_8(CO)_{24}C_6]$ has been determined by X-ray crystallography[24]. The molecule consists of a $[CCo_3(CO)_9]$ group at each end of a four-carbon chain containing two acetylene bonds, one of which forms a bridge with a $Co_2(CO)_6$ group.

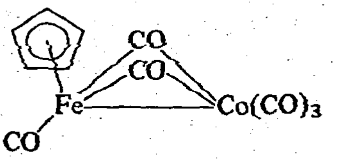
Crystal structure determinations have also been reported for derivatives of $[YCCo_3(CO)_9]$, which all contain the tetrahedral CCo_3 cluster of the parent compound[25]. Thus, in $[PhCCo_3(CO)_6(\pi\text{-}C_6H_3Me_3)]$ a mesitylene group is π-bonded to a single cobalt, having replaced three carbonyl groups; in $[PhCCo_3(CO)_6(\pi\text{-}C_8H_8)]$, a cyclooctatetraene molecule has replaced the three axial carbonyl groups and is π bonded to the Co_3 triangle through three of its double bonds. The preparation and spectral properties of the complex $[PhCCo_3(CO)_6(C_8H_8)]$ have also been described[26]. It is formed by treatment of $[PhCCo_3(CO)_9]$ or $[PhCCo_3(CO)_6(arene)]$ with C_8H_8 in refluxing ether.

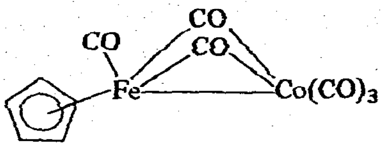
An X-ray crystallographic study of the diamagnetic complex $[FeCo_2(CO)_9S]$ together with a detailed comparison of its molecular dimensions with those of the isomorphous, paramagnetic $[Co_3(CO)_9S]$ has been reported[27]. The conclusion is drawn that electrons in excess of a closed-shell electronic configuration of each metal atom in an organometallic cluster system occupy strongly anti-bonding metal orbital combinations. The formal substitution of an Fe for a Co may be regarded as equivalent to removal of the unpaired electron from $[Co_3(CO)_9S]$ and results in a large decrease in metal–metal bond distances. X-ray analyses of the related complexes $[Co_3(CO)_9Se]$, $[FeCo_2(CO)_9Se]$ and $[FeCo_2(CO)_9Fe]$ support the previously demonstrated anti-aromatic character of the unpaired electron in the Co_3 fragment of the $Co_3(CO)_9S$ molecule[28]. This investigation demonstrates that excess electrons in a triangular metal-cluster system will occupy primarily the antibonding σ-orbitals and will thereby reduce the net metal–metal bond order to less than one. The effect is less for the selenium than for the sulphur complex.

The infrared band near 1900 cm^{-1} in the spectrum of $NaCo(CO)_4$ has been examined in different solvent systems[29]. The band envelope is simple in DMF, DMSO and wet THF, but shows varying degrees of complexity in pyridine, piperidine, THF, DME and water. The results are discussed in terms of the differing multiplicities and differing nature of the anion environment. A more detailed study of the carbonyl stretching region for $NaCo(CO)_4$ in THF has been carried out, using infrared and laser-Raman spectroscopy[30]. The spectrum is temperature dependent, revealing two kinds of anion environment. The major anion sites are identified as solvent-separated ion pairs and contact ion pairs.

The infrared spectra of the complexes $[(\pi\text{-ring})Fe(CO)_2Co(CO)_4]$ (where ring = C_5H_5, MeC_5H_4 and indenyl C_9H_7) have been investigated[31]. In the solid state they exist as carbonyl-bridged species, which probably possess puckered di-μ-carbonyl bridging systems. In solution, one non-bridged and two bridged isomers are present. The proportion of the former decreases with decreasing temperature in polar solvents, and along the series $C_5H_5 > MeC_5H_4 > C_9H_7$. Only the non-bridged form of the ruthenium compound has been observed.







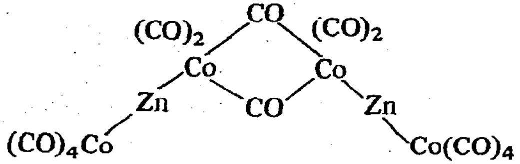
Addition of $[Ph_4As][Co(CO)_4]$ to a methylene chloride–heptane solution of an excess of $[In\{Co(CO)_4\}_3]$ or $[Tl\{Co(CO)_4\}_3]$ yields red crystals of $[Ph_4As][In\{Co(CO)_4\}_4]$ or $[Ph_4As][Tl\{Co(CO)_4\}_4]$ respectively[32]. The infrared spectra indicate that the four M–Co bonds (M = In, Tl) are in a tetrahedral array. In polar organic solvents, there is some dissociation, although the positions of equilibria are very solvent dependent:

$$[M\{Co(CO)_4\}_4]^- \rightleftharpoons [M\{Co(CO)_4\}_3] + [Co(CO)_4]^-$$

$$[M\{Co(CO)_4\}_3] \rightleftharpoons M^{3+} + 3[Co(CO)_4]^-$$

Single crystal X-ray analyses of $[Co(Ph_3PAu)(CO)_4]$ and ({bis(*o*-dimethylarsinophenyl)-methylarsine}argentio)tetracarbonylcobalt] have been reported[33]. In both compounds the cobalt atom is 5-coordinated in a trigonal bipyramidal form with a gold or silver atom in an apical position.

The irradiation of a solution of $[Zn\{Co(CO)_4\}_2]$ in hexane at 20° affords orange crystals of the condensation product $[Zn_2Co_4(CO)_{15}]$ accompanied by loss of CO[34]. This condensation also proceeds under conditions of thermolysis and even on storage in the dark. The infrared and Raman spectra are complex, and the observed diamagnetism suggests a Co–Co bond. The proposed structure is:



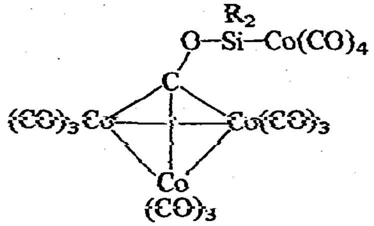
As might have been predicted, this complex proves to be an effective catalyst for the dimerisation of bicyclo[2.2.1]heptadiene to Binor-S.

Treatment of $[HCo(CO)_4]$ with NH_3 affords $NH_4Co(CO)_4$ and this has been observed to react with aromatic aldehydes[35].

The reactions of $[Cl_3MCo(CO)_4]$ (M = Si, Ge, Sn) with $P(OEt)_3$, P-n-Bu_3 and PPh_3 have been studied[36]. Treatment of $[Cl_3SnCo(CO)_4]$ with $P(OEt)_3$, P-n-Bu_3 or NEt_3 in hexane or with THF in the neat solvent leads to formation of $[SnCl_2\{Co(CO)_4\}_2]$, the reaction appearing to proceed via attack of the base at the tin atom, displacement of $[Co(CO)_4]^-$ and subsequent displacement of Cl^- from $Cl_3SnCo(CO)_4$ by $Co(CO)_4^-$. In the presence of excess base, products of the form $[Cl_3MCo(CO)_3L_2]$ (M = Sn and Ge; L = P-n-Bu$_3$, and PPh$_3$) were obtained. Infrared data leads to their formulation as ionic species $[MCl_3]^-[Co(CO)_3L_2]^+$. Under different conditions, the complexes $[Cl_3MCo(CO)_3L]$ were obtained, adjudged to be the *trans* isomer.

The complete absorption spectra (33000–55000 cm^{-1}) for the complexes $[X_3MCo(CO)_4]$ (X = Br, I; M = Sn, Ge) have been reported[37].

Ph_2SiH_2 and Et_2SiH_2 react with excess of $Co_2(CO)_8$ to give $[R_2SiCo_4(CO)_{14}]$[38]. High resolution infrared and mass spectra suggest that these derivatives contain nonacarbonyltricobaltmethoxy and tetracarbonylcobalt groups directly bonded to Si:



The corresponding $H(CO)_4CoSi$ and $(CO)_7Co_2Si$ compounds appear to be intermediates.

The ultraviolet irradiation of $[\pi\text{-}C_5H_5Co(CO)_2]$ with Cl_3SiH has been observed to afford $[Cl_3SiCoH(CO)(C_5H_5)]$[39].

Reaction of Me_2NSiMe_3 with $HCo(CO)_4$ and $HCo(PF_3)_4$ leads to the formation of $[Me_2N(H)SiMe_3]^+[Co(CO)_4]^-$ and $[Me_2N(H)SiMe_3]^+[Co(PF_3)_4]^-$ respectively, as white solids[40]. The former complex may also be obtained from the reaction of Me_2NH with $[Me_3SiCo(CO)_4]$.

The complexes $[CoH_2(SiR_3)(PPh_3)_3]$ (R = F, OEt) are formed by an oxidative-elimination reaction between R_3SiH and $[CoH(N_2)P_3]$; the reaction is reversible when R = OEt[41]. The complex $[CoH_2\{Si(OEt)_3\}P_3]$, which may also be obtained by the reaction of $[CoH_3P_3]$ with $(EtO)_3SiH$, functions as an efficient catalyst for *o*-silylation of, for example, EtOH, and for the reaction of $SiH(OEt)_3$ with 1-hexene. The olefin is also isomerised in this reaction at about half the rate of hydrosilylation.

Passage of carbon monoxide through an aqueous solution of $[Co(CN)_5]^{3-}$ yields the anion $[Co^I(CN)_3(CO)_2]^{2-}$ which demonstrates a relatively weak basicity towards protonation and a weak nucleophilicity towards alkyl halides, this possibly reflecting the tendency of carbon monoxide to stabilise Co^I with regard to oxidation[42]. Treatment of the dianion with tertiary phosphines affords the species $[Co(CN)_2(CO)_2(PR_3)]^-$, $[Co(CN)_2(CO)(PR_3)_2]^-$ and $[Co(CN)(CO)_2(PR_3)_2]$ (where R = $MePh_2$, Me_2Ph, Et, Ph, cyclohexyl). A ready oxidation of coordinated carbon monoxide is the result of the reaction of $[Co(CN)_2(CO)(PEt_3)_2]^-$ with alkaline $Fe(CN)_6{}^{3-}$:

$$[Co(CN)_2(CO)P_2]^- + Fe(CN)_6{}^- + OH^- \rightarrow Fe(CN)_6{}^{4-} + CO_3{}^{2-} +$$
$$+ [(CN)_5FeCNCo(CN)_2P_2(H_2O)]^{3-}$$

A variable temperature infrared spectral study between −78° and +40° of tricarbonyl acylcobalt derivatives has revealed rotational isomerism owing to hindered rotation about the Co–C_{acyl} bond axis[43]. The derivatives were prepared from substituted acetic anhydrides and $[Co(CO)_3(PPh_3)]^-$:

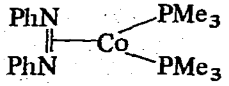
$$(XFHCCO)_2O + Na[Co(CO)_3(PPh_3)] \rightarrow [XFHCCOCo(CO)_3P] \; (X = H, F).$$

Kinetic studies of the isotopic exchange reaction:

$$[Co(CO)_2(NO)L] + {}^{14}CO \rightleftharpoons [Co({}^{14}CO)_2(NO)L] + CO$$

(where $L = PPh_3$, $P\text{-}n\text{-}Bu_3$, $P(OPh)_3$ or $P(OMe)_3$) have previously shown that it follows a two-term rate law of the type $\nu = k_1$ [complex] + k_2 [complex][CO]. Further investigations in different solvents have demonstrated that the second-order rate constant is influenced by the solvent to a negligible extent, while k_1 varies with the solvent's nucleophilicity and steric requirements[44]. In solvents possessing good donor properties k_1 is increased, which correlates with a solvent-assisted dissociative mechanism for the first-order path.

The paramagnetic species $[Co(PMe_3)_4]$ has been obtained as dark-brown needles by sodium amalgam reduction of anhydrous cobalt halides in the presence of the phosphine[45]. Solution molecular weight determinations gave the monomeric value, a contrast to the ready dimerisation of the species $[Co(CO)_4]$ and $[Co(PF_3)_4]$. In absence of a catalyst, $[Co(PMe_3)_4]$ does not react with hydrogen, but if the above preparation is conducted in an H_2 atmosphere, a biproduct is $[HCo(PMe_3)_4]$. Solutions of $[Co(PMe_3)_4]$ rapidly absorb NO to form diamagnetic $[Co(NO)P_3]$, and with azobenzene gives dark violet crystals of the complex:



Sodium borohydride reduction in ethanol of $CoCl_2$ in the presence of excess PEt_2OPh affords orange prisms of $[CoH(PEt_2OPh)_4]$[46]. The ^1H NMR spectrum at 25° shows the hydride resonance as a quintet but cooling to –55° is accompanied by loss of resolution, the signal eventually becoming a single broad band. An X-ray structure determination shows the coordination about the cobalt to be approximately trigonal bipyramidal with the hydrogen in an apical position. The approximately tetrahedral disposition of the four phosphine ligands suggests the barrier to intramolecular rearrangements via a tetrahedral CoP_4 transition state would be very low, with the hydrogen possibly tunnelling between triangular face (edge) positions. The NMR data require the barrier to be higher than in $HCo[P(OPh)_3]_4$ or $HCo[P(OEt)_3]_4$.

Reaction of cobalt salts with excess $Ph_2PCH_2CH_2PPh_2$ (diphos) in polar solvents gives the ionic species $[Co(diphos)_2]^+X$ (where $X = Br$, ClO_4, BPh_4)[47]. The bromide is 4-coordinated in polar solvents but 5-coordinated in non-polar solvents, whereas the ClO_4^- and BPh_4^- salts are 4-coordinated in solution and in the solid state. The cations easily afford 1/1 adducts with H_2, CO or SO_2. Carbon monoxide is extracted from PhCOCl to give $[Co(CO)(diphos)_2]^+$, which is in contrast to the simple oxidative addition observed for the Rh and Ir analogues. NO displaces one diphos ligand to give $[Co(diphos)(NO)_2]^+$.

The olefinic ditertiary arsine 1,2-bis(dimethylarsino)ethylene (edas) (90% *trans* and 10% *cis*) reacts under UV irradiation with CoX_2 to give[47a] $CoX_2(cis\text{-edas})_2$ (X = Cl, Br, T, NO). These complexes behave as 1/1 electrolytes in nitromethane and should probably be represented as $[CoX(cis\text{-edas})_2]^+X^-$.

Using aqueous alcohol as the solvent for the above photolysis, a species formulated as $[CoCl_2(cis\text{-edas})]$ was obtained, and this was considered to be $[Co(cis\text{-edas})_2][CoCl_4]$ in the solid state.

The synthesis and some reactions of a bis(pentafluorophenyl)cobalt complex have been described[48]. Thus the reaction:

$$C_6F_5MgBr + CoBr_2 \rightarrow (C_6F_5)_2Co$$

is proposed to occur, although the stable blue solid product has not yet been obtained pure; several of its reactions imply facile liberation of the C_6F_5 radical.

$$(C_6F_5)_2Co \left\{ \begin{array}{l} \xrightarrow{H_3O^+} C_6F_5H \\ \xrightarrow{O_2} C_{12}F_{10} \\ \xrightarrow{240°} C_6F_5H + C_{12}F_{10} \\ \xrightarrow{S} C_6F_5SH + C_6F_5SSC_6F_5 \\ \xrightarrow{I_2} C_6F_5I \\ \xrightarrow{ICN} C_6F_5I. \end{array} \right.$$

with P-n-Bu_3, however, the complex $[(C_6F_5)_2CoP_2]$ is obtained.

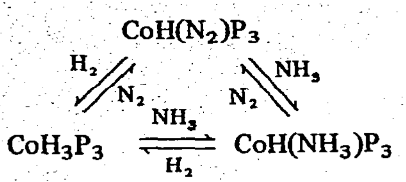
The complexes $[(\pi\text{-}C_5H_5)_2M(SR)_2]$ (M = Mo or W; R = Me, Et, n-Bu) act as ligands to cobalt to form the complexes $[(\pi\text{-}C_5H_5)_2M(SR)_2CoX_2]$ (X = Cl, Br, I or SCN)[49]. Solution molecular weight determinations show monomeric character. Magnetic moment values and electronic spectra are typical of pseudo-tetrahedral Co^{II} compounds.

Dinitrogen complexes of Co^0 and Co^{-1} have been prepared by reduction of $[CoClP_3]$ (P = PEt_2Ph or PPh_3) with Na metal in THF or toluene under N_2[50]. Thus, reaction between $[CoCl_2(PEt_2Ph)_2]$, PEt_2Ph and Na metal in 1/1/2 molar ratio in THF leads, via $[CoClP_3]$ to a bridged N_2 complex of Co^0, $[P_3Co(N_2)CoP_3]$, obtained as dark-brown crystals, unstable in air. The infrared spectrum does not show N-N stretching bands, indicating a symmetric bridging conformation. Use of the same reagents in the molar ratio 1/1/3 afforded $Na[Co(N_2)P_3]$ as black, diamagnetic crystals, whose infrared spectrum showed a very strong ν(NN) at 1840 cm^{-1}. The N_2 ligand is readily displaced by carbon monoxide, but with water the complex $[CoH(N_2)P_3]$ is obtained.

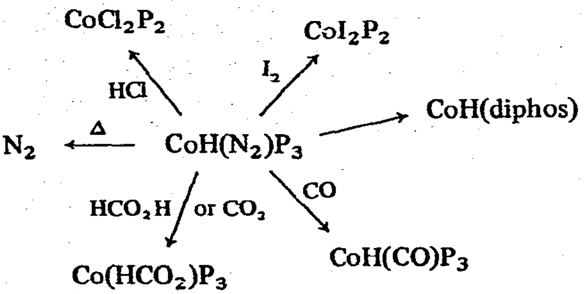
Another preparation of the PPh_3 complex $[CoH(N_2)(PPh_3)_3]$ involves reduction of Co^{II} or Co^{III} acetylacetonates with trialkylaluminium reagents in the presence of PPh_3 under N_2[51]. Use of $AlMe_2OMe$ or $ALEt_2OEt$ in an argon atmosphere afforded $[MeCo(PPh_3)_3]$

and $[Co(C_2H_4)(PPh_3)_3]$ respectively. This suggests that the N_2 complex is formed via an intermediate alkyl–cobalt complex. The reactions may be divided into those involving reversible exchange of N_2, and irreversible reactions:

(i)

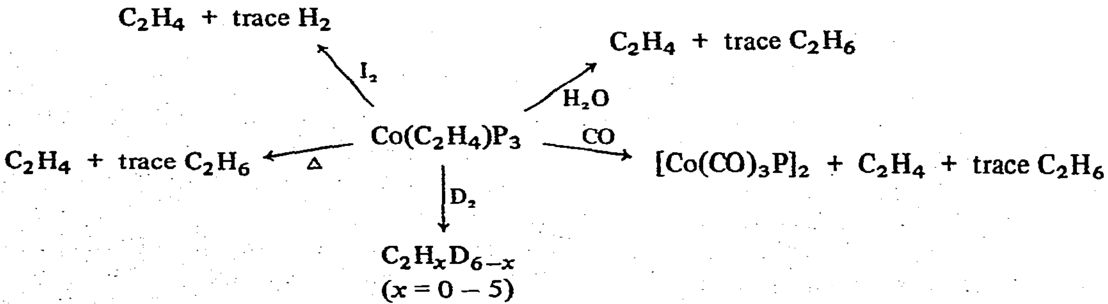


(ii)



The N_2 complex functions as a catalyst for a variety of transformations *viz.*, oxidation of PPh_3, reduction of N_2O to N_2 with concomitant oxidation of PPh_3; hydrogenation of C_2H_4; dimerisation of C_2H_4 and propene, via $HCoP_3$ intermediate; isomerisation of 1-butene; and polymerisation of acrylonitrile, methacrylonitrile and methylmethacrylate.

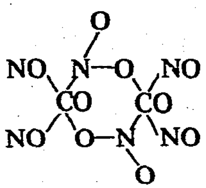
The ethylene complex exhibits reactions consistent with its formulation as a zerovalent complex:



The nitrogen ligand in $[CoH(N_2)(PPh_3)_3]$ has been reduced by sodium naphthalenide, PhLi or Li/naphthalene in the presence of $TiCl_4$[52]. Hydrolysis of the reaction mixture liberates NH_3 as the reduction product. No reduction occurs in the absence of the titanium compound and it may proceed either through an intermediate Co—N═N—Ti or through transfer of N_2 from Co to a low-valence complex of Ti.

Treatment of a hexane solution of $Co_2(CO)_8$ with excess NO at room temperature results in the formation of a black, diamagnetic complex characterised as $Co(NO)_2NO_2$

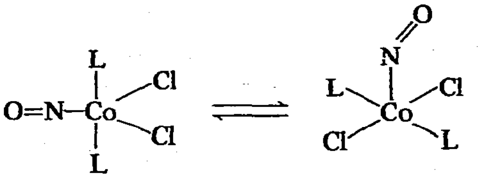
by X-ray and infrared studies[53]. In the solid state a chain structure exists involving $Co(NO)_2$ moieties linked by nitrile groups. The similarity of the solid and solution infrared spectrum and the difference of the NO_2 frequencies from those of nitro- or nitrito-groups indicates a bridging configuration in solution and a dimeric structure is suggested:



A nitrosylnitro complex $[Co(NO_2)(PPh_3)(NO)_2]$ is also obtained from reaction of $[CoP_3(NO)]$ with NO[54]. Nitrogen is also evolved and the reaction may be considered as the result of a disproportionation of NO to $NO^+NO_2^-$ and N_2 followed by an oxidative addition. The complex may also be prepared by:

$$[CoP_2(NO)_2]^+ClO_4^- + KNO_2 \rightarrow [Co(NO_2)P(NO)_2]$$

The possibility of conformational equilibria between the two forms of metal–nitrosyl bonding (NO^+ linear and NO^- bent) has been previously discussed. In this way the co-ordination geometry about the metal would change as the metal and nitrosyl undergo a formal internal oxidation–reduction reaction. Variable temperature infrared data for the complexes $[CoCl_2(NO)L_2]$ [L = P-n-Bu_3, $PMePh_2$, PPh_3, PEt_3, $P(p\text{-}MeC_6H_4)_3$] suggest that there is a rapid equilibrium in solution between a trigonal bipyramidal Co^I complex containing a linear nitrosyl, and a square pyramidal Co^{III} species with a bent nitrosyl[55]:



The relative intensities of the ν(NO) bands are dependent on the nature of the phosphine; more basic ligands increasing the intensity of the lower (NO^-) frequency. Cooling of the solution of $[CoCl_2(NO)(PMePh_2)]$ caused an increase in intensity of the higher (NO^+) frequency band.

Polarographic studies of the reduction of complexes of the type $[Co(CO)_{3-n}P_n(NO)]$ ($n = 1, 2$) (P = phosphine) show that they are reversibly reduced to the radical anion, which is irreversibly inactivated[56].

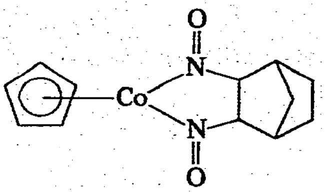
The measured changes of half-wave potentials correspond to changes of standard redox potentials and a correlation of these quantities with ν(NO) indicates a considerable degree of delocalisation of the redox orbital. This correlation is based on a simplified model according to which changes in ν(NO) are primarily due to varying degrees of back-donation into π^*(NO), which is at the same time a significant component of the redox orbital.

Halonitrosyldicarbonylcobalt anions $[Co(NO)(CO)_2X]^-$ have been obtained from $[Co(NO)(CO)_3]$ and X^- [57]. Reaction with benzyl halides results in nitrosylation of the aromatic species to afford benzaldoximes, possibly via intermediate benzylation of the metal.

$$PhCH_2Cl + [Co(NO)(CO)_2X]^- \rightarrow PhCH_2NO + [Co(CO)_2X]$$

An unusual reaction is reported involving $[CpCo(NO)]_2$ and bicyclo[2.2.1]heptene in the presence of NO which affords a 90% yield of dark red crystals of $[\pi\text{-}C_5H_5Co(NO)_2\text{-}(C_7H_{10})]^{58}$.

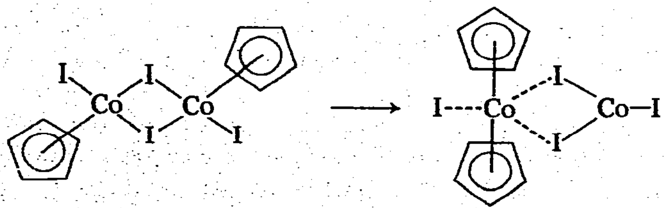
^{1}H NMR, mass and infrared spectral evidence (ν(NO) 1357 cm^{-1}) suggests the structure below involving bridging nitrosyl groups:



The Diels–Alder adduct from C_5H_6 and $C_2(CO_2Me)_2$ reacts similarly to bicyclo[2.2.1]-heptene, but only the unsubstituted double bond reacts.

The syntheses and characterisation of a series of mixed 1,1-/1,2-dithiolene complexes $[Co(S_2CNR_2)\{S_2C_2(CN)_2\}_2]^{2-}$ (R = Me or Et) and $[Co(S_2C{=}X)\{S_2C_2(CN)_2\}_2]^{2-}$ (X = $C(CN)_2$, $C(CN)CO\cdot OEt$, $C(CN)CO\cdot NH_2$, $CH\cdot NO_2$ or $N(CN)$) have been described[59]. A voltammetric examination in CH_2Cl_2 established that the trianionic species and $[Co(S_2CNR_2)\{S_2C_2(CN)_2\}]^{2-}$ could be oxidised in a one electron step, the $E_{\frac{1}{2}}$ values showing a small but significant dependence on R and X. The dithiocarbamate adducts and $[Co\{S_2C{=}C(CN)_2\}\{S_2C_2(CN)_2\}_2]^{2-}$ could be further oxidised. Chemical oxidation of the complexes was achieved using iodine.

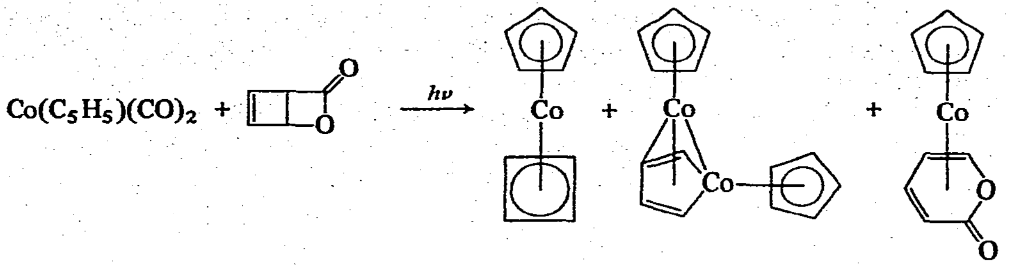
Diiodocyclopentadienylcobalt has been prepared as a grey black solid $[Co(C_5H_5)I_2]_n$ (where n is probably 2) from the reaction of $[Co(C_5H_5)(CO)_2]$ with iodine[61]. Lewis base ligands such as PPh_3 and pyridine, break the iodide bridge to afford $[Co(C_5H_5)I_2L]$. Whereas $[Co(C_5H_5)I_2]_n$ is insoluble in non-complexing solvents, it decomposes in coordinating solvents to give the cobaltocenium ion and cobalt(II). The bromide analogue disproportionates more rapidly, even in light petroleum, and the chloride could not be prepared, only the cobalticenium salt being formed. The disproportionation mechanism for the iodide is suggested to involve intramolecular transfer of a $C_5H_5^-$ ligand:



$$[Co(C_5H_5)_2]^+I^- + CoI_3$$

Neither the rhodium analogues, nor the complex $[Co(C_5Me_5)I_2]$ show this behaviour under these conditions.

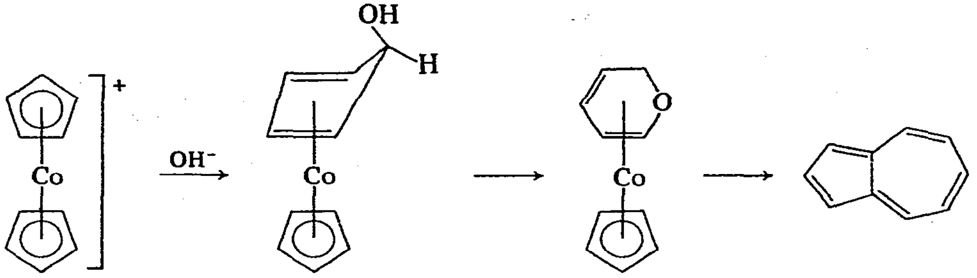
Photolysis of photo-α-pyrone in the presence of $[Co(C_5H_5)(CO)_2]$ has been shown to give three products[62]:



(I) (II) (III)

The structure illustrated for (II) has been confirmed by X-ray study and in solution it exhibits a novel fluxional behaviour, which is interpreted as involving exchange of the nonequivalent C_5H_5 groups together with exchange of σ- and π-bonding between the two cobalt atoms and the C_4H_4 moiety.

Reaction of hydroxide or amide ion with cobaltocenium cation has been observed to give good yields of azulene[63]. The suggested mechanism envisages initial nucleophilic attack followed by ring expansion with a final condensation reaction between the 6-membered ring intermediate and a second $C_5H_5^-$ ion.

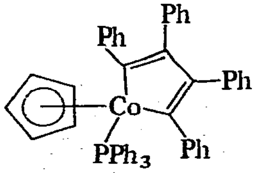


The expansion of the C_5H_5 ring to incorporate the oxygen is comparable to similar rearrangements previously observed for $[Co(C_5H_5)(C_5H_5CH_2X)]$.

Although only one of the carbonyl ligands in $[Co(C_5H_5)(CO)_2]$ may be directly displaced by PPh_3, the complex $[Co(C_5H_5)(PPh_3)_2]$ has been prepared by reduction of $Co(C_5H_5)PPh_3I_2$[64].

$$Co(C_5H_5)PPh_3I_2 + i\text{-}PrMgBr + PPh_3 \xrightarrow{C_6H_6} Co(C_5H_5)(PPh_3)_2 \cdot C_6H_6$$

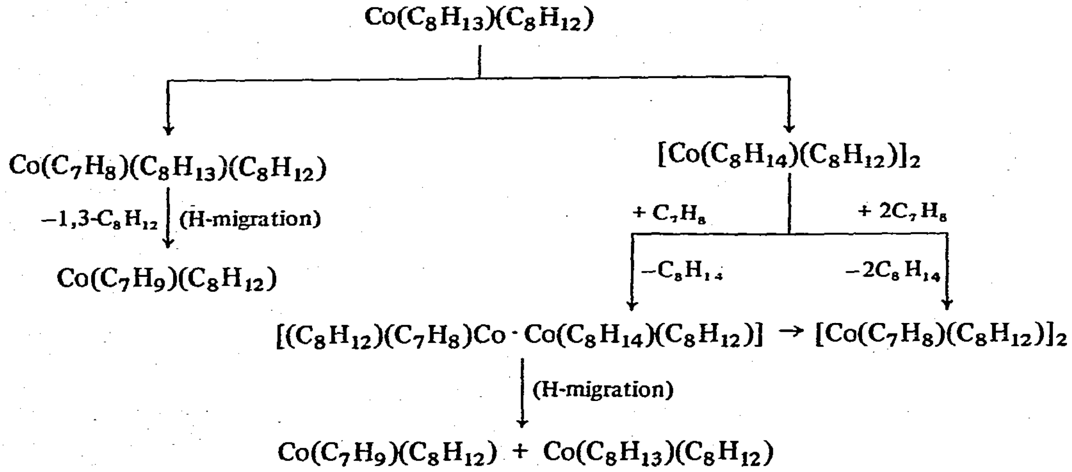
The rhodium analogue may be similarly obtained. One of the phosphines of the cobalt complex is labile and is displaced by CO, CS_2 or two moles of PhC≡CPh, the latter affording a tetraphenylmetallocyclopentadiene ring:



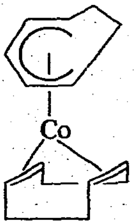
Butadiene reacts with a suspension of $[CoH(N_2)(PPh_3)_3]$ in ether at room temperature to give directly the orange red diamagnetic complex $[Co(C_4H_7)(C_4H_6)(PPh_3)]$, which on the basis of its ^{1}H NMR is formulated as π-crotyl-π-butadienetriphenylphosphinecobalt^I [65]. This reacts with carbon monoxide to displace butadiene and form $[Co(\pi\text{-}C_4H_7)(CO)_2PPh_3]$, detected by infrared spectroscopy.

Treatment of $[Co(C_8H_{13})(C_8H_{12})]$ with cycloheptatriene affords red-brown needles of $[Co(C_7H_9)(C_8H_{12})]$ from which may be derived $[Co(C_7H_9)(CO)_2]$, both containing a π(h^5)-cycloheptadienyl ligand[66]. The formation of $Co(C_7H_9)(C_8H_{12})$ in n-heptane at 65° follows a composite rate equation, $R = k[Co][C_7H_8] + k'[Co]^{\frac{1}{2}}$ (where $[Co] \equiv [Co(C_8H_{13})(C_8H_{12})]$).

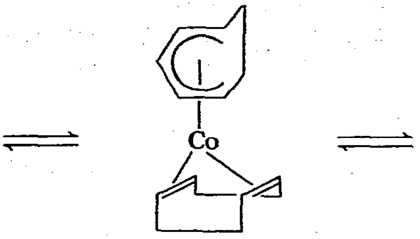
The first term represents an associative mechanism common to substitution reactions of square planar complexes, this type of configuration being approximately attained by the C_8H_{13} and C_8H_{12} ligands. Formation of the final product would require rapid transfer of the hydrogen from C_8H_{13} to C_7H_8 and evidence for this is supplied by the detection of 1,3-C_8H_{12} as the major C_8 hydrocarbon. The virtual absence of any 1,5-C_8H_{12} precludes a mechanism involving initial displacement of the 1,5-C_8H_{12} ligand by C_7H_8. The second term in the rate equation implies rapid formation of a dinuclear intermediate containing C_7H_8. The reaction scheme deduced is illustrated in the scheme below.



The complex $Co(C_7H_9)(C_8H_{12})$ also exhibits a temperature-dependent ^{1}H NMR spectrum in solution indicative of proton averaging, between −25 and + 75° [67]. This is in contrast to the rigid structure maintained in solution by $[Co(C_8H_{13})(C_8H_{12})]$. The limiting spectrum at −25° led to the molecular conformation below being proposed as the stable configuration:



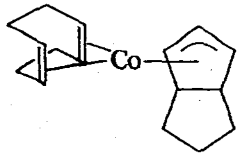
The observed fluxional behaviour results from rotation of the C_8H_{12} ligand, the C_7H_9 ring being unaffected:



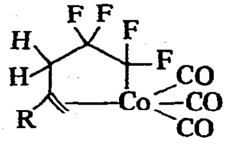
The contrast with $Co(C_8H_{13})(C_8H_{12})$ is assigned to the different characters of the ligand and metal orbitals used in the two complexes. It is postulated that $[Co(C_7H_9)(C_8H_{12})]$ contains certain metal orbitals which form essentially a non-bonding core which is more isotropic than the analogous orbitals in the square planar $[Co(C_8H_{13})(C_8H_{12})]$.

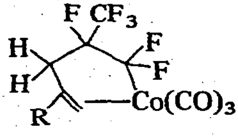
By reduction of $CoCl_2$ with $NaBH_4$ in the presence of cyclooctatetraene the similar complex $[Co(C_8H_8)(C_8H_9)]$ has been prepared[68]. This is thought to contain a fluxicnal h^4-1,2,3,4-cyclooctatetraene cobalt system. The ^{1}H NMR data does not allow a firm decision between the two modes of coordination possible for the C_8H_9 moiety, namely, h^5-1,2,3,4,5- or h^5-1,2,5,6,7. The latter π-allylic mode of bonding is thought to be present in the cationic species $[Ru(C_8H_9)(CO)_3]^+$. Carbon monoxide displaces C_8H_8 from $[Co(C_8H_8)(C_8H_9)]$ to give a tricarbonyl-π-h^3-cyclooctatrienyl cobalt. In the discussion of the ^{1}H NMR spectrum of $[C_8H_9Co(CO)_3]$, it is suggested that the previously reported $C_7H_7Co(CO)_3$ does in fact contain a h^3-1,4,5-cycloheptatrienyl system. Cyclopentadiene and indene react with $[Co(C_8H_8)(C_8H_9)]$ to form respectively, 1,3,6-cyclooctatriene-π-cyclopentadienylcobalt and 1,3,6-cyclooctatriene-π-indenyl cobalt. In these reactions it is suggested that C_8H_8 is first displaced by the C_5H_6 or indene followed by a cobalt assisted H migration. This is related to the formation of $[Co(C_7H_9)(C_8H_{12})]$ described above.

The previously mentioned π-allylic cobalt(I) complex $[Co(C_8H_{13})(C_8H_{12})]$ has been prepared by electrolysis of $Co^{II}(acac)_2$ in the presence of 1,5-C_8H_{12}[69]. It is also reported that heating (60°) of $[Co(C_8H_{13})(C_8H_{12})]$ in 1,5-C_8H_{12} produces cyclooctene and a π-bicyclo[3.3.0]octadienyl-1,5-cyclooctadienecobalt.



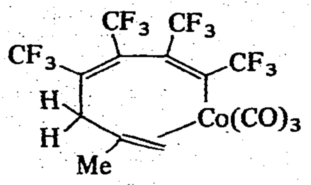
Reaction of [π-allylCo(CO)$_3$] and [(π-C_4H_7)Co(CO)$_3$] with C_2F_4 and CF_3—CF=CF_2 results in a formal insertion of the fluoroolefin into the C–Co σ-bond of the allyl system to give stable σ,π-alkylCo(CO)$_3$ complexes[70].





R = H or Me

These compounds react with PPh_3 to form σ-bonded derivatives such as $CH_2{=}C(R)CH_2CF_2CF_2Co(CO)_3PPh_3$ (R = H, Me). Insertion reactions of π-allylic complexes have been implicated in the catalytic formation of hexadienes with both Rh and Ni catalysts. It was also found that $CF_3C{\equiv}CCF_3$ reacts with $[(\pi\text{-}C_4H_7)Co(CO)_3]$ to form the illustrated complex in which two molecules of the acetylene are inserted between the cobalt atom and the allyl group.



It is suggested that an ionic mechanism can best explain the formation of this complex.

When cationic Co^I derivatives such as $[Co(bipy)_3]^+$ or $[Co(o\text{-}phen)_3]^+$ are treated with H_2 in the presence of PR_3, the cationic species $[Co^{III}(chel)(PPh_3)_2H_2]^+$ are obtained[71] (chel = bipy or *o*-phen).

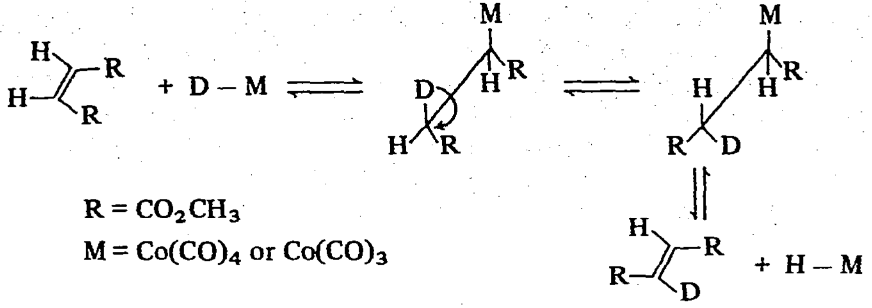
Reaction of this with butadiene or isoprene affords $[Co(chel)L(diene)]^+$ species which can also be obtained directly from the $[Co(chel)_3]^+$ cations. All these reactions may be reversed by addition of excess chelate.

Using a variety of complexes $[MX_2(PPh_3)_2]$ (where M = Fe, Co, Ni; X = Cl, Br, I) as catalysts for the homogeneous hydrogenation of 1,3- and 1,5-C_8H_{12} and cyclooctane, organic compounds have been used as hydrogen sources[73]. The main advantage of this type of transfer-hydrogenation is that milder reaction conditions are possible. As hydrogen donors, *o*- and *p*-dihydroxybenzene were found to be superior to alcohols.

The hydrogenation of butadiene by $[Co^{II}(CN)_5]^{3-}$ selectively produces 1-butene in the presence of excess CN^-, and *trans*-2-butene in the presence of a smaller quantity of CN^- ($CN^-/Co > 5$). Proposed mechanisms involve intermediate formation of σ-2-butenyl, π-(1-methylallyl)- or σ-1-methyl-2-propenylcobalt derivatives. A ^1H NMR study of the reaction in D_2O and H_2O at 0° under an atmosphere of H_2 and butadiene has been carried out[74]. For a ratio $CN/Co > 5$ the spectra revealed two complexes in similar amounts, postulated to be *cis*- and *trans*-σ-2-butenylpentacyanocobaltate(III). The spectrum for a ratio $CN/Co < 5$ showed that the complex formed is *syn*-π-(1-methylallyl)tetracyanocobaltate(III). Addition of excess CN^- caused the first demonstration of the conversion of a π-1-methylallyl to a σ-2-butenyl complex. Preliminary rate comparisons with that of butene formation suggests that σ-2-butenyl complexes are not direct intermediates in 1-butene formation and that the π-1-methylallyl complex is the most probable intermediate for formation of *trans*-2-butene.

The selectivity of the hydrogenation has also been found to be solvent dependent[75]. Studies of water and alcohol solvents show that the former promotes 1-butene formation, whereas methanol and ethylene glycol give higher yields of *cis*-2-butene.

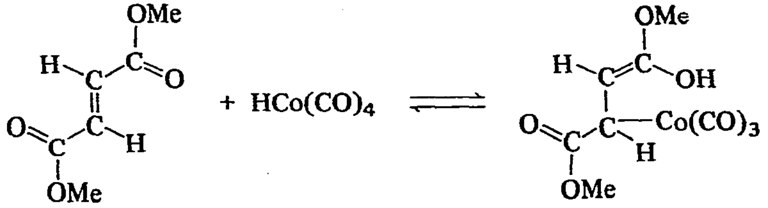
Homogeneous olefin isomerisation catalysed by $[HCo(CO)_4]$ has provided evidence for at least three mechanisms; 1,3-internal hydride shift, external 1,3-allyl exchange and 1,2-addition–elimination. The isomerisation of dimethylmaleate by $[DCo(CO)_4]$ has been studied and yields deuterated dimethylfumarate and dimethylsuccinate and undeuterated dimethylmaleate[76]. Such results are compatible with a 1,2-*cis*-addition–elimination of $DCo(CO)_4$.



$R = CO_2CH_3$

$M = Co(CO)_4$ or $Co(CO)_3$

The hydrogenation of the maleate and fumarate catalysed by $[HCo(CO)_4]$ was also investigated and led to the conclusion that whereas addition of the hydride to maleate proceeded predominantly via 1,2-addition, the fumarate was attacked in a 1,4-fashion.



Cobalt hydrides of the general formula $[CoH(CO)_{4-n}(P(n\text{-}Bu)_3)_n]$ ($n = 2, 3$) have been prepared[77]:

$$[Co(CO)_3P]_2 + H_2 + P \rightarrow CoH(CO)_2P_2$$

$$(RCOO)_2Co + P + CO + H_2 \rightarrow \text{dark yellow oil}$$

$$\Big\downarrow \begin{array}{l} P,\ H_2 \\ CH_3CH{=}CH_2 \\ 120° \end{array}$$

$$[CoH(CO)P_3]$$

The triphosphine complex is capable of abstracting CO from linear aldehydes; a reaction known for rhodium and ruthenium phosphine complexes.

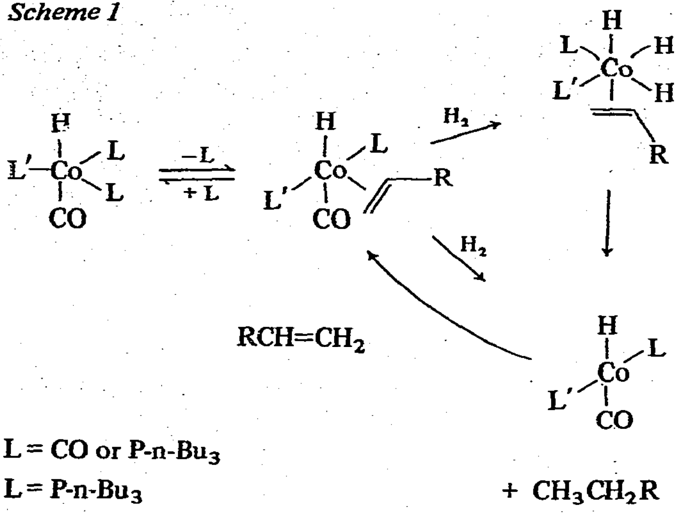
$$[CoH(CO)P_3] + RCH_2CH_2CHO \rightleftharpoons [CoH(CO)_2P_2] + RCH{=}CH_2 + H_2 + P$$

In the presence of carbon monoxide, a series of reversible reactions occurs at room temperature involving stepwise replacement of phosphine ligands. Reaction of the cobalt hydrides with butadiene affords π-allyl complexes:

$[HCo(CO)_{4-n}P_n] + C_4H_6 \longrightarrow$  $-Co(CO)_{4-n}P_{n-1}$

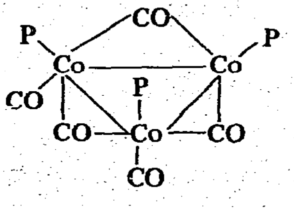
The hydrides also function as catalysts for the homogeneous hydrogenation of olefins, alkynes and aldehydes, and the isomerisation of olefins. The observed overall rates are diminished by excess phosphine, a fact that implies a dissociative pathway. The complex $[CoH(CO)_2P_2]$ has a lower selectivity than the Rh and Ir analogues, which only hydrogenate terminal double bonds, this probably reflecting less steric hindrance in the cobalt complex. The cobalt systems show a low mobility of the cobalt–hydrogen bond in the presence of olefins and H_2. This would exclude an insertion mechanism of olefin into the M–H bond as has been postulated for the Rh and Ir complexes. The mechanism suggested for the hydrogenation is summarised in Scheme 1, but the isomerisation pathway is as yet unclarified.

Scheme 1

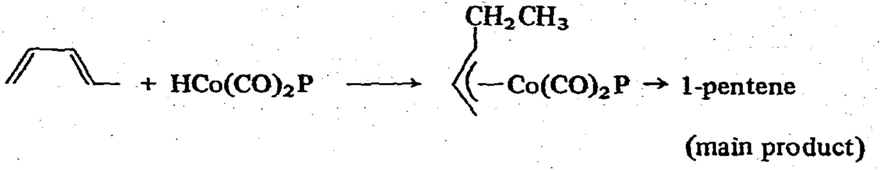


L = CO or P-n-Bu_3
L = P-n-Bu_3

The hydrogenation of aldehydes is also thought to proceed via coordination at the vacant site of the metal. During the hydroformylation of olefins catalysed by the system $Co_2(CO)_8/PR_3$ at temperatures > 110°, trimeric complexes have been obtained, formulated as $[Co(CO)_2PR_3]_3$ (where R = n-Bu, Ph)[78]. These complexes are also formed by direct hydrogenation of $[(\pi\text{-allyl})Co(CO)_2(PR_3)]$. An X-ray study has confirmed the structure as being:

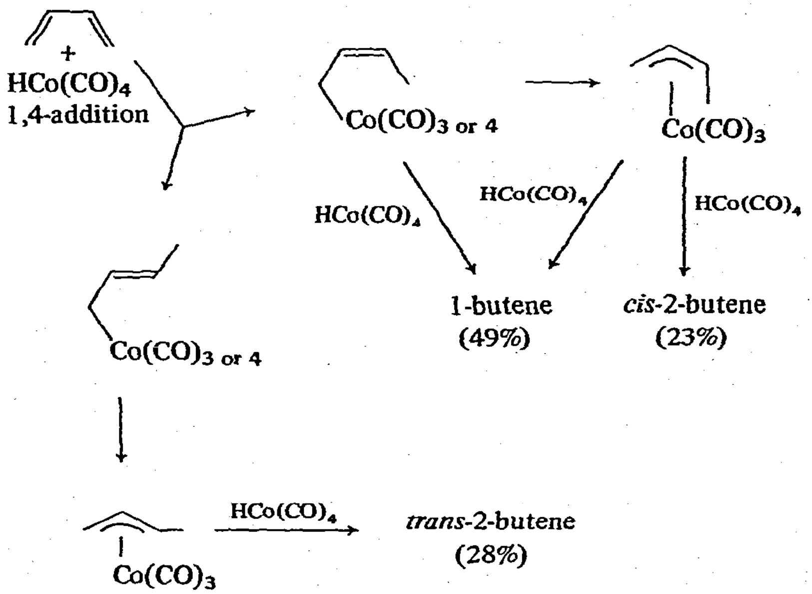


Its reactions are typical of coordinate unsaturation; CO, phosphines, dienes and H_2 being readily added. Under a pressure of H_2, the trimeric species exhibit catalytic activity towards the hydrogenation and isomerisation of olefins, and the hydrogenation of aldehydes. The hydrogenation reactions are effectively catalysed by an initially formed hydrido species [CoH(CO)$_2$P]. Conjugated dienes are reduced selectively, and the results indicate a preferential 3,4-addition of the Co–H system via a π-allylic intermediate:



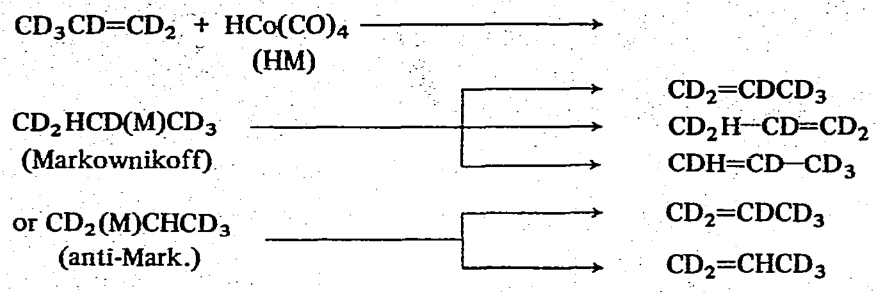
The isomerisation system appears complex and isomeric activity is very high under a N_2 atmosphere.

The species [HCo(CO)$_4$] is regarded as a catalytic intermediate in high-pressure hydroformylation reactions involving cobalt systems, but whereas dihydroformylation of butadiene has been achieved with a Rh catalyst, this does not occur with [HCo(CO)$_4$] since hydrogenation to butenes is the first reaction, the monoolefins then being hydroformylated. The mechanism of hydrogenation of butadiene catalysed by [HCo(CO)$_4$] has been studied. Reaction of the diene + HCo(CO)$_4$ was found to yield *syn* + *anti* (π-1-methylallyl)Co(CO)$_3$, which react with more [HCo(CO)$_4$] to give butenes. However, the butene isomeric distribution obtained in hydrogenation requires another intermediate, postulated as a σ-allyl species.



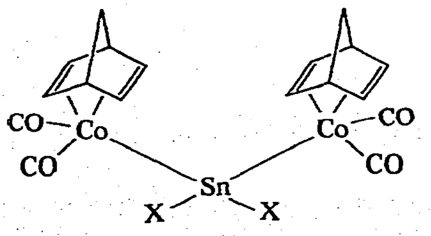
The range of butene isomers formed contrasts with the selectivity shown by the cobalt systems [HCo(CO)$_2$P] described above.

Further evidence for a 1,2-addition–elimination mechanism for the isomerisation of olefins catalysed by [HCo(CO)$_4$] has been provided by using the substrate propene-d_6[80]. The experiments, conducted in the vapour-phase in order to control the concentration of CO, resulted in considerable incorporation of H on to the central carbon atom. In the absence of CO, analysis of the aldehydic products showed approximately 70% of the addition of [$HCo(CO)_4$] which occurred in the Markownikoff manner.



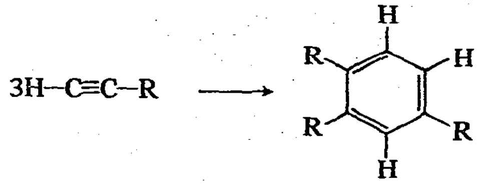
The formation of by-products in the one-step synthesis of primary alcohols from olefins and H_2/CO (synthesis gas) is completely suppressed by use of a catalytic system consisting of a mixture of $Co_2(CO)_8$, $Fe(CO)_5$ and *N*-methylpyrrolidine[81]. This complex catalyst strongly favours hydrogenation of the aldehyde intermediates to the alcohols, avoiding side reactions such as aldol condensation.

$Co_2(CO)_8$ has been shown to be a catalyst for the hydrogenation of acid anhydrides[82]. The reduction of aromatic nitrogen compounds by $NaBH_4$ is catalysed by either $CoBr_2$ or [$Co(DMG)_2$][83]. The effect of the cobalt may either be due to complexation with the nitrogen-containing species, thus facilitating reduction, or the reducing system may be a cobalt hydride. Investigation of the catalytic dimerisation of propene using catalysts of the type alkylaluminium halides, cobalt (or nickel) halides–alkylaluminiums, $CoCl_2$–$AlCl_3$, $CoCl_2$–$AlCl_3$–Al-alkyls or NiO–alumina–silica has shown that the cobalt and nickel salts cause a high selectivity[84]. Typical reactions yield a mixture of 30% n-hexenes and 70% methylpentenes, and a cationic mechanism is postulated for the process. The complexes [$X_2Sn\{Co(CO)_4\}_2$] (X = Cl, or Ph) are known to behave as multicentre catalysts for the dimerisation of bicyclo[2.2.1]heptadiene and NBD complexes have been isolated [$X_2Sn\{Co(CO)_2C_7H_8\}_2$]. Single-crystal X-ray diffraction studies of these two NBD complexes have been carried out[85]. Coordination at tin is approximately tetrahedral and the Co–Sn–Co angle is less for X = Ph than for X = Cl, a variation that was previously postulated on the basis of second-order hybridisation effects. This difference in angle, and the shorter Co–Sn bond distances for X = Cl are probably relevant to the catalytic behaviour of the two systems, since, for X = Cl, the dimerisation is stereospecific giving only Binor-S, whereas, for X = Ph, a mixture of dimers is obtained.



The catalytic system produced *in situ* by reduction of CoX_2 with powdered Mn or Fe–Mn alloys causes trimerisation of acetylenes[86]. Another catalytic species is

$[(CoL_2)(S)_x]$ (where L = maleic, fumaric or acrylic ester and (S) = solvent, *e.g.* DMF, MeCN). The trimerisation is highly selective and no other oligomeric or polymeric species are formed



(95%)

The synthesis of the first examples of perchlorato $M^I(d^8)$ (M = Co, Ph or Ir) complexes have been reported[87].

$$[CoCl(CO)_2(PPh_3)_2] + AgClO_4 \rightarrow [Co(OClO_3)(CO)_2(PPh_3)_2]$$

$$\underset{\text{(or Ir)}}{[RhCl(CO)(PPh_3)_2]} + AgClO_4 \rightarrow \underset{\text{(or Ir)}}{[Rh(OClO_3)(CO)(PPh_3)_2]}$$

Infrared spectra indicate a covalent linkage of perchlorato ligand and this is readily displaced by, for example, PPh_3. The complexes thus serve as versatile precursors for a variety of complexes. In polar solvents such as acetone, nitromethane, methanol, the rhodium and iridium complexes undergo complete dissociation.

$$[M(OClO_3)(CO)P_2] + (S) \rightarrow [M(S)(CO)P_2]^+ClO_4^-$$

M = Rh, Ir; (S) = solvent; P = PPh_3

Reaction of the complexes $[M(NO)(PPh_3)_3]$ (M = Co, Rh or Ir) with *o*- or *p*-quinones (L) leads directly to the complexes $[M(NO)P_2L]$[88].

The preparation of $[Rh_2(OAc)_2(DMG)(PPh_3)_2]$ from $[Rh_2(OAc)_4(H_2O)_2]$ by successive reactions with dimethylglyoxime and PPh_3 has been reported, together with the determination of its structure by X-ray diffraction[89]. The molecule is shown to contain bridging acetate linkages with staggered DMG groups.

Treatment of $[Rh(CO)_2Cl]_2$ with CN^- results in the formation of $[RhH(CN)_5]^{3-}$ which has been isolated as the sodium, potassium, rubidium and caesium salts[90]. The ^1H NMR, Raman and infrared spectra of the reactions reveal the existence of the three long-lived solution species $[Rh(CO)_2(CN)Cl]^-$, *trans*-$[Rh(CO)_2(CN)_2]^-$ and $[Rh(CO)(CN)_3]^{2-}$.

In the presence of base, bidentate salicylaldimines, H Sal=NR (R = alkyl, aryl), react with $[Rh(CO)_2Cl]_2$ or $[M(C_8H_{12})Cl]_2$ (M = Rh, Ir) to yield the chelate compounds $[Rh(CO)_2(Sal{=}NR)]$ and $[M(C_8H_{12})(Sal{=}NR)]$[91]. A more efficient route to these compounds involves bridge-splitting reaction of the chlorobridge with thallium(I) Schiff-base derivatives $Tl^ISal{=}NR$. The potential tetradentate Schiff-base *N,N'*-ethylenebis(salicylaldimine), H_2Salen, yields the binuclear derivatives $[M(CO)_2]_2$Salen and $[Rh(C_8H_{12})]_2$Salen.

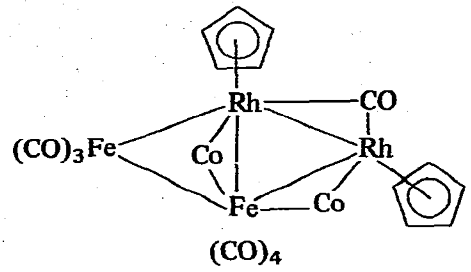
An improved synthesis of $[Rh_4(CO)_{12}]$ has been reported[92]. This is conducted at atmospheric pressure and room temperature and involves reduction of $[Rh^{III}Cl_6]^{3-}$ to

$[Rh(CO)_2Cl_2]^-$ followed by further reduction with CO and H_2O in presence of sodium citrate buffer, giving yields of approximately 90%.

$$\begin{array}{c} [RhCl_6]^{3-} + Cu + CO \rightarrow [Rh(CO)_2Cl_2]^- \\ \qquad\qquad\qquad\qquad\downarrow \text{CO, } H_2O \\ \qquad\qquad\qquad\qquad Rh_4(CO)_{12} \end{array}$$

The structure of $[N\text{-}n\text{-}Bu_4][Rh_6(CO)_{15}I]$ has been determined by X-ray methods[93]. The cluster anion $[Rh_6(CO)_{15}I]$ has a structure closely related to that of $[Rh_6(CO)_{16}]$, with four CO ligands each bridging three metal atoms on alternate faces of the octahedron and the remaining CO groups and the iodine acting as unidentate ligands.

X-ray diffraction studies have also been used to determine the molecular structure of $[(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8]$[94]. The metal atoms define an irregular tetrahedron and the $\pi\text{-}C_5H_5$ and a bridging CO group associated with the two Rh atoms. An unusual feature is the presence of two asymmetric carbonyl bridges between Fe and Rh:

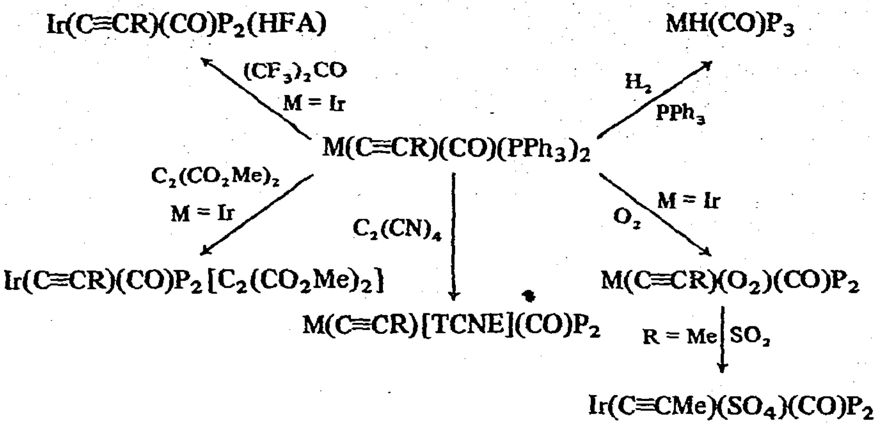


When rhodium and platinum halides are heated in DMF as solvent, the resulting solutions have been found to contain carbonyl halo species[95]. These solutions prove to be convenient starting materials for the synthesis of a variety of carbonyl complexes, for example, $[Rh(CO)_2Cl_2]^-$, *trans*-$[RhL_2(CO)Cl]$, and $[RhL(PPh_3)(CO)]$.

The acetylide complexes $[M(C{\equiv}CR)(CO)(PPh_3)_3]$ and $[M(C{\equiv}CR)(CO)(PPh_3)_2]$ (M = Rh or Ir; R = alkyl) have been prepared by direct reaction of 1-alkynes with $[MH(CO)P_3]$ and $[IrH(CO)_2P_2]$[96]. These reactions probably involve the oxidation addition of $RC{\equiv}CH$ to the metal to give a *cis*-dihydride complex followed by elimination of hydrogen. The acetylide complexes may also be prepared by direct reaction of the 1-alkyne with the π-allyl species $[Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2]$, when propene is eliminated, presumably by a similar oxidative-addition route involving a transient σ-allyl species:

$$\begin{array}{ccc} Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2 & \xrightarrow{RC\equiv CH} & [IrH(\sigma\text{-}C_3H_5)(C{\equiv}CR)(CO)(PPh_3)_2] \\ & & \downarrow -C_3H_6 \\ & & [Ir(C{\equiv}CR)(CO)(PPh_3)_2] \end{array}$$

However, even in the presence of Et_3N, *trans*-$[IrCl(CO)(PPh_3)_2]$ failed to form an adduct with 1-propyne:



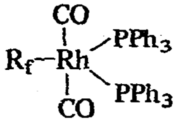
Hexafluoro-1,3-butadiene and $CF_3CF{=}CFCF_3$ react similarly to hexafluoroacetone, in affording 1/1 adducts, but $CF_3C{\equiv}CCF_3$ polymerises as well as forming an adduct.

Treatment of $[Rh(CO)_2Cl]_2$ with PPh_3 or PMe_3(L) has been reported to give a mixture of complexes, including *cis*-[Rh(CO)₂LCl] and the dimeric species $[Rh(CO)LCl]_2$[97].

Studies of the complex previously formulated as *trans*-$[Rh(CO)_2(PPh_3)Cl]$ have led to the revision of its formulation as the dimer $[RhCl(CO)PPh_3]_2$[98]. Evidence for this is provided by the molecular weight in $CHCl_3$ or C_6H_6 and the reaction with Lewis base ligands without evolution of CO:

Complex + L $\rightarrow$ *trans*-$[Rh(CO)Cl(PPh_3)L]$
(where L = $AsPh_3$, py, or Me_2S).

The anion $[Rh(CO)_2(PPh_3)_2]^-$ has been shown to be a strong nucleophile of similar power to that of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ or $[(\pi\text{-}C_5H_5)Ru(CO)_2]^-$[99]. It is formed by sodium amalgam reduction of $[Rh(CO)_2(PPh_3)_2]_2$. The anion reacts with perfluoroaromatics to afford σ-Rh complexes as yellow air-stable crystalline solids.



(where $R_f = C_6F_5$, *p*-C_6F_4X, *m*-$C_6F_3(NC)_2$, C_5F_4N, or $C_5F_3(NC)N$).

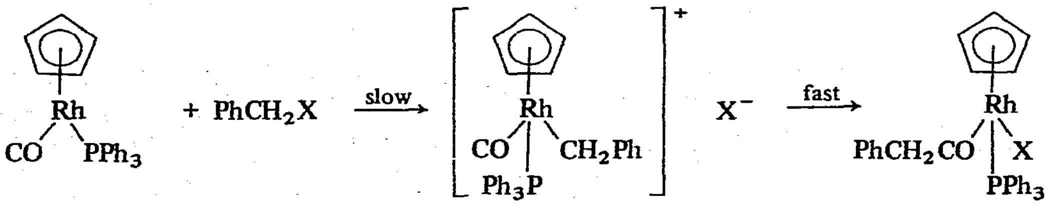
Use of the molecular fluoro-complexes *trans*-$[MF(CO)(PPh_3)_2]$ (M = Rh, Ir) as substrates for reactions with a wide variety of univalent anions (X^-) has led to the isolation of the complexes *trans*-$[M(X)(CO)(PPh_3)_2]$[100]. Correlation of ν(CO) with the "total electronegativity" of X has been suggested and leads to the order of π-acidity $I > SePh > Br > SPh > CN > Cl > NO_2 > NCS \sim N_3 > ONO_2 > NCO > OCO(Me) > OCOPh > OPh > OH = F$ for both Rh and Ir complexes. The complexes *trans*-$[MX(CO)P_2]$ (where M = Rh, Ir; X = BH_3CN or BH_4; P = PPh_3, or $P(C_6H_{11})_3$) have been prepared directly from the perchlorato derivatives $[M(OClO_3)(CO)P_2]$[101]. Infrared spectra indicate that BH_4^- is coordinated through a double hydrogen bridge, *i.e.* MH_2BH_2. The BH_3CN anion is apparently coordinated to the metal via the N-atom. The isolation of metal hydrido derivatives from the syntheses under certain conditions suggests that reaction with BH_4^- and BH_3CN^- proceeds via metal–hydroborato intermediates.

In benzene solution at 20°, the complexes $[MCl(CO)P_2]$ (where M = Rh or Ir; P = PPh_3 or $P(OPh)_3$) exchange their phosphine ligands with $P(C_6H_{11})_3$ and PPh_3, the former phosphine exchanging only with the Rh complex[102].

The dissociation of the phosphines is much greater in the rhodium complexes than in the analogous iridium compounds and this observation is relevant to the greater catalytic activity of the rhodium complex towards hydrogenation.

The low temperature ^{31}P NMR spectra of the complexes *trans*-$[MCl(CO)(PR\text{-}t\text{-}Bu_2)_2]$ (M = Rh, Ir; R = Me, Et or n-Pr) show the presence of three rotamers with very different chemical shifts[103]. It is suggested that in complexes of this type an energy barrier to rotation about the M–P bond of several $kcal \cdot mol^{-1}$ exists due to interaction with the *cis* Cl or CO ligands. For complexes of the type *trans*-[RhCl(CO)(t-phosphine)$_2$] there is a linear correlation between the ^{31}P chemical shifts for the free phosphine and the change in chemical shift on coordination. At present this linear relationship cannot be explained theoretically[104].

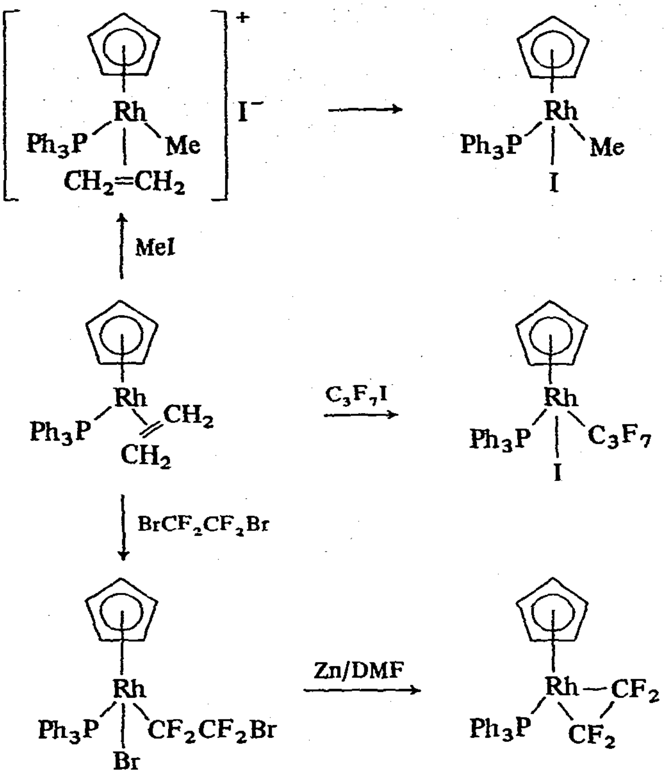
The oxidative addition of benzyl and alkyl halides (RX) to $[Rh(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]$ yields acyl complexes of the form $[Rh(COR)X(PPh_3)\text{-}\pi\text{-}C_5H_5]$. In the case of the benzyl halides, which have the relative reactivities $Cl \ll Br < I$, the rate-determining step involves the formation of a cationic alkyl to rhodium σ-bonded complex via an S_N2 type transition state; the benzyl group rapidly migrating on to the coordinated carbon monoxide to give the isolated acyl complex.



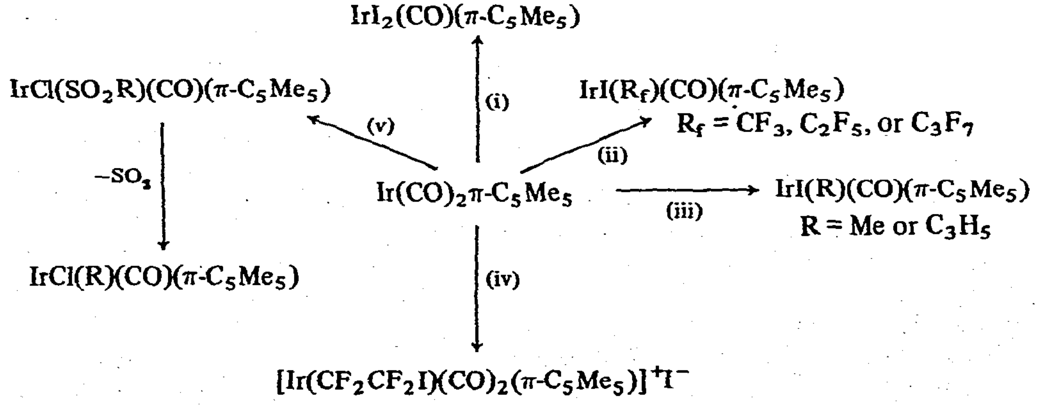
In contrast, allyl bromide and chloride undergo a rapid reversible reaction to form a cationic complex, which only slowly affords the acyl complex[105].

Whereas, chloroacetonitrile and benzenesulphonyl chloride undergo the expected oxidative reactions with $[Rh(CO)_2\text{-}\pi\text{-}C_5H_5]$ and $[Rh(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]$, hydrogen chloride reacts but with cleavage of the cyclopentadienyl group as C_5H_6, and the formation of $[Rh(CO)_2Cl]_2$ and $[Rh(CO)(PPh_3)Cl]_2$ respectively[106]. The intermediacy of a cationic hydride in these reactions is indicated by the isolation of $[IrH(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]^+$ on reaction of $[Ir(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]$ with HCl. It was concluded that the oxidation of rhodium(I) complexes containing the C_5H_5 ligand is not as easy as that of complexes of the type $[RhXL_3]$ and *trans*-$[RhX(CO)L_2]$, and that the nucleophilicity of the metal is greater in $[Rh(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]$ than in $[Rh(CO)_2\text{-}\pi\text{-}C_5H_5]$.

It is suggested[107a] that ionic intermediates are also involved in oxidative-elimination reactions of $[Rh(C_2H_4)(PPh_3)\text{-}\pi\text{-}C_5H_5]$, although as illustrated only in the case of the reaction with methyl iodide were these isolated. Whereas, the ethylene complex reacts with HI to give only $[RhI_2(PPh_3)\text{-}\pi\text{-}C_5H_5]$, the corresponding reaction of the tetrafluoroethylene complex gives a tetrafluoroethylene derivative $[Rh(CF_2CF_2H)I(PPh_3)\text{-}\pi\text{-}C_5H_5]$.



The development of synthetic routes to pentamethylcyclopentadienyl-rhodium and -iridium dicarbonyl complexes has led to the examination of their oxidative-addition reactions.



Reagents (i) I_2; (ii) R_fI; (iii) RI; (iv) ICF_2CF_2F; (v) RSO_2Cl

Whereas King and Efraty[107b] report that the reaction of $[Ir(CO)_2(\pi\text{-}C_5Me_5)]$ with MeI give a σ-methyliridium complex and $[IrI_2(CO)(\pi\text{-}C_5Me_5)]$, Maitlis and Kang[107c] obtained a cationic adduct $[Ir(Me)(CO)_2(\pi\text{-}C_5Me_5)]^+I^-$, which reverted to the starting materials in the solid state. The rhodium complex $[Rh(CO)_2(\pi\text{-}C_5Me_5)]$ reacted with MeI to give an acetyl complex $[RhI(COMe)(CO)(\pi\text{-}C_5Me_5)]$.

An X-ray crystal structure determination of chlorocarbonyl(sulphurdioxide)bis-(triphenylphosphine)rhodium indicated an unusually long and presumably weak metal–sulphur bond. Following this, calorimetric studies suggest that the rhodium to sulphur bond strength is approximately 30 kcal less than *trans*-Rh–S bonds in, for example, thiourea complexes[108].

Paramagnetic rhodium(II) complexes of the type *trans*-$[RhCl_2(P\text{-}t\text{-}Bu_2R)_2]$ (R = Me, Et, or n-Pr) are rapidly formed on treating ethanolic rhodium(III) chloride trihydrate with the tertiary phosphine at 25° [109]. The complexes have low magnetic movements in the solid state but in solution *trans*-$[RhCl_2(P\text{-}t\text{-}Bu_2Me)_2]$ has the expected moment of 2.12 B.M. A square planar *trans*-stereochemistry is suggested. A similar bivalent rhodium complex, *trans*-$[RhCl_2\{P(o\text{-}tolyl_3\}_2]$, has been obtained by the reaction of an excess of tri-*o*-tolylphosphine with rhodium trichloride.

Examination of molecular models suggests that in complexes of the type *trans*-$[RhCl_2(P\text{-}t\text{-}Bu_2R)_2]$, the t-butyl groups lie above and below the plane of the complex and block the two octahedral sites. The stability of these complexes is attributed to this effect. The reaction of rhodium trichloride trihydrate with t-butylphosphine in refluxing 2-propanol gives square pyramidal hydridorhodium(III) complexes $[RhHCl_2L_2]$. The five-coordinate species $[RhHCl_2(P\text{-}t\text{-}Bu\text{-}n\text{-}Pr_2)_2]$ reacts with various donor ligands to give six-coordinate complexes. Addition of strong base to solutions of complexes of the type $[RhHCl_2L_2]$ in ethanol or methanol gives *trans*-$[RhCl(CO)L_2]$.

The dissociation of $[RhCl(PPh_3)_3]$ in solution [into $RhCl(PPh_3)_2$ and PPh_3] has been a subject of considerable interest and controversy. Recent NMR measurements[110] and chemical evidence[111] indicate that the degree of dissociation in solvents such as benzene and chlorinated hydrocarbons is much smaller than suggested by earlier molecular weight measurements. This is supported by a spectrophotometric measurement[112] of the equilibrium constant for the dissociation $[RhCl(PPh_3)_3] \rightleftharpoons [RhCl(PPh_3)_2] + PPh_3$, which gave a value of $(1.4 \pm 0.4) \times 10^{-4} M$ in benzene at 25°.

An X-ray crystal structure determination of bromo(tri-*o*-vinylphenyl)-phosphinerhodium(I) has shown that the six olefinic carbons are almost coplanar with and equidistant from the rhodium; the geometry around the rhodium being essentially trigonal bipyramidal[113].

A detailed paper on the atmospheric pressure synthesis of a number of PF_3 complexes of rhodium and iridium has appeared[114]. A quantitative yield of $[RhCl(PF_3)_2]_2$, which was previously accessible in only low yield, is obtained by displacement of cyclooctene from $[RhCl(C_8H_{14})_2]_2$ with phosphorus trifluoride. A similar reaction with $[IrCl(C_8H_{14})_2]_2$ gives as a formal product a five coordinate complex $[IrCl(PF_3)_4]$, which on warming affords $[IrCl(PF_3)_2]_2$. The preparation of mononuclear complexes such as $[M(acac)(PF_3)_2]$ and $[Rh(PF_3)_2\text{-}\pi\text{-}C_5H_5]$ is also described. The complexes $[RhCl(PF_3)_2]_2$ (in the presence of PF_3) and $[IrCl(PF_3)_4]$ are reduced by K/Hg in ether to give $K[M(PF_3)_4]$ via $Hg[M(PF_3)_4]_2$. The latter react with $[RhCl(PF_3)_2]$ (with PF_3) or $[IrCl(PF_3)_4]$ to give the dimeric metal–metal bonded complexes $[Rh_2(PF_3)_8]$ and

$[Ir_2(PF_3)_8]$, which are probably isostructural to the isomer of $Co_2(CO)_8$ without bridging carbonyl ligands. Five-coordinate metal-metal bonded complexes of general formula $[RM(PF_3)_4]$ [M = Rh, Ir; R = Ph_3Sn or Ph_3PAu; M = Ir; R = Ph_3Pb] can be made by reaction of $[M(PF_3)_4]^-$ with RCl. A more general route to compounds containing bonds between rhodium or iridium and Group IV elements is the reaction between $[M_2(PF_3)_8]$ and the Group IV hydrides:

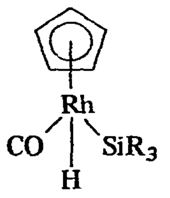
$$[M_2(PF_3)_8] + RH - [RM(PF_3)_4] + [HM(PF_3)_4]$$

$R = Ph_3Si, (EtO)_3Si, Cl_3Si$ or Ph_3Ge

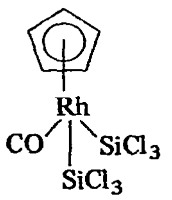
The preparation of some chlororhodium(I) complexes with diethylaminodifluorophosphine, $PF_2 \cdot NEt_2$ have been described[115]. Treatment of $[RhCl(PPh_3)_3]$ with PF_2NEt_2 (1/1 mol ratio) gives $[RhCl(PF_2NEt_2)(PPh_3)_2]$, however, excess PF_2NEt_2 affords *cis*-$[RhCl(PF_2NEt_2)_2(PPh_3)]$, whose X-ray crystal structure is reported. The ethylene complex $[RhCl(C_2H_4)_2]_2$ reacts with excess PF_2NEt_2 to give the chloro-bridged dimer $[RhCl(PF_2NEt_2)_2]_2$, which reacts with PPh_3 to form *cis*-$[RhCl(PF_2NEt_2)_2(PPh_3)]$. It is concluded that in its chemistry PF_2NEt_2 resembles phosphites, which form both $[RhClL'_3]$ and $[RhClL'_2]_2$ (L' = phosphite) derivatives, rather than PF_3.

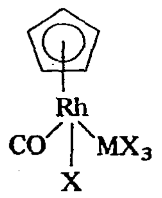
The variable temperature NMR spectra of the complexes $[HM(PF_3)_4]$ (M = Co, Rh, Ir) have been examined[116]. A preliminary analysis, with the Eyring equation of the ^{19}F NMR line shape has provided an estimate of the barrier to rearrangement, which is considered to involve a hydrogen atom traverse of MP_4 "tetrahedral" faces; the barriers largely reflect the force constants for the MP bending modes involved in the changes in the phosphorus position during the rearrangement.

Ultraviolet irradiation of solutions of $[Rh(CO)_2\text{-}\pi\text{-}C_5H_5]$ and triphenyl- and tribenzylsilane leads to the formation of the hydrido complexes illustrated[117].



(R = Ph, $PhCH_2$)





(M = Ge, Sn; X = Cl, Br, I)

In contrast, trichlorosilane, gives a bis-silyl derivative, which is presumably formed via a Ph–H species. The germanium and tin halides MX_4 react oxidatively with $[Rh(CO)_2\text{-}\pi\text{-}C_5H_5]$ to afford the illustrated Rh^{III} complexes.

A series of neutral and anionic rhodium–germanium bonded compounds have been obtained by oxidative-addition, for example $[RhCl(EPh_3)] + R_3GeH \rightarrow [RhH(Cl)(GeR_3)(EPh_3)]$ (E = P, As; R = Me, Et, Cl). The stannane $n\text{-}Bu_3SnH$ reacts in a similar way, but Me_3SnH is decomposed to hydrogen and Me_6Sn_2. Trichlorosilane and $[RhCl(C_8H_{12})]_2$ afford $[RhCl(SiCl_3)_2(C_8H_{12})]$, whereas, with $[Rh(1,5\text{-}C_8H_{12})\text{-}\pi\text{-}C_5H_5]$ a cyclooctene derivative $[Rh(SiCl_3)_2(C_8H_{14})\text{-}\pi\text{-}C_5H_5]$ is formed[118].

Hexamethylditin reacts with dicarbonyl-π-cyclopentadienylcobalt or -rhodium to form $[M(CO)(SnMe_3)\text{-}\pi\text{-}C_5H_5]$. In addition the dinuclear complexes $[M(CO)(SnMe_2)\text{-}\pi\text{-}C_5H_5]_2$

were formed by extrusion of $SnMe_4$. The dinuclear complexes, which contain the previously unreported four-membered $\overline{\text{SnCoSnCo}}$ ring structure are formed as a mixture of *cis* and *trans* isomers[119]. A similar oxidative reaction was observed with $Fe(CO)_5$ and Me_6Sn_2 to give the known complex $[Fe(SnMe_3)_2(CO)_4]$.

The reaction of $SnCl_2$ with $[RhCl(C_7H_8)]_2$ in the presence of a tertiary phosphine or arsine ligand (L) leads to a variety of five-coordinate monomers of the type $[RhSnCl_3(C_7H_8)L_2]$[120]. The preparation of $[RhSnCl_3(\text{butadiene})_2]$ and $[RhSnCl_3(CO)(SbPh_3)]$ is also described.

Rhodium(I) and iridium(I) complexes of the tripodal ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (TDPME) of the type [MCl(CO)(TDPME)] have been synthesised[121]. The iridium(I) complex appears to be five-coordinate in the solid state but to be capable of dissociating a phosphine ligand in solution. The rhodium(I) complex is a mixture of four- and five-coordinate isomers (with TDPME) as either a bidentate or a tridentate ligand, both in the solid state and in solution. Both the rhodium and iridium complexes react with carbon monoxide to form dicarbonyl species. Reactions with oxygen, sulphur dioxide–oxygen, and *p*-nitrobenzoyl azide, which yield (bidentate) carbonato, sulphato, and isocyanato complexes, have also been examined.

A series of complexes of the type $[M(TTAS)X_3]$ (TTAS = bis(*o*-dimethylarsinophenyl)-methylarsine, M = Rh; X = Cl, Br, I or NO_3; M = Ir; X = Cl) have been prepared. The complexes are non-electrolytes, and some exist in both *fac*- and *mer*-isomeric forms[122].

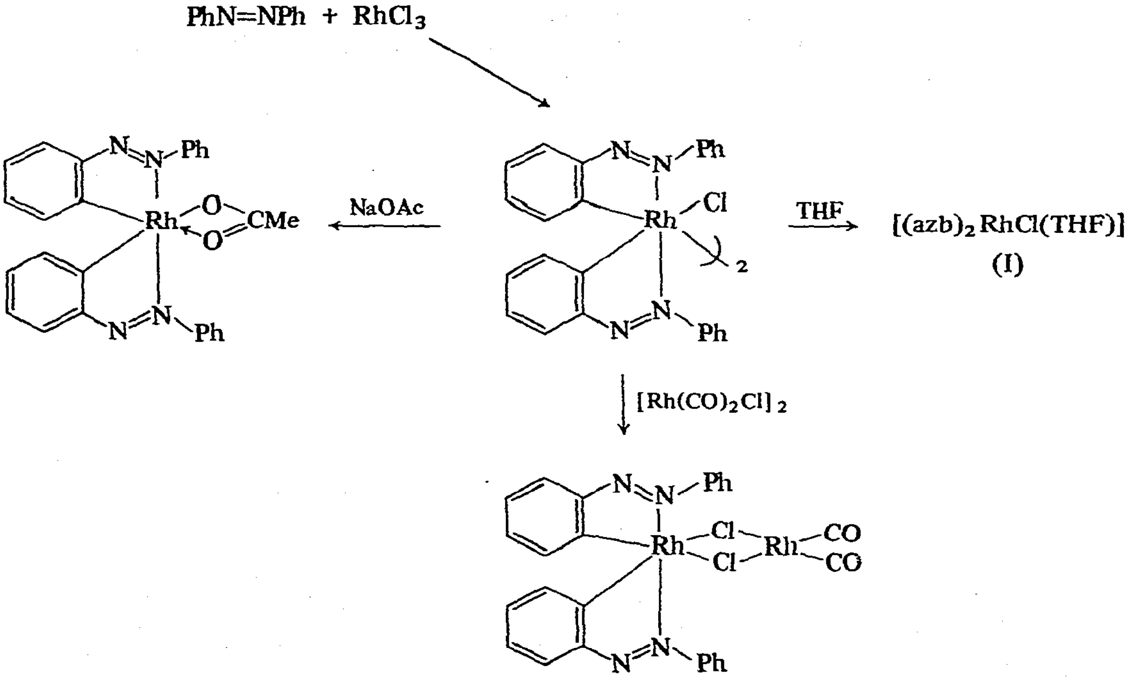
The characterisation of several monomeric, diamagnetic complexes which appear to contain an intact P_4 molecule bonded to a rhodium atom, has been reported[123]. Reaction of compounds of the type $[RhClL_3]$ (L = PPh_3, $P(C_6H_4Me)_3$(*p*- and *m*-) and $AsPh_3$) with white phosphorus in methylene chloride afforded the air-sensitive compounds. The P_4 is easily displaced by carbon monoxide, and PEt_3 or diphos displace both P_4 and triphenylphosphine.

$$\begin{tikzcd}
{[RhClL_3] + P_4} \arrow[r, "-L"] & {[RhCl(P_4)L_2]} \arrow[r, "CO"] \arrow[d, "\text{diphos}"] & {[RhCl(CO)L_2]} \\
 & {[Rh(\text{diphos})_2Cl]} &
\end{tikzcd}$$

It is suggested that the P_4 remains intact, and is bonded to the rhodium through a face of the P_4 tetrahedron. The failure to observe ^{31}P NMR lines due to P_4 in the complexes is interpreted in terms of either an inter- or intra-molecular exchange process.

One equivalent of methylisocyanide reacts with $[RhCl(PPh_3)_3]$ to afford $[RhCl(MeNC)(PPh_3)_2]$, whose chemical behaviour resembles $[RhCl(CO)(PPh_3)_2]$ although it is somewhat more reactive. Reaction with iodine and tetracyanoethylene affords respectively $[RhCl(MeNC)(PPh_3)_2]$ and $[RhCl(TCNE)(MeNC)(PPh_3)_2]$; both of these reactions occur with $[RhCl(CO)(PPh_3)_2]$. However, mercuric chloride and oxygen also react with the isocyanide complex to give $[RhCl_2(HgCl)(MeNC)(PPh_3)_2]$ and $[RhCl(O_2)(MeNC)(PPh_3)_2]$; reactions which do not occur with the corresponding carbonyl analogue. The cation $[Rh(MeNC)_4]^+$ prepared by reaction of methylisocyanide with $[RhCl(1,5\text{-}C_8H_{12})]_2$, also undergoes oxidative addition reactions. With iodine, $[RhI_2(MeNC)_4]^+$, is formed, whereas, methyl iodide adds without methyl migration to yield $[RhMe(I)(MeNC)_4]^+$. Oxygen does not react with $[Rh(MeNC)_4]^+$ [124]. The complex $[Rh(PhNC)_2(PPh_3)_2]Cl$ also reacts with tetracyanoethylene to give the neutral complex $[RhCl(TCNE)(PhNC)_2(PPh_3)]$. TCNE also replaces one isocyanide ligand in $[Rh(PhNC)_4]Cl$ to give $[RhCl(TCNE)(PhNC)_3]$[125]. In a more extensive investigation, it has been reported that the tetrakis-isocyanide complexes $[M(RNC)_4]^+PF_6^-$ (M = Rh, Ir; R = alkyl or aryl) readily undergo oxidative-addition reactions giving a variety of six-coordinate mono-cations, *trans*-$[M(RNC)_4XY]^+PF_6^-$ (X = Me, C_3F_7, or I, and Y = I; X = MeCO, $CH_2{=}CHCH_2$, HgCl, $SnCl_3$, $SnPh_3$). When the counter-anion was Cl^-, oxidative-addition of halogens (X_2) to $[Rh(RNC)_4]^+$ occurred with loss of isocyanide and formation of $[Rh(RNC)_2X_2Cl]_2$. Some oxidative-reactions of $[M(RNC)_2(PPh_3)_2]^+$ and $[M(RNC)_3(PPh_3)_2]^+$ were also described[126].

The reaction between azobenzene (azbH) and ethanolic rhodium(III) chloride affords a red dimeric complex containing a chelating phenylazophenyl group, which on recrystallisation from tetrahydrofuran (THF) gives the previously described mononuclear THF adduct[127](I).



Treatment of the initial product with $[Rh(CO)_2Cl]_2$ gives the illustrated chlorine bridged dicarbonyl species, which contains both Rh^I and Rh^{III} [127]. This complex has also been obtained directly from azobenzene and $[Rh(CO)_2Cl]_2$ [127].

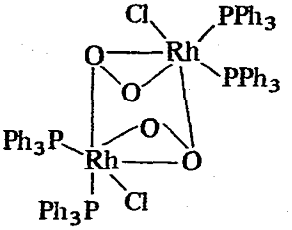
X-ray crystallographic study[128] of the acetate complex has confirmed the illustrated structure, in which the rhodium bonds to two azobenzene ligands each of which acts as a bidentate ligand with the metal bonded to an *ortho* carbon of one phenyl group, and the further nitrogen thus forming a five-membered ring. The two Ph–C bonds are *cis* and the two Ph–N bonds *trans* to one another. From the reaction between azobenzene and

$[Rh(CO)_2Cl]_2$ the volatile deep violet complex $[(PhNH_2)_2Rh(CO)_2Cl]_2$ was obtained[127]. In an aprotic solvent, *e.g.* C_6F_6, the aniline complex was still isolated, suggesting that reduction and cleavage of the N=N bond occurred via a metal-assisted hydrogen transfer from the *ortho*-position of the phenyl ring. Interestingly, addition of a catalytic amount of $[Rh(CO)_2Cl]_2$ to a mixture of $LiAlH_4$ and azobenzene gave a quantitative yield of hydrazobenzene, no trace of aniline being formed[127].

The reaction of allylamine with rhodium(III) chloride has been examined; the products of the reaction can contain one, two, three or five molecules of the amine which is considered on the basis of infrared spectra to be coordinated via the NH_2 lone pair and not by the olefinic double bond. At 20° in ethanol the complexes afforded acrolein, *N*-propylideneallylamine, propionaldehyde and propylene[129].

An ^{18}O isotopic infrared study of various dioxygen complexes including $[RhX(O_2)L_2(t\text{-}BuNC)]$ ($X = Cl, Br$; $L = PPh_3, AsPh_3$) prepared with a heavy dioxygen mixture ($^{16}O_2$, $^{16}O\text{-}^{18}O$, and $^{18}O_2$) revealed the geometry of the O_2 coordination to be a side-on isosceles structure. The effect of various auxiliary ligands on the metal–oxygen vibrations was examined, and the nature of the metal–oxygen bond discussed[130].

An X-ray crystal structure determination of the complex obtained by bubbling oxygen through solution of the red form of $[RhCl(PPh_3)_3]$ in methylene chloride has established the unusual illustrated structure, in which the overall geometry of each rhodium atom can be described in terms of trigonal bipyramid.

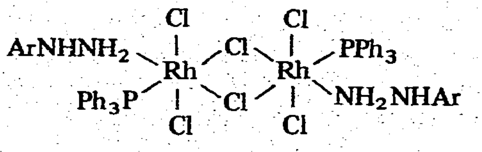


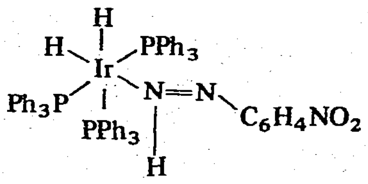
The preference for the oxygen bridge over the relatively common chlorine bridge suggests, perhaps, a particularly favourable energy relationship between the occupied π^* orbital of the coordinated oxygen molecule and the $d_z{}^2$ orbital of the rhodium atom[131].

Sulphato complexes of rhodium and iridium have been prepared by reaction of the appropriate dioxygen complex with sulphur dioxide[132].

Cyclooctasulphur and cyclooctaselenium react with $[Rh(DMPE)_2]^+Cl^-$ (DMPE = $Me_2PCH_2 \cdot CH_2PMe_2$) and $[Ir(diphos)_2]^+Cl^-$ to form the complexes $[Rh(S_2)(DMPE)_2]^+Cl^-$, $[Ir(S_2)(diphos)_2]^+Cl^-$, $[Ir(Se_2)(diphos)_2]^+Cl^-$.[133] It is suggested that these complexes contain the unknown dimers S_2 and Se_2 stabilised by coordination to the metal.

Aryldiazonium cations react with the hydrido species $[RhH_2Cl(PPh_3)_2(S)]$ (S = solvent) and *mer*-$[IrH_3(PPh_3)_3]$ to form respectively a hydrazine derivative or a simple insertion product[134].





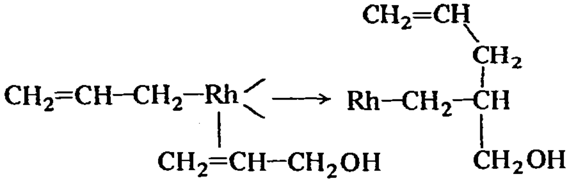
On insertion the diazonium group undergoes a two-electron reduction with consequent rehybridization and bond-order lowering making it susceptible to further reduction. If the activating complex is also able to function as a promotion centre for the hydrogenation of the coordinated diimide, a simple reduction of diazonium cation to the corresponding hydrazine derivative occurs.

A convenient single-stage synthesis has been described[135] involving addition of rhodium or iridium halides and *N*-methyl-*N*-nitroso toluene *p*-sulphonamide to a solution of the appropriate phosphine (or arsine) in a boiling alcoholic solvent, giving the halonitrosyl complexes $[MX_2(NO)(PR_3)_2]$ and $[MX_2(NO)(AsPh_3)_2]$ (M = Rh, Ir; X = Cl, Br, I; R = alkyl, aryl or mixed alkyl, aryl). It is suggested that the reactions involve as intermediates the hydrides $[MX_2H(ER_3)_3]$ (E = P, As).

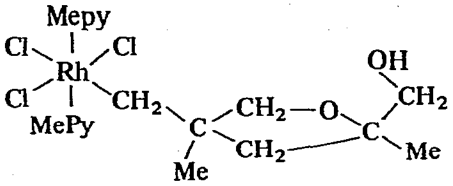
It is suggested that the reaction $[RhHX_2(CO)(PPh_3)]$ (X = Cl, Br) with diazoketones affords an ionic species $[RC(OH){=}CRN_2]^+[RhX_2(CO)(PPh_3)]^-$ [136].

The sulphides PhSR (R = Me, Et, n-Pr, or n-Bu) react with rhodium trichloride trihydrate in refluxing methanol to give *mer*-$[RhCl_3(PhSR)_3]$. The reaction of sodium chloroiridate with sulphides did not proceed as readily. No products were isolated using isopropylphenyl sulphide, a diphenyl sulphide and methylphenyl sulphide gave only a 20% yield of $[IrCl_3(PhSMe)_3]$[137].

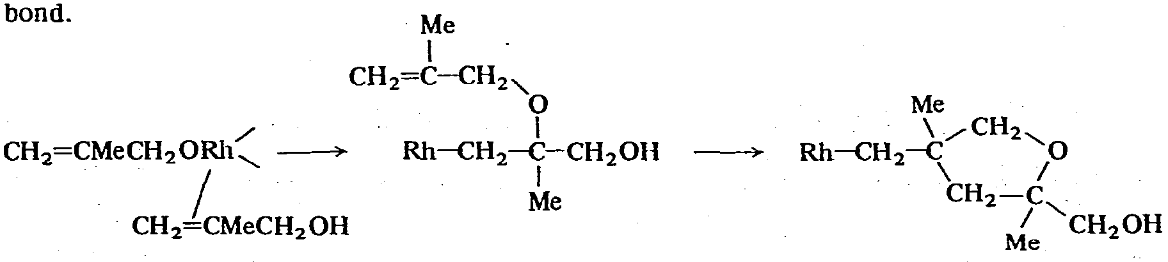
An X-ray crystallographic study of the reaction product $[Rh_2Cl_4(C_6H_{11}O)_2]MeOH$ obtained on refluxing $RhCl_3 \cdot 3H_2O$ in a mixture of allyl alcohol and methanol shows the presence of the tridentate ligand C_6H_{11}, which is thought to be formed via the 1,2-addition of a σ-allylrhodium system to an allyl alcohol[138].



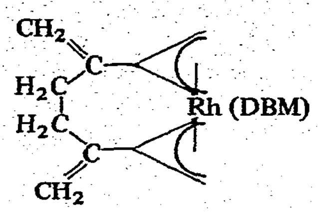
In contrast, a similar reaction with $RhCl_3 \cdot 3H_2O$ and 2-methylallyl alcohol affords $[RhCl_2(C_8H_{15}O_2)]_n$, which with 4-methylpyridine gives $[RhCl_2(C_8H_{15}O_2)(4\text{-methylpyridine})]$, for which the illustrated structure has been determined by X-ray diffraction[139].



In this case it is suggested that the furan-ring arises by an insertion reaction into a Rh-O bond.

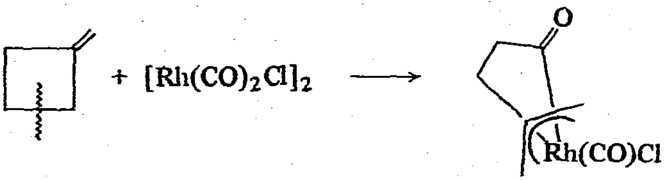


There is currently considerable interest in the reaction of allene with rhodium complexes and various kinds of reactions have been observed. It is reported[140] that allene reacts with $[Rh(C_2H_4)_2(acac)]$ and $[Rh(C_2H_4)_2(DBM)]$ (DBM = 1,3-diphenylpropane-1,3-dionato) to form an unusual complex of rhodium(III), in which a linear allene tetramer is bonded to the metal by two π-allylic bonds; the structure being established by X-ray crystallography.

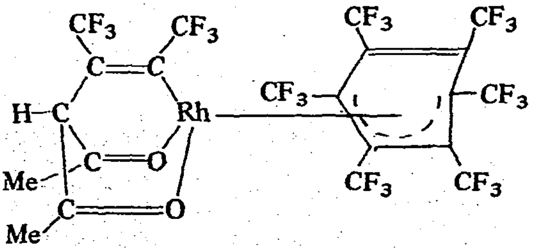


Several reactions of rhodium(I) complexes of 1,2,5,6,8-pentamethylenecyclodecane (allene pentamer) have been described[141]. Reaction of the chloride $[RhClC_{15}H_{20}]$ with C_6F_5Li gave the stable σ-bonded complex $[Rh(C_6F_5)C_{15}H_{20}]$. Sodium cyclopentadienide afforded $[Rh\text{-}\pi\text{-}C_5H_5(C_{15}H_{20})]$ formulated as a h^4-1,2,5,6,8-pentamethylcyclodecane, h^5-cyclopentadienyl bonded complex. Reaction of $[RhClC_{15}H_{20}]$ with $HgPF_6$ in acetone gave the cationic complex $[RhC_{15}H_{20}]^+PF_6^-$, which reacts with carbon monoxide to give the yellow monocarbonyl $[Rh(CO)C_{15}H_{20}]^+PF_6^-$.

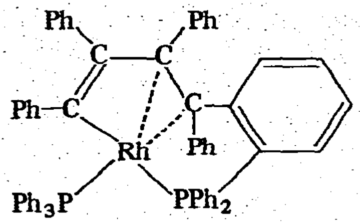
The reaction of methylenecyclobutane with $[Rh(CO)_2Cl]_2$ results in ring-fission and the formation of an acyl-π-allylic complex:[142]



A crystal structure determination[143] of the product of the reaction of hexafluoro-2-butyne with acetylacetonato(1,5-cyclooctadiene)rhodium shows that three molecules of C_4F_6 have trimerised and the resultant hexakis(trifluoromethyl)benzene replaces 1,5-cyclooctadiene, coordinated to the rhodium as a diene, as in the complex $[Rh\text{-}\pi\text{-}C_5H_5\{C_6(CF_3)_6\}]$. A fourth C_4F_6 adds 1,4 to the acetylacetonatorhodium ring forming a bicyclo-system:

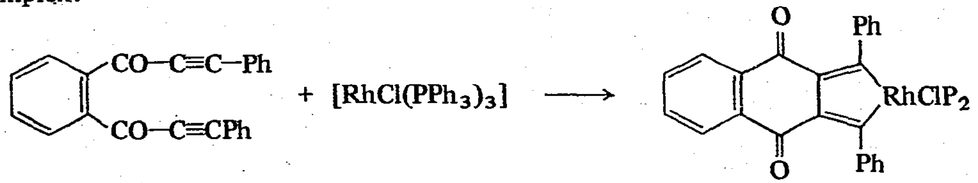


An X-ray structural study[144] has shown that the product of the reaction of $[Rh(PPh_3)_2(PPh_2C_6H_4)]$ with two molecules of diphenylacetylene has the illustrated novel structure rather than the expected rhodiocyclopentadiene structure.



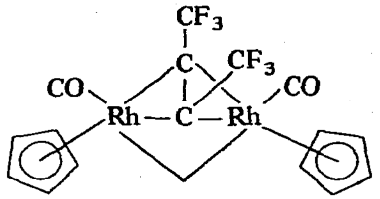
A similar structure seems likely for the product of the corresponding reaction with hexafluoro-2-butyne.

A crystal structure determination[145,146] has also elucidated the nature of the product from the illustrated reaction, which was originally thought to form a cyclobutadiene complex:



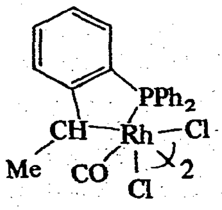
The reaction of diphenylacetylene with $[RhMe(PPh_3)_3]$ has been studied in detail; the main product of the reaction is *trans*-α-methylstilbene[147].

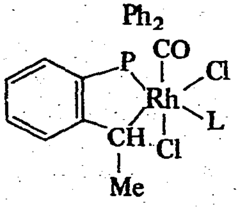
Previously, reaction of $[Rh(CO)_2\text{-}\pi\text{-}C_5H_5]$ and hexafluoro-2-butyne has been shown to give π-cyclopentadienyl-π-hexakis(trifluoromethyl)cyclopentadienonerhodium and π-cyclopentadienyl-π-hexakis(trifluoromethylbenzene)rhodium. When the reaction is conducted in hexane a bridged acetylene species is formed[148].



Treatment of a boiling ethanolic solution of $RhCl_3 \cdot 3H_2O$ with carbon monoxide followed by *o*-styryldiphenylphosphine(SP) affords a chlorine-bridged species, which undergoes bridge splitting on treatment with monodentate phosphine ligands (L = PPh_3, $PMePh_2$ or PMe_2Ph). It is suggested that an initial Rh^I-olefin complex reacts with HCl to form a rhodium to carbon σ bond[149].

The complex $[RhCl(SP)_2]$ has been obtained by reaction of SP with $[RhCl(C_8H_{14})_2]_2$ or more satisfactorily by reducing ethanolic $RhCl_3 \cdot 3H_2O$ with formaldehyde in the

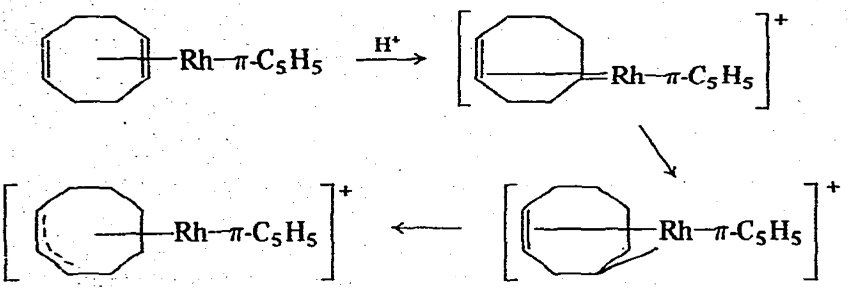




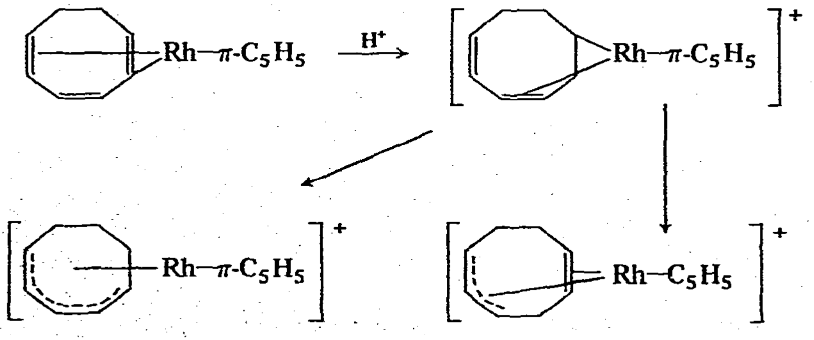
presence of SP[150]. The complex shows a low conductivity in nitromethane and in nitrobenzene suggesting that ionisation to $[Rh(SP)_2]^+Cl^-$ is incomplete. Treatment of $[Rh(CO)_2Cl]_2$ with SP in benzene gives a five-coordinate cationic species $[Rh(CO)(SP)_2]^+Cl^-$, which loses carbon monoxide in solution to give $[RhCl(SP)_2]$. The planar cation $[Rh(SP)_2]^+$ can be isolated as its tetraphenylborate salt by treating $[RhCl(SP)_2]$ with $NaBPh_4$; this reacts reversibly with ethylene to give $[Rh(C_2H_4)(SP)_2]^+$.

Complexes of bicyclo[3.3.1]-2,6-nonodiene of formula $[RhCl(diene)]_2$ have been prepared and characterised[151].

Protonation of 1,5-cyclooctadienecyclopentadienylrhodium in CF_3CO_2H leads (30 min) to the initial formation of a mixture of the h^3-1,4,5- and h^3-1,3,4-bonded cations, which are slowly converted via thermodynamically controlled prototropic rearrangements to the h^3-1,2,3-bonded isomer:

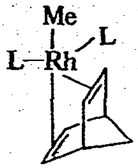


Similarly, protonation of 1,3,5-cyclooctatrienecyclopentadienylrhodium leads initially to a h^3-1,3,4-bonded cation, which rearranges to a mixture of h^5-1,2,3,4,5- and h^5-1,2,4,5,6-bonded isomeric cations[152].



Previously, a series of pentacoordinate iridium(I) complexes of the type $[RIr(1,5\text{-}C_8H_{12})L_2]$ (R = H, Me; L = tertiary phosphine) had been described, in which rapid intramolecular rearrangement was found to occur. These studies have been extended to bicyclo[2.2.1]heptadiene rhodium complexes $[MeRh(C_7H_8)L_2]$ (L = phosphine or arsine), which were prepared by treating $[Rh(C_7H_8)Cl]_2$ with methyllithium in toluene in the presence of a stoichiometric amount of the ligand L. ^{1}H NMR measurements at different temperatures indicated that the trigonal bipyramidal molecules undergo an intramolecular rearrangement as found with the Ir^I system when L = $PMePh_2$, PMe_2Ph or $AsMe_2Ph$. In contrast when L = PPh_3 or with the corresponding 1,5-cyclooctadiene and L = PMe_2Ph,

PMe_2Ph, $AsMe_2Ph$ there is an intermolecular exchange process, which is independent of the intramolecular rearrangement[153].

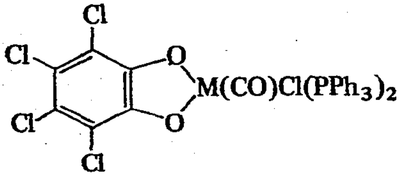


The effect of substituents in the cyclopentadienyl ring of the free rotation of the ethylene in $[Rh(C_2H_4)_2\text{-}\pi\text{-}C_5H_5]$ has been examined. Electronegative substituents weaken the π-bond between the rhodium and ethylene, whereas, a methyl group strengthens the bond[154]. The molecular geometries of acetylacetonatodiethylenerhodium and acetylacetonatoethylenetetrafluoroethylenerhodium show that C_2F_4 is more closely bonded to rhodium than C_2H_4, a consequence of increased π-back-bonding[155].

The reaction of $Fe_2(CO)_9$ with 3,5,7-triphenyl-4*H*,1,2-diazepine proceeds via cleavage of the N–N bond with the formation of a novel nitrogen-bridged metallobicyclo system. In contrast, chlorodicarbonylrhodium dimer reacts with this diazepine without cleavage of the N–N bond to afford chloro-*cis*-dicarbonyl(3,5,7-triphenyl-4*H*,1,2-diazepine)rhodium, in which the diazepine (in a twisted boat conformation) is coordinated to the rhodium(I) atom via only one nitrogen atom[156].

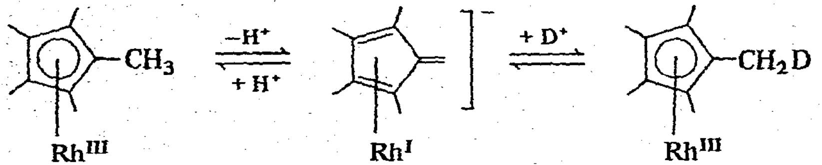
Gas chromatography of C_2–C_4 olefins using squalene and 0.117*M* solution of [dicarbonylrhodium(3-trifluoroacetylcamphorate)] provides evidence for coordination of these lower olefins and also indicates a useful analytical procedure for the detection of olefins[157]. Thermodynamic data have been collected and compared for the reversible addition of small molecules to isostructural d^8 complexes of Rh^I and Ir^I. The results have been assessed in terms of the role of the metal in these interactions which are interpreted as generalised acid–base reactions[158].

Recently, the photo-induced addition of 9,10-phenanthroquinone and 1,2-naphthaquinone to *trans*-$[IrCl(CO)(PPh_3)_2]$ has been reported. In contrast, the strongly oxidizing quinones tetrachloro- and tetrabromo-1,2-benzoquinone readily react at 25° with both *trans*-$[RhCl(CO)(PPh_3)_2]$ and *trans*-$[IrCl(CO)(PPh_3)_2]$ to form respectively the illustrated 1/1 adducts. Similar reactions occur with other d^8 complexes known to be susceptible to oxidative addition reactions, for example, $[RhCl(PPh_3)_3]$ forms green $[RhCl(1,2\text{-}Cl_4C_6O_2)(PPh_3)_2]$, and the complexes $[MCl(1,5\text{-}C_8H_{12})]_2$ (M = Rh, Ir) give $[MCl(1,5\text{-}C_8H_{12})(1,2\text{-}Cl_4C_6O_2)]_n$[159].



The (pentamethylcyclopentadienyl)rhodium and -iridium chloride $[MCl_2(\pi\text{-}C_5Me_5)]_2$ reacted with silver acetate to give the acetates $[M(OAc)_2\text{-}\pi\text{-}C_5Me_5\cdot H_2O]$ (M = Rh, Ir), which in turn gave the trifluoroacetates $[M(O_2CCF_3)_2\text{-}\pi\text{-}C_5Me_5\cdot H_2O]$ with CF_3CO_2H.

The rhodium acetate was relatively stable, but the iridium complex was readily hydrolysed to the dihydroxo compound. Reaction of $[RhCl_2\text{-}\pi\text{-}C_5Me_5]_2$ with aqueous base gave the complexes $[(\pi\text{-}C_5Me_5Rh)_2(OH)_3]^+X^-$, which are formulated with three bridging hydroxo groups. The complex $[\{\pi\text{-}C_5Me_5Rh\}_2(OH)_3]Cl$ gave $[\{C_5(CD_3)_5Rh\}_2(OD)_3]Cl$ on heating with OD^- in D_2O; it is suggested[160] that the exchange reactions proceed via the illustrated reaction sequence.



The complexes $[MCl(diene)]_2$ (M = Rh, diene = bicycloheptadiene, dicyclopentadiene; M = Ir, diene = 1,5-cyclooctadiene) react with carboxylate ions to give the carboxylate-bridged complexes $[M(O_2CR)(diene)]_2$; there was no evidence for nucleophilic attack on the olefin[161].

Reaction of allene or 1,3-butadiene with $[RhH(CO)(PPh_3)_3]$ affords $[Rh(\pi\text{-allyl}(CO)\text{-}(PPh_3)_2]$ or $[Rh(\pi\text{-1-methylallyl})(CO)(PPh_3)_2]$. The complex $[IrH(CO)_2(PPh_3)_2]$ reacts similarly, but more slowly, to give the corresponding π-allylic complexes; isoprene gives the allylic group $CH_2\text{---}C(Me)\text{---}CHMe$, whereas in contrast the addition to $[CoH(CO)_4]$ yields only the isomeric product with a $\pi\text{-}CH_2\text{---}CH\text{---}CMe_2$ group. The complexes $[Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2]$, $[Rh(\pi\text{-}C_3H_5)(CO)(PPh_3)_2]$, $[Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2]$, and $[Ir(\pi\text{-}C_4H_7)(CO)(AsPh_3)_2]$ were also obtained by reaction of the appropriate Grignard reagent with *trans*-$[MCl(CO)L_2]$ (M = Rh, or Ir; L = PPh_3 or $AsPh_3$)[162]. The reaction of these π-allylic species with CO, H_2 and HCl was also studied. The $[IrR(CO)_2(PPh_3)_2]$ complexes have σ-allyl groups in the solid state, but exist largely in solution as dynamic π-allyl systems.

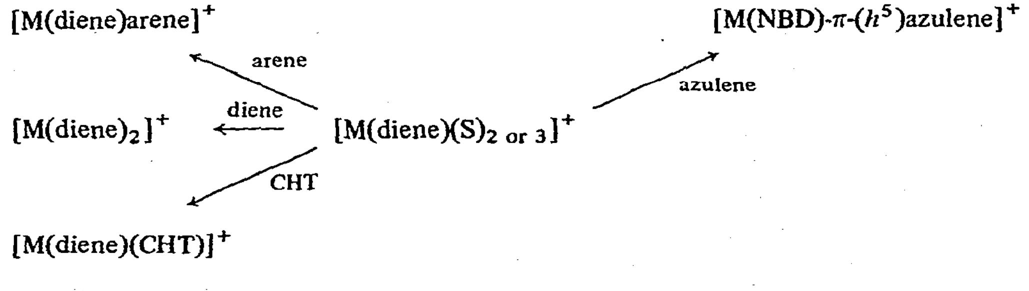
There has been a growing interest in cationic Rh^I and Ir^I complexes, particularly in their possible use as homogeneous catalysts. Hydrogen reversibly displaces carbon monoxide from the thiocarbonyl Ir^I complex $[Ir(CO)_2(CS)(PCy_3)_2]^+ClO_4^-$ (PCy_3 = tricyclohexylphosphine) to give the Ir^{III} dihydride $[IrH_2(CO)(CS)(PCy_3)_2]^+ClO_4^-$; as would be expected on the basis of the decreased nucleophilicity of the metal, the bis-triphenylphosphine analogue does not react with molecular hydrogen[163]. Treatment of a solution of $[Rh(NBD)(PPh_3)_2]^+$ (NBD = bicycloheptadiene) with H_2 generates $[RhH_2(PPh_3)_3(S)_2]^+$ ((S) = solvent), with elimination of bicyclo[2.2.1]heptane[164]. The dihydride reacts with carbon monoxide to displace H_2 and forms various cationic carbonyl–phosphine–rhodium(I) complexes. The four-coordinate cationic complex $[Rh\{P(OMe)_3\}_4]^+[BPh_4]^-$ readily undergoes oxidative addition reactions with the acetylenes C_2R_2 (R = CF_3 or CO_2Me) to give $[Rh\{P(OMe)_3\}_4(C_2R_2)]^+[BPh_4]^-$[165]. Hydrogen adds reversibly to $[Rh\{P(OMe)_3\}_4]^+\text{-}[BPh_4]^-$ to form a *cis*-dihydride, whereas, the more reactive cation $[Rh(P\text{-n-}Bu_3)_4]^+\text{-}[BPh_4]^-$ adds hydrogen irreversibly to form *cis*-$[RhH_2(P\text{-n-}Bu_3)_4]^+$. Treatment of the five-coordinate complex $[Rh\{P(OMe)_3\}_5]^+[BPh_4]^-$ with HBr or HI gives *trans*-$[RhHBr\text{-}\{P(OMe)_3\}_4]^+[BPh_4]^-$. The cations $[RhL_4]^+$ [L = $P(OR)_3$; R = Me, Et, or Ph] react with allyl halides C_3H_5X (X = Cl, Br) to give $[Rh(\pi\text{-}C_3H_5)L_4]^{2+}$ or $[RhX(\pi\text{-}C_3H_5)L_3]^+$, the product depending on the nature of the ligand L. The reactions of $[RhCl(1,5\text{-}C_8H_{12})_2]_2$

with excess of the ligands L = PMe_2Ph and $AsMe_2Ph$ in methanol in the presence of air afford[166] the stable oxygen-containing cations $[RhL_4(O_2)]^+$.

The four-coordinate species $[Rh(CO)L_3]^+$ have been obtained by warming a suspension of $[RhCl(CO)L_2]$ (L = PEt_2Ph, $PMePh_2$) in hot methanol with the ligand L followed by addition of the anions $[PF_6]^-$ on $[BPh_4]^-$. In contrast, the corresponding reaction with L = PMe_2Ph or $AsMe_2Ph$ gives the five-coordinate cationic derivatives $[Rh(CO)L_4]^+$ [167]. The previously described iridium(III) hydride $[IrHCl(CO)(PMe_2Ph)_3]^+[BPh_4]^-$ is more readily prepared by treating $[IrHCl_2(CO)L_2]$ or $[IrHCl_2(CO)_2]_2 \cdot H_2O$ with one or three moles of the ligand L. The complexes $[Ir(CO)L_4]^+[BPh_4]^-$ (L = PMe_2Ph, $AsMe_2Ph$) are formed by an analogous procedure or by dehydrohalogenation[168] of the cations $[IrHCl(CO)L_3]^+$ with triethylamine. Corresponding salts of formula $[Ir(CO)L_3]^+[PF_6]^-$ (L = $PMePh_2$, PEt_2Ph) are formed by the addition of L to a suspension of the cyclooctene complex $[IrCl(CO)(C_8H_{14})_2]_2$. A solution of the complexes $[M(CO)L_4]^+[BPh_4]^-$ [M = Rh, Ir; L = PMe_2Ph, $AsMe_2Ph$] in acetone reacts with oxygen to give the stable adducts $[ML_4(O_2)]^+[BPh_4]$[167].

The reaction of [M(diene)acac] (M = Rh, Ir; diene = 1,5-C_8H_{12} or bicycloheptadiene) with $Ph_3C^+BF_4^-$ in the presence of an excess of diene affords $[M(diene)_2]^+[BF_4]^-$, from which diene is readily displaced by acetonitrile to form $[M(diene)(CH_3CN)_2]^+[BF_4]^-$ [169]. Reaction of $[M(diene)(CH_3CN)_2]^+$ with phosphines and dipyridyl were also examined to give complexes of the type $[M(diene)L_2]^+[BF_4]^-$ and $[ML_4]^+[BF_4]^-$. In a related investigation[170] the reaction of $[Rh(1,5\text{-}C_8H_{12})acac]$ with $[Ph_3C]^+[BF_4]^-$ in methylene chloride followed by the addition of ligand (L) gives the cationic complexes $[Rh(1,5\text{-}C_8H_{12})L_2]^+$-$[BF_4]^-$ (L = PPh_3, $PEtPh_2$, PEt_2Ph, $AsPh_3$).

Abstraction of chloride anion from $[Rh(diene)Cl]_2$ (diene = 1,5-cyclooctadiene or bicycloheptadiene) with $AgPF_6$ in tetrahydrofuran affords the reactive species $[Rh(diene)(S)_{2\text{ or }3}]^+$((S) = tetrahydrofuran), which has been shown to undergo a wide range of displacement reactions[171].

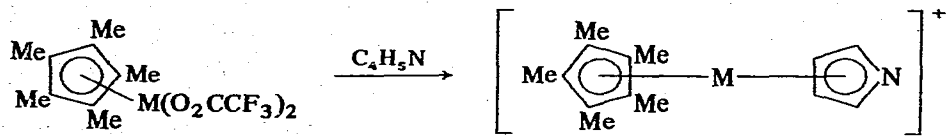


(CHT = cycloheptatriene, M = Rh, Ir)

The species $[Rh(NBD)_2]^+PF_6^-$ was also shown to catalyse the dimerisation of NBD to form the dimers previously formed on refluxing NBD over a 5% Rh/C catalyst. Significantly addition of 1 mole (per Rh) of L (L = PPh_3, $PPh_2C_6H_{11}$ or $P(OPh)_3$ led to the catalytic formation of the dimer Binor-S.

Rhodium(I) carboxylates of stoichiometry $[Rh(O_2CR)(PPh_3)_3]$ (R = allyl, aryl, or substituted alkyl) have been prepared by the reaction of the dirhodium(II) cation Rh_2^{4+}, with a stoicheiometric amount of triphenylphosphine, and an excess of the lithium salt of the appropriate carboxylic acid[172]. The reactions of the carboxylates with H_2, O_2, CO and aldehydes, were described. In benzene solution the Rh^I carboxylates catalyse the homogeneous hydrogenation of alkenes and alkynes. The acetate, for example, is less than 25% as effective as chloride for hydrogenation of 1-hexene and 1-hexyne, and only 2% as effective for cyclohexene. The nature of the R group has little effect. Reaction with carbon monoxide affords *trans*-$[Rh(O_2R)(CO)(PPh_3)_2]$.

A new method for the preparation of π-arene and π-pyrrolyl complexes of Rh^{III} and Ir^{III} has been described[173]. The trifluoroacetates $[M(O_2CCF_3)_2\text{-}\pi\text{-}C_5Me_5]\cdot H_2O$ (M = Rh, Ir) in trifluoroacetic acid react with a variety of methylated benzenes to give $[M(\pi\text{-}C_5Me_5)(\text{Arene})]^{2+}$. The π-arene complexes of Ir^{III} are more stable than those of Rh^{III} and their stability increases with increasing methylation. The complex $[Rh(\pi\text{-}C_5Me_5)(p\text{-xylene})]^{2+}$ readily reacts with dimethylsulphoxide to give $[Rh(\pi\text{-}C_5Me_5)(Me_2SO)_3]^{2+}$. Nucleophiles ($NaBH_4$, MeLi) attack the arene ring to give π-cyclohexadienyl complexes where the nucleophile becomes the *exo* substituent. The reaction of the bis(trifluoroacetate) with pyrrole afforded good yields of the π-pyrrolyl complexes, which did not react with sodium borohydride.

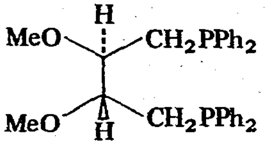


(M = Rh, Ir)

Complexes of rhodium(I) and iridium(I) containing the ligand diphenylphosphine (Ph_2PH) have been described. Rhodium trichloride and ammonium hexachloroiridate react with Ph_2PH to give $[MCl_3(HPPh_2)_3]$; however, $[RhCl(PPh_3)_3]$ and *trans*-$[RhCl(CO)(PPh_3)_2]$ react with Ph_2PH to give tetrakis(diphenylphosphine)rhodium chloride. Similarly, *trans*-$[IrCl(CO)(PPh_3)_2]$ reacts to give salts of the cations $[Ir(CO)(HPPh_2)_4]^+$. The complex $[Rh(HPPh_2)_4]^+[BF_4]^-$ does not react with H_2 or CO, but reacts with HCl or HBr to give complexes, which are tentatively formulated as $[Rh_2HX_2(HPPh_2)_6]^+[BF_4]^-$ (X = Cl, or Br)[174].

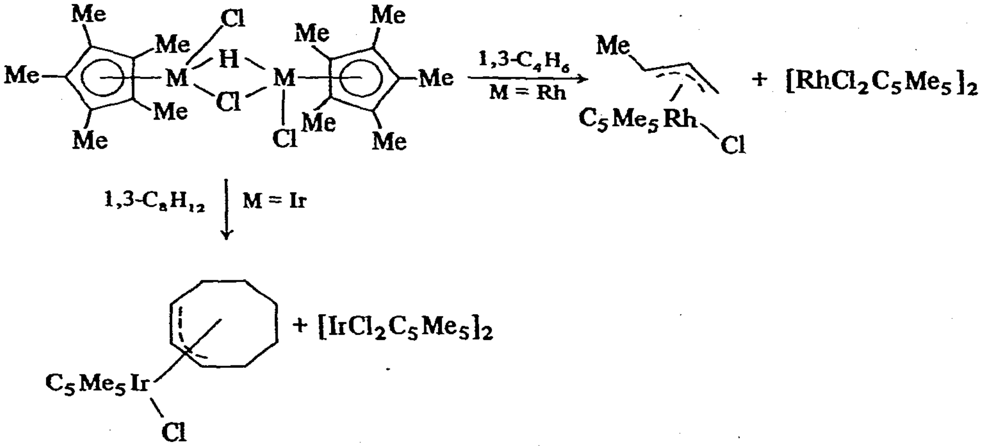
The catalytic hydrogenolysis of molecular oxygen by triphenylphosphine complexes of platinum, iridium, rhodium and ruthenium in toluene under ambient conditions has been reported. Although heterogeneous reaction cannot be completely discounted the available evidence points to a homogeneous reaction[175].

Recently there has been interest in asymmetric hydrogenations catalysed by soluble rhodium catalysts[176,177]. For example, asymmetric hydrogenation of α-phenylacrylic acid was accomplished with a rhodium complex of (*R*)-methylpropylphenylphosphine in an ethanol-benzene solution containing triethylamine; (*S*)-Hydratropic acid (15% enantiomeric excess) was obtained. Similarly α-ethylstyrene was reduced to 2-phenylbutane (about 8% enantiomeric excess). Instead of using tertiary phosphines, which are asymmetric at phosphorus, attention has been focused on chiral rhodium complexes containing phosphine ligands which are asymmetric at carbon and are therefore more accessible. Reaction of lithium diphenylphosphide with menthyl chloride or bromide forms neomenthyldiphenylphosphine, which forms species of the type $[RhClL_3]$ (L = chiral phosphine). Reduction of (*E*)-β-methylcinnamic acid in a 1/1 benzene–ethanol solution of prereduced tris-(neomenthyldiphenylphosphine)rhodium chloride in the presence of Et_3N gave 3-phenylbutanoic acid containing 61% enantiomeric excess (ee) of the *S* isomer. Similarly, reduction of (*E*)-methylcinnamic and atropic acids gave (*R*)-2-methylphenylpropanoic (52%ee) and (*S*)-hydratropic acid (28%ee)[178]. In a related investigation reduction of atropic acid with a rhodium complex prepared by addition of the illustrated diphosphine to $[RhCl(C_8H_{14})_2]_2$



in 1/2 benzene–ethanol gives (*S*)-hydratropic acid with an optical purity of 63%[179]. α-Acetamidocinnamic acid is reduced by the same catalytic system to give (*R*)-*N*-acetylphenylalanine with an optical purity of 72%.

The bridged hydrides $[MHCl_3(\pi\text{-}C_5Me_5)]$ (M = Rh, Ir), for which the illustrated structure is proposed, and which are formed by reaction of $[MCl_2(\pi\text{-}C_5Me_5)]$ with either hydrogen in the presence of base, or sodium borohydride, or isopropyl alcohol and base react with 1,3-dienes to give enyl complexes[180].



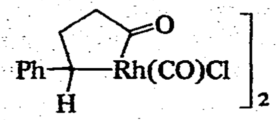
The bridged hydrides are good catalysts in the presence of Et_3N for the homogeneous hydrogenation of olefins. The iridium complex was generally more active than the rhodium complex, but the activity of the latter was greatly increased on addition of base. Functional groups (COR, NO_2 or aryl) were not reduced, but their presence on the olefin deactivated it towards hydrogenation.

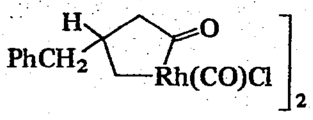
Complexes of the type *trans*-$[RhCl_2L_2]$, $[RhHCl_2L_2]$, $[RhH_2ClL_2]$ and *trans*-$[RhCl(CO)L_2]$ have been prepared from the phosphines di-t-butyl(alkyl)phosphines, $P\text{-t-}Bu_2R$ (R = Me, Et, or n-Pr) and rhodium trichloride in ethanol. Addition of base (NaOMe) to $[RhHCl_2L_2]$ gives the complexes *trans*-$[RhCl(CO)L_2]$. The complex $[RhHCl_2(P\text{-t-Bu-n-}Pr_2)_2]$ in 2-propanol with NaOPr-i is an active hydrogenation catalyst. The related complexes $[RhHCl_2L_2]$ also have catalytic activity but not as good as the above system[181].

4-Vinylcyclohexene is reported[182] to be converted quantitatively into equimolar quantities of ethylbenzene and ethylcyclohexene in a refluxing ethanol solution of $RhCl_3$. It is suggested that 1,3-hydride shifts lead to ethylcyclohexadienes, which in turn readily undergo disproportionation with the same catalyst.

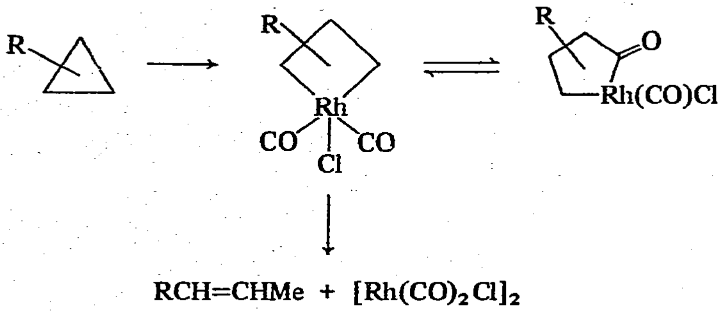
It is reported[183] that $[RhH(CO)(PPh_3)_3]$ in toluene isomerises 1-heptene faster under an atmosphere of H_2 than N_2, and isomerises the olefin faster than hydrogenates. In benzene, 1-pentene isomerises and hydrogenates very rapidly under both N_2 and H_2.

The metal catalysed conversion of hexamethyl-Dewar-benzene to hexamethylbenzene has been examined on an empirical basis using a wide range of metal complexes including rhodium and iridium species[184]. The recent interest in the reaction of Rh^{I} species with strained carbon–carbon bonds as present in cyclopropane, quadricyclene and cubanes, the reaction of $[Rh(CO)_2Cl]_2$ with substituted cyclopropanes has been studied[185]. Thus phenyl- and benzyl-cyclopropane differ in reacting at the more and the less substituted edge of the cyclopropane ring to give the illustrated acyl complexes.

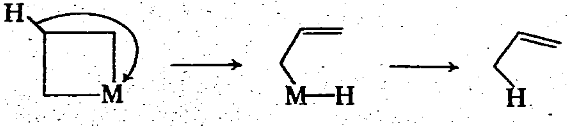




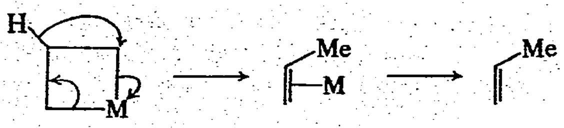
Concurrent with the formation of the above species, phenylcyclopropane gave propenylbenzene and a little α-methyl styrene. Benzylcyclopropane gave 2-methyl-3-phenyl-1-propene. These observations suggest a common reaction pathway, in which an intermediate may be trapped by carbonyl insertion, or isomerised by hydrogen transfer.



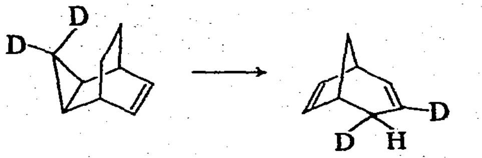
There are two alternative ways in which hydrogen isomerisation could take place, which are shown below:



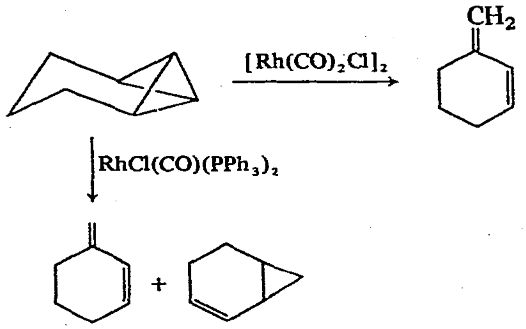
or

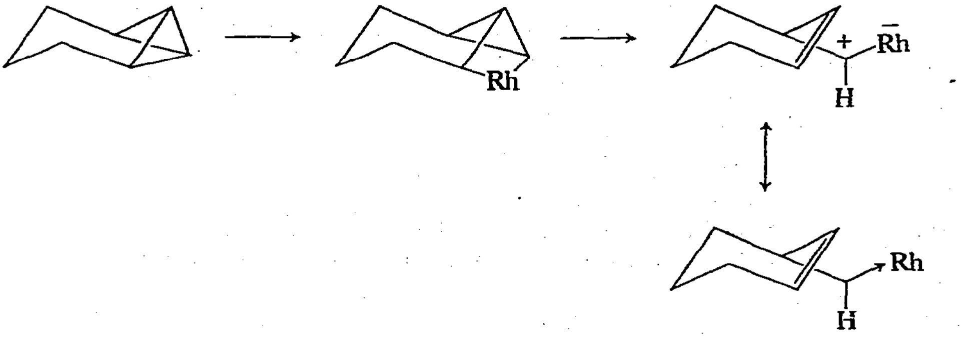


A study[186] of the $[RhCl(PPh_3)_3]$ promoted isomerisations of the illustrated deuterium labelled cyclopropane showed that the product was mainly a bicyclo[3.2.1]octadiene, a result which implies the stereospecific transfer of hydrogen across the face of the molecule, *i.e.* the first process.

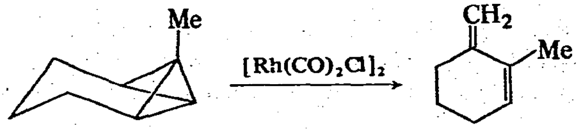


Treatment of a solution of tricyclo[4.1.0.0^{2,7}]heptane with $[Rh(CO)_2Cl]_2$ in acetonitrile results in a rapid conversion to 3-methylenecyclohexene. In contrast *trans*-$[RhCl(CO)(PPh_3)_2]$ effected only a slow conversion, giving also a small amount of 2-norcarene. It is suggested[187] that these reactions involve the intermediacy of a rhodium-carbene complex; possibly via an initial oxidative insertion reaction; a hydrogen shift leading to the observed products.

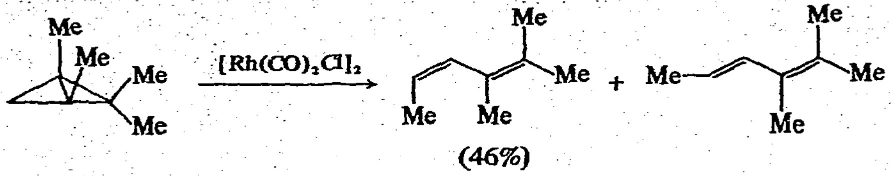




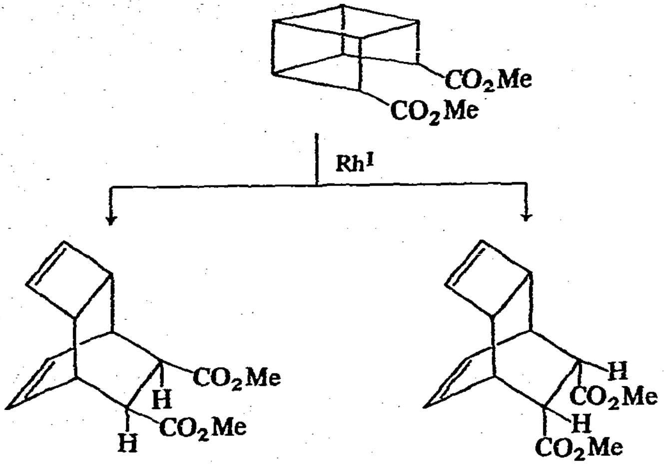
The course and stereospecificity of these rearrangements is sensitive to the presence of alkyl substituents on the bicyclo[1.1.0]butane ring system. For example, although the following reaction:



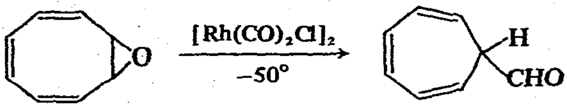
occurs stereospecifically the presence of an additional bridgehead methyl substituent leads to a lack of specificity[188].



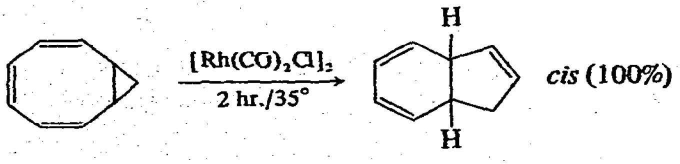
The 1,1'-bishomocubane system readily rearranges in the presence of the rhodium(I) species $[RhCl(PPh_3)_3]$, $[Rh(C_7H_8)Cl]_2$, *trans*-$[RhX(CO)(PPh_3)_2]$ (X = Cl, Br, I) to afford the illustrated diene systems[189].



The rhodium(I) catalysed rearrangement of cyclooctatetraene epoxide has been rationalised in terms of an initial oxidative-addition reaction[190].



It is also reported[190] that the stereochemistry of the isomerisation of bicyclo[6.1.0]-nonatrienes to 8,9-dihydro indenes can be controlled by use of a Rh(I) catalyst.



Without a catalyst, a higher temperature is required and the reaction is less specific.

The decomposition of formic acid to hydrogen and carbon dioxide has been observed in the presence of homogeneous catalysts consisting of rhodium or iridium iodocarbonyls and hydriodic acid[191].

$$[M(CO)_xI_4]^- + HCO_2H \rightarrow [M(CO)_xI_2]^- + 2HI + CO_2$$
$$[M(CO)_xI_2]^- + 2HI \rightarrow [M(CO)_xI_4]^- + H_2$$
$$(M = Rh, Ir; x = 1 \text{ or } 2)$$

Following the earlier report of the decarbonylation of aldehydes by $[RhCl(PPh_3)_3]$, a series of aldehydes differing in the hybridisation of the carbon atom to which the carbonyl group is attached, *i.e.*, (–)-(*R*)-2-methyl-2-phenylbutanol, (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxaldehyde and (*E*)-α-ethylcinnamaldehyde was decarbonylated using tris(triphenylphosphine)rhodium chloride. The products (+)-(*S*)-2-phenylbutane, (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane and (*Z*)-1-phenyl-1-butene were formed with 81, 94 and 100% retention of optical activity. A cleavage radical pair disproportionation mechanism is proposed[192].

Chlorocarbonylbis(triphenylphosphine)iridium catalyses selectively, and under mild conditions, the transformation of aliphatic acid halides into mixtures of olefins. Aroyl halides are not affected. The species $[Rh(CO)_2Cl]_2$ $[RhCl(PPh_3)_3]$ and $[RhCl_3(AsPh_3)_3]$ catalyse the decarbonylation and dehydrohalogenation of acyl chlorides in the presence of PPh_3 to give terminal olefins selectively[193].

The catalytic reduction of nitro compounds to amines with water and carbon monoxide has been studied[194]:

$$ArNO_2 + CO + H_2O \rightarrow ArNH_2 + CO_2$$

The reaction, which is conducted in an aqueous organic base (Me_3N, Et_3N, DMF or *N*-methylpyrrolidine) is catalysed by the species $Rh_6(CO)_{16}$ (50 atm CO/50°), and $[Rh(CO)_2Cl]_2$ (120 atm CO/150°).

The previously reported iridium hydride $[HIr(CO)_3(PPh_3)]$ and $[Ir_2(CO)_6(PPh_3)_2]$, can be prepared more conveniently by refluxing $[IrI(CO)(PPh_3)_2]$, in benzene suspension with sodium ethoxide[195]. A benzene suspension of the dinuclear species reacts reversibly[195,196] with hydrogen to give a yellow solution of the unstable monohydride. Further reaction with hydrogen affords the trihydride *fac*-$[IrH_3(CO)_2(PPh_3)]$.

$$[Ir_2(CO)_6(PPh_3)_2] \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} [IrH(CO)_3(PPh_3)] \overset{+H_2}{\rightleftharpoons} [IrH_3(CO)_2(PPh_3)]$$

The use of a high pressure spectrophotometric cell has led to a more detailed understanding of the formation of the mono-hydride[196].

$$\begin{tikzcd}
[IrH(CO)(PPh_3)_3] \arrow[r, "420\text{ atm }CO/H_2", "50\text{–}60°"'] & {[IrH(CO)_2(PPh_3)_2]} \arrow[r, "450\text{ atm}", "80\text{–}120°"'] & {[IrH(CO)_3PPh_3]} \arrow[d, "210\text{ atm}"', "90\text{–}120°"'] \\
& & {[Ir_2(CO)_6(PPh_3)_2]}
\end{tikzcd}$$

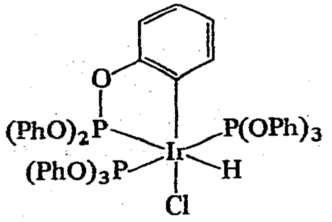
Tetranuclear phosphine-substituted iridium carbonyl derivatives of the types $[Ir_4(CO)_8L_4]$ ($L = PEt_3$, P-n-Bu_3), and $[Ir_4(CO)_9(P\text{-i-}Pr_3)_3]$ also react with carbon monoxide and hydrogen under pressure in liquid paraffin–heptane to give the monomeric hydride derivatives as the predominant final products[196].

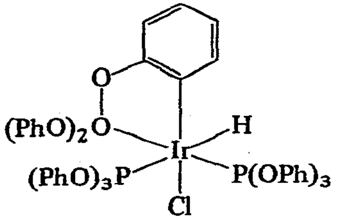
Reaction of the hexachloroiridite ion (or $IrCl_3$) with bulky phosphines especially those with t-butyl substituents does not form simple substitution products $[IrCl_3L_3]$ such as one gets with triethylphosphine or dimethylphenylphosphine[197]. Instead five-coordinate purple hydrides of the type $[IrHCl_2(P\text{-t-}Bu_2R)_2]$ (R = Me, Et or n-Pr) are formed. Interestingly, these hydrides show an ^1H NMR resonance at $\tau 60$; the largest τ-values yet observed. On heating $[IrHCl_2(P\text{-t-}Bu_2\text{-n-}Pr)_2]$ in boiling 2-methoxy-ethanol for 15 h it gives ($>90\%$) *trans*-$[IrCl(CO)(P\text{-t-}Bu_2\text{-n-}Pr)_2]$.

Ultraviolet irradiation of $[IrH(PF_3)_4]$ affords $[Ir_2(PF_3)_8]$ and hydrogen[198]. The dinuclear species can also be obtained more easily by the reaction of $K^+[Ir(PF_3)_4]^-$ with $[IrCl(PF_3)_4]$.

Reaction of aliphatic alkynes with $[IrH(CO)(PPh_3)_3]$ or $[IrH(CO)_2(PPh_3)_2]$ results in the overall loss of hydrogen and the formation of the acetylides $[Ir(C{\equiv}CR)(CO)(PPh_3)_{2\text{ or }3}]$. It is suggested that these reactions proceed via an oxidative-addition of $RC{\equiv}CH$ (R = Me, Et, n-Bu, t-Bu, C_6H_{11}) to the metal to give a *cis*-dihydrido complex, which then readily loses hydrogen. The acetylides $[Ir(C{\equiv}CR)(CO)(PPh_3)_3]$ are bright yellow, whereas the square planar bis(triphenylphosphine) species are orange yellow. In solution the two complexes are in equilibrium. The square-planar complexes are analogous to *trans*-$[IrCl(CO)(PPh_3)_2]$ and undergo a similarly wide range of oxidative addition reactions with O_2, SO_2, TCNE and $MeO_2C{-}C{\equiv}C{-}CO_2Me$[199].

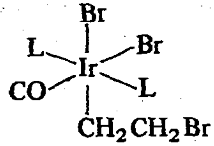
Attempts[200] to prepare the triphenylphosphite complex $[IrCl\{P(OPh)_3\}_3]$ by reaction of triphenylphosphite with $[IrCl(C_8H_{14})_2]_2$ led instead to the formation of a complex with either of the two illustrated formulas. The same complex has been reported as formed by treatment of $P(OPh)_3$ with $[IrHCl_2(1,5\text{-}C_8H_{12})]_2$, $[IrCl(C_8H_{12})]$, or $[IrCl(CO)\{P(OPh)_3\}_2]$[201]. An X-ray crystal structure study of the complex obtained by heating $[IrCHCl_2\{P(OPh)_3\}_3]$ in boiling decalin has confirmed the presence of an iridium–carbon σ-bond in the product[202].





The complexes $[IrCl(L)(1,5\text{-}C_8H_{12})]$ (L = PPh_3, $AsPh_3$, $PMePh_2$) undergo oxidative-addition and halide-exchange with HX (X = Cl, Br, I, CN) to give $[IrHX_2L(1,5\text{-}C_8H_{12})]$, in which the hydride is *trans* to X. The complexes with L = pyridine or quinoline react differently, to give $[IrX_3(Py)(1,5\text{-}C_8H_{12})]$ or $[IrX_4(LH)(1,5\text{-}C_8H_{12})]$ (X = Cl, Br). Halogens convert the complexes $[IrCl(L)(1,5\text{-}C_8H_{12})]$ into $[IrX_3(L)(1,5\text{-}C_8H_{12})]$ (X = Cl, Br; L = PPh_3, $AsPh_3$, Py) or $[IrCl_4(\text{quinoline-H})(1,5\text{-}C_8H_{12})]$[203].

The cationic complex $[Ir(CO)(PMe_2Ph)_2(C_2H_4)_2]^+[BPh_4]^-$ prepared by treatment of *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ with C_2H_4 in the presence of $NaBPh_4$ reacts with HCl to form $[IrHCl_2(CO)(PMe_2Ph)_2]$, with 2-methylallylchloride to give $[IrCl(\pi\text{-2-methylallyl})(CO)(PMe_2Ph)_2]^+[BPh_4]^-$ and with iodine to give $[IrI_3(CO)(PMe_2Ph)_2]$. In contrast, Br_2 in ethanol-free chloroform and the bis-ethylene complex gives the 2-bromo-ethyliridium complex:



($L = PMe_2Ph$)

which reacts with methylalcohol to give the corresponding 2-methoxyethyl complex[204].

Hydrogen reversibly displaces carbon monoxide from the thiocarbonyl Ir^I complex $[Ir(CO)_2(CS)(PCX_3)_2]^+[ClO_4]^-$ (PCX_3 = tricyclohexylphosphine) to give the Ir^{III} dihydride $[IrH_2(CO)(CS)(PCX_3)_2]^+[ClO_4]^-$. As would be expected on the basis of the decreased nucleophilicity of the metal the bis-triphenylphosphine analogue does not react with molecular hydrogen[205].

Somewhat unexpectedly the red cation $[Ir(PMePh_2)_4]^+$ does not react with molecular oxygen in marked contrast to $[Ir(diphos)_2]^+$. This difference has been shown by X-ray crystallography to lie in a tetrahedral distortion, which results in a hindered approach by reacting ligands[206]. In the synthetic studies leading to these observations the species $[IrCO(MeCN)L_2]^+[ClO_4]^-$ ($L = PPh_3, PMePh_2$) were prepared and some of their reactions explored.

In a study[207a] of the reaction of molecular hydrogen with Ir^I species the species $[IrCl(CO)(PMe_2Ph)_3]$ was found to be more reactive towards H_2 than the four-coordinate species $[IrCl(CO)(PMe_2Ph)_2]$. This enhanced reactivity is attributed to the presence of a small amount of the ionic complex $[Ir(CO)(PMe_2Ph)_3]^+$ present as undissociated ion pairs. The kinetics and mechanism of the reaction of hydrogen with $[IrH(CO)(PPh_3)_3]$ and of the catalytic hydrogenation of ethylene have been studied. The active catalyst is $[IrH(CO)(PPh_3)_2]$[207b].

Following earlier studies of the reactivity of complexes of the type *trans*-$[IrCl(CO)L_2]$ towards oxidative-addition of benzoic or acetic acids, in which it was found that the "basicity" of the metal decreased along the series $L = PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$, the corresponding investigation with tertiary t-butyl-phosphine ligands has been reported[208]. The relative order of the extent of protonation is $L = PMe_2Ph > P\text{-t-BuMe}_2 > P\text{-t-BuEt}_2 > P\text{-t-Bu-n-Pr}_2 > P\text{-t-Bu}_2Me > P\text{-t-Bu}_2\text{-n-Pr} > P\text{-t-Bu}_2Et$; the bulky t-butyl group having a marked effect. In the same paper the synthesis of the complexes required for this study are described.

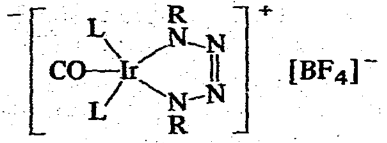
The rates of oxygen addition to *trans*-$[IrCl(CO)L_2]$ (L = tertiary phosphine) and the stability of the resulting dioxygen adducts $[IrO_2(Cl)(CO)L_2]$ increase with increasing basicity of the substituent R, provided the substituents have comparable structures; the geometry of R exerts a large steric effect on the rates of reaction[209].

In a recent reinvestigation[210] of a reaction of *trans*-$[IrCl(CO)(PMe_3)_2]$ with an alkyl halide purporting[211] to establish inversion of configuration at carbon, no reaction at all was observed, not even under much more severe conditions.

σ-2-Methylallyliridium(III) complexes of the type $[IrX_2(CH_2{=}CMe{-}CH_2)(CO)L_2]$ ($X = Cl, Br$; $L = PMe_2Ph, AsMe_2Ph$) are isomerised to the corresponding σ-2-methyl-1-

propenyl complexes in the presence of dry hydrogen chloride, thus providing the first example of the conversion of a σ-allyl– to an alkenyl–metal complex[212]. The σ-allyl complex $[IrCl_2(allyl)(CO)(PMe_2Ph)_2]$ adds on hydrogen chloride to give the 2-chloropropyl-iridium complex $[IrCl_2(C_3H_6Cl)(CO)(PMe_2Ph)_2]$, which with triethylamine reverts to the σ-allyl complex.

The complex *trans*-$[IrCl(CO)(PPh_3)_2]$ undergoes an unusual oxidative reaction on treatment with a benzene–ethanol solution of *p*-fluorophenyldiazonium tetrafluoroborate to give the illustrated iridium-1,4-*p*-fluorophenyltetrazene, which was structurally characterised by X-ray crystallography. The environment of the iridium is irregular, but may be viewed as based upon a square-pyramid geometry. Bond-lengths suggest that the tetrazene is bonded as shown, rather than as an Ir^I complex.



($L = PPh_3$, $R = p\text{-}C_6H_4F$)

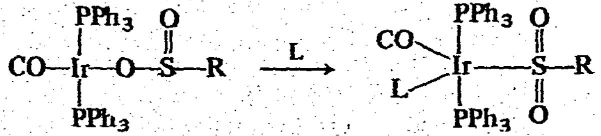
The oxidation of cyclohexene catalysed by low oxidation state phosphine–transition metal complexes has been shown to be a radical reaction; the effective action of transition metal complexes is related to their interaction with preformed hydroperoxide to form radicals[214].

The selective isomerisation of vinylcycloalkenes and vinylcycloalkanes to compounds containing an *exo*-cyclic double bond has been studied[215] using (a) $[RuCl_2(PPh_3)_3]$ in air or with hydroperoxides, (b) $[PtCl_2L_2]$ and $SnCl_2$ under hydrogen and (c) with $[IrCl(CO)(PPh_3)_2]$.

The photochemical isomerisation of complexes of the types *mer*-$[IrX_3L_3]$, $[IrHX_2L_2]$ and $[IrX_3(CO)L_2]$ (X = Cl, Br, I; L = tertiary phosphine) has been reported. Complexes of the type *fac*-$[IrX_3(PEt_3)_3]$ (X = CNO, SCN, N_3) have also been made from *mer*-$[IrCl_3(PEt_3)_3]$ by a light-induced reaction. The complexes *mer*-$[IrCl_3L_3]$ ($L = PEt_3$, P-n-Bu_3 or $AsMe_2Ph$) react with PMe_2Ph in light to give $[IrCl_3L_2(PMe_2Ph)]$[216].

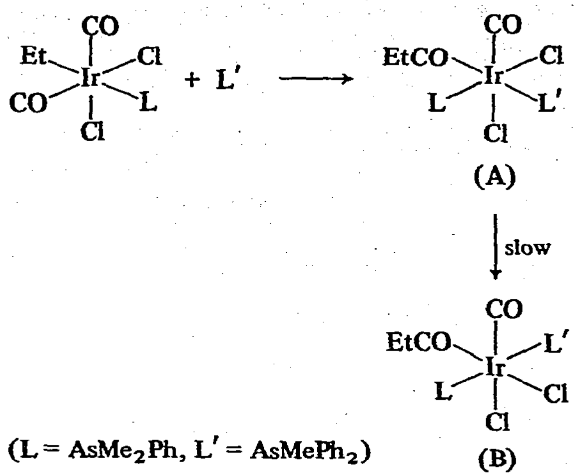
The synthetic value of nitrate complexes of Ir^{III} has been demonstrated[217]. Complexes of the type $[IrX_2(NO_3)L_3]$ (X = halogen, $L = PMe_2Ph, PEt_2Ph, AsMe_2Ph$) have been prepared from $AgNO_3$ and the corresponding trichloro species. The nitrate ligand is readily displaced by neutral ligands, Q, to give cations of the type $[IrX_2QL_3]^+$ ($Q = CO, PMe_2Ph, AsMe_2Ph$, pyridine, 3-methylpyridine, 4-methylpyridine or NH_3). Complexes of type $[IrX_2(CO)L_3]^+$, with two different configurations were prepared. $[IrCl_2(CO)L_3]^+$ reacts with NaOMe to give $[IrCl_2(CO_2Me)L_3]$, which on heating gives the hydride $[IrHCl_2(PMe_2Ph)_3]$.

The four-coordinate iridium(I) compound $[Ir(O_2S\text{-}p\text{-tolyl})(CO)(PPh_3)_2]$ has *O*-bonded sulphinate but uptake of carbon monoxide or O_2 results in isomerisation to *S*-bonded sulphinate



while addition of methyl iodide leaves the ligand *O*-bonded[218].

The mechanism and stereochemistry of carbonyl insertion reactions of Ir^{III} complexes has been studied[219].



($L = AsMe_2Ph$, $L' = AsMePh_2$)

The hypothesis of alkyl migration does not account for the spectroscopically inferred structure of isomer (A), which is the kinetically controlled product; subsequent slow isomerisation affords isomer (B). The stereoselective formation of (A) may be rationalised on the basis of the intermediacy of a square-pyramidal intermediate, which arises via a concerted approach of Et and CO accompanied by the opening of the Cl—Ir—L bond angle.

From measurement of infrared intensities on the complexes $[IrCl(CO)(PPh_3)_2]$ and $[IrCl(N_2)(PPh_3)_2]$ it is concluded that the N_2 σ-donor strength is less than that of coordinated carbon monoxide[220].

The crystal and molecular structures of the nitrosyl complexes $[IrI(Me)(NO)(PPh_3)_2]$[221], $[IrCl_2(NO)(PPh_3)_2]$[222] and $[IrH(NO)(PPh_3)_3]^+[ClO_4]^-$[223] have been reported. These papers include important discussion of the various modes of nitrosyl bonding.

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