COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1972

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Reviews have been published concerned with various aspects of the hydroformylation reaction [1,2].

The cleavage of cobalt—carbon bonds in organocobalt compounds is a subject of considerable current interest. Several modes of cleavage have been described including homolysis, photolysis, and reductive dealkylation. In a study [3] of the reaction of $[Co(DH)_2(H_2O)R]$ with $IrCl_6^{2-}$ a further reaction path for cleavage of Co—C bonds has been identified involving the initial one-electron oxidation of an aquocobalt(III) species. 1-Adamantylpentacyanocobaltate has been prepared by reaction of 1-adamantyl iodide with $K_3Co(CN)_5$ and isolated as a yellow crystalline solid stable in both neutral or alkaline solution. Its stability is comparable with that of methyl and (pyridylmethyl)pentacyanocobaltates [4].

In the presence of excess base, carbon monoxide reacts with hydridopentacyanocobaltate in aqueous solution to give the anionic species $[Co(CN)_3(CO)_2]^{2-}$. The kinetics of this reaction have been investigated and the mechanism discussed [5].

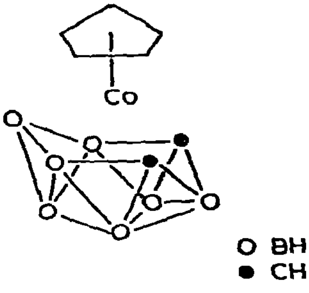
Methylcobaloximes (axial bases H_2O, imidazole, pyridine and triphenylphosphine) have been shown to C-methylate quinones; addition of Pd^{II} salts enhances the yield [6].

Hawthorne and his co-workers have continued to develop the field of metallocarborane chemistry with particular emphasis on cobalt containing species. The compound $[(\pi\text{-}C_5H_5)Co(\pi\text{-}CB_7H_8)]^-$ is obtained by a polyhedral contraction of $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_2B_{10}H_{12})$ upon degradation with base [7]. An X-ray diffraction study of $Me_4N^+[Co(C_2B_7H_9)_2]^-$ has shown that the cobalt is sandwiched by two carborane polyhedral fragments in the shape of two distorted bicapped square antiprisms with one common vertex occupied by the cobalt atom [8].

The direct synthesis of a bimetallic carborane complex, $[(C_5H_5)Co(C_2B_8H_{10})\cdot Co(C_5H_5)]$, by polyhedral expansion of $[(C_5H_5)Co(C_2B_9H_{10})]$, was carried out by treating the latter complex with sodium naphthalide followed by an excess of $CoCl_2$ and NaC_5H_5 [9].

The alkaline degradation of $[LCo\{\pi\text{-}(3)\text{-}1,2\text{-}C_2B_9H_{11}\}]^z$ followed by oxidation results in a polyhedral contraction to give $[LCo\{\pi\text{-}(1)\text{-}2,4\text{-}C_2B_8H_{10}\}]^z$

[L = C_5H_5, $z = 0$, or L = (3)-1,2-$C_2B_9H_{11}^{2-}$ and $z = -1$] [10,11]. Further degradation of these complexes by reaction with $FeCl_3$ gives [(π-C_5H_5)Co(π-$C_2B_7H_{11}$)] and [{π-(3)-1,2-$C_2B_9H_{11}$}Co(π-$C_2B_7H_9$)]$^-$. The former species eliminates H_2 at 150°C to yield I which can be rearranged to [(π-C_5H_5)Co{π-(2)-1,10-$C_2B_7H_9$}] [11].



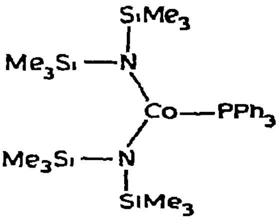
(I)

The crystal structure of [Et_4N]$^+$[(π-$C_2B_9H_{11}$)Co(π-$C_2B_8H_{10}\cdot C_5H_5N$)]$^-$ shows that the d^6 Co^{III} ion is sandwiched between mutually staggered $C_2B_9H_{11}^{2-}$ and $C_2B_8H_{10}\cdot C_5H_5N^{2-}$ anions; the latter of these has a C_2B_8 skeleton which defines an icosahedron from which two adjacent apices have been removed [12].

Rearrangement of [(π-C_5H_5)Co{π-(3)-1,2-$C_2B_9H_{11}$}] in the vapour phase at 400—700°C leads to the formation of six isomers, in which migration of the dicarbollyl carbon atoms has occurred over the polyhedral surface [13]. The chemical decomposition of [RN_2][(π-7,8-$C_2B_9H_{11}$)$_2$Co] (R = C_6H_5, C_6H_4Me) in aromatic solvents has been shown to give the complexes [Me_4N][(π-7,8-$C_2B_9H_{10}$)$_2$-C_6H_4Co] and [Me_4N][(π-7,8-$C_2B_9H_{10}$)$_2$$C_6H_3$MeCo], in which the aryl group is thought to occupy a bridging position between two $C_2B_9H_{10}$ cages [14]. Isomerisation of 1,2-$C_2B_{10}H_{12}$ to the 1,7-isomer occurs at lower temperatures by proceeding through a cobalt(III) derivative which is subsequently oxidised with $CuCl_2$ to give the free carborane [15]. A crystal structure determination of the complex [(π-C_5H_5)Co(π-7,9-$C_2B_{10}H_{12}$)] has shown that an apical cobalt(III) atom is linked to a six-atom C_2B_4 hexagonal face [16].

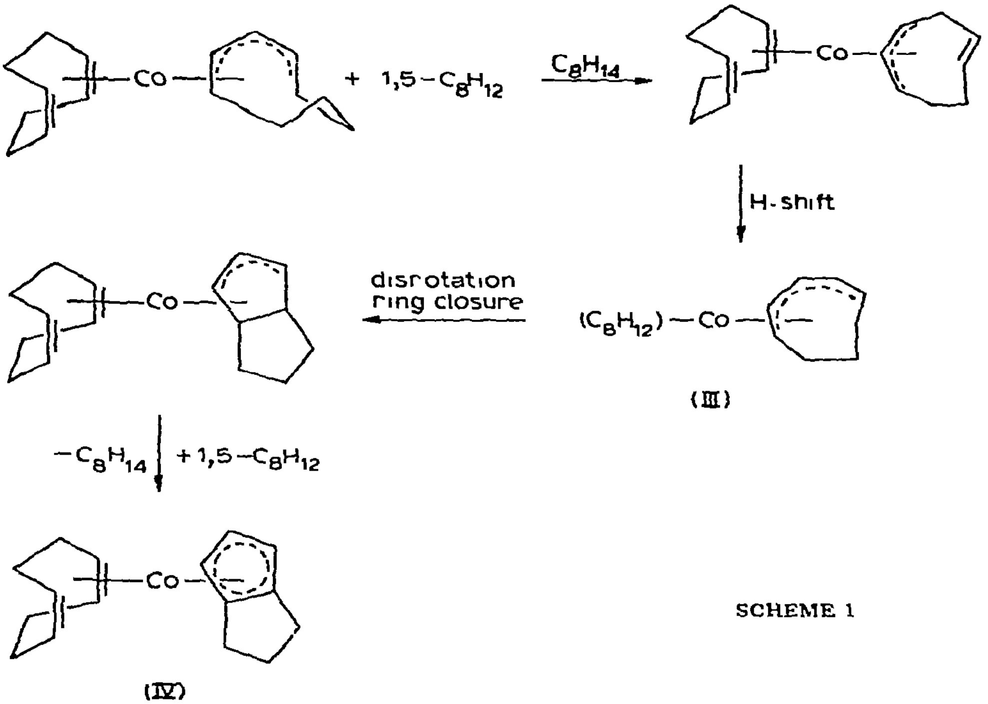
The coordination about the central Co^{III} atom of [Co{($B_{10}C_2H_{10}$)$_2$}$_2$]$^-$-[NEt_4]$^+$ consists of four Co—C σ-bonds and one Co—H—B bridge bond in a badly distorted square pyramidal structure [17]. Of all the bis-carborane complexes reported, the Co^{III} species is unique in that it is the only one whose ^{11}B NMR spectrum shows a doublet at very low field. This doublet was assigned to the two boron atoms in each icosahedron, which are simultaneously bonded to two carbon atoms, and are within bonding distance of the cobalt.

A novel three-coordinate complex II of Co^{II} has been obtained by treatment of $CoCl_2(PPh_3)_2$ with $LiN(SiMe_3)_2$; an X-ray crystal structure determination has established the illustrated structure [18].



(II)

The reaction of cyclooctenyl-1,5-cyclooctadienecobalt with 1,5-cyclooctadiene gives (4)-bicyclo[3.3.0]-2,4-octadiene-1-yl(1,5-cyclooctadiene)cobalt; the reaction proceeding via the characterised intermediate 1-3-η-1,5-cyclooctadienyl-(1,5-cyclooctadiene)cobalt [19]. It is suggested that this interesting reaction involves the steps shown in Scheme 1. In order to account for the formation of IV



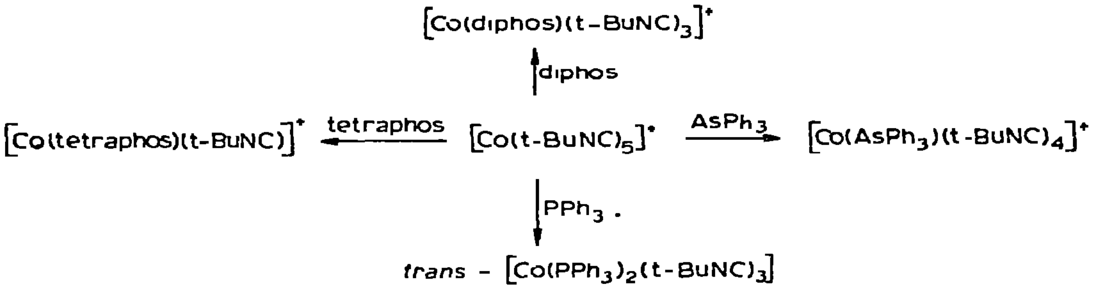
SCHEME 1

from III a ring closure with a dehydrogenation process must be postulated. It is suggested that an allowed disrotatory ring closure is involved.

The system $CoCl_2$/diphos/Et_3 Al in 1,2-dichloroethane has been shown to have high catalytic activity and selectivity for the formation of *cis*-1,4-hexadiene from 1,3-butadiene and ethylene. The temperature of the reaction appears to be critical; between 80 and 110° *cis*-1,4-hexadiene is formed in high yield, whereas, below 80° more ethylene than 1,3-butadiene is consumed, with the result that C_8 compounds are produced. Above 110° 1,4-hexadiene is isomerised to 2,4-diene. Possible mechanisms are discussed, and it is suggested that the catalytic species is an octahedral complex of cobalt(I) hydride [20].

Molecular oxygen reacts irreversibly with the Co^I cation $[Co\text{-}cis\text{-}(Ph_2PCH{=}CHPPh_2)_2]^+BF_4^-$ to form a 1/1 adduct [21]. A single crystal X-ray diffraction study has established an octahedral geometry for the adduct. It is interesting that the Co—O bond distance is significantly shorter than the previously reported Rh—O and Ir—O distances, but this decrease can however be explained by consideration of the relative covalent radii. The O—O bond distance is essentially identical with that found in $[Rh(O_2)(diphos)_2]^+$ and comparable with those in $[Ir(O_2)Cl(CO)(PEtPh_2)_2]$ and $[Ir(O_2)Br(CO)(PPh_3)_2]$.

The substitution reactions of the pentakis(t-butylisocyanide)cobalt cation with phosphines and arsines have been investigated [22], and are summarised in Scheme 2. Also investigated were the corresponding reactions with *trans*-Ph_2-

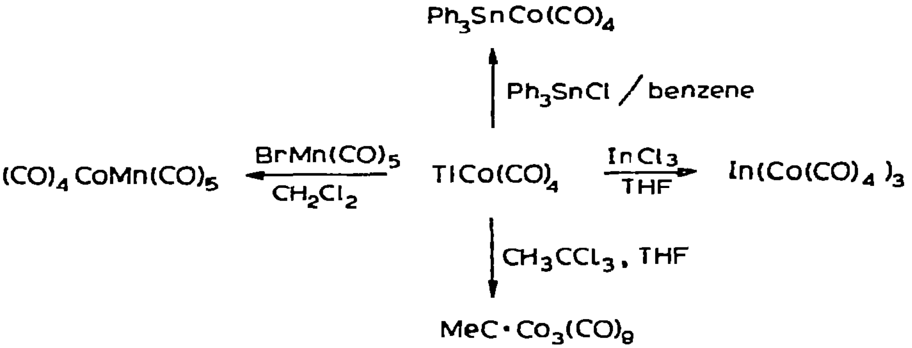


tetraphos = P$(CH_2CH_2PPh_2)_3$

Scheme 2

$PCH{=}CHPPh_2$, $(Ph_2ECH_2CH_2)_2PPh$ (E = P or As), $Ph_2PCH_2CH_2P(Ph)CH_2CH_2$-$P(Ph)CH_2CH_2PPh_2$. Variable temperature ^1H NMR observations with the parent cation $[Co(t\text{-}BuNC)_5]^+$ are interpreted in terms of a relatively high-energy dynamic process, which averages axial and equatorial environments.

Thallous tetracarbonylcobaltate prepared by reaction of thallium metal with $Co_2(CO)_8$ in toluene, is a convenient and versatile source of the tetracarbonylcobaltate anion [23]. As illustrated in Scheme 3, $TlCo(CO)_4$ undergoes a variety of reactions analogous to the less easily handled $NaCo(CO)_4$. The simplicity of its preparation is an added advantage.



Scheme 3

Reaction of germyl bromide with $NaCo(CO)_4$ in diethyl ether has been shown [24] to afford germyltetracarbonylcobalt $GeH_3Co(CO)_4$ as a relatively stable material. The $[^2H_3]$-germyl analogue was obtained similarly, and the ^1H NMR and vibrational and mass spectra discussed. Reaction with mercuric chloride leads to cleavage of the Ge—Co bond and the formation of GeH_3Cl. The other products are assumed to be a mixture of $Hg[Co(CO)_4]_2$ and $ClHg[Co(CO)_4]$ The reaction with HCl also involves predominant cleavage of the Ge—Co bond. In general, $GeH_3Cl(CO)_4$ also reacts with nitrogen bases to give 1/2 adducts, this again is similar to $SiH_3Co(CO)_4$.

Reaction of $[NiX(L)\text{-}\pi\text{-}C_5H_5]$ (L = phosphine or arsine; X = Cl or Br) with $NaCo(CO)_4$ affords the complex $[Ni(\pi\text{-}C_5H_5)Co(CO)_4L]$. IR studies indicate that these compounds contain both bridging and terminal carbonyl ligands. Thus it appears they have structures, which are intermediate between those of $[\pi\text{-}C_5H_5\text{-}Ni(CO)_2]_2$ and $Co_2(CO)_8$ which, in the solid state, contain $M(CO_\mu)_2M$ moieties.

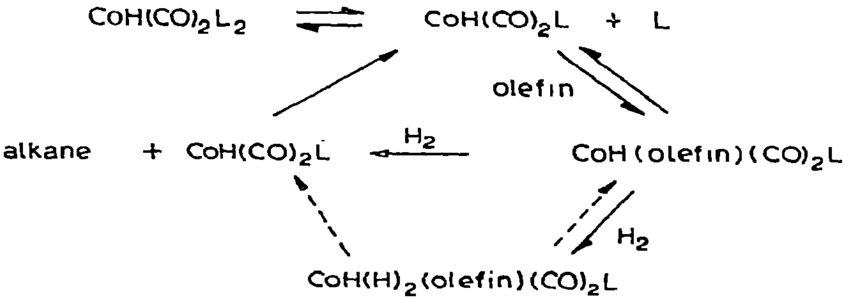
If it is assumed that the EAN rule is obeyed, the most reasonable structures are those of the type π-$C_5H_5Ni(CO_\mu)_2Co(CO)_3L$ with a non-planar bridging system and a Ni—Co bond. Thus the ligand L appears to have migrated from the nickel to the cobalt. Careful examination of the IR spectra suggests that these compounds exist in solution as mixtures of carbonyl bridged and non-bridged species [25].

The reaction of $Hg[Co(CO)_4]_2$ with various phosphines in the absence of light give $Hg[Co(CO)_3L]_2$ and under more vigorous conditions $Hg[Co(CO)_2L_2]$ derivatives (L = PEt_3, P-n-Bu_3, PMe_2Ph, P-i-Pr_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OMe)Ph_2$, $P(OCH_2)_2OPh$ or $P(OPh)_3$). The bidentate ligand diphos yields $[(diphos)Co_2(CO)_6Hg]$ and $Hg[(diphos)Co(CO)_2]_2$. Analogous arsenic compounds are also described. The reaction of some of these compounds with mercury(II) halides or tin(IV) chloride have also been examined. The complex $Hg[Co(CO)_2(diphos)]$ yields $[CoX(CO)_2(diphos)]$ (X = HgCl, HgBr, HgI or $SnCl_3$), whereas (diphos)-$Co_2(CO)_6Hg$ gives a mixture of $[CoX(CO)_2(diphos)]$ and $[XCo(CO)_4]$ [26].

X-ray crystallographic studies [27] have shown that heating the complex $Co_2(CO)_6(f_4fars)$ [$f_4fars = Me_2As\overline{C=C(AsMe_2)CF_2CF_2}$] under reflux in hexane results in the cleavage of a Me_2As group from $f_4$fars with subsequent dimerisation to form $\{(Me_2As)\overline{C=CCF_2CF_2}\}_2(Me_2As)_2Co_4(CO)_9(H)_2$. One cobalt atom has a very distorted octahedral environment formed by the π-bond of a fluorocyclobutenyl ring, a terminal carbonyl group, a postulated hydrogen atom, and a dimethylarsine group, which is also linked to the second type of cobalt atom; this latter has a trigonal bipyramidal environment with axial (bridging) dimethylarsine and carbonyl groups and equatorial terminal carbonyl groups, and the arsenic atom attached to the fluorocyclobutenyl ring.

The equilibrium and the rates of the reaction between $Co_2(CO)_8$ and H_2 to form $HCo(CO)_4$ have been studied in n-heptane [28]. The formation of $HCo(CO)_4$ is first-order in both $Co_2(CO)_8$ and H_2, and at a low partial pressure of CO is inversely proportional to carbon monoxide concentration. The rate-determining step is the reaction of H_2 with $Co_2(CO)_7$, where the latter is formed in a fast pre-equilibrium.

An investigation has been described of the kinetics of homogeneous cyclohexene hydrogenation catalysed by $CoH(CO)_2\{P(n\text{-}C_4H_9)_3\}$. The results are summarised in Scheme 4 [L = $P(n\text{-}Bu)_3$]. It is suggested that olefin insertion into the

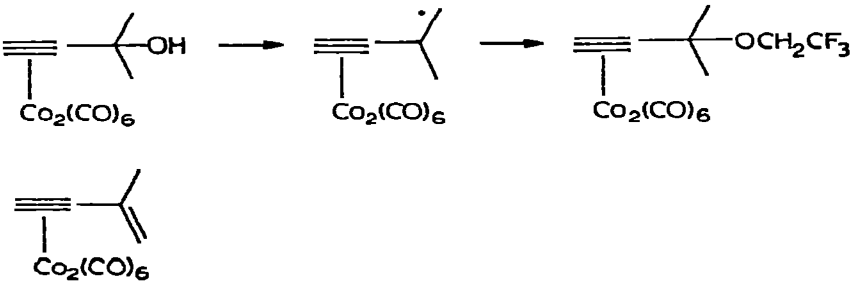


Scheme 4

initial cobalt—hydrogen bond is not an important step, possibly because the hydrido and olefin ligands have a relative *trans*-configuration. The rate-determining step is assumed to be the direct hydrogen interaction with the cobalt-coordinated olefin. The absence of a detectable isotope effect is interpreted as evidence that this interaction proceeds via instantaneous H_2 bond breaking and C—H bond making. These ideas contrast with the suggestion that in the $[RhH(CO)(PPh_3)_2]$-catalysed hydrogenation of olefin an initial insertion occurs into a Rh—H bond to form a σ-alkyl, which is then broken by H_2 after activation by the metal.

The kinetics of the reaction of $Co_2(CO)_8$ with alkynes to give hexacarbonyl-μ-alkyne dicobalt have been reexamined [30,31]. In contrast to earlier interpretations involving a "reactive form" of $Co_2(CO)_8$ the reaction is shown to involve initial dissociation of CO to give $Co_2(CO)_7$, which rapidly adds alkynes.

The greatly enhanced stability of carbonium ions α to an organometallic substituent is widely recognised, and recently experiments have been directed towards an evaluation of the stability of hexacarbonyl α-alkynyldicobalt carbonium ions [32]. Treatment of the carbinol (Scheme 5) with a catalytic amount of CF_3CO_2H in trifluoroethanol led to the quantitative formation of the trifluoroethyl ether; under identical conditions only about 10% of the ene—yne V reacted.



(V)

Scheme 5

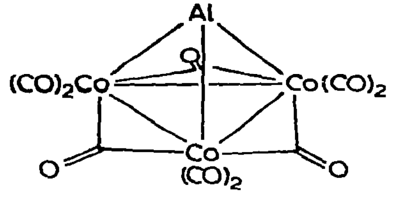
Dicobalt octacarbonyl and some of its derivatives $NaCo(CO)_4$, $Co_4(CO)_{12}$, $Hg[Co(CO)_4]_2$, $[Co(CO)_3PPh_3]_2$ and $NaCo(CO)_3PPh_3$ react with activated *gem*-dihalides R_2CX_2, such as dichlorodiphenylmethane, 9,9-dihalofluorenes and dimethyldibromomalonate to give the olefin $R_2C{=}CR_2$ [33]. The isolation of 9,9'-dichlorobisfluorenyl together with the expected olefin from the reaction of 9,9'-dichlorofluorene with $Co_2(CO)_8$ ruled out the possibility of a carbene complex intermediate, and suggested a stepwise process: $R_2CX_2 \rightarrow R_2C(X)C(X)R_2 \rightarrow R_2C{=}CR_2$. The formation of $Co_2(CO)_6(PPh_3)_2$ in the reaction of $NaCo(CO)_3PPh_3$ with Ph_2CHBr and Ph_2CCl_2, and the formation of *trans*-stilbene in the reaction of $Co_2(CO)_8$ with *D,L*-dibromostilbene suggests the possibility of a radical mechanism. It is also noted that the formation of alkylidyne tricobalt nonacarbonyl from RCX_3 and $Co(CO)_4^-$ could also proceed via radical intermediates.

The addition of CCl_4 to olefins is catalysed by $Co_2(CO)_8$. It is assumed that initiation is promoted by metal—metal bond homolysis. This investigation has been extended to include the reaction (150°) of methyl trichloroacetate with 1-hexene; a reaction which occurs stereospecifically to give $C_4H_9CHClCH_2CCl_2CO_2Me$ [34].

Reactions of *trans*-$[^2H_2]$ethylene with solutions of $CoH(N_2)(PPh_3)_3$ and

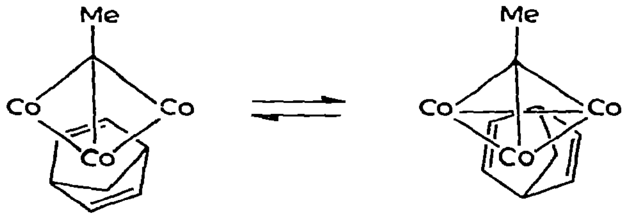
$RhH(PPh_3)_3$ in benzene at 50° have been investigated. Redistribution of hydrogen isotopes is discussed in terms of reactions proceeding via ethyl intermediates [35].

Treatment of sublimed aluminium trichloride with an excess of sodium tetracarbonyl cobalt in dry benzene gives a deep red, moisture sensitive complex $AlCo_3(CO)_9$, for which structure A is proposed [36]. This is related to $Co_4(CO)_{12}$ in that a $Co(CO)_3$ group is replaced by an aluminium atom.



(A)

Arenes coordinate to methinyltricobaltenneacarbonyls $YCCo_3(CO)_9$, thrpu one cobalt atom, whereas, cyclooctatetraene is linked symmetrically to the basal cobalt triangle. These studies have been extended to other polyenes, dienes and olefins [37]. Cyclopentadiene does not act as a diene, but instead undergoes hydrogen abstraction to form cyclopentadienyl complexes $YCCo_3(CO)_4(\pi\text{-}C_5H_5)_2$ The norbornadiene (nbd) complexes $YCCo_3(CO)_7(nbd)$ undergo an interesting non-rigid behavior illustrated by the process VI ⇌ VII.



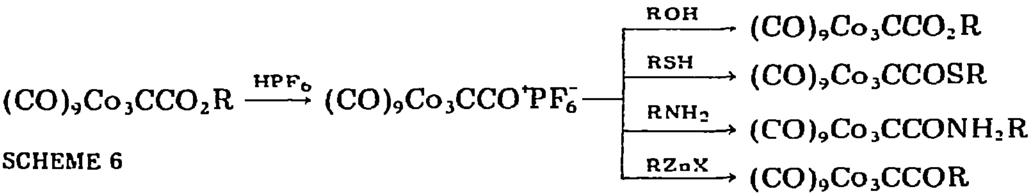
(VI) (VII)

Both $ClCCo_3(CO)_9$ and $BrCCo_3(CO)_9$ react with arenes in the presence of a Lewis acid such as $AlCl_3$ or BF_3 forming the aryl clusters $RCCo_3(CO)_9$ in high yield [38]. Methylene chloride is a convenient solvent for this reaction. Deactivated and hindered or polysubstituted arenes failed to react or the product yield was low. As is normally observed in the alkylation of arenes *ortho—para* substitution is the rule, and the same holds true for the cluster reactions except that steric hinderance generally prevents *ortho*-substitution.

$$\begin{tikzcd}
(CO)_9Co_3CCl + AlCl_3 \rightleftharpoons & (CO)_9Co_3C{-}Cl\cdots AlCl_3 \arrow[d, "RH"] \\
RCCo_3(CO)_9 & {[HRCCo_3(CO)_9]^+AlCl_4^-} \arrow[l, "-HCl"']
\end{tikzcd}$$

A structure determination of the complex $[CCo_3(CO)_9]_2$ obtained by heating $BrCCo_3(CO)_9$ in toluene confirmed the structure, in which two $CCo_3(CO)_9$ units are formed by a carbon—carbon bond. The two Co_3 triangles are semi-eclipsed to minimize non-bonded interactions [39].

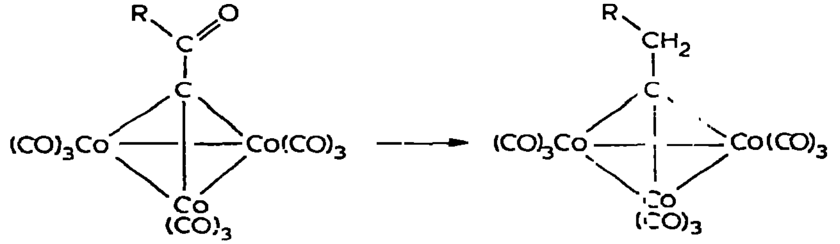
Addition of HPF_6 in propionic anhydride to carboalkoxymethylidynetricobalt nonacarbonyl results in the formation of the stable but reactive carbatricobalt decacarbonyl cation [40]. As illustrated (Scheme 6) this cation undergoes a wide variety of reactions with nucleophilic reagents.



SCHEME 6

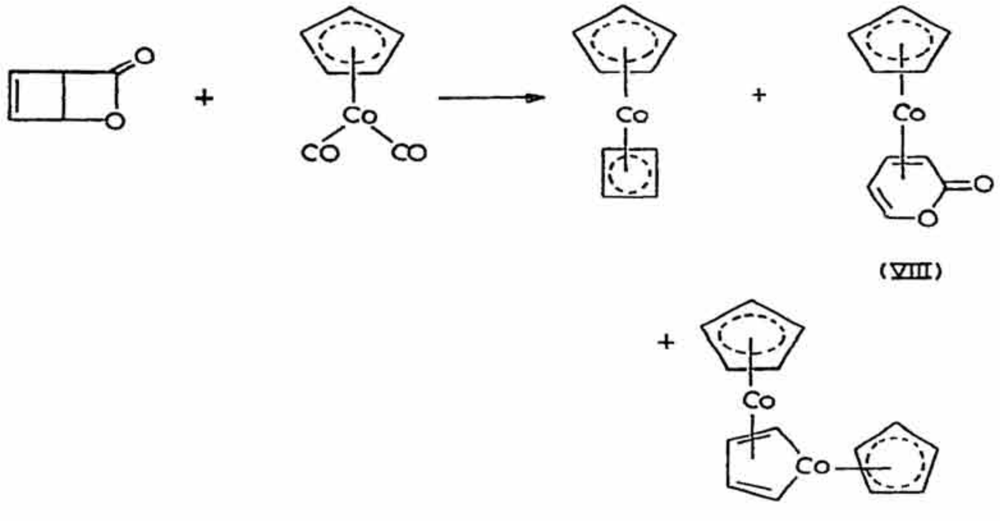
An alternative, and interesting synthesis of the acylating reagent is the treatment of $ClCCo_3(CO)_9$ with $AlCl_3$ in methylene chloride; a reaction which involves the transfer of CO to the apical carbon atom and which is not facilitated by carrying out the reaction in an atmosphere of carbon monoxide [41].

The ketones $RC(O)CCo_3(CO)_9$, prepared by reaction of trichloromethyl ketones, $RC(O)CCl_3$, with $Co_2(CO)_8$ or by reaction of mild alkylating agents such as RZnX or R_4Sn with the acylium salts $[(CO)_9Co_3CCO]^+$, are reduced in high, often quantitative, yield to alkylidynetricobalt nonacarbonyls by triethylsilane in trifluoroacetic acid in THF medium [42].



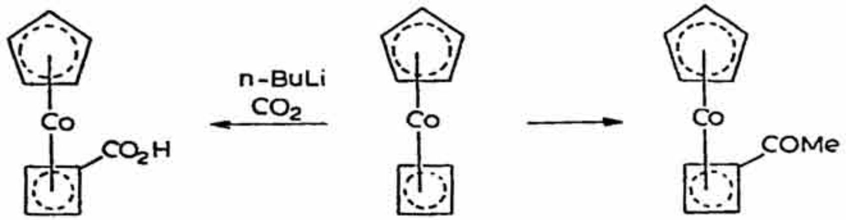
The reactions of $[(\pi\text{-dienyl})FeCo(CO)_6]$ (dienyl = C_5H_5, MeC_5H_4 and C_9H_7) with various dienes gives $[(\pi\text{-dienyl})FeCo(CO)_4(\text{diene})]$ complexes (diene = norbornadiene, 1,3-cyclohexadiene or 2,3-dimethyl-1,3-butadiene). In the solid state these complexes exist as either *cis*- or *trans*-carbonyl bridged tautomers similar to those of related $[\{(\pi\text{-dienyl})Fe(CO)_2\}_2]$ and $[\{(\pi\text{-diene})Co(CO)_2\}_2]$ complexes. In solution the two isomers are in equilibrium [43].

Cyclobutadiene(cyclopentadienyl)cobalt has been prepared by photochemical reaction of $[Co(CO)_2\text{-}\pi\text{-}C_5H_5]$ with photo-α-pyrone [44]. The complexes VIII and IX are also formed in this reaction, and it is interesting that the dicobalt species exhibit fluxional behavior at elevated temperatures involving the interchange of the cobalt atom with concurrent exchange of metal—carbon σ- and π-bonds. Similar behaviour is exhibited by a carbomethoxy substituted derivative. The complex $[Co(\pi\text{-}C_4H_4)(\pi\text{-}C_5H_5)]$ undergoes Friedel—Crafts acetylation and metallation with n-BuLi/TMED preferentially on the cyclobutadiene ring. The preferential reaction of the four-membered ring in these reactions is most plausibly attributed to the greater acidity of the protons in this ring due to the increased s-character of its C—H bonds.

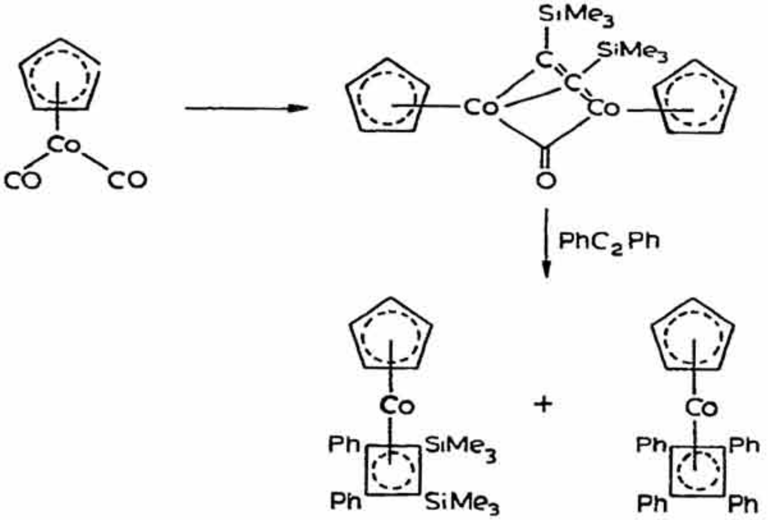


(VIII)

(IX)



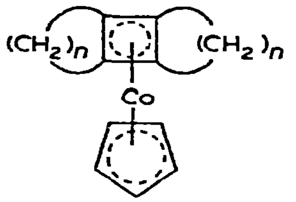
Whereas, diphenylacetylene reacts with $[Co(CO)_2\text{-}\pi\text{-}C_5H_5]$ to form $[Co\text{-}(\pi\text{-}C_4Ph_4)(\pi\text{-}C_5H_5)]$ extensions of the reaction to other acetylenes, for example, $CF_3C_2CF_3$ or MeC_2Me affords cyclopentadienone complexes. However, $PhC{\equiv}CSiMe_2Ph$ (R = Me, $SiMe_3$) gives two isomeric cyclobutadiene complexes, *cis*- and *trans*-$[\pi\text{-}C_5H_5Co\{Ph_2C_4(SiMe_2R)_2\}]$ in almost quantitative yield [45]. In contrast, the corresponding reaction with $RMe_2SiC{\equiv}CSiMe_2R$ (R = Me, Ph) led to the formation of dinuclear complexes.

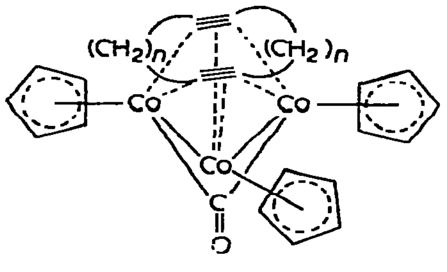


Because the dinuclear complexes react with diphenylacetylene to give a cyclobutadiene complex, related dinuclear species are speculated to be intermediates in the formation of other cyclobutadienecobalt species.

Related to this investigation is the confirmation by X-ray crystallography of the structure of *trans*-[π-$C_5H_5Co\{\pi$-$Ph_2C_4(SiMe_3)_2\}$] previously deduced on the basis of mass-spectral studies [46].

The macrocyclic alkadiynes 1,7-cyclododecadiyne, 1,7-cyclotridecadiyne, 1,7- and 1,8-cyclotetradecadiyne, and 1,8-cyclopentadecadiyne react with $Co(CO)_2$-π-C_5H_5 or, in some cases $Co(1,5$-$C_8H_{12})$-π-C_5H_5, in boiling octane or cyclooctane to give complexes Co(alkadiyne)(π-C_5H_5), in which the macrocyclic alkadiyne has undergone an intramolecular transannular cyclisation reaction to form a tricyclic cyclobutadiene derivative [47]. The reaction of 1,8-cyclotetradecadiyne with $Co(CO)_2$-π-C_5H_5 also gives the black trimetallic derivative X, for which the illustrated structure is proposed, in which an intact 1,8-diyne is bonded to a triangle of cobalt atoms. This reaction of an alkadiyne is clearly different from known interactions of simple alkynes with transition metals.





(X)

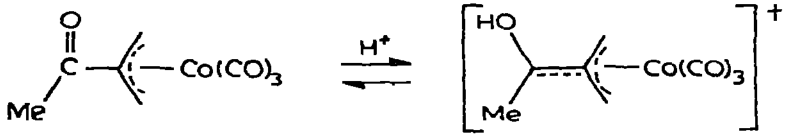
A versatile synthesis of pentamethylcyclopentadienyl complexes has been developed involving the reaction of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene with metal carbonyls. As part of this investigation the reaction of $Co_2(CO)_8$ with Me_5C_5COMe has been shown to give the red crystalline complex $Co(CO)_2$-π-C_5Me_5 [48].

The structure of cyclopentadienyl(duroquinone)cobalt dihydrate XI has been determined by X-ray crystallography, and a detailed comparison made of the molecular parameters of this complex with those of closely related complexes [49]. Evidence that the metal-duroquinone interaction in XI is considerably stronger than that in the electronically-equivalent 1,5-cyclooctadiene(duroquinone)nickel is given not only by the metal—C(olefin) distances being shorter in the duroquinone—cobalt complex, but also by the much greater C_{2v}-type distortion of the duroquinone ring from the planar D_{2h} configuration in free duroquinone.

Equimolar amounts of dicarbonyl-π-cyclopentadienylcobalt and mercuric chloride react to give a 1/1 adduct. X-ray analysis shows this to be a true adduct containing a metal donor Co—Hg bond. By the reaction of excess of $HgCl_2$ with either the 1/1 adduct or $Co(CO)_2$-π-C_5H_5 crystals of $Co(CO)_2(\pi$-$C_5H_5)\cdot 3HgCl_2$ are obtained. In principle this compound could be a 1/1 adduct containing an additional $HgCl_2$ molecule in the lattice or a salt as in the ruthenium and osmium complexes $[M(CO)_3(PPh_3)_2HgCl]^+HgCl_3^-$. An X-ray diffraction study has confirmed the former possibility [50,51].

The cyclopentadienyl di- and tri-cyanides of cobalt π-$C_5H_5Co(CN)_2(PPh_3)$ and $[\pi$-$C_5H_5Co(CN)_3]^-$ have been prepared by reaction of cyanide with π-C_5H_5-$CoI_2(PPh_3)$ and π-$C_5H_5CoI_2(CO)$ respectively [52]. The anionic tricyanide is most easily isolated as its benzyltriphenylphosphonium salt. Alkylation of the anionic species with MeI or trimethyloxonium tetrafluoroborate affords the neutral mono- and di-catonic tris(alkylisocyanide) complexes π-$C_5H_5Co(CO)_2$-$(CNMe)$ and $[\pi$-$C_5H_5Co(CNEt)_3]^{2+}$.

The relatively stable tricarbonyl(2-acetyl-π-allyl)cobalt is reversibly protonated in concentrated sulphuric acid to form a cationic species, which on the basis of the ^1H NMR spectrum is considered to be a cationic trimethylenemethane cobalt species. It was found that the introduction of an electron-withdrawing acyl group into the allyl moiety improves the air stability of the tricarbonyl π-allyl cobalt system. Further the 2-acetyl-π-allyl group does not undergo an insertion reaction with isocyanides or carbon monoxide; the reaction with t-BuNC or PPh_3 merely results in the substitution of one of the carbonyl groups [53].



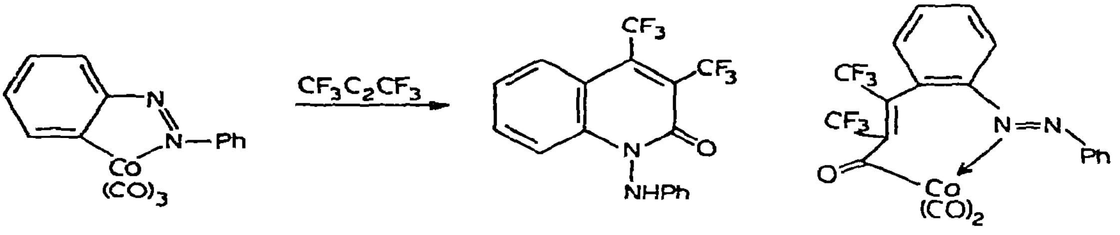
The reaction of cobaltocene with organoboron dihalides ($PhBCl_2$, $PhBBr_2$, $MeBBr_2$) affords a synthetic route to the paramagnetic complexes $Co(\pi$-$C_5H_5)$-(C_5H_5BR) and $Co(C_5H_5BR)_2$ as well as the diamagnetic cations $[Co(C_5H_5)$-$(C_5H_5BR)]^+$ (R = Ph, Me) [54]. In these complexes the borinate anion $[C_5H_5$-$BR]^-$ is bonded to the cobalt as a 1-6η bonded ligand. An X-ray crystallographic study [55] of bis(methoxoborinato)cobalt, $[Co(MeOBC_5H_5)_2]$ confirms the mode of bonding. The cobalt—boron distance (2.348 Å) although considerably longer than the Co—B distance in carborane complexes, is, however, indicative of bonding.

Examination of the carbonyl and nitrosyl stretching frequencies of the complexes $Co(NO)(CO)_2L$ obtained by the reaction of the cyanophosphines $(CF_3)_2PCN$, $CF_3P(CN)_2$ and $P(CN)_3$ with $Co(NO)(CO)_3$ shows that these ligands bond through the phosphorus and are extremely good π-acceptors. However, it should be noted that in the reaction with $P(CN)_3$, extensive polymerisation occurs [56].

The known complex cations $[Co(NO)_2L_2]^+$ [L = PPh_3, $P(OPh)_3$ and PPh_2-Me or L_2 = diphos] are conveniently prepared in high yield from $Co(NO)(CO)L_2$ and $NOPF_6$ in methanol/toluene mixtures. The triphenylphosphine cation reacts with bromide anion to give $[Co(NO)_2(PPh_3)Br]$. However, the corresponding diphos cation reacts to give $[Co(NO)_2(diphos)Br]$, which it is suggested contains both linear and bent nitrosyl ligands. It is interesting that the reaction of $[Co(NO)_2(PPh_3)_2]^+$ with $NaBH_4$ gives the mono-nitrosyl $Co(NO)(PPh_3)_3$ with evolution of NH_3; the ammonia being presumed to arise by reduction of a coordinated nitrosyl ligand [57].

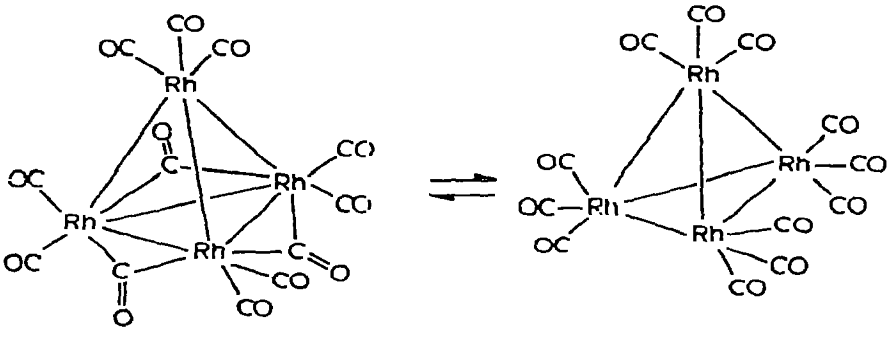
An improved synthesis and single-crystal X-ray diffraction study of bis-(dimethyldithiocarbamato)nitrosyl cobalt has been described. The coordination geometry about the cobalt is a tetragonal pyramid with the bent nitrosyl group at the apex [58].

It is well known that azobenzenes can be carbonylated to form indazolones and dioxoquinazolines in the presence of $Co_2(CO)_8$. Later, Heck showed [59] that carbonylation of a presumed intermediate XII, in methanol, afforded instead 2-methoxycarbonylhydrazone benzene. It has now been found that XII reacts with hexafluoro-2-butyne to form XIII and XIV. The reaction leading to XIII and XIV has been shown to occur with substituted azobenzenes, and in all cases analogous compounds are formed thus providing a route to substituted quinolines [60].



(XII) (XIII) (XIV)

An important ^{13}C Fourier transform NMR study of the cluster compound $Rh_4(CO)_{12}$ has demonstrated the possible generality of rapid permutational isomerisation reactions (fluxionality) through the agency of bridge-terminal interconversions of carbonyl groups [61]. It is suggested that the mechanism for CO scrambling in the Rh_4 cluster involves a sequence of XV ⇌ XVI interconversions.

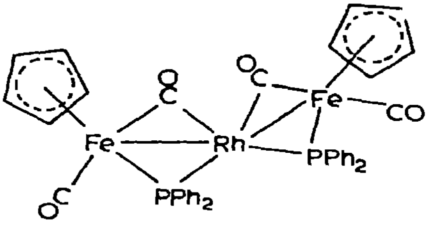


(XV) (XVI)

It had been earlier reported that $[Rh(CO)_2Cl]_2$ reacted with carbon monoxide at atmospheric pressure to produce $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, the proportions depending on the solvent system. With hexane as solvent, and in the presence of $NaHCO_3$, $Rh_4(CO)_{12}$ was reported to be the predominant product. It has now been found that water is a necessary component for the reaction to occur, and reaction is rapid in its presence. This has been used as the basis for a convenient low pressure synthesis of $Rh_4(CO)_{12}$.·Evidence was obtained in this reaction for a transient bridging carbonyl species [62].

Previously, $Rh_4(CO)_{12}$ has been used as a hydroformylation catalyst at elevated pressures (50—100 atm) and temperatures (75°). It has now been reported [63] that a solution of $Rh_4(CO)_{12}$ in toluene reacts rapidly with a mixture of propene and hydrogen (atm. pressure and room temperature) to give in a stoicheiometric reaction 90—95% yield of the aldehydes (1/1, n/iso). In the absence of one of the gases only a slow formation of $Rh_6(CO)_{16}$ is observed. In more polar solvents such as methanol or acetone only traces of aldehydes are formed, the reaction products being $Rh_6(CO)_{16}$ and acyl derivatives of the type $[Rh_6(CO)_{15}(COR)]^-$; using ethylene it was possible to isolate the salt $[Rh_6(CO)_{15}(COEt)]^-[NMe_4]^+$. Treatment of $Rh_4(CO)_{12}$ with PPh_3 gives $[Rh_2(CO)_4(PPh_3)_4]$; which is a hydroformylation catalyst. Interestingly, hydroformylation becomes catalytic on using $Rh_4(CO)_{10}(PPh_3)_2$. During these reactions hydrocarbons are formed corresponding to the radicals of the phosphine, for example, using a $PPh_3/Rh_4(CO)_{12}$ ratio of 2, about one molar equivalent of benzene is formed suggesting that the formation of the phosphido bridges is important in the catalytic reaction.

The reaction of $[Rh(1,5\text{-}C_8H_{12})Cl]_2$, $[Rh(CO)_2Cl]_2$ or $RhCl_3 \cdot 3H_2O$ in methanol or $[Rh(1,5\text{-}C_8H_{12})(THF)_2]^+$ in tetrahydrofuran with an excess of $[Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_4Me)]$ affords the cationic species $[Rh\{Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_4Me)\}_2]$. An X-ray diffraction study shows that the cation does not contain a $RhFe_2$ cluster, instead the structure determination established the illustrated open structure XVII. It is suggested that a triangular structure is unstable with respect to the open arrangement, because of the presence of the strongly basic phosphido-groups [64].



(XVII)

In hexane, $M_4(CO)_{12}$ (M = Co, Rh) undergo phosphine substitution reactions to afford $Co_4(CO)_{12-n}L_n$ (L = $P(OMe)_3$, n = 1—4; L = PEt_3, n = 2 or 3) and $Rh_4(CO)_{12-n}L_n$ (n = 1 or 2). The infrared spectra of the rhodium derivatives suggest that substitution occurs at basal metal atoms as opposed to the unique apical atom. In the presence of excess L and under carbon monoxide pressure $Rh_2(CO)_6L_2$, which readily revert to the tetranuclear derivatives, are formed. From an IR study of the effect of carbon monoxide pressure on $Rh_4(CO)_{12}$, evidence has been obtained for the formation of $Rh_2(CO)_8$ [65].

An X-ray crystallographic study of the species $Rh(CO)_2(PPh_3)_2 \cdot 2CH_2Cl_2$, first reported by Wilkinson et al. [66] shows that the complex is dimeric, and that there are two bridging carbonyl groups per dimer. The Rh—Rh separation of 2.630(2) Å is in the range (2.618—2.796 Å) reported for other Rh—Rh bonds, and confirms the existence of a rhodium—rhodium bond. It is interesting that there is no interaction between the metal atoms and the solvent molecule showing that the complex is, therefore, coordinatively unsaturated [67].

The complexes $[Rh_2(CO)_3(PPh_3)(O_2CR)_2]_2$ (R = Me, Et) have been prepared from the corresponding dinuclear carboxylatorhodium carbonyls by treatment with the controlled amount of triphenylphosphine. Both the substituted and unsubstituted dinuclear complexes are converted by an excess of the ligand into the mononuclear complex $[Rh(CO)(PPh_3)_2(O_2CR)]$ [68].

The complex $Rh_2(PF_3)_8$, which resembles $Co_2(CO)_8$ in many chemical respects, reacts with a variety of acetylenes to give volatile complexes of formula $[Rh_2(PF_3)_6(ac)]$. An X-ray crystallographic study of $[Rh_2(PF_3)_4(PPh_3)_2(PhC_2Ph)]$ confirms the structural analogy between $[Rh_2(PF_3)_6(ac)]$ and $[Co_2(CO)_6(ac)]$; the overall geometry being similar. If it is assumed that all of the $[Rh_2(PF_3)_6(ac)]$ complexes are structurally analogous then it would be expected that complexes containing unsymmetrical disubstituted acetylenes should have three non-equivalent PF_3 groups, two of these become equivalent when the acetylene is symmetrically disubstituted. However, variable ^{19}F NMR studies show that the molecules are stereochemically non-rigid. The non-rigidity can be explained by assuming a propeller-like rotation of the PF_3 ligands about the Rh—Rh bond with the acetylene remaining stationary. Alternatively, or in addition, there could be a concerted rotation of the $Rh_2(PF_3)_6$ unit with respect to the acetylene [69].

The synthesis and some ligand exchange reactions of $[RhX(PF_3)_2]_2$ (X = Cl, Br or I) have been reported. The complexes $[Rh(CO)_2X]_2$ (X = Cl, Br or I) react with an excess of PF_3 at room temperature to afford the red, volatile, crystalline di-μ-halogenotetrakis(trifluorophosphine)dirhodium(I) complexes in almost quantitative yield. Treatment of $[Rh(CO)_2Cl]_2$ with smaller amounts of PF_3 affords $[Rh_2Cl_2(PF_3)_x(CO)_{4-x}]$ (x = 1, 2, 3), which are also produced as a result of ready intermolecular ligand exchange reactions between $[Rh(CO)_2Cl]_2$ and $[RhCl(PF_3)_2]_2$ in solution at room temperature. The complex $[RhCl(PF_3)(CO)]_2$ has one PF_3 group coordinated to each rhodium atom. The complexes $[RhX(PF_3)_2]_2$ react further with PF_3 to yield yellow $[RhX(PF_3)_4]$ compounds, which are stable at room temperature only under a pressure of PF_3.

The complex $[RhCl(PF_3)_2]_2$ has also been obtained by the ready displacement of ethylene from $[RhCl(C_2H_4)_2]_2$ under mild conditions. ^{19}F NMR studies show that $[RhCl(PF_3)_2]_2$ readily undergoes a rapid intermolecular exchange reaction with PF_3 and carbon monoxide. The binuclear complex $[RhCl(C_2H_4)(PF_3)]_2$ formed by mixing a solution containing equimolar amounts of $[RhCl(C_2H_4)_2]$ and $[RhCl(PF_3)_2]_2$ has been shown to have one ethylene and one PF_3 ligand attached to each rhodium atom. Whereas, $[RhCl(PF_3)_2]_2$ reacts with carbon monoxide to give $[Rh(CO)_2Cl]_2$, triphenylphosphine cleaves the halogen bridge affording the square-planar complex *trans*-$[RhCl(PF_3)(PPh_3)_2]$, which can also be obtained by reaction of $RhCl(PPh_3)_3$ with PF_3. Although $[RhCl(PF_3)(PPh_3)_2]$ does not dissociate in solution it does undergo a rapid intermolecular exchange reaction of coordinated PF_3 or PPh_3 ligands [70,71].

In an important investigation some variable temperature NMR studies with the stereochemically non-rigid five-coordinate hydrides $HM(PF_3)_4$ (M = Co, Rh or Ir), $[HM\{P(OEt)_3\}_4]$ (M = Co, Rh), $[HM\{Ph_2PCH_2\}_2]$ and $[HIr(CO)_2(PR_3)_2]$ are discussed in terms of possible reaction paths. The limitations of idealized rearrangement mechanisms are discussed, and the probable multi-reaction path character of these rearrangements is emphasized. A new rearrangement mechanism is discussed, which is described as tetrahedral tunneling [72].

The confusion over reactions of $[Rh(CO)_2Cl]_2$ with phosphorus ligands L appears to be only partially resolved. Agreement seems to have been reached on the existence of *trans*-$[RhCl(CO)L_2]$, *trans*-$[RhCl(CO)L]_2$ and $[Rh_2Cl_2(CO)_3L]$, and the probable non-existence of *trans*-$[RhCl(CO)_2L]$, but such species as *cis*-$[RhCl(CO)_2L]$, are also said to be found under certain conditions [73,74].

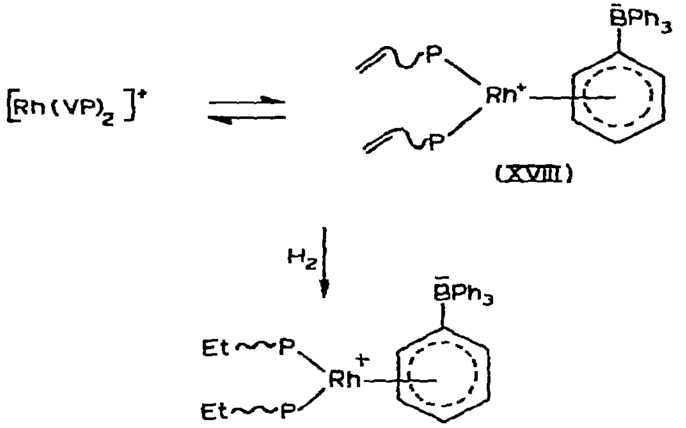
Tris(trimethylsilyl)phosphine (siphos) reacts with $[Rh(CO)_2Cl]_2$ to give *trans*-$[RhCl(CO)(siphos)_2]$, which reacts with ethanolic sodium borohydride in the presence of the phosphine to give the tetrahydroborate complexes $[Rh(BH_4)(CO)(siphos)_2]$. Similar reactions are reported for the corresponding iridium system. Reaction of siphos with rhodium trichloride and tribromide gives respectively the dimeric $[RhCl_2(siphos)_2]_2$ and the monomeric *trans*-$[RhBr_2(siphos)_2]$ complexes [75].

Two common starting points for the preparation of Rh^I complexes are $[Rh(CO)_2Cl_2]^-$ and $[Rh(CO)_2Cl]_2$. Preparation of the latter species, though not difficult, is rather time consuming while the former can be obtained very quickly. However, the use of the anionic species has the disadvantage that the elements of HCl are present in the reduced solution, and can be expected to add oxidatively to any derivative of $[Rh(CO)_2Cl_2]^-$, which is readily susceptable to oxidative addition. The difficulty can be avoided by treating the reduced solution with a suitable base ($NaHCO_3$) prior to adding the ligand. In this way convenient syntheses have been developed of the cations $[Rh(vdiars)_2]^+$ and $[Rh(MPPE)_2]^+$ [vdiars = *cis*-1,2-bis(diphenylarsino)ethylene; MPPE = 1,2-bis(methylphenylphosphino)ethane] [76].

Treatment of $[RhCl(C_2H_4)_2]_2$ with $[Cu(MeCN)_4]^+BF_4^-$ in methylene chloride saturated with ethylene gives cuprous chloride and yellow crystals of the five-coordinate cationic complex $[Rh(C_2H_4)_3(MeCN)_2]^+BF_4^-$. An X-ray crystallographic study has established that the cation has a trigonal bipyramidal structure, the three ethylene C—C axes being coplanar with the trigonal plane; the two MeCN ligands occupy the axial position. Unfortunately, the low stability of the complex precluded NMR studies [77].

A range of complexes $[Rh(arene)(diene)]^+$ (diene = nbd or 1,5-cyclooctadiene) is obtained by treating $[Rh(diene)_2]^+$ with the arene; the ease of formation increases with increasing alkyl substitution on the arene. The reactions are reversible, and the arene ligands are also displaced by ligands such as MeCN and Me_2SO. The NMR evidence suggested that the arenes are symmetrically bonded to the metal. Related reactions occur with cycloheptatriene to afford $[Rh(1,5\text{-}C_8H_{12})(C_7H_8)]^+$, in which the cycloheptatriene is considered to be bonded in the $\pi(h^6)$ form. 1,3-Cyclohexadiene is disporportionated by $[Rh(nbd)_2]^+BF_4^-$ to cyclohexene and benzene, the 1,4-diene undergoes isomerisation before disproportionation [78].

The olefinic phosphine ligand *o*-vinylphenyldiphenylphosphine (VP) reacts with $[RhCl(1,5\text{-}C_8H_{12})]_2$ to give $RhCl(VP)_2$, which has been shown to be pentacoordinate, with two rhodium—olefin bonds. With VP the complexes $[RhCl(1,5\text{-}C_8H_{12})(PPh_3)]$ and $[RhCl(PPh_3)(C_7H_8)]$ give $[RhCl(diene)VP]$. With stannous chloride in methanolic solution $RhCl(VP)_2$ gives yellow crystals of $[RhCl(SnCl_3)(VP)_2]$, a pentacoordinate, diolefinic complex having a rhodium—tin bond. Sodium tetraphenylborate reacts with $RhCl(VP)_2$ in methylene chloride to give a deep orange-red solution, which is thought to contain the four-coordinate cation $[Rh(VP)_2]^+$ in equilibrium with the arene cationic complex XVIII. Treatment with molecular hydrogen leads to the rapid hydrogenation of the free double bonds of the vinylphosphine. Carbon monoxide and pyridine (L) react with this system to give the salts $[Rh(VP)_2L]^+BPh_4^-$. Similar but less stable adducts are formed with C_2H_4, CS_2 and SO_2 [79].



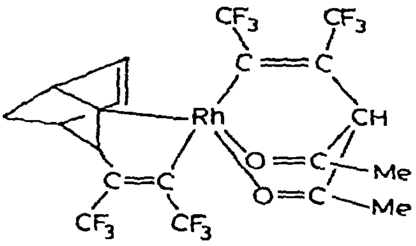
(XVIII)

The oxidative-addition of bromine or iodine to the complexes $[Rh(RNC)_4]^+$, *trans*-$[Rh(R^1NC)_2(R^2_3P)_2]^+$, and *trans*-$[RhX(CO)(R^1NC)_2]$ (R^1 =*p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-ClC_6H_4; R^2_3 = Ph_3 or Ph_2Me; X = Cl or Br) has been shown to involve a *trans*-addition. None of these complexes reacts with HCl or HBr, although the complex *trans*-$[RhCl(CO)(p\text{-}MeOC_6H_4NC)_2]$ reacts with MeI to form the five-coordinate acetyl complex $[Rh(COMe)I_2(p\text{-}MeOC_6H_4NC)_2]$. In a partly complementary study [82] the addition of I_2, MeI, EtI, n-PrI, n-BuI, $PhCH_2I$ or $PhCH_2Cl$ to $[Rh(t\text{-}BuNC)_4]^+BF_4^-$ has been shown to give the octahedral Rh^{III} species *trans*-$[Rh(t\text{-}BuNC)_4XY]^+BF_4^-$. Trimethyloxonium and nitrosyl tetrafluoroborate react with $[Rh(t\text{-}BuNC)_4]^+BF_4^-$ to form; respectively, the dications $[RhMe(t\text{-}BuNC)_4]^{2+}$ and $[Rh(NO)(t\text{-}BuNC)_4]^{2+}$. The former reacts with iodide anion to give the methyl iodide adduct. The carbene complex $[Rh(t\text{-}BuNC)_3\{C(NHBu\text{-}t)NHR\}]^+BF_4^-$ formed by the addition of primary amines RNH_2 to $[Rh(t\text{-}BuNC)_4]^+BF_4^-$ also undergoes oxidative addition reactions with I_2, MeI and $PhCH_2I$ to form $[Rh(t\text{-}BuNC)_3\{C(NHBu\text{-}t)NHR\}XY]^+BF_4^-$.

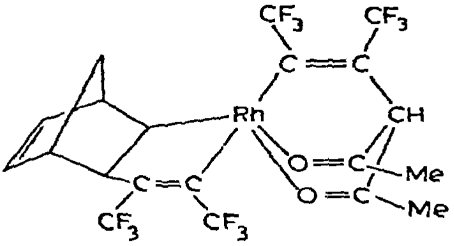
The reaction of methyl substituted 1,3-dienes with $(C_2H_4)_2Rh(acac)$ has been studied. The results show that the corresponding reactions with $Fe(CO)_5$ are kinetically rather than thermodynamically controlled [82].

Asymmetric complexes of Rh^I with a monothio-β-diketonate ligand and one of the chelating diolefins norbornadiene, 1,5-cyclooctadiene, cyclooctatetraene or duroquinone have been synthesised and studied by ^1H NMR spectroscopy. The compounds show thermally induced intramolecular proton exchange between nonequivalent sites. In the presence of Me_2SO or Ph_3As the exchange is accelerated, and a mechanism is discussed involving a fluxional five-coordinate intermediate [83].

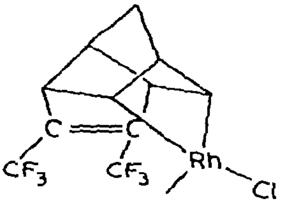
Reaction of hexafluoro-2-butyne with acetylacetonato(1,5-cyclooctadiene)-rhodium leads to the 1,4-addition of the acetylene to the acac ring, and the replacement of the 1,5-cyclooctadiene by hexakis(trifluoromethyl)benzene. A similar reaction of the acetylacetonato(norbornadiene)rhodium gives either XIX or XX, in which one molecule of the acetylene links the diene to the rhodium via a rhodiacyclopentene ring. In contrast, hexafluoro-2-butyne and chloro-(norbornadiene) rhodium dimer gives the tetramer XXI [84,85].



(XIX)



(XX)



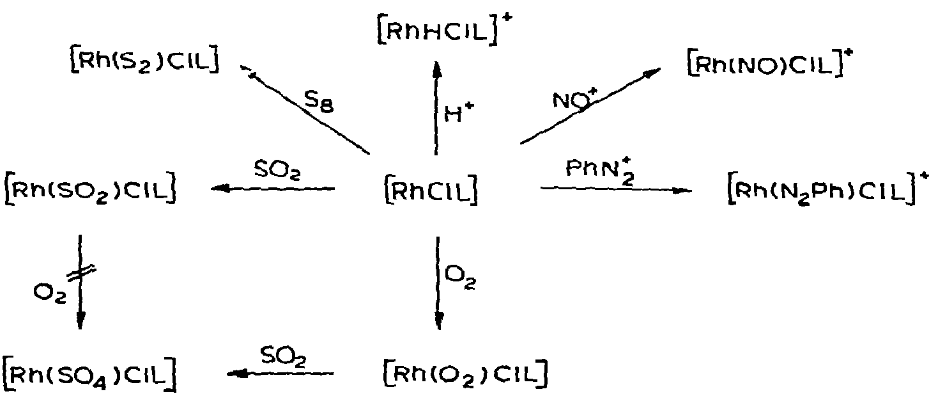
(XXI)

Unlike the complexes $RhX(CO)(PPh_3)_2$, five-coordinate compounds RhX(CO)(dupp) [dupp = (o-$CH_2{=}CHC_6H_4)_2PPh$: X = Cl, Br or I] formed by the reaction of $[RhX(dupp)]_2$ with carbon monoxide, readily lose the carbonyl ligand to yield [RhXL(dupp)] when treated with ligands such as PPh_3 or pyridine. The difference in behaviour is suggested to result from the electron-withdrawing character of the coordinated vinyl groups [86].

The cations NO^+ and Et_3O^+ abstract azide ion from $[M(N_3)(CO)(PPh_3)_2]$ (M = Rh, Ir) leaving bridging products $[(Ph_3P)_2(CO)MN_3M(CO)(PPh_3)_2]^+$. The observation of three ^{14}N NMR signals for the rhodium complex is interpreted as evidence that both metal atoms are attached to the same nitrogen atom [87].

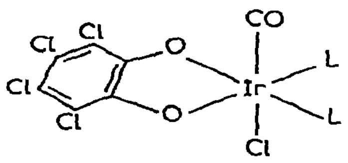
Treatment of $[M(NCO)(CO)(PPh_3)_2]$ [M = Rh, Ir] with HBF_4 in ethanol produces $[M(CO)(PPh_3)_2\{O{=}C(NH_2)OEt\}]^+$. The carbamic ester is bonded through the carbonyl oxygen and can be displaced by PPh_3 [88].

The Rh^I complex [RhClL] [L = $PhP(CH_2CH_2CH_2PPh_2)_2$] has been shown to undergo a variety of oxidative-addition reactions (Scheme 7). In general the rhodium in this system functions as a stronger Lewis base, it forms qualitatively more stable adducts and it simplifies the stoichiometry of the products, as all three phosphine groups remain bonded in the resulting complexes [89].

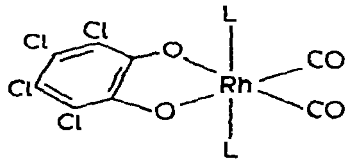


Scheme 7

Tetrachloro-1,2-benzoquinone adds to the complexes *trans*-[$MCl(CO)L_2$] (M = Rh, Ir; L = Ph_3P or Ph_2MeP) to yield the six-coordinate complexes [$M(1,2\text{-}O_2C_6Cl_4)Cl(CO)L_2$] [90]. It is interesting that the stereochemistry of this reaction is dependent on the nature of the metal. As illustrated iridium reacts with retention of the relative stereochemistry of the Cl and CO (XXII) but, in the case of rhodium, the phosphines have a relative *trans*-configuration (XXIII). The reactions of a variety of other quinones with *trans*-[$IrCl(CO)(PPh_3)_2$] were also examined. It was found that the kinetics of the addition are strongly affected by the oxidising ability of the quinone. The reaction of various other rhodium(I) complexes with tetrachloro-1,2-benzoquinone were also studied.



(XXII)

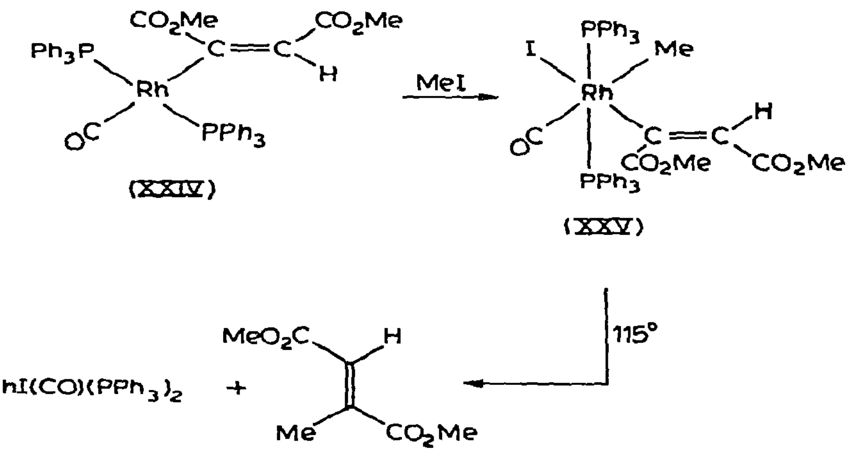


(XXIII)

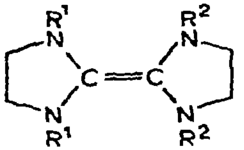
The anions [$Rh(CO)_2(PPh_3)_2$]$^-$ and [$Ir(CO)_3(PPh_3)$]$^-$ react with RHgCl to afford $Hg[Rh(CO)_2(PPh_3)_2]_2$ and $Hg[Ir(CO)_3(PPh_3)]_2$. In the case of the iridium complex, the unstable intermediate [$RHgIr(CO)_3(PPh_3)$] has been isolated [91].

Hydrogen chloride or bromide reacts with the square-planar Rh^I complexes [Rh(acac)(CO)L] (L = PPh_3 or $AsPh_3$) to give the halogen-bridged dimers [$RhX(CO)L$]$_2$ (X = Cl, Br), which are cleaved by donor ligands L^1 to give the mixed ligand complexes [$RhX(CO)LL^1$] [L = PPh_3; L^1 = $AsPh_3$, $SbPh_3$ or $P(OPh)_3$; L = $AsPh_3$, L^1 = $SbPh_3$ or $P(OPh)_3$]. Methyl iodide readily adds oxidatively *trans* to [$Rh(acac)(PPh_3)_2$] to give an octahedral complex without loss of triphenylphosphine [92].

In an investigation concerned with developing new methods of forming carbon—carbon bonds under relatively mild conditions the vinylrhodium(I) complex XXIV formed by the stereospecific addition of $RhH(CO)(PPh_3)_2$ to dimethylacetylenedicarboxylate was treated with MeI to form a rhodium(III) adduct of uncertain stereochemistry. Pyrolysis (115°) of XXV gave dimethyl citraconate (> 98%) and dimethyl mesaconate (< 2%), i.e. essentially a stereospecific reaction [93].



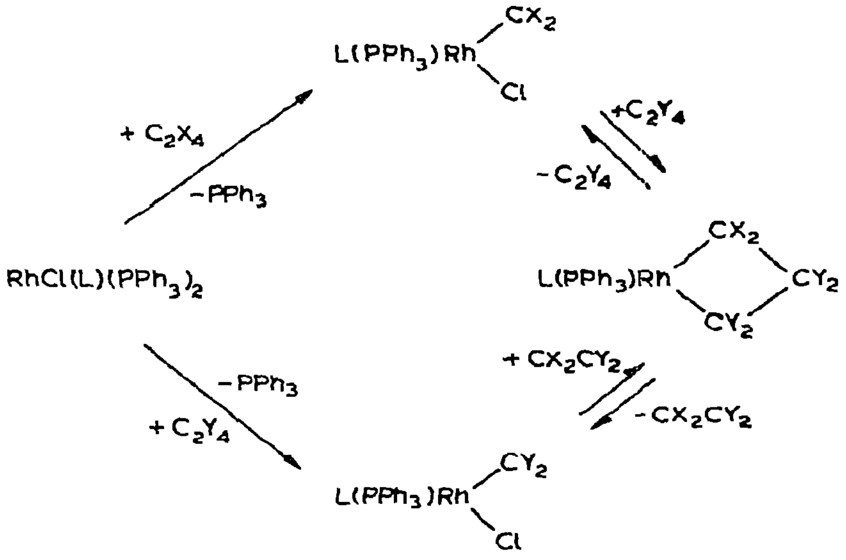
Rhodium(I) carbene complexes have been proposed as intermediates in electron-rich olefin dismutation [94]. The olefins XXVI and XXVII do not undergo a cross-over reaction to give XXVIII even on heating under reflux in xylene. However, catalysis of this reaction has been observed with the complexes [$RhCl(L)(PPh_3)_2$] (L = PPh_3 or CO). It is suggested that the dismutation reaction involves formation of a Rh^I carbene complex (Scheme 8) followed by a reversible oxidative step giving an intermediate rhodacyclobutane. In support of this proposal it is noted that the carbene complex [$(Ph_3P)_2RhCl(NPhCH_2)_2$] is a catalyst for dismutation, and that *trans*-[$PtCl_2\{C(NPh)CH_2\}_2(Et_3P)$], which is known to be unreactive towards oxidative addition, is not a dismutation catalyst.



(XXVI) $R^1 = R^2 = Ph$

(XXVII) $R^1 = R^2 = p\text{-}MeC_6H_4$

(XXVIII) $R^1 = Ph$; $R^2 = p\text{-}MeC_6H_4$



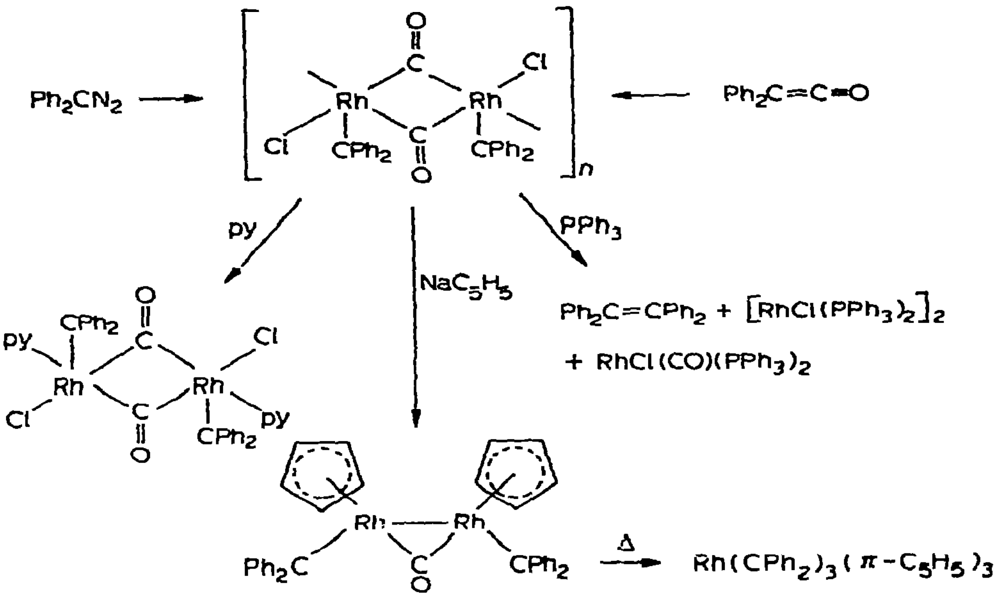
Scheme 8

Rhodium(III) and iridium(III) carbene complexes have been prepared by the oxidative reaction of chloro-formiminium or -amidinium chloride with Rh^I, or Ir^I compounds [95].

$$RhCl(CO)(PPh_3)_2 + [(PhNH)_2CCl]^+Cl^- \rightarrow [RhCl_3(CO)\{C(NHPh)_2\}(PPh_3)_2]$$

$$IrCl(N_2)(PPh_3)_2 + [Me_2N{=}CHCl]^+Cl^- \rightarrow [IrCl_3(CHNMe_2)(PPh_3)_2]$$

Stable diphenylcarbene complexes of rhodium have been reported (Scheme 9) [96]. Previously carbene complexes have only been obtained when an oxygen or nitrogen atom is adjacent to the carbenoid carbon atom.



Scheme 9

Confirmation by X-ray crystallography of these interesting structures is clearly required.

The reaction of *mer*-RhCl$_3$(PMe$_2$Ph)$_3$ with dibenzoylhydrazine in refluxing ethanol in the presence of a base is reported to give a complex [(PMe$_2$Ph)(CO)-RhN(COPh)]$_2$, which is considered to contain dibenzoyldiimide as a bridging ligand [97].

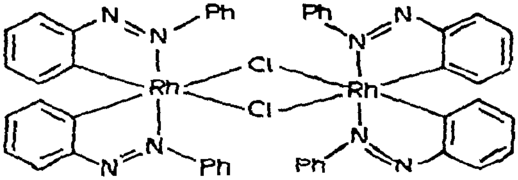
Di-t-butylsulphurdiimine and di-t-butylcarbodiimine react with [Rh(CO)$_2$-Cl]$_2$ to form complexes of Rh^I of the type [RhCl(L)(CO)$_2$]. From variable temperature NMR data it was shown that both intra- and inter-molecular exchange reactions occur with these adducts [98].

The reaction of 3,5,7-triphenyl-4*H*-1,2-diazepine with [Rh(CO)$_2$Cl]$_2$ does not lead to N—N bond cleavage; the products are analogous to other square-planar Rh^I complexes of the type [RhCl(L)(CO)$_2$] where L = NH$_3$, pyridine etc. In this investigation evidence was also obtained for related complexes, in which the diazepine functions as a bidentate ligand [99].

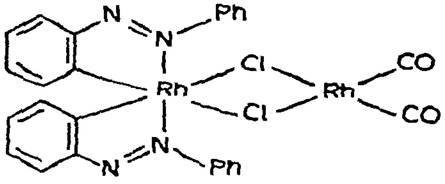
Addition of 2,2'-bipyridyl to a methanol solution of [RhCl(1,5-C$_8$H$_{12}$)$_2$]$_2$ followed by NaClO$_4$, NaPF$_6$ or NaBPh$_4$ affords the red crystalline cationic complexes [Rh(bipyridyl)(1,5-C$_8$H$_{12}$)]$^+$. The cation is kinetically labile and reacts with CO, C$_8$H$_8$, and *N*-methylimidazole. In general the π-acceptor ligands displace the coordinated 1,5-cyclooctadiene, whereas mainly σ-donor ligands displace bipyridyl. The reaction with trialkylphosphines affords the corresponding pentacoordinated adducts [Rh(bipyridyl)(1,5-C$_8$H$_{12}$)(PR$_3$)]$^+$. If these reactions are carried out in a H$_2$ atmosphere complexes of the type *cis*-[RhH$_2$(PR$_3$)$_4$]$^+$ are formed [100].

The reduction of rhodium(III) bipyridyl solutions with NaBH$_4$ in methanolic media affords labile-hydrido species, which on addition of organic halides RX affords the Rh^{III} complexes [Rh(bipy)$_2$(R)X]$^+$ClO$_4^-$. The same compounds are formed when sodium amalgam is used instead of $NaBH_4$, and are considered to arise from the oxidative addition of RX to a mono(bipyridyl)rhodium(I) species [101].

Reaction of rhodium complexes with azobenzenes have been described in detail [102]. With $RhCl_3$ the aniline complex $RhCl_3(PhNH_2)_2$ is accompanied by the bisphenylazophenyl complex XXIX. The structure of the related acetate has been determined by X-ray crystallography [103]. With $[Rh(CO)_2Cl]_2$ three compounds are obtained, $[RhCl(CO)_2(PhNH_2)]$, $[RhCl(CO)(azb)_2]$ (XXX), and an unidentified polymeric material. Complex XXX has the structure shown [104], and is unusual in containing both Rh^I and Rh^{III}. In accord with this XXX can be prepared from XXIX and $[Rh(CO)_2Cl]_2$.

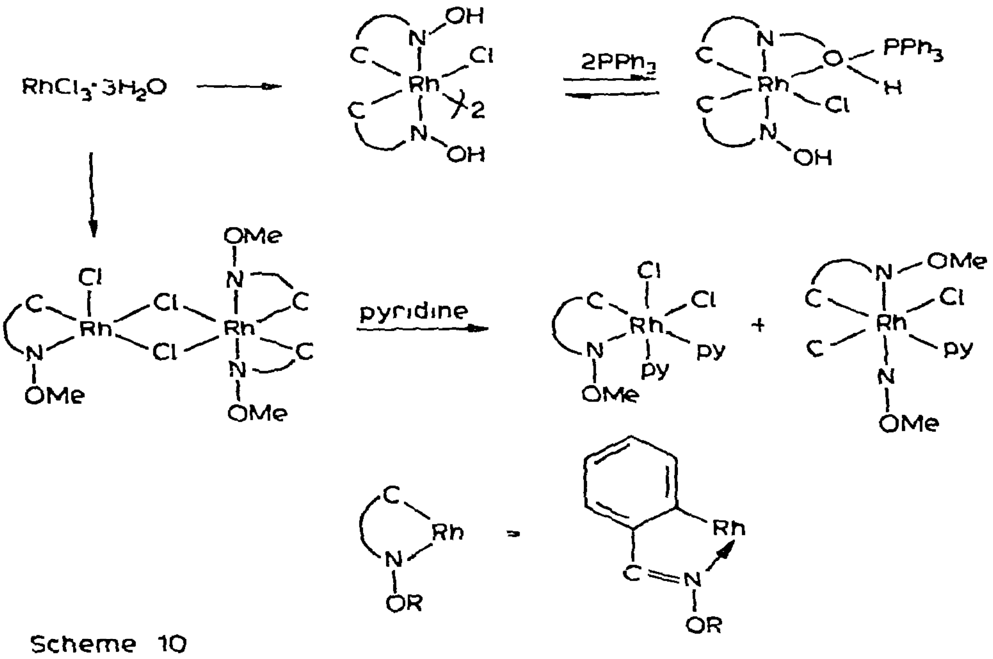


(XXIX)



(XXX)

In a related investigation [105] aromatic ketoximes, and their *o*-methyl derivatives have been shown to react with $RhCl_3\cdot3H_2O$, $[Rh(1,5\text{-}C_8H_{12})Cl]_2$ or $[Rh(C_2H_4)_2Cl]_2$ to give *ortho*-metallated five-membered chelate rings (Scheme 10).

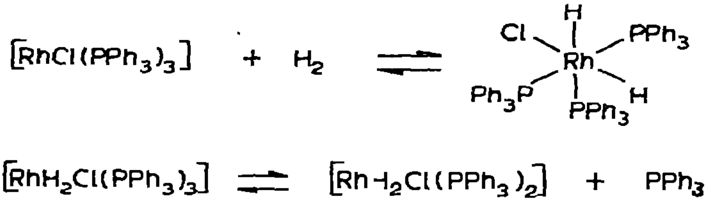


Scheme 10

The complex $[RhCl(PPh_3)_3]$ has been shown to be an extremely effective catalyst for the hydrosilation of carbonyl compounds [106]. For example, reaction (ice-temperature) of Ph_2SiH_2 with cyclohexanone is catalysed to give

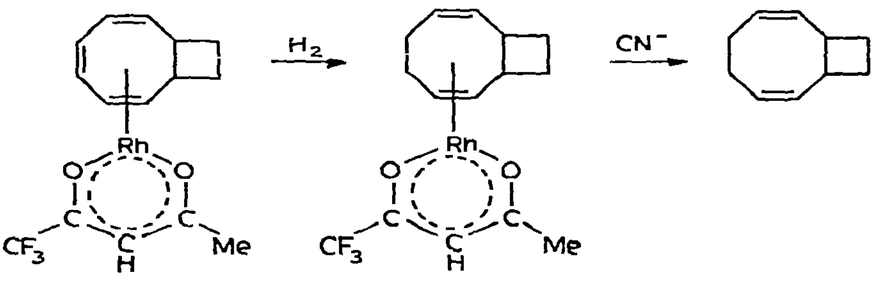
(10 min) a 98% yield of the cyclohexyloxydiphenylsilane. Since silyl enol ethers are readily hydrolysed to give saturated ketones or aldehydes this reduction method has wide potential. The selective hydrogenation of the olefinic double bond of α,β-unsaturated carbonyl compounds by triethylsilane in the presence of catalytic amounts of $[RhCl(PPh_3)_3]$ affords a silyl enol ether. For example α-ionone gives dihydroionone, there being no evidence for isomerisation of the remaining double bond. The corresponding reaction of β-ionone affords a mixture of dihydro-β-ionone and an allylic alcohol, the relative proportions depending on the silane used. Thus, the selective hydrogenation of β-ionone was achieved with phenyldimethylsilane [107,108].

Solutions of $[RhCl(PPh_3)_3]$ are among the most efficient hydrogenation catalysts yet discovered. Until recently the initial suggestion that the first step in the reaction of this complex with H_2 involves an initial dissociative loss of PPh_3, has been accepted. However, recent experiments [109] have shown that the degree of dissociation is, in fact, very small. In a ^{31}P NMR study it has been established that Scheme 11, represents the first two steps in the 'hydride' route to hydrogenation of olefins. The subsequent step is presumed to be coordination of the olefin to the vacant site followed by migration of hydrogen onto the olefin.



Scheme 11

An interesting use of a Rh^I species as a built-in hydrogenation catalyst is reported in a synthesis of *cis*-bicyclo[6.2.0]-2,6-decadiene. Treatment of *cis*-bicyclo[6.2.0]-2.4.6-decatriene with dicarbonyltrifluoroacetylacetonatorhodium leads to loss of two moles of carbon monoxide, and the formation of complex XXXI, which smoothly absorbs 1 mole equivalent of hydrogen to give XXXII in high yield; decomposition of the complex in aqueous KCN affords the required hydrocarbon [110].

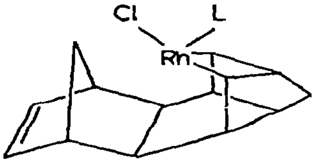


(XXXI) (XXXII)

The homogeneous catalysis by $[RhCl(PPh_3)_3]$ of the hydrogenation of allenes to give alkenes has been studied [111]. It was found that the reaction is stereospecific, substitution leads to a slower reaction, and in the case of unsymmetrical substituted acyclic allenes the least-substituted double bond is reduced preferentially.

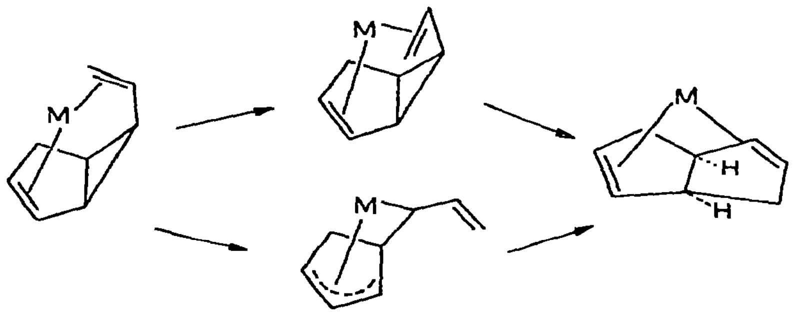
There has been considerable interest in the homogeneous catalytic formation of a chiral carbon centre using an optically active catalyst. Knowles and coworkers have described [112] a direct route to optically active α-amino acids by hydrogenation of α-acylaminoacrylic acids. For example the cationic complex $[Rh(1,5\text{-}C_8H_{12})L_2]^+BF_4^-$ [L = (—)-PMe(*o*-anisyl)(cyclohexyl)] has been found to catalyse the conversion of $3\text{-MeO-4-(OH)}C_6H_3CH{=}C(NHCOPh)CO_2H$ into $2\text{-MeO-4-(OH)}C_6H_3CH_2CH(NHCOPh)CO_2H$ with a 90% optical purity. It is suggested that the high efficiency of the process depends on the presence of two optically active phosphines in the catalyst. A catalyst system prepared by the addition of (—)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane to $[Rh(C_8H_{14})_2Cl]_2$ has been used for the hydrogenation of various precursors of alanine, phenylalanine, tyrosine, dopa and leucine. Optical yields in the range 70—80% are reported [113]. The cationic complex $[Rh(nbd)L_2]^+ClO_4^-$ (L = benzylmethylphenylphosphine) has also been shown to catalyse the asymmetric hydrogenation of phenylmethylketone and 2-butanone to 1-phenylethanol and 2-butanol with optical yields of 8.6 and 1.9% respectively [114].

Norbornadiene is dimerised and trimerised by catalytic amounts of $[RhCl(PPh_3)_3]$ giving isomeric hydrocarbons, which have been characterised by X-ray crystallography and NMR spectroscopy. It is speculated that the intermediate XXXIII plays a key role in these reactions [115].



(XXXIII)

Coordination of *endo*-6-vinylbicyclo[3.1.0]-2-hexene to Rh^I inhibits Cope rearrangement to bicyclo[3.2.1]-2,6-octadiene. At elevated temperatures a vinylcyclopropanecyclopentene isomerisation is the dominant reaction course (Scheme 12). Thermolysis of the hexafluoroacetylacetonato analogue occurred almost ten times more rapidly, and with greater selectivity. Because the prefer-

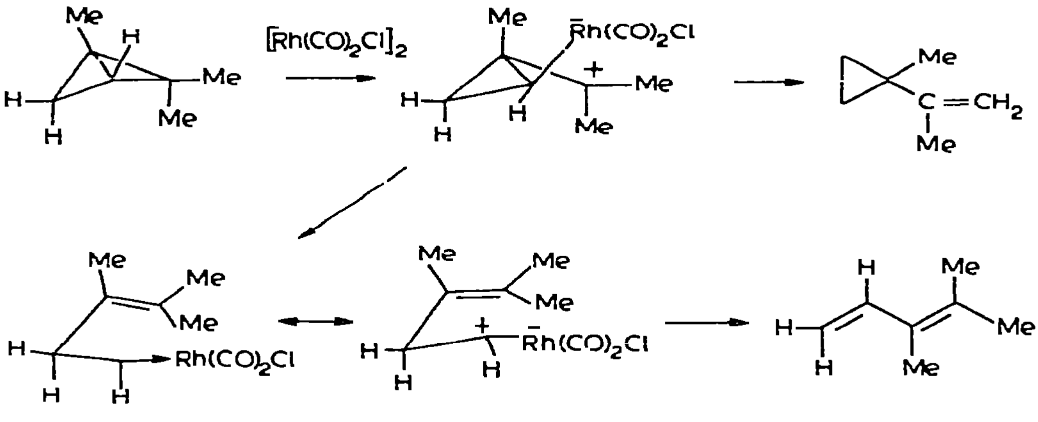


Scheme 12 M = Rh(acac)

red configuration of the starting complex is likely to be boat-like, direct rearrangement is impossible. For this reason possible reaction paths as reversible isomerisation to a chair configuration, and a subsequent $[2\sigma_s + 2\pi_s]$ sigmatropic shift, or alternatively, antarafacial opening of the cyclopropane ring could give a σ,π-bis-allyl-rhodium intermediate, with the proper geometry for closure to the observed product [116].

The reaction of $[Rh(CO)_2Cl]_2$ with various vinyl epoxides to give α,β-unsaturated aldehydes, and cleavage of oxetans to olefins and aldehydes have been discussed in terms of Rh^I acting as a weak Lewis acid, and coordinating to the ether oxygen atom; this being followed by C—O cleavage to give the most stable carbonium ion [117].

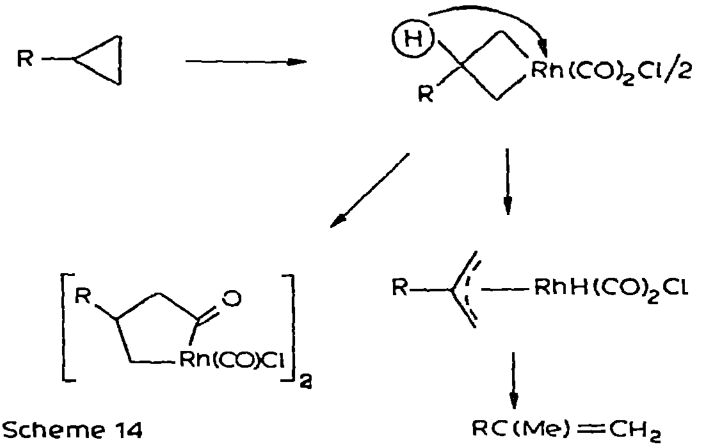
In an important series of papers Gassman and coworkers have detailed their studies on the isomerisation of bicyclo[1.1.0]butanes and tricyclo[4.1.0.$0^{2,7}$]-heptane promoted by a wide variety of transition metal complexes including $[Rh(CO)_2Cl]_2$. An overall mechanism is suggested, which is shown (Scheme 13) for isomerisation of 1,2,2-trimethyl[1.1.0]butane, and where formation of a metal—carbene complex is postulated as a key step, although as depicted such a species can also be written as a carbonium ion complex. Evidence has in fact been described for the capture by methanol of a carbonium ion intermediate; however, there is now some doubt as to the implications of these experiments [118—122].



Scheme 13

In a further investigation of the reactions of cyclopropanes, the $[Rh(CO)_2Cl]_2$ promoted isomerisation of bicyclo[2.1.0]pentane is described. It is suggested that a Rh^{III} hydride is involved as an intermediate [123].

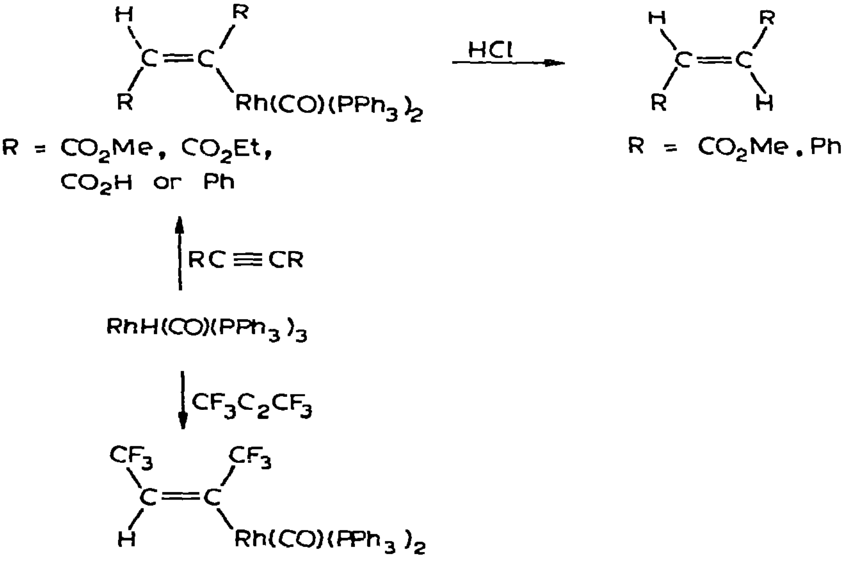
The insertion reaction between $[Rh(CO)_2Cl]_2$ and phenylcyclopropane, benzylcyclopropane and bicyclo[4.1.0]heptane have been investigated [124]. The structures of resultant rhodacyclopentanones are deduced by $NaBH_4$ reduction. Evidence was also found for cyclopropane to olefin isomerisation, and an overall mechanism for insertion and isomerisation is outlined in Scheme 14. Refluxing 1-chloro-1-carbonylphenylrhodacyclopentane with triphenylphosphine gives propenylbenzene and $RhCl(CO)(PPh_3)_2$. *o*-Tolylphosphines, $(o\text{-}MeC_6H_4)_3P$, $Ph(o\text{-}MeC_6H_4)_2P$ and $Ph_2(o\text{-}MeC_6H_4)P$ have been shown [125] to under-



Scheme 14

go coupling and dehydrogenation on heating with $RhCl_3 \cdot 3H_2O$ in high boiling alcohols to give Rh^I complexes [RhCl(Ligand)] derived from the tridentate olefinic tertiary phosphines. It has now been reported that [RhCl(*o*-$Ph_2C_6H_4$-$CH=CHC_6H_4PPh_2$-*o*)] is conveniently obtained by reaction of 2,2′-bis(diphenylphosphino)bibenzyl with $RhCl_3 \cdot 3H_2O$, $RhCl(PPh_3)_3$ or $[Rh(1,5\text{-}C_8H_{12})Cl]_2$.

The reaction of hydridocarbonyltris(triphenylphosphine)rhodium with disubstituted acetylenes has been studied (Scheme 15) [126]. Cleavage of the adducts obtained with $C_2(CO_2Me)_2$ and PhC_2Ph gives dimethyl fumarate and *trans*-stilbene. If it is assumed that in these reactions the hydrogen transfer to the σ-alkenyl carbon atom occurs with retention of configuration about the double bond, then this suggests that the reaction of the hydride with the acetylene involves a *trans*-addition. In contrast, the corresponding reaction with hexafluoro-2-butene is shown by NMR spectroscopy to involve a *cis*-addition. This difference in stereochemistry is indicative of a change in reaction mechanism.



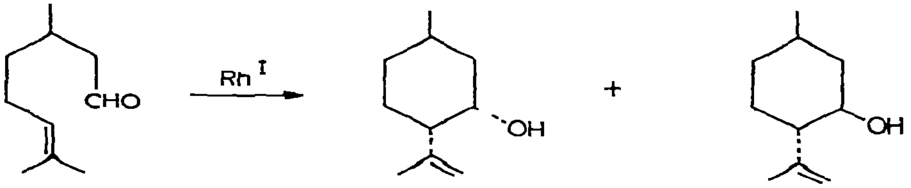
Scheme 15

In a kinetic study of the isomerisation of the three isomers of methylbutenoate using the catalyst system $RhCl(PPh_3)_3 \cdot 4SnCl_2 \cdot 2H_2O$ it is concluded that the reversible addition of a rhodium hydride to a coordinated olefin is involved [127].

A variety of new dioxygen complexes of Rh^I of formula $[RhX(O)_2)(PPh_3)_2(RNC)]$ have been prepared by the following methods: (a) exposure of a solution of $[RhX(PPh_3)_2(RNC)]$, $[RX(PPh_3)_2(t\text{-}BuNC)_2]$ or $[RhCl(AsPh_3)_2(t\text{-}BuNC)]$ to air, (b) introduction of air into a reaction mixture of $RhX(PPh_3)_3$ with RNC in benzene. These dioxygen complexes are thermally stable in the solid state [128]. 1-Hexene, 1-heptene and 1-octene are reported to react with O_2 in the presence of $RhH(CO)(PPh_3)_3$ or $RhCl(PPh_3)_3$ to give 2-hexanone (20—25%), 2-heptanone (20—25%) and 2-octanone (35—50%). There was no evidence for these oxygenated products arising from a free-radical chain process. These reactions are suggested to involve a metal-ion activated process and the intermediate formation of an epoxide [129]. The catalytic activity of $RhCl(PPh_3)_3$ for oxidations of styrene and cinnamaldehyde have also been studied [130]. The reactions are complicated because decarbonylation reactions take place with oxidation, and the carbonyl complex is thought to play a role in the catalytic oxidation.

At somewhat high temperatures (180°) $RhCl(PPh_3)_3$ has been reported to catalyse the hydrogen transfer from dioxane to cyclopentene; the dioxane being converted to dioxene [131].

The treatment of (+)-citronellal with $RhCl(PPh_3)_3$ in chloroform solution at room temperature (15 h) is reported to afford a mixture of (+)-neoisopulegol and (—)-isopulegol, the former being the major product (Scheme 16). It is suggested that this interesting cyclisation reaction involves the initial formation of an acylrhodium species [132].



Scheme 16

Secondary amines and a number of primary aromatic amines may be alkylated with butadiene using $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$ or $RhCl_3$ $3H_2O/PPh_3$ as catalysts. The reaction is suggested to involve the intermediacy of π-allylic rhodium(I) complexes formed via a rhodium hydride intermediate by treatment of an ethanolic solution of $RhCl_3 \cdot 3H_2O$ with C_4H_6. Also formed in the reaction are octadienyl adducts, the yield of which is increased by the presence of triphenylphosphine. The corresponding reaction of morpholine with isoprene and piperylene has also been studied, but it was found that the extent of reaction decreases in the order butadiene > piperylene > isoprene. Furthermore addition of PPh_3 only reduces the extent of reaction without forming any octadienyl derivatives [133].

The methyl groups of duroquinone in the complex cyclopentadienylduroquinone-cobalt, -rhodium and -iridium have been shown to be activated toward both acid- and base-catalysed reactions. For example, dimethylaminomethylation (Mannich reaction) affords dimethylaminomethyl derivatives in high yield, and the rhodium complex readily exchanged the methyl hydrogens of the coordinated duroquinone on treatment with sodium deuteroxide-methanol-*d* [134].

The molecular and crystal structure of $[Rh(C_2H_4)(C_2F_4)(\pi\text{-}C_5H_5)]$ has been determined. The stereochemical implications with respect to bonding are examined. The large differences in rhodium—olefin distances are discussed in terms of increased π-bonding to the C_2F_4 ligand, which exerts a significant *trans*-influence on the cyclopentadienyl ring [135].

The inertness of $[Rh(C_2H_4)_2\text{-}\pi\text{-}C_5H_5]$ to S_N2 attack by nucleophiles provided an opportunity for a study of a dissociative mechanism for substitution. Cramer [136] has found that this reaction path becomes available above 115°, and by studying the kinetics of the first step in the gas phase has tentatively evaluated the strength of the rhodium—ethylene bond in $Rh(C_2H_4)_2\text{-}\pi\text{-}C_5H_5$ as 31 kcal.

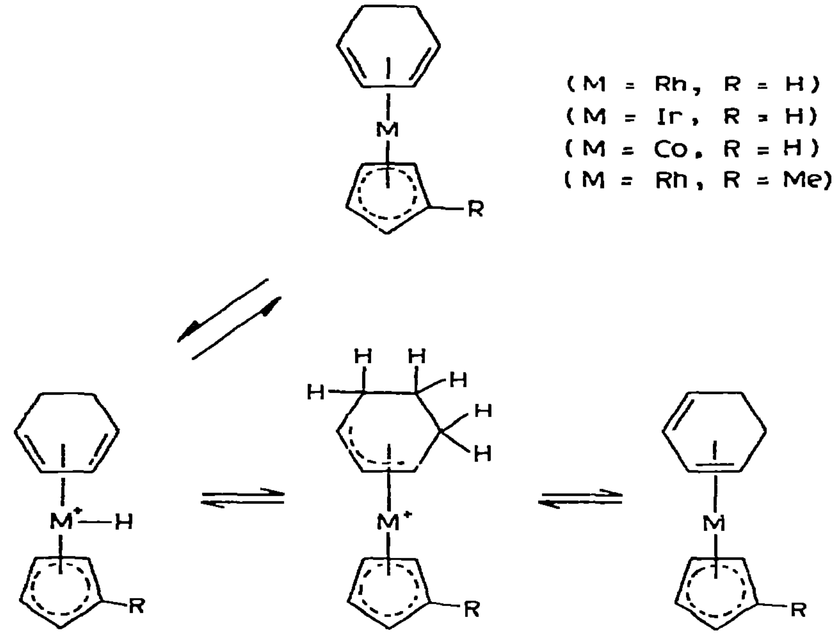
$$Rh(C_2H_4)_2\text{-}\pi\text{-}C_5H_5 \rightarrow Rh(C_2H_4)\text{-}\pi\text{-}C_5H_5 + C_2H_4$$

$$Rh(C_2H_4)\text{-}\pi\text{-}C_5H_5 + L \rightarrow RhL(C_2H_4)\text{-}\pi\text{-}C_5H_5$$

Treatment of $[Rh(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]$ with $ClCH_2CN$ has been previously shown to lead to an oxidative-addition reaction and the formation of the cation $[Rh(CH_2CN)(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]^+$. An analogous reaction with the corresponding iridium system affords $[Ir(CH_2CN)(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]^+$. Reaction of the rhodium cation with SCN^-, $SeCN^-$ or halide anion leads to displacement of CO and the formation of the expected neutral complexes, whereas, MeO^- and N_3^- react at the carbonyl group to form respectively $[Rh(CO_2Me)(CH_2CN)(PPh_3)\text{-}\pi\text{-}C_5H_5]$ and $[Rh(NCO)(CH_2CN)(PPh_3)\text{-}\pi\text{-}C_5H_5]$. In the latter reaction an initially formed acyl azide is considered to lose N_2 and rearrange to the isocyanate. The corresponding iridium cation reacts at room temperature only with MeO^- and N_3^- to give the expected products. However, even in refluxing acetone there was no evidence for a reaction with the other anions. This lower reactivity of the iridium complex is interpreted in terms of the stability of the cationic complex and the strength of the metal—CO bond. The reaction of $[Rh(CH_2CN)(CO)(PPh_3)\text{-}\pi\text{-}C_5H_5]^+$ with $C_6H_5SO_2^-$ gives $[Rh(CH_2CN)(Ph)(PPh_3)\text{-}\pi\text{-}C_5H_5]$, formed by loss of SO_2 from the initially formed $[Rh(CH_2CN)(SO_2Ph)(PPh_3)\text{-}\pi\text{-}C_5H_5]$ [137].

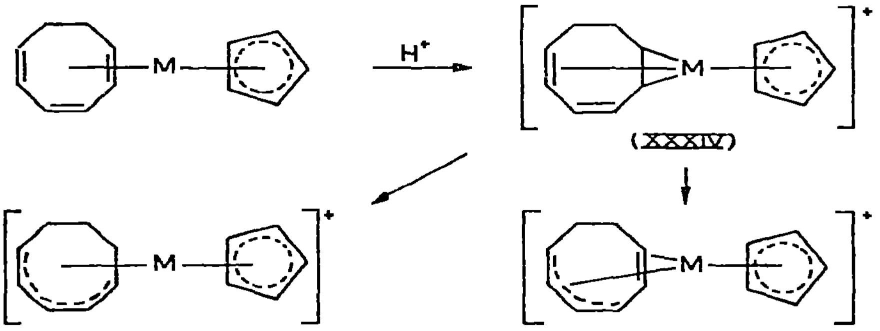
Protonation and deuteration studies have been carried out on the complexes (1,3-cyclohexadiene)(π-cyclopentadienyl) M (M = Rh, Ir). A mechanism is suggested which involves initial protonation of the metal followed by the reversible transfer of the proton to the cyclohexadiene to form a cationic allylic complex. As is indicated in Scheme 17, a sufficiently rapid exchange will equilibrate three protons between *endo*-methylene and metal hydride environments [138,139].

Reaction of the cyclohexadiene complex (M = Rh, R = H) with $Ph_3C^+BF_4^-$ affords the coordinated cyclohexadienium cation, which undergoes nucleophilic attack to form *exo* derivatives. The protonation studies parallel the findings of Whitesides and coworkers in their study of the protonation of tricarbonylcyclohexadieneiron, where *endo*-proton attack was also established. The protonation of (1,3,5-cyclooctatriene)(π-cyclopentadienyl)-cobalt(I), -rhodium(I), or -iridium-



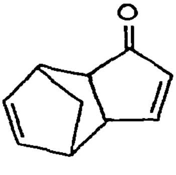
Scheme 17

(I) leads to the formation of cations of the type $[C_8H_{11}M(\pi\text{-}C_5H_5)]^+$. The C_8H_{11} entity adopts a variety of bonding modes and interconversion between these various species readily occurs (Scheme 18). In the case of the Rh^I and Ir^I cations the kinetics of these rearrangements have been examined by ^1H NMR spectroscopy. Reversible protonation of $[Co(C_8H_{10})(\pi\text{-}C_5H_5)]$ affords a 1-5-η^5-cyclooctadienyl cation, which is also formed from bicyclo[4.2.0]-2,4-octadiene(π-cyclopentadienyl)cobalt. Treatment of (1,3,5-cyclooctatriene)(π-cyclopentadienyl)-rhodium with CF_3CO_2H gives initially a 1,3,4-η-bonded system, which isomerises to a mixture of an octadienyl complex and an allylolefin complex. The corresponding iridium system, which also forms an air-stable white salt with HPF_6 dissolves in CF_3CO_2H to a mixture of XXXIV and the octadienyl cation. Nucleophilic addition to these cations gives the expected neutral complexes of formula $[M(C_8H_{11}Y)(\pi\text{-}C_5H_5)]$, the mode of bonding of which depends on the reaction temperature employed [140].

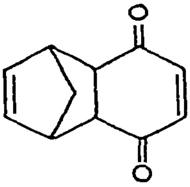


Scheme 18

The preparation and reactions of $[RhCl(ligand)]_2$ and $[Rh\text{-}\pi\text{-}C_5H_5(ligand)]$ where ligand is XXXV or XXXVI has been examined [141]. Both complexes undergo several reactions characteristic of ketones. The ketone group of the $[Rh\text{-}\pi\text{-}C_5H_5(ligand)]$ undergoes nucleophilic attack by carbanions to give the corresponding alcohol, which can be readily converted into stable cationic complexes.



(XXXV)



(XXXVI)

The reaction between the readily available $[RhCl_2\text{-}\pi\text{-}C_5Me_5]_2$ and $Ni(PF_3)_4$ provides a facile synthesis of $[Rh(PF_3)_2\text{-}\pi\text{-}C_5Me_5]$. This has provided an opportunity for a study of oxidative-addition reactions of metal—trifluorophosphine complexes. Iodine reacts with $[Rh(PF_3)_2\text{-}\pi\text{-}C_5Me_5]$ in benzene at room temperature to give the deep red crystalline diiodide $[RhI_2(PF_3)\text{-}\pi\text{-}C_5H_5]$. In an attempt to prepare the dibromide the reaction with Br_2 was also investigated. However, this reaction led to the complete loss of PF_3 and the formation of $[RhBr_2\text{-}\pi\text{-}C_5H_5]_2$. The perfluoroalkyl iodides R_fI ($R_f = CF_3, C_2F_5$, n-C_3F_7 and n-C_7H_{15}) also react at room temperature to give the orange to deep red complexes $[RhR_f(I)(PF_3)\text{-}\pi\text{-}C_5Me_5]$ [142].

Although there is indirect evidence for participation of a π-allylmetal hydride in the isomerisation of olefins, only in one case has an equilibrium been established between a π-allylmetal hydride complex and the corresponding olefin metal(0) complex. Further evidence for this reaction path has been obtained from a study [143] of the reaction of HCl with a series of π-allylic rhodium trifluorophosphine complexes:

$$\pi\text{-allylic } Rh(PF_3)_2 + HCl \xrightarrow{PF_3} \text{olefin} + [RhCl(PF_3)_2]_2$$

Low temperature ^{19}F NMR studies show that in this reaction an intermediate π-allylrhodium(III) hydrido complex is formed by oxidative addition of HCl. In systems containing symmetrically bonded π-allylic groups only one olefin product is obtained, but with the asymmetrically bonded 1-methylallyl and 1-methyl-3-ethylallyl complexes an almost 1/1 mixture of isomeric olefins is formed, indicating hydrogen migration from rhodium to both terminal carbon atoms has occurred almost equally. The 1,1-dimethylallyl compound affords 2-methyl-2-butene and 3-methyl-1-butene in an approximately 2/1 ratio, indicating some preference for hydrogen migration to the least hindered carbon atom.

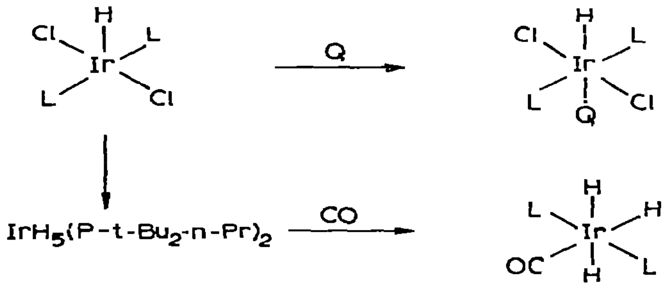
Convenient single stage syntheses of $Rh(NO)L_3$ ($L = P(p\text{-}ClC_6H_4)_3$ or $P(p\text{-}MeC_6H_4)_3$ have been described involving the reaction of $RhCl_3 \cdot 3H_2O$ in ethanol with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in the presence of the respective phosphine [144].

In the high pressure infrared spectral study of the reactions of $Ir_4(CO)_{12}$ with carbon monoxide and hydrogen no evidence was obtained for the existence of $Ir_2(CO)_8$, either during the preparation of $Ir_4(CO)_{12}$ or from the reaction of $Ir_4(CO)_{12}$ with carbon monoxide at various pressures and temperatures. Treatment of $Ir_4(CO)_{12}$ with CO/H_2 at high pressures and temperatures strongly suggests the formation of the mononuclear hydrido carbonyl $HIr(CO)_4$. During the course of this work a convenient synthesis of $Ir_4(CO)_{12}$ was devised involving the carbonylation of a chloroiridiate salt, preferentially $Na_2IrCl_6 \cdot 6H_2O$, in 2-methoxyethanol as solvent at 80—100 atm. pressure and 100° for 12—16 h in the presence of copper bronze as a halogen acceptor [145].

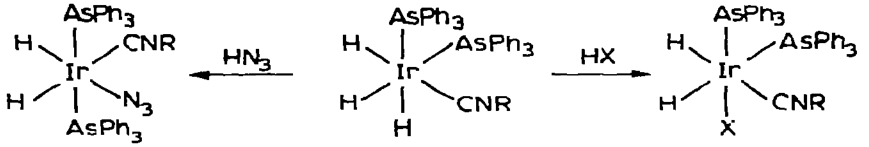
In principle homogeneous transition metal catalysts bound to a resin may exhibit properties different from those in solution. Since the active form of homogeneous catalysts are unsaturated, immobilisation on a solid support might prevent self-aggregation. It has been shown that this effect is difficult to achieve with phosphine-substituted polystyrene [146].

Treatment of a solution of chloroiridous acid obtained by heating a solution of chloroiridic acid in isopropyl alcohol, with di-t-butyl-n-alkylphosphines (4 mole equivalents) in boiling isopropyl alcohol gives purple. five-coordinate square pyramidal hydrides $IrHCl_2(P\text{-}t\text{-}Bu_2R)_2$ (R = Me, Et, n-Pr). These compounds are analogous to the rhodium complexes $[RhHCl_2L_2]$, for which the illustrated square pyramidal structure has been established when L = $P\text{-}t\text{-}Bu\text{-}n\text{-}Pr_2$ by X-ray crystallography. The iridium complexes have a hydride resonance at τ 60. With 2—3 mole equivalents of $P\text{-}t\text{-}Bu_2\text{-}n\text{-}Pr$ chloroiridous acid gives $[P\text{-}t\text{-}Bu_2\text{-}n\text{-}PrH]^+$-$[Ir_2Cl_7(P\text{-}t\text{-}Bu_2\text{-}n\text{-}Pr)_2]^-$, but with 2 equivalents of $P\text{-}t\text{-}Bu_2Me$ a hydride is formed, possibly $[P\text{-}t\text{-}Bu_2MeH]^+[Ir_2HCl_6(P\text{-}t\text{-}Bu_2Me)_2]^-$ [147].

The bulky di-t-butylalkylphosphines, $P\text{-}t\text{-}Bu_2R$ (R = Me, Et or n-Pr) react with the $[IrCl_6]^{2-}$ anion in isopropyl alcohol to give complexes $[IrHCl_2(P\text{-}t\text{-}Bu_2R)_2]$, with the illustrated square-pyramidal structure. These five-coordinate complexes readily take up CO or MeNC(Q) to give six-coordinate species. The complex $[IrHCl_2(P\text{-}t\text{-}Bu_2Me)_2]$ will also add pyridine, methylpyridine or $P(OMe)_3$ to give similar adducts, but with $[IrHCl_2(P\text{-}t\text{-}Bu_2R)]$ (R = Et, n-Pr) these ligands displace $P\text{-}t\text{-}Bu_2R$ to give $[IrHCl_2Q_2(P\text{-}t\text{-}Bu_2R)]$. $IrHCl_2(P\text{-}t\text{-}Bu_2\text{-}n\text{-}Pr)_2$ in the presence of sodium isoproxide takes up H_2 to give $IrH_5(P\text{-}t\text{-}Bu_2\text{-}n\text{-}Pr)_2$, which in turn reacts with carbon monoxide to give $[IrH_3(CO)(P\text{-}t\text{-}Bu_2\text{-}n\text{-}Pr)_2]$ [148].



Treatment of $[IrH_3(AsPh_3)_3]$ with alkyl- or aryl-isocyanides leads to the displacement of one triphenylarsine ligand, and the formation of a trihydride, which in the case of the *p*-tolylisocyanide has the illustrated stereochemistry [149]. Treatment with HX (X = Cl, Br, I, F) results in the replacement of hydrogen by a halide ligand. It is interesting that a different isomer is obtained in the corresponding reaction with HN_3.



A series of four- and five-coordinate iridium(I) salts of the type $[Ir(1,5\text{-}C_8H_{12})L_2]^+X^-$ and $[Ir(1,5\text{-}C_8H_{12})L_3]^+X^-$ and $[IrL_5]^+X^-$ (L = phosphite, phosphine or arsine; X = BPh_4, PF_6 or ClO_4) have been prepared from the reactions of $[Ir(1,5\text{-}C_8H_{12})Cl]_2$ with L in a polar solvent [150]. For L = PMe_2Ph and $AsMe_2Ph$ the dioxygen adducts $[Ir(O_2)L_4]^+BPh_4^-$ have been characterised. When longer reaction times are used for the reaction of $[Ir(1,5\text{-}C_8H_{12})Cl]_2$ with L (L = PEt_2Ph and P-n-Bu_3) in ethanol, the deep red solution containing the cations $[IrL_4]^+$ gradually turn white, and addition of $NaBPh_4$ gives the dihydrides $[IrH_2L_4]^+BPh_4^-$, for which a *cis*-configuration is assigned. The variable temperature ^1H NMR spectra of the reactions $[Ir(1,5\text{-}C_8H_{12})L_3]^+$ [L = $P(OMe)_3$ and $P(OMe)_2Ph$] and $[Ir\{P(OMe)_3\}_5]^+$ indicate that these species undergo a Berry pseudo-rotation process.

The photolysis of $[Ir(NH_3)_5N_3]^{2+}$ is consistent with the formation of an intermediate containing a coordinated nitrene. A similar process is suggested to occur on irradiation of $[Rh(NH_3)_5N_3]^{2+}$ when N_2 is evolved and the chloramine product is formed [151].

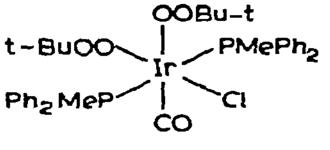
$$\begin{tikzcd}
{[(NH_3)_5IrN_3]^{2+}} \arrow[r, "h\nu", "-N_2"'] & {[(NH_3)_5IrN]^{2+}} \arrow[d, "+H^+"] & \\
& {[(NH_3)_5IrNH]^{3+}} \arrow[r, "HCl"] & {[(NH_3)_5IrNH_2Cl]^{3+}}
\end{tikzcd}$$

The ^{17}O NMR spectra of the adducts of $^{17}O_2$ with *trans*-$[IrX(CO)L_2]$ [X = Cl, I; L = PPh_3 or $P(p\text{-}MeC_6H_4)_3$] have been examined in the belief that the bond characteristics of coordinated oxygen might be revealed by its chemical shift. However, no resonance attributable to bound $^{17}O_2$ could be detected 20000 ppm up- and down-field from the resonance of $H_2{}^{17}O$. This failure to observe the ^{17}O resonance is attributed to a slow tumbling effect which broadens the resonance beyond detection [152].

The synthesis of the acetylide complexes $[Ir(C{\equiv}CPh)(CO)(PPh_3)_2]$ and $[Ir(C{\equiv}CH)(CO)(PPh_3)_3]$ have been reported. The former compound reacts irreversibly with molecular oxygen to give a 1/1 adduct [153].

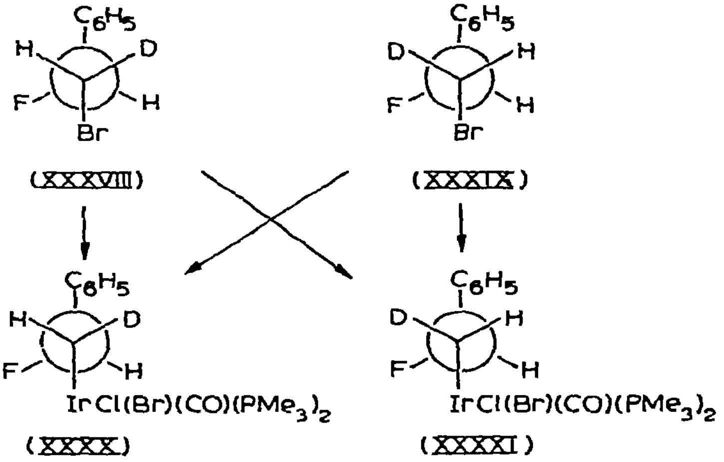
It has been reported [154] that the cation $[Ir(O_2)(CO)(PMePh_2)_3]^+$ acts as a homogeneous catalyst for the oxidation of diphenylmethylphosphine by O_2. The kinetics of the irreversible uptake of O_2 by $[Ir(CO)(PMePh_2)_3]^+$ have now been studied. Qualitative measurements on the homogeneous oxidation of PPh_3 and $PMePh_2$ by the above dioxygen complex show that in a variety of solvents this is an inefficient catalyst.

A catalytic amount of *trans*-$[IrCl(CO)(PPh_3)_2]$ rapidly causes the decomposition of the hydroperoxides ROOH (R = t-Bu or $PhMe_2C$) to give oxygen and the corresponding alcohol as the major products. When the reaction is carried out in toluene, diperoxy complexes can be isolated. In the case of the related reaction of $IrCl(CO)(PMePh_2)_2$ with t-BuOOH a complex is isolated, which is assigned the structure XXXVII, in which the peroxy ligands have a relative *cis*-configuration. Although the peroxy-iridium complexes are secondary products, they are not intermediates in the decomposition of the peroxides, since they do not catalyse the rapid decomposition of t-BuOOH. However, it is suggested that they are structurally related to the actual intermediates involved [155].



(XXXVII)

Two general mechanisms have been proposed for the oxidative addition of alkyl halides to square planar Ir^I complexes: (1) an S_N2 process in which Ir^I acts as a nucleophile; (2) a concerted, three-centre addition. It is interesting that recently evidence has been obtained that oxidative addition to Ir^I can proceed via a free-radical pathway. It has been found [156] that $[IrCl(CO)(PMe_3)_2]$ reacts with either XXXVIII or XXXIX to give an identical equimolar mixture of the two diastereoisomers XXXX and XXXXI. The lack of stereospecificity strongly indicates a free-radical pathway, which is further suggested by the observation that O_2, AIBN or benzoyl peroxide initiate the reaction. Moreover small quantities of radical scavangers such as duroquinone or hydroquinone retard the oxidative addition reaction. In analogy with related reactions of alkyl halides with complexes of Co^{II} and Cr^{II} which occur via radical pathways an attractive mechanism for oxidative addition to Ir^I is:



$$Ir^I + Q^{\cdot} \rightarrow Ir^{II} - Q$$

$$Ir^{II} - Q + RBr \rightarrow Br - Ir^{III} - Q + R^{\cdot}$$

$Ir^{I} + R^{\bullet} \rightarrow Ir^{II} - R$

$Ir^{II} - R + RBr \rightarrow Br - Ir^{III}R + R^{\bullet}$

$Q^{\bullet}$ = initiator

However, it is significant that MeI reacts extremely rapidly with $[IrCl(CO)(PMe_3)_2]$ even in the presence of radical inhibitors, suggesting that alternative pathway(s) can be operative for certain substrates.

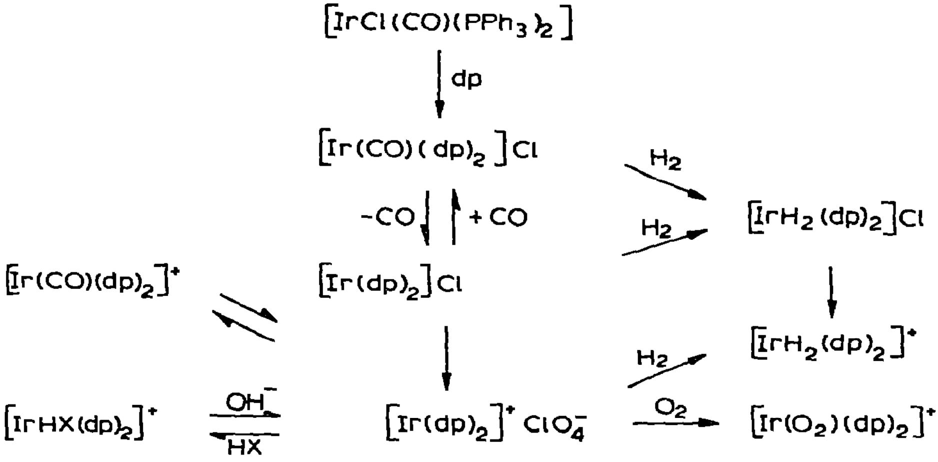
A kinetic study [157] of the reactions:

$[IrH(CO)(PPh_3)_2] + PPh_3 \rightleftharpoons [IrH(CO)(PPh_3)_3]$ and

$IrH(CO)(PPh_3)_2 + Me_n(EtO)_{3-n}SiH \rightleftharpoons [IrH_2\{Si(OEt)_{3-n}Me_n\}CO(PPh_3)_2]$

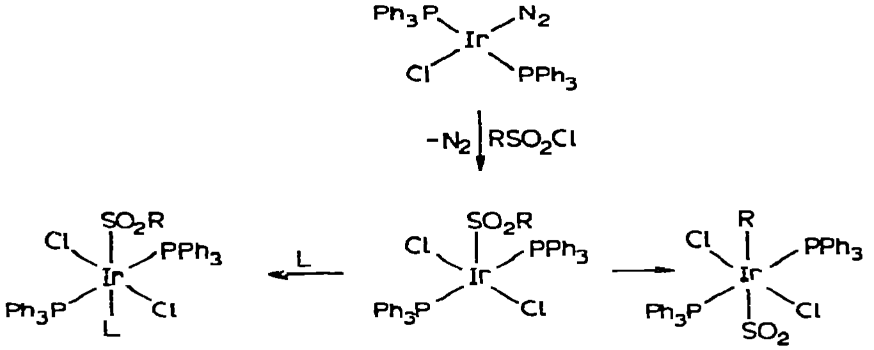
shows that for the case where $n = 3$, the kinetic parameters for the phosphine and silane reactions are almost identical. For the case where $n = 1$ and $n = 0$, the activation enthalpies for addition were again 23 kcal/mol, but for the elimination reaction substantially larger values of ΔH were observed, in agreement with an earlier investigation. These results are interpreted to mean that phosphine addition and silane are mechanistically similar processes, and that the observed activation enthalpies are largely due to an initial deformation of the square-planar iridium complex.

Reaction of Vaska's complex with *cis*-vinylenebis(diphenyl)phosphine (dp) affords an air-stable, five-coordinate carbon monoxide adduct, which on heating undergoes a reversible loss of carbon monoxide to give the illustrated (Scheme 19) 4-coordinate species. Comparison of the $[Ir(dp)_2]^+$ system with the corresponding diphos complexes suggests that the unsaturated dp ligand is more effective in the delocalisation of the d_π electrons of the metal [158].



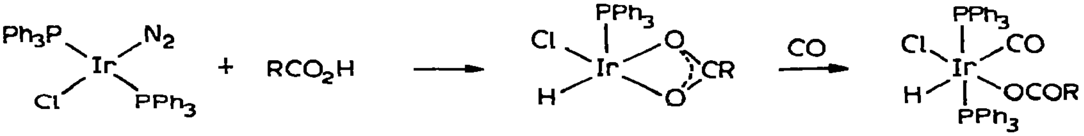
Scheme 19

The reaction of *trans*-$[IrCl(N_2)(PPh_3)_2]$ with alkyl- and aryl-sulphonyl chlorides leads to the evolution of nitrogen and formation of five-coordinate *S*-sulphinato complexes. These complexes rearrange under mild conditions to the corresponding alkyl- or aryl-iridium complexes; kinetic studies indicate that electron-withdrawing substituents on the R substituent enhance the rate of this rearrangement. This effect contrasts to the observation that electron-withdrawing substituents on R led to a decreased rate of migration from carbon monoxide to iridium. The five-coordinate sulphinato complexes react with ligands such as pyridine to afford six-coordinate adducts [159].



Scheme 20   L = CO, pyridine, PhCN

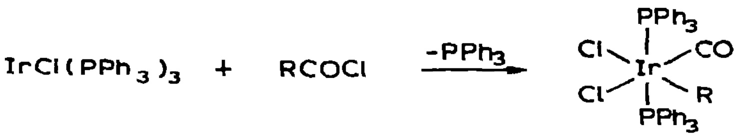
Weak carboxylic acids react reversibly with Ir^I—carbonyl complexes. However, it has not been possible to isolate stable carboxylatohydrido carbonyl iridium complexes [160]. In contrast, addition of carboxylic acids to *trans*-$[IrCl(N_2)(PPh_3)_2]$ leads to the displacement of N_2 and the formation of stable carboxylate complexes. Carbonylation of these compounds leads to the addition of CO to a site *trans* to the strongly *trans*-directing hydrido ligand. It is suggested that other nucleophiles such as pyridine, benzonitrile and dimethylphenylphosphine add similarly.



Cationic hydrido complexes of Rh and Ir have been prepared by treatment of Rh^I and Ir^I complexes with trifluoroacetic acid. For example, treatment of $[IrH(CO)(PPh_3)_3]$ with CF_3CO_2H gives $[IrH_2(CO)(PPh_3)_3]^+[(CF_3CO_2)_2H]^-$; the anion being a hydrogen bonded trifluoroacetate [161].

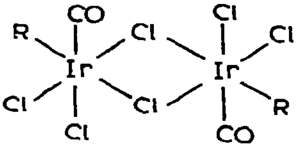
The oxidative addition of acyl and aryl halides to *trans*-$[IrCl(N_2)(PPh_3)_2]$ has been shown to give initially five-coordinate acyliridium(III) complexes, which rearrange to six-coordinate alkyl- or aryl-iridium(III) species. In a related investigation the addition of acyl halides to $IrCl(PPh_3)_3$ has been studied. Interestingly, if R in the acyl halide RCOCl is branched at the α-carbon atom, the resulting alkyl iridium(III) complex is exclusively the isomeric straight-chain derivative. Thus addition of 2-methylpropanoyl chloride in refluxing benzene gives the n-propyl complex. It is suggested that the initial product of reaction with branched acyl chlorides is the appropriate *sec*-alkyliridium(III) complex, and that this rapidly isomerises to the n-alkyl derivative via a hydrido-olefin

$$IrCl(N_2)(PPh_3)_2 + RCOCl \xrightarrow{-N_2} [IrCl_2(COR)(PPh_3)_2] \rightarrow [IrCl_2R(CO)(PPh_3)_2]$$

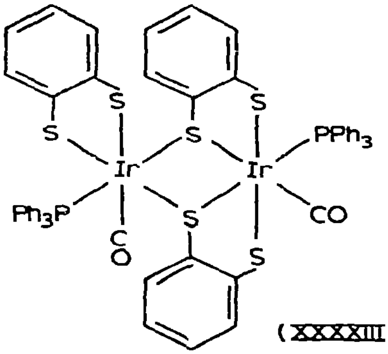


intermediate. Molecular models suggest that the instability of the *sec*-alkyls with respect to the n-alkyls may be due to non-bonding interactions of the branched alkyl chain with the phenyl rings of the PPh_3 ligands. Support for this hypothesis is provided by the observation that the cyclooctene complex $[IrCl(CO)(C_8H_{14})_2]_2$ reacts with acyl chlorides to give dimeric chlorine-bridged alkyliridium(III) complexes (XXXXII). For example, methylpropanoyl chloride reacts to give the isopropyl complex (XXXXII, R = $CHMe_2$), but after 90 min in refluxing benzene a mixture of the isopropyl and n-propyl (XXXXII, R = CH_2CH_2Me) complexes are obtained [162].

The reaction of $[IrCl(CO)(PPh_3)_2]$ with toluene-3,4-dithiol has been investigated as a means of synthesising new iridium—dithiolene complexes [163]. In addition to the simple oxidative addition product, an unidentified polynuclear complex and a dinuclear complex are formed. An X-ray crystal structure determination showed that the dinuclear complex has the illustrated structure XXXXIII.

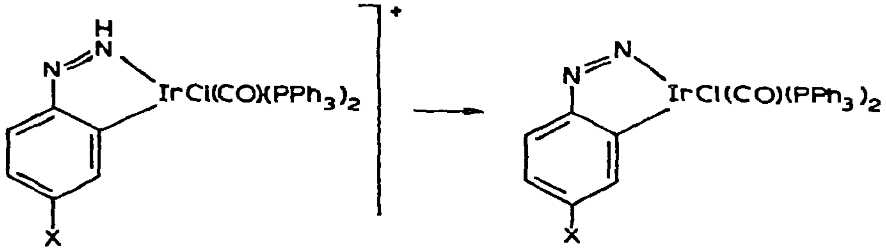


(XXXXII)



(XXXXIII)

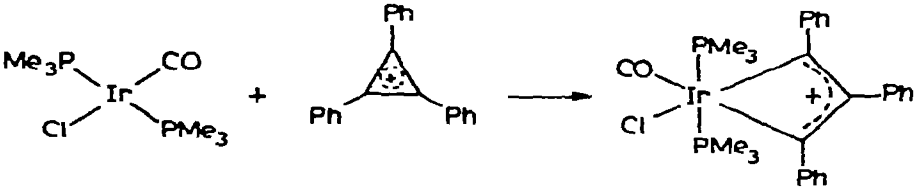
In a further investigation [164] of the reaction of aryldiazonium ions with Vaska type Ir^I complexes, the *ortho*-metallated complex XXXXIV has been obtained in addition to the tetrazene complex; the identity of XXXXIV was established by X-ray crystallography. Deprotonation of XXXXIV with bases affords the neutral species XXXXV.



(XXXXIV) X = F, Br

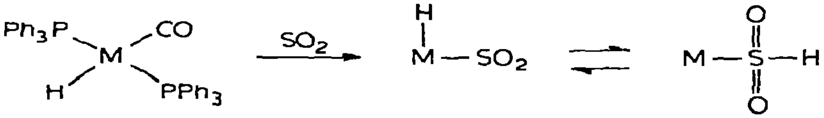
(XXXXV) X = F, Br

A single crystal X-ray diffraction study [165] has confirmed that the reaction of triphenylcyclopropenium cation with *trans*-[$IrCl(CO)(PMe_3)_2$] leads to the opening of the 3-membered ring and the formation of a four-membered iridocycle. Examination of the carbon—carbon bond lengths in the propenylium group suggests that there is a 1,3-($p_\pi p_\pi$) interaction.

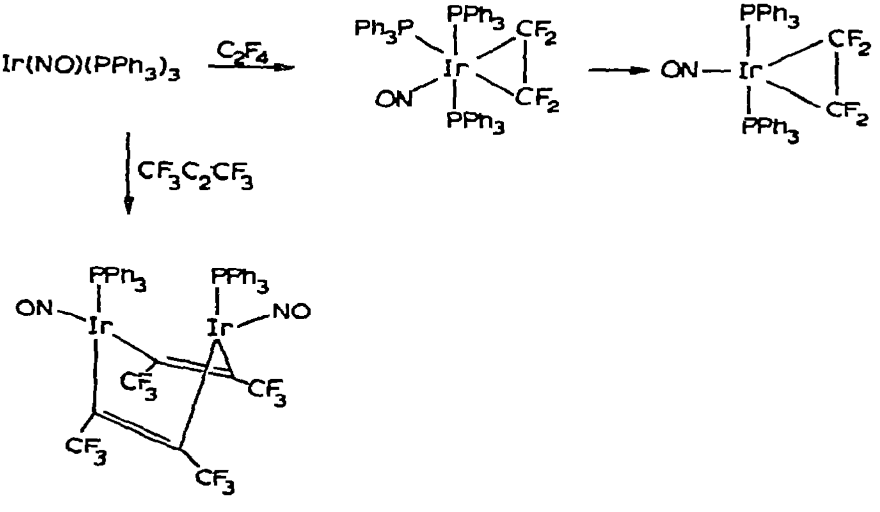


Reaction of dimethyl(1-naphthyl)phosphine with $IrCl_3$ in 2-methoxyethanol affords [$IrCl_2(P\text{-}C)L_2$], metallation occurring in the 8-position. Further metallation occurs with base in alcohol, giving [$IrCl(P\text{-}C)_2L$] and [$IrH(P\text{-}C)_2L$], and finally pyrolysis (2%, 10 mm) give *fac*-[$Ir(P\text{-}C)_3$]. Related rhodium(III) complexes were prepared by similar routes. Reversal of the metallation reaction occurs on treatment of some of these complexes with HCl; a hydride addition—elimination mechanism is suggested as a possible reaction pathway [166].

The rhodium and iridium hydrides [$MH(CO)(PPh_3)_3$] (M = Rh, Ir) react with SO_2 to give sulphur dioxide derivatives. To account for the absence of discernable high field NMR signals, it is suggested that in solution there is an equilibrium mixture of tautomers [167].



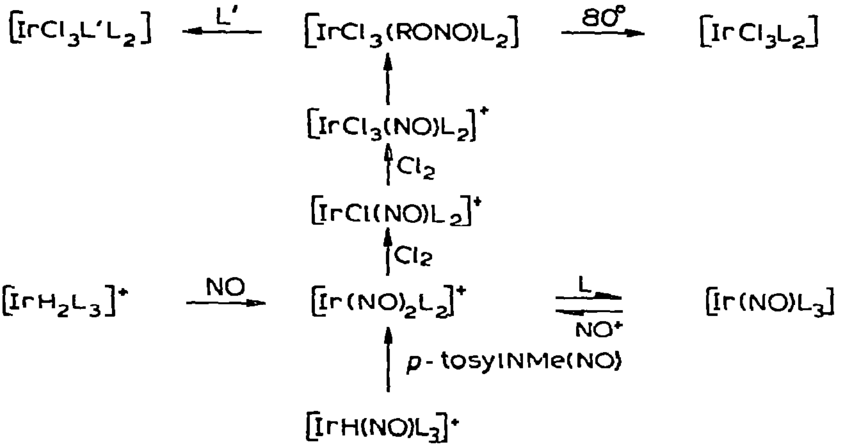
Although tetrafluoroethylene reacts straightforwardly with [$Ir(NO)(PPh_3)_3$] to displace PPh_3 and form an adduct, the corresponding reaction with hexafluoro-2-butyne gives an unusual dinuclear complex XXXXVI whose structure was established by X-ray crystallography [168].



(XXXXVI)

The complex $[IrCl(NO)(PPh_3)_2]^+$, a nitrosyl analog of Vaska's compound, can be readily prepared (90% yield) by treatment of $[IrCl(N_2)(PPh_3)_2]$ with $NOBF_4$ in chloroform. Tetracyanoethylene adds to the cation to form a stable 1/1 adduct [169].

The cationic nitrosyls $[IrCl_3(NO)L_2]^+$ (L = PPh_3, $AsPh_3$) react with alcohols to give neutral iridium(III) complexes containing bound alkyl nitrites $[IrCl_3(RONO)L_2]$ (R = Me, Et, Pr) [170]. These reactions (Scheme 21) parallel the formation of complexes containing alkoxycarbonyl groups as ligands by alkoxide-ion attack on cationic carbonyl complexes. The nitrite complexes revert to the parent nitrosyls with acids. It is suggested that this reaction bears upon the mechanism of formation of nitrosyl complexes in the frequently used preparation, which makes use of alkyl nitrites, *N*-nitroso reagents and nitrous acid. As illustrated new routes to the dinitrosyl cations required for the synthesis of $[IrCl_3(NO)L_2]^+$ cation, were examined.

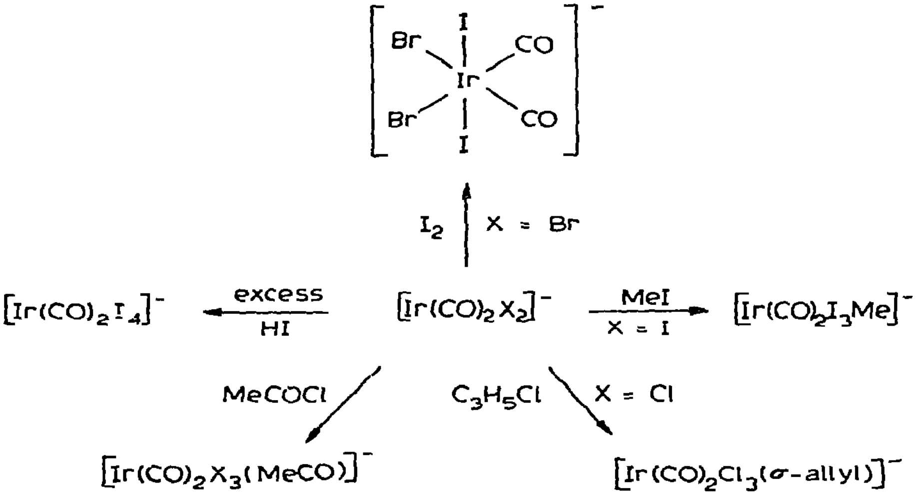


Scheme 21

Even though hydrido π-olefinic complexes of transition metals are often cited as probable intermediates in homogeneous catalytic reactions, only a few such compounds have been isolated. With this view the reaction of various activated olefins with $[IrH(CO)(PPh_3)_3]$, $[IrH(CO)_2(PPh_3)_2]$ and $[IrH_3(CO)(EPh_3)_2]$ (E = P, As) have been studied leading to the isolation and characterisation of the olefin complexes $[IrH(CO)(olefin)(EPh_3)_2]$. An X-ray study of the fumaronitrile complex has shown that in the solid state a trigonal bipyramidal configuration exists around the iridium with the olefin and phosphine ligands in the equatorial plane. Attempts to convert the olefin complex via H-migration into a σ bonded alkyl were unsuccessful. In the case of $IrH(CO)(PPh_3)_3$ a 1,4 addition of TCNE is observed [171, 172].

The crystal structure of carbonylchloro(tetracyanoethylene)bis(triphenylarsine)iridium has been determined [173].

Oxidative-addition reactions of the dihalodicarbonyliridate ions have been studied [174] and are summarised in Scheme 22. The reaction with methyl iodide contrasts with the corresponding rhodium system where the methylrhodium species, presumed to form initially rapidly isomerised to a dimeric acetyl species; the $[Ir(CO)_2I_3Me]^-$, in the form of its tetraphenylarsonium salt shows no tendency to isomerise up to 150°. Acetyl chloride adds rapidly to $[Ir(CO)_2X_2]^-$ at room temperature, which contrasts with the lack of reactivity towards acyl halides shown by the corresponding rhodium system.



Scheme 22

There are many examples of the labilisation of substituents on an alkyl ligand, which is bonded to a transition metal. A further illustration of this principle is provided by the observation that σ-allyl complexes of the type $[IrCl_2(CH_2CH{=}CH_2)(CO)L_2]$ (L = phosphine) react with HCl to give the 2-chloropropyliridium complexes [175]. These are readily converted into the 2-methoxy or 2-ethoxy derivatives (X = OMe or OEt) when treated with methanol or ethanol to the 2-hydroxy complex (L = PMe_2Ph with Na_2CO_3 in aqueous acetone) or to the 2-acetoxy complex (with NaOAc). Following an earlier investigation it was established that *mer*-$[IrCl_3(PEt_2Ph)_3]$ when treated with KOH in allyl alcohol, and then with dilute HCl and MeOH gives a mixture of $[IrCl_2(CH_2CHXCH_3)(CO)(PEt_2Ph)_2]$ with X = $OCH_2CH{=}CH_2$ and OMe.

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