COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1986*

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CONTENTS

Reviews

A review is available on alkyl complexes of cobalt (ref. 1) as are two on cyclometallated compounds including those of the cobalt group (refs. 2,3). The synthesis of some aryl rhodium complexes by decarboxylation reactions (ref. 4) and of bimetallic species containing a saturated hydrocarbon bridge (ref. 5) have also been reviewed. Three more accounts cover

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*No reprints available. Previous Survey, J. Organometal. Chem., 305(1987)57.

aspects of the activation of carbon-hydrogen bonds by transition metal complexes (refs. 6-8) while others describe radical processes in organometallic and bioorganometallic chemistry (ref. 9) and some chemistry of rhodium complexes of octaethylporphyrin (ref. 10).

Two reviews cover the chemistry of iridium carbene complexes (refs. 11, 12) while in the area of carbonyl complexes are reviews dealing with organometallic sonochemistry (ref. 13), complexes containing multiple bonds between main group elements and transition metals (ref. 14) and clusters containing open metal polyhedra (ref. 15). Also described are other classes of cluster complexes (ref. 16) and the bonding in such clusters and its relationship to that in the bulk metals (ref. 17). Phase-transfer catalyzed carbonylation reactions in the presence of $[Co_2(CO)_8]$ (ref. 18) and various aspects of hydroformylation processes are the subjects of further reviews (refs. 19, 20). Also of interest is a series of short accounts appearing in the March 1986 issue of J. Chem. Educ. describing the use of organotransition metal compounds as industrial catalysts.

Heterometallic clusters are reviewed (refs. 21, 22) as is the coordination chemistry of ligands derived from pyrazole (ref. 23) and from compounds of silicon, germanium, tin and lead (ref. 24). Also appearing is an account of polynuclear rhodium complexes of nitrogen-donor ligands (ref. 25). Compounds of the cobalt group are included in a review of the catalysis of ethylene and propylene dimerization by transition metal complexes (ref. 26), a further review discusses the catalysis of carbon-carbon bond formation by $[RhCl(PPh_3)_3]$ and $[Rh(COD)(PPh_3)_2]^+$ (ref. 27) and two more cover catalysis of asymmetric hydrogenation by chiral rhodium complexes (refs. 28, 29).

A short account of $[cpCo(CO)_2]$-mediated [2+2+2] cycloaddition processes in steroid synthesis has appeared (ref. 30) as have reviews on acyclic pentadienyl complexes (ref. 31), [m,m]metallocenophanes (ref. 32) and borabenzene complexes (ref. 33) all three of which include compounds of the cobalt group. Finally there are articles dealing with metallaboranes (ref. 34, 35), the burgeoning area of the reactions of gas phase metal ions with organic molecules (ref. 36), ^{59}Co and ^{103}Rh NMR studies on various organometallic complexes of these elements (ref. 37) and the use of $[RhH(PPh_3)_4]$ as a catalyst for the hydrogenation of aldimines by hydrogen transfer from formic acid (ref. 38).

Dissertations

A total of forty seven dissertations has been reported this year and many of their subjects should be familiar to readers of previous Surveys. The first group covers the synthesis of cobalt alkyl complexes containing

1,2-bis(dimethylphosphino)ethane ligands (ref. 39), the kinetics of the carbonylation of iridium alkyl complexes (ref. 40), the reactivity of $[Ir(CH_2SiMe_3)(PMe_3)_3]$ towards carbon-hydrogen bonds (ref. 41), the analysis of the ^{13}C NMR spectrum of $[Ir(Hbipy-C^3-N')(bipy)_2]^{3+}$ (ref. 42) and the synthesis and reactivity of binuclear, μ-alkylidene complexes of cobalt (ref. 43) and of binuclear alkyl complexes of rhodium derived from $[cp'_2Rh_2(\mu\text{-}CO)_2]$ (ref. 44). In the area of isocyanide complexes is one reporting the synthesis of [cpCo(CNMe)(CO)] from $[cpCo(CN)(CO)]^-$ and trimethyltin chloride (ref. 45), another concerned with the fluxional behavior and reactivity towards dihydrogen of isocyanide derivatives of $[Rh_2(\mu\text{-}H)_2(P(OPr^i)_3)_4]$ (ref. 46) and a third on the synthesis of the linear chain compounds $[(OC)_5ReRh(\mu\text{-}L_2)_4RhRe(CO)_5]^{2+}$ (L_2 = br, TMB) and related species (ref. 47).

Dissertations concerned with carbonyl complexes include ones on the synthesis and reactivity of carbonyl metallates including $[M(CO)_3]^{3-}$ (M = Co, Ir) (ref. 48), the reactions of $[Co_2(CO)_6L_2]$ (L = CO, PPh_3, PBu_3^n) with lithium aluminum hydride to form C_1-C_3 hydrocarbons (ref. 49), the reactions of $[Co_2(CO)_8]$ with $[HM(CO)_4L]^-$ (M = Cr, W; L = CO, $P(OMe)_3$, PPh_3, PMe_3) to form $[Co(CO)_4]^-$ and $[M_2(\mu\text{-}H)(CO)_{10}]^-$ (ref. 50) and radical reactions of $[HCo(CO)_4]$ with olefins and acetylenes (ref. 51). Other dissertations report Fenske-Hall molecular orbital calculations to assess protonic vs hydridic behavior of various transition metal hydride complexes including $[HCo(CO)_4]$ and its phosphine derivatives (ref. 52), the kinetics of substitution reactions of $[Co_4(CO)_9(TPM)]$ (ref. 53), the synthesis of other cobalt and rhodium complexes of TPM (ref. 54) and a study of electron-transfer-catalyzed substitution reactions of $[YCCo_3(CO)_9]$ (Y = Ph, Cl) (ref. 55). The mechanisms of carbon monoxide exchange processes of rhodium and cobalt carbonyl clusters in the solid state and in solution are described (ref. 56) as is a spectroscopic and electrochemical study of $[Ir_4(CO)_{12}]$ and $[IrCl(CO)_3]_n$ in molten $AlCl_3$/NaCl mixtures (ref. 57).

Heterometallic cluster systems are the subjects of four more dissertations including those on the synthesis of $[LMFeCo_3(CO)_{12}]$ (M = Au, Ag; L = PPh_3. M = Cu; L = PPh_2(p-tolyl), CNPh. M = Hg; L = Cl, Br, I, $Mn(CO)_5$, $cpFe(CO)_2$, $Co(CO)_4$, $Fe(CO)_3(NO)$, $FeCo_3(CO)_{12}$) (ref. 58), the chemistry of $[Pr^iO_2CCCo_3(CO)_9]$ and the synthesis of chiral, mixed metal clusters (ref. 59), the synthesis of $[(cpMe)_2Co_2Mo_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)(CO)_4]$ and related compounds (ref. 60) and the formation of $RhOs_3$ and Rh_2Os_2 clusters from $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (ref. 61).

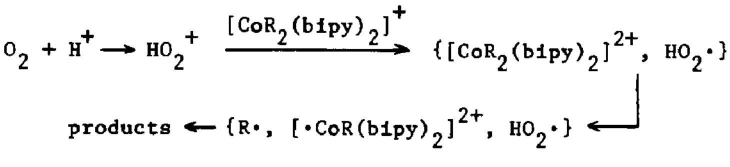
The final set of dissertations concerned with carbonyl complexes includes those on the synthesis of rhodium complexes of 2-pyridyl-bis-(diphenylphosphino)methane (ref. 62), flash and continuous photolysis studies on $[MCl(CO)(PPh_3)_2]$ (M = Rh, Ir), $[RhCl(PPh_3)_3]$ and $[IrH_2Cl(CO)(PPh_3)_2]$ (ref. 63), the synthesis of phosphide-bridged binuclear complexes of iridium with chromium, molybdenum or tungsten (ref. 64), the formation of $[M_2(\mu\text{-}AsBu^t{}_2)_2(CO)_4]$ (M = Co, Rh, Ir) and larger clusters (ref. 65) and on the results of Fenske-Hall molecular orbital calculations on heterobimetallic complexes including $[RhCo(CO)_5(PH_3)_2]$ and $[(OC)_4\overline{M(\mu\text{-}PR_2)M'}(CO)_3]$ (M = Fe; M' = Co, Ir. M = Ru; M' = Co) (ref. 66).

In the area of alkene complexes there are dissertations on the preparation of $[Rh_3(COD)_3(\mu_3\text{-}S)_2(\mu\text{-}H)]$ (ref. 67), the oxidative addition of nitrogen-hydrogen bonds to rhodium and iridium (ref. 68) and the use of $[Rh(NBD)L_2]^+$ (L_2 = various ferrocenylphosphines or o-1-dimethylaminoethyldiphenylphosphine and related ligands) as asymmetric hydrogenation catalysts (refs. 69, 70). Three more dissertations report on the use of $[Co_2(CO)_8]$ to catalyze the cocyclization of acetylenes with carbon monoxide to form cyclic enones (ref. 71), the intramolecular cyclization of α,ω-enynes (ref. 72) and on the use of $\{Co_2(CO)_6\}$-stabilized propargyl cations in organic synthesis (ref. 73). Also appearing is a report on the use of η^3-allyl complexes of rhodium and iridium containing chiral phosphine ligands which catalyze the rearrangement of allylic thionobenzoates (ref. 74).

Further dissertations describe the synthesis and reactivity of complexes of the type $[cp_2Co_2(\mu\text{-}PR_2)_2]$ (ref. 75), the synthesis of chiral (ref. 76) and helical (ref. 77) cobaltacenes, the preparation of pentamethylcyclopentadienyl polyhydride and polyphosphine complexes of iridium (ref. 78) and routes to cobaltacarbaboranes (ref. 79) and cobaltaboranes (ref. 80). The final set reports on chemistry of $[RhH_3(triphos)]$ (ref. 81), the oxidative addition of dihydrogen to $[RhCl(P(p\text{-}tolyl)_3)_2L]$ (L = $P(p\text{-}tolyl)_3$, thf, py, N-methylimidazole) (ref. 82), the reaction of hydrogen sulfide with phosphine complexes of rhodium and iridium (ref. 83), the use of $[RhCl(PPh_3)_3]$ to mediate the coupling of arylmercurials with vinyl halides to form aryl olefins (ref. 84) and the catalysis of hydrogenation reactions with rhodium complexes of 1,2-bis(diphenylphosphino)benzene and a macrocyclic tridentate phosphine ligand (ref. 85).

Metal-carbon σ-bonded Complexes

Tested syntheses are available for several perfluorophenylcobalt complexes including $[Co(C_6F_5)_2]$, $[Co(C_6F_5)(CO)_4]$ and phosphine derivatives of the latter (ref. 86). Treatment of $[Co(acac)_3]$ with trimethyl- or tris(trimethylsilyl)aluminum in the presence of phosphine ligands forms $[Co(R)L_3]$ (R = Me, $SiMe_3$; L = PPh_3. R = Me; L = PPh_2Me, $PPhMe_2$, PPh_2GeMe_3, PPh_2SnMe_3). The analog $[Co(Ph)(PPh_2Me)_3]$ can be generated from cobalt(II) chloride, phenyllithium and the phosphine. The complexes are thermally unstable in solution and cleavage and rearrangements of the ligands accompany the decomposition. In the presence of p-bromotoluene $[Co(Me)(PPh_3)_3]$ forms both p-xylene and 4,4'-dimethylbiphenyl but with 1- or 2-bromonaphthalene only methylation is seen and no coupling products are found. As noted above, decomposition of the phosphine ligand occurs here too and interferes with the methylation reaction in some instances (refs. 87, 88). The acid-promoted oxidation of cis-$[CoR_2(bipy)_2]ClO_4$ (R = Me, Et, bz) by dioxygen has been studied and the mechanism of Scheme I proposed.



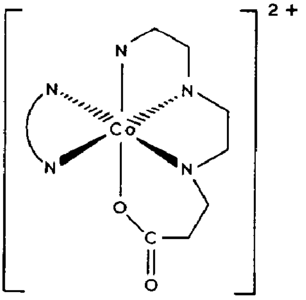
$$O_2 + H^+ \longrightarrow HO_2^+ \xrightarrow{[CoR_2(bipy)_2]^+} \{[CoR_2(bipy)_2]^{2+}, HO_2\cdot\}$$

$$\text{products} \longleftarrow \{R\cdot, [\cdot CoR(bipy)_2]^{2+}, HO_2\cdot\}$$

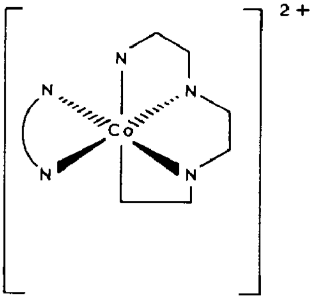
Scheme I

This seems appropriate when R = bz since significant amounts of benzyl hydroperoxide are seen. However when R = Et butane is a major product suggesting the proposed $[CoEt_2(bipy)_2]^{2+}$ intermediate undergoes a rapid reductive elimination. Photolysis of the same dialkyl complexes in the presence of benzyl and allyl bromides causes carbon-carbon bond formation with the formation of 1,2-diphenylethane and hexa-1,5-diene respectively. Here it is proposed that the photolysis generates $[\cdot CoR(bipy)_2]^+$ which then selectively reduces the organic halide (refs. 89, 90).

Photolytic decarboxylation of [1] ($\overset{\frown}{NN}$ = ophen) forms [2] (ref. 91) while oxidation of $[Co(dacoda)(H_2O)]$ with hydrogen peroxide in the presence

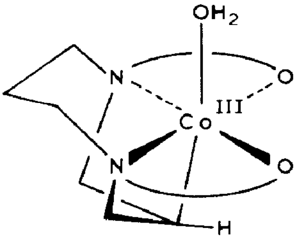


[1]



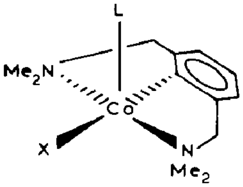
[2]

of cyanide ion forms [3] which contains one of the shortest cobalt(III)-carbon bonds (1.941 Å) yet reported. It is proposed that the cyanide ion first replaces water in the starting complex following which the cobalt is oxidized and then activation of the carbon-hydrogen bond occurs. This is supported by the observation that when the oxidation is performed in the



[3]

presence of sulfite ion, the reaction stops with the formation of the cobalt(III) complex with an axial sulfite ligand. In this complex there is an agostic interaction of a ligand hydrogen atom with the metal and [3] can be generated by subsequent reaction with sodium methoxide (ref. 92). The extremely air-sensitive complexes [4] (L = py, PPh_3; X = Cl, Br, I. L =



[4]

PEt_3; X = Cl) are prepared from $[CoX_2L_2]$ and 2,6-bis(dimethylaminomethyl)-phenyllithium. A square pyramidal structure is proposed on the basis of EPR studies (ref. 93).

Slow crystallization of PPN$[Co(1\text{-norbornyl})_4]$ from diethyl ether at -35°C is accompanied by its oxidation to $[Co(1\text{-norbornyl})_4]$ which contains a slightly distorted tetrahedral coordination of the cobalt. The formally cobalt(IV) complex exhibits a magnetic moment corresponding to one unpaired electron and is therefore the first example of a low-spin tetrahedral complex (ref. 94). A variable temperature NMR study of $[cp'Co(Et)(PMe_2Ph)]$-BF_4 which contains an agostic ethyl group indicates that three dynamic processes are occurring in solution. These are, in order of increasing $\Delta G^{\dagger}$, an averaging of the three protons of the methyl group, an inversion at cobalt which equilibrates the diastereotopic methyl groups on the phosphine ligand and an equilibration between the ethyl complex and an ethylene hydride complex. The last process has been probed by EHMO calculations which show that the structure corresponding to the agostic ethyl group represents an energy minimum. At this stage, there is still significant carbon-hydrogen bonding but cobalt-hydrogen bonding is also definitely present. The depth of this minimum is predicted to be sensitive to the nature of the other ligands on the metal (refs. 95, 96).

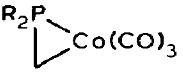
The mechanism of the cobalt-catalyzed olefin hydroformylation reaction continues to attract attention and three papers explore the final stage where an acyl cobalt complex is reduced to the product aldehyde. In the first, $[MeC(O)Co(CO)_3(PPh_3)]$ was reacted with HMR_3 (M = Si, Sn; R = Bu^n, Ph) to form acetaldehyde and $[R_3MCo(CO)_3(PPh_3)]$ with the rate increasing in the order H_2<$HSiR_3$<$HSnR_3$ which parallels the decrease in the element-hydrogen bond strength. A mechanism involving reversible loss of carbon monoxide followed by oxidative addition of the silicon- or tin-hydrogen bond and reductive elimination of aldehyde is proposed (ref. 97). In the others $[RC(O)Co(CO)_4]$ (R = Pr^n, Pr^i) was reacted with dihydrogen, hydrogen halides and $[HCo(CO)_4]$ and in all instances, aldehyde formation was inhibited by the presence of carbon monoxide indicating again that carbon monoxide dissociation is the initial step. Use of D_2 and $[DCo(CO)_4]$ demonstrated the existence of an inverse isotope effect which is thought to be thermodynamic in origin. In the reaction with hydrogen iodide, $[ICo(CO)_4]$ was detected as an intermediate. Although $[HCo(CO)_4]$ reacts with the acyl complex 20-30 times faster at 25°C than does dihydrogen, the reaction rates are strongly temperature dependent and extrapolation of the data obtained here to conditions prevailing in the industrial hydroformylation process suggests that dihydrogen rather than $[HCo(CO)_4]$ is the primary reductant. Also noted was the reaction of $[Co_2(CO)_8]$ with hydrogen halides which is one half order in $[Co_2(CO)_8]$ suggesting that the reaction is initiated by cleavage to $[\cdot Co(CO)_4]$ (refs. 98, 99). Reaction of several ketenes with $[HCo(CO)_4]$ proceeds at dry ice temperature to form $[RR'CHC(O)Co(CO)_4]$ (R = R' = H, Me. R = H; R' = Me, Et) in high yield provided strict 1:1 stoichiometry is maintained. A low yield of $[Me(Ph)CHC(O)Co(CO)_4]$ was obtained after prolonged reaction at 10°C but no acyl could be formed with diphenyl ketene (ref. 100).

Reduction of $[Co_2(CO)_6(PMePh_2)_2]$ with sodium amalgam followed by reaction with alkyl halides forms $[Co(R)(CO)_3(PMePh_2)]$ (R = Me, CH_2OMe, CH_2CO_2Et) which slowly decomposes on storage. Successive treatment of $Hg[Co(CO)_2(PMePh_2)_2]_2$ with sodium amalgam and chloromethyl methyl ether forms $[Co(CH_2OMe)(CO)_2(PMePh_2)_2]$ which is less stable than the monophosphine analog due to ligand dissociation. While $[Co(R)(CO)_3(PMePh_2)]$ converts to $[RC(O)Co(CO)_2(PMePh_2)L]$ (R = Me, CH_2Me; L = CO, $PMePh_2$) on addition of L, when R = CH_2CO_2Et this does not occur. In fact when $[EtO_2CCH_2C(O)Co(CO)_3(PMePh_2)]$ is prepared from $Na[Co(CO)_3(PMePh_2)]$ and carbethoxyacetyl bromide it readily reverts to $[EtO_2CCH_2Co(CO)_3(PMePh_2)]$ (ref. 101). Whilst $Na[Co(CO)_4]$ reacts with methyl iodide in diethyl ether at 0°C to form $[MeCo(CO)_4]$, $PPN[Co(CO)_4]$ and methyl iodide in THF or acetonitrile at 0°C gives the iodoacetyl complex $PPN[MeC(O)Co(I)(CO)_3]$. The latter reaction in dichloromethane however also forms some $[MeC(O)Co(CO)_4]$, a species which is the sole product if $K[Co(CO)_4]$ is reacted with methyl iodide in THF. It is apparent that the course of this reaction is sensitive to the nature of the cation and the solvent. Some chemistry of PPN[MeC(O)Co(I)$(CO)_3$] is outlined in Scheme II (ref. 102). Reduction of $[Co(CO)_3(R_2P(CH_2)_nCl)]_2$ (R = Ph; n = 1, 3. R = cy; n = 3) with sodium amalgam forms [5] when n = 1 but [6] when n = 3. Complex [5] is unreactive towards carbon monoxide but [6] reacts reversibly at -10°C to give [7] (R = Ph, cy) while with triphenylphosphine the low temperature product is [8] (R = Ph) and at 60°C [9] (R = cy) forms. From NMR and structural data, [5] is considered to be a chelating phosphorus ylide (ref. 103).

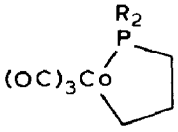
$$\begin{tikzcd}
 & {[MeC(O)Co(CO)_3(PPh_3)]} & \\
CH_3CO_2Me & {[MeC(O)Co(I)(CO)_3]^-} \arrow[l, "d"'] \arrow[u, "a"'] \arrow[r, "b"] \arrow[d, "c"] & CH_3CHO(42\%) \\
 & CH_3CHO(24\%) &
\end{tikzcd}$$

a) PPh_3, THF, 0°C. b) H_2SO_4, THF, 0°C. c) H_2(50 atm), THF, 50°C. d) CO, MeOH, py, THF, 25°C.

Scheme II



[5]



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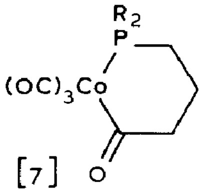

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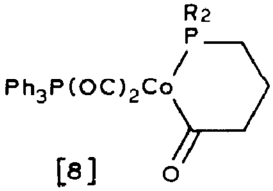

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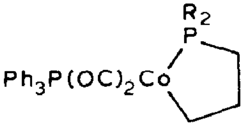
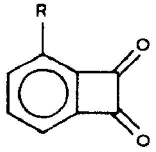
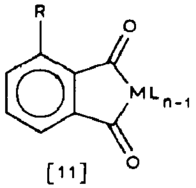


[9]

Further studies of the use of phthaloyl complexes of cobalt in the synthesis of naphthoquinones have been reported. Thus reaction of [10] with ML_n (ML_n = $RhCl(PPh_3)_3$, $CoCl(PPh_3)_3$, $cpCo(CO)_2$) forms [11] (R = H). Treatment of [11] (R = H; ML_{n-1} = $CoCl(PPh_3)_2$) in acetonitrile with acetylenes in the presence of one equivalent of silver tetrafluoroborate gives

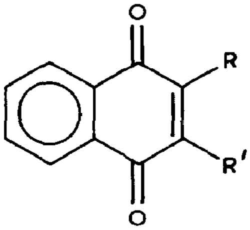


[10]

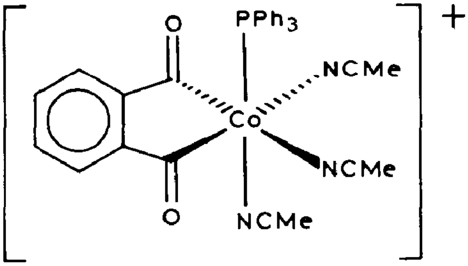


[11]

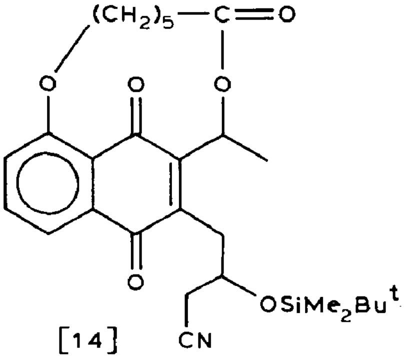
[12] (R = R' = Me, Et, Ph. R = H; R' = Bu^n, Ph among others). The role of the silver ion is to convert [11] to [13] in which at least one acetonitrile ligand is labile thereby providing a site for acetylene coordination. Treatment of [11] (ML_{n-1} = $CoCl(PPh_3)_2$; R = $O(CH_2)_5C(O)OC(Me)C{\equiv}CCH(CH_2CN)OSiMe_2Bu^t$) with silver tetrafluoroborate in acetonitrile promotes an internal cyclization to form [14] which is a synthon for nanomycin-A.



[12]

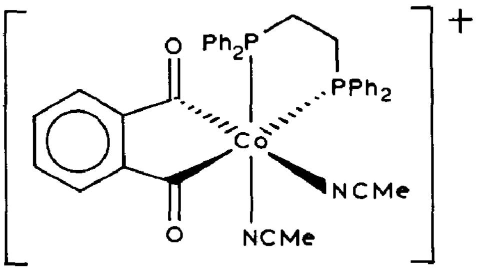


[13]



[14]

Modifications of this system involve reaction of [13] with DPPE to form a species now shown to be [15] and of [11] (R = H; ML_{n-1} = $CoCl(PPh_3)_2$) with pyridine and dimethylglyoxime to form [16]. Both are also suitable substrates for reaction with acetylenes to form naphthoquinones with [16] requiring activation by Lewis acids. Particularly effective ones are $[Co(H_2O)_6]Cl_2$ and tin(IV) chloride (refs. 104, 105). Methylphenylacetylene reacts with either $[CoMn(CO)_9]$ or $[CoMn(CO)_7(PhC_2Me)]$ in refluxing hexane to produce [17] (ref. 106).



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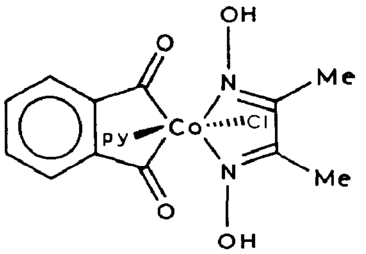

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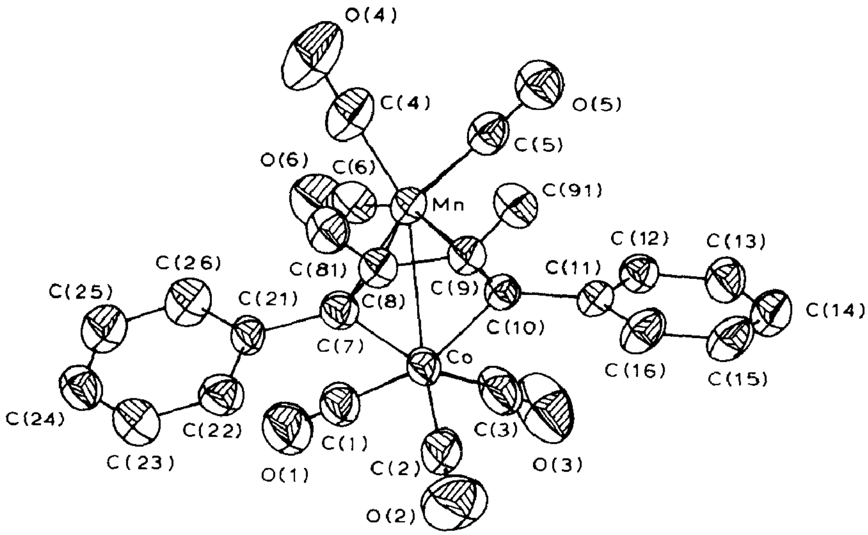
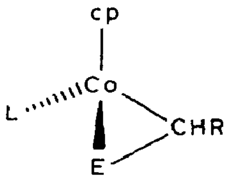
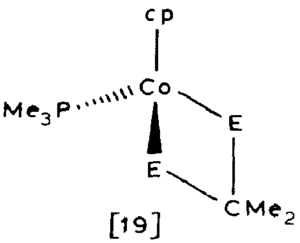


[17]

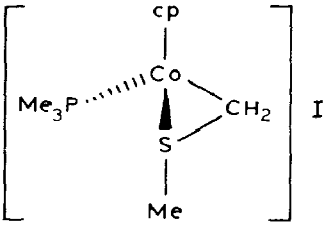
The complexes [cpCo(CO)L] (L = PMe_3, PMe_2Ph) can be converted to [18] (L = PMe_3, PMe_2Ph; R = H; E = S, Se. L = PMe_3; R = Me) by successive reaction with $CHRBr_2$ and NaEH but with L = PMe_3 reaction with CMe_2Br_2 and NaEH forms [19]. Protonation of [18] (L = PMe; R = H; E = S) with tetrafluoroboric acid forms $[cp_2Co_2(PMe_3)_2(\mu\text{-}SMe)_2](BF_4)_2$ while reaction with methyl iodide forms [20] which is in equilibrium with $[cpCo(I)(PMe_3)(CH_2SMe)]$ and reacts with TFA and sodium iodide to give $[CpCo(I)(PMe_3)(SMe_2)]^+$. Protonation of [21] (R = Ph, R' = Me) with TFA forms [22] after addition of hexafluorophosphate ion which converts to [23] in refluxing acetone. Methylation of [21] (R = Me, R' = Ph) with trimethyloxonium tetrafluoroborate however forms [24] which is converted to [25] by TFA. The chloromethyl ligand in



[18]



[19]



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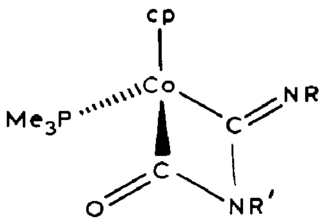

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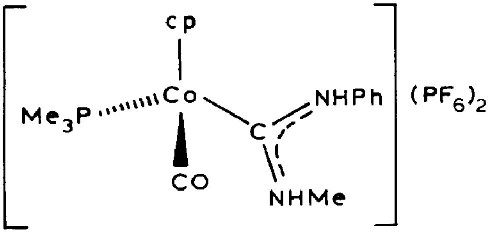

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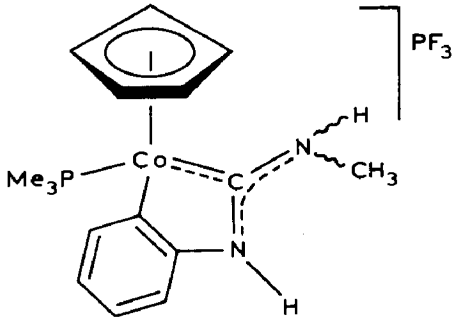

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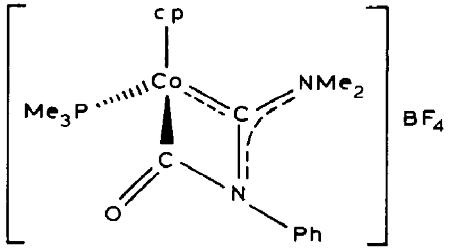

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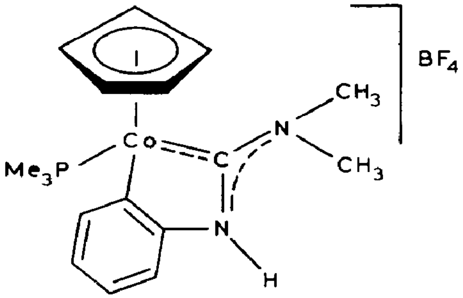
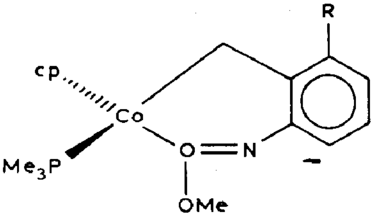


[25]

[cpCo(CH$_2$Cl)(PMe$_3$)(CNMe)]PF$_6$ was expected to be susceptible to nucleophilic attack by hydroxide ion to give an analog of [18] (L = PMe$_3$; E = O; R = H) but no reaction occurred. To check if this failure was due to a high Lewis basicity of the methylisocyanide ligands, analogs with phenyl- and p-tolylisocyanide were prepared and reacted with methanolic potassium hydroxide. The desired cobaltaoxetane again did not form and instead the product was [26] (R = H, Me) for which the mechanism of Scheme III (L = PMe$_3$) was proposed (refs. 107-109). In related work, photolysis of a mixture of



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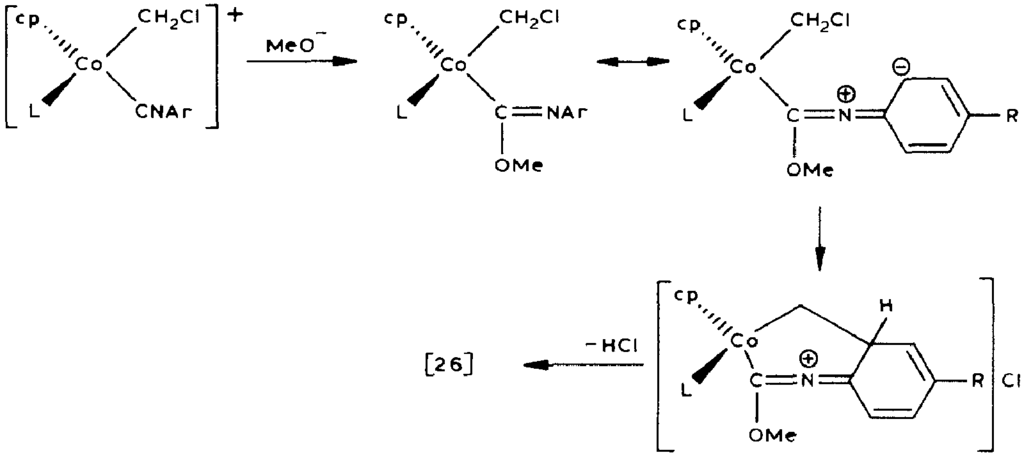


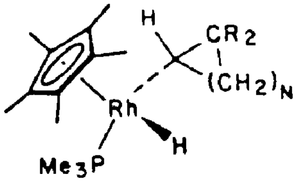
Scheme III

$[cp'Co(CO)_2]$ and dichloromethane in diisopropyl ether forms $[cp'Co(CH_2Cl)$-$(Cl)(CO)]$ which decomposes on extended photolysis. The success of the synthesis is attributed to the choice of solvent since the product precipitates as it forms and therefore is not photodegraded. The structure has been determined and shows a slight electronically induced distortion of the pentamethylcyclopentadienyl ring from symmetrical η^5-bonding (ref. 110).

In a study of the synthesis of trifluoromethyl cobalt complexes it was determined that $[Hg(CF_3)_2]$ is not a suitable synthon but using $[Cd(CF_3)_2 \cdot DME]$ and $[cpCo(CO)I_2]$ in a 3:1 ratio forms $[cpCo(CF_3)_2(CO)]$ plus small amounts of $[cpCo(CF_3)(I)(CO)]$. Separation of the latter and reaction with more $[Cd(CF_3)_2 \cdot DME]$ affords overall high yields of the bis(trifluoromethyl) complex. This is more thermally robust than the dimethyl analog but when it is thermolyzed some hexafluoroacetone forms suggesting that both may decompose by the same process (ref. 111). Halide abstraction from $[cpCo(L_2)I]I$ (L_2 = DPPE, DPPP) with silver tetrafluoroborate or hexafluorophosphate in acetone containing a small amount of phenylacetylene under carbon monoxide forms $[cpCo(L_2)(CO)]X_2$ (X = BF_4, PF_6). In refluxing alcohols conversion to $[cpCo(DPPE)(C(O)OR)]X$ (R = Me, Et, Pr^n, Bu^n, n-pentyl, n-hexyl) occurs while with aniline the product is $[cpCo(DPPE)(C(O)NHPh)]X$. Pentamethylcyclopentadienyl analogs of the dications were also prepared. It was not determined what is the role of the phenylacetylene in the formation of the dicationic complexes but in its absence it was not possible to obtain pure products (ref. 112).

A β-hydrogen is abstracted from the ethyl group in $[cpRh(Et)(PMe_3)_2]I$ on treatment with trityl tetrafluoroborate to give $[cpRh(C_2H_4)(PMe_3)_2](BF_4)_2$.

The coordinated ethylene is susceptible to nucleophilic attack leading to the formation of [cpRh(CH$_2$CH$_2$Nu)(PMe$_3$)$_2$](BF$_4$)$_2$ (Nu = NEt$_3$, PMe$_3$, PPr$^i{}_3$, PPh$_3$, P(OMe)$_3$). The trimethylphosphite adduct undergoes an Arbusov reaction with iodide ion to give [cpRh(CH$_2$CH$_2$P(O)(OMe)$_2$)(PMe$_3$)$_2$]BF$_4$ while [cpRh(C$_2$H$_4$)(PMe$_3$)$_2$](BF$_4$)$_2$ itself yields a mixture of [cpRh(I)(PMe$_3$)$_2$]BF$_4$ and [cpRh(CH$_2$CH$_2$I)(PMe$_3$)$_2$]BF$_4$ when the reaction is run at room temperature but only the former at 55°C. Reaction of [cpRh(C$_2$H$_4$)(P(OMe)$_3$)] with methyl iodide and hexafluorophosphate ion forms [cpRh(Me)(C$_2$H$_4$)(P(OMe)$_3$)]PF$_6$ in which the ethylene molecule is attacked by phosphorus ligands to give [cpRh(Me)(CH$_2$CH$_2$PR$_3$)(P(OMe)$_3$)]PF$_6$ (R = Me, OMe) (ref. 113). Further work on the activation of aryl carbon-hydrogen bonds at rhodium centers showed that photolysis of [cp'RhH$_2$(PMe$_3$)] (to presumably generate {cp'Rh(PMe$_3$)}) in a benzene/deuterobenzene mixture at 10°C forms both [cp'Rh(H)(C$_6$H$_5$)-(PMe$_3$)] and [cp'Rh(D)(C$_6$D$_5$)(PMe$_3$)] with a very small isotope effect (k_H/k_D = 1.05). The same reaction in 1,3,5-trideuteriobenzene at -40°C forms [cp'Rh(H)(C$_6$H$_2$D$_3$)(PMe$_3$)] and [cp'Rh(D)(C$_6$H$_3$D$_2$)(PMe$_3$)] with k_H/k_D = 1.4. The results are interpreted to support previous proposals that the reaction proceeds via an η^2-benzene intermediate rather than via a direct insertion of the metal into a carbon-hydrogen(deuterium) bond. The reductive elimination of m-xylene from [cp'Rh(H)(3,5-C$_6$H$_3$Me$_2$)(PMe$_3$)] gave k_H/k_D = 0.51. Taken together, all the kinetic data suggest that the transition state for oxidative addition of a carbon-hydrogen bond of the η^2-coordinated arene occurs at a relatively early stage and conversely that in the reductive elimination significant carbon-hydrogen bonding must develop by the time the transition state is reached (ref. 114). The same rhodium complex, [cp'RhH$_2$(PMe$_3$)], on photolysis in saturated hydrocarbons at -40°C forms the alkyl hydride complexes [cp'Rh(R)(H)(PMe$_3$)] (R = Me, Et, Pr^n, Bu^n, n-pentyl, n-hexyl, n-octyl, Bu^i, SiMe$_3$, cyclopropyl, 1-methylcyclopropylmethyl, 2,2-dimethylcyclopropyl, cyclobutyl, cyclopentyl). Some of these complexes can also be prepared from [cp'Rh(R)(Br)(PMe$_3$)] and butyllithium at -78°C followed by protonation with ethanol at -90°C, from [cp'RhH$_2$-(PMe$_3$)] and butyllithium followed by reaction with the appropriate alkyl tosylate or from thermolysis of [cp'Rh(H)(Np)(PMe$_3$)] at -60°C in the presence of the appropriate alkane. Kinetic studies indicate that the presumed reactive intermediate, {cp'Rh(PMe$_3$)}, inserts into all possible carbon-hydrogen bonds but rapid intramolecular rearrangements ensue to give the observed primary alkyl products. This selectivity therefore appears to be thermodynamic rather than kinetic in origin. If the oxidative addition of the alkanes is carried out at -90°C it is possible to regiospecifically form ^{2}H and ^{13}C labelled products which rearrange at -80°C faster than they undergo reductive elimination. This was demonstrated by showing that even in aromatic solvents, some rearranged alkyl hydride complex formed. Since the aryl hydride complex which would form on reaction of {cp'Rh(PMe$_3$)} with the solvent is more stable than the alkyl hydride complex, no rearranged alkyl hydride complex should be seen if the rearrangement were to go exclusively via reductive elimination to form a free {cp'Rh(PMe$_3$)} moiety. From a consideration of labelling studies and kinetic isotope effects it was concluded that the most consistent mechanism for rearrangement of the alkyl hydride complex involves a reductive elimination of alkane but with the latter remaining associated with the metal via an η^2-C-H attachment. This would also suggest that such a species should also be a precursor to the oxidative addition of sp^3 carbon-hydrogen bonds to a transition metal. In further work, the cycloalkyl complexes [27] (n = 1; R = H, Me. n = 2; R = H), prepared from [cp'Rh(H)(Np)(PMe$_3$)] as described above, rearrange to [28] at 20°C in the corresponding cycloalkane as solvent. From labelling and kinetic studies an intramolecular process is again indicated which is proposed to involve migration of the {cp'Rh(PMe$_3$)} moiety to the α-carbon-carbon bond of the cycloalkane ring. The fact that these cycloalkyl hydride complexes form prior to any appearance of the metallacycles indicates that the former are the kinetic products and are formed by carbon-hydrogen oxidative addition. That no initial carbon-carbon bond cleavage occurs, even in the cyclopropane reaction, was taken to suggest that activation of carbon-carbon bonds in alkanes by transition metals may occur by a prior activation of a carbon-hydrogen bond. In another part of this work, [29] (R = H, Me) is converted by silver tetrafluoroborate to [30] which in turn reacts with lithium triethylborohydride or -deuteride to form [31] (R = H, X = D; R = Me, X = H). This provides a second example of nucleophilic attack at the central carbon atom of an η^3-allyl ligand (refs. 115, 116).



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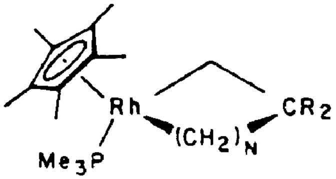

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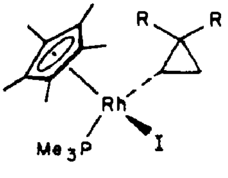

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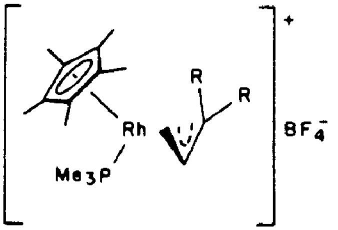

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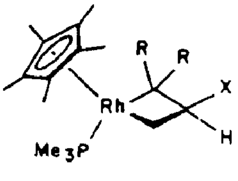
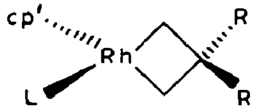


[31]

The course of the reaction of [cp'RhCl$_2$(PPh$_3$)] with neopentyl and trimethylsilylmethyl reagents is dependent on the nature of the metal they contain and the solvent. With neopentyl magnesium chloride in pentane the product is [32] (L = PPh$_3$; R = Me) while in diethyl ether [32] (R = Me) [33] (R = Np) and [cp'Rh(C$_2$H$_4$)(PPh$_3$)] form. In dichloromethane the products are [32] (R = Me), [cp'Rh(C$_2$H$_4$)(PPh$_3$)] and [cp'Rh(Np)(Cl)(PPh$_3$)] while



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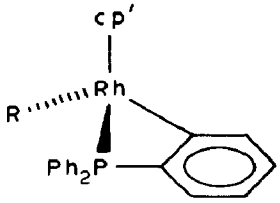
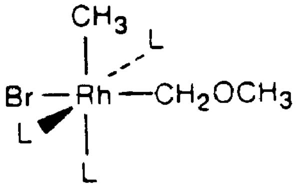


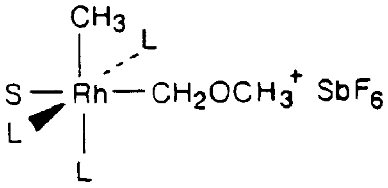
[33]

with neopentyllithium in pentane [32] (R = Me) and [33] (R = Np) are obtained. With trimethylsilylmethyl magnesium chloride in diethyl ether, the product is [cp'Rh(CH$_2$SiMe$_3$)$_2$(PPh$_3$)] but with trimethylsilylmethyl lithium, [33] (R = CH$_2$SiMe$_3$) is formed, a result which is attributed to the lithium reagent being a stronger base than the Grignard and preferentially abstracting a proton from the o-position of a phenyl group of the phosphine. Reaction of [cp'RhCl$_2$(PPh$_3$)] with one equivalent of trimethylsilylmethyl magnesium chloride in dichloromethane forms [cp'RhCl(CH$_2$SiMe$_3$)-(PPh$_3$)] which is converted to [cp'Rh(CH$_2$SiMe$_3$)$_2$(PPh$_3$)] by a second equivalent of the Grignard in diethyl ether and to the o-metallated complex by trimethylsilylmethyllithium in ether. Complex [32] (R = Me) decomposes to form 1,1-dimethylcyclopropane in CF$_2$ClCFCl$_2$ and in the same solvent reacts with bromine to give a 2:1 yield of the same cyclopropane and 1,3-dibromo-2,2-dimethylpropane. Thermolysis of [cp'Rh(CH$_2$SiMe$_3$)$_2$(PPh$_3$)] in cyclohexane forms tetramethylsilane while its iridium analog, which was synthesized by the same route, is thermolyzed in benzene to give iridium metal, an unidentified iridium complex and tetramethylsilane. The same complex on heating to 50°C in cyclohexane forms tetramethylsilane and the iridium analog of [32] (R = SiMe$_3$). Treatment of [cp'IrCl$_2$(PPh$_3$)] with neopentylmagnesium chloride in pentane forms the iridium analog of [33] (R = Np) while with one equivalent of trimethylsilylmethyl magnesium chloride the products are the iridium analog of [33] (R = CH$_2$SiMe$_3$) and a minor amount of [cp'Ir(Me)Cl(PPh$_3$)] (refs. 117, 118).

Reaction of [Rh(Me)(PMe$_3$)$_{3,4}$] with bromomethyl methyl ether forms [34] (L = PMe$_3$) which decomposes on treatment with silver hexafluoroantimonate in dichloromethane but in acetonitrile [35] (L = PMe$_3$; S = MeCN) can be

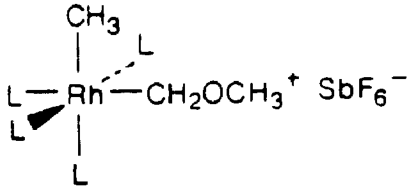


[34]



[35]

isolated. The latter converts to [36] (L = PMe$_3$) on treatment with trimethylphosphine and to [37] (L = PMe$_3$; S = MeCN) when reacted with [RhCl(cyoct)$_2$]$_2$ in acetonitrile. Analogs of [36] and [37] with a methyl group



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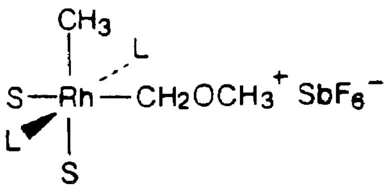
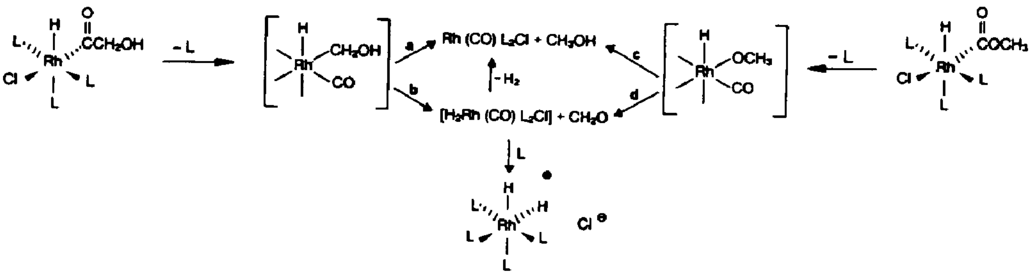


[37]

in place of the methoxymethyl moiety can be prepared similarly and are more stable. Complex [34] also reacts with bromotrimethylsilane to form *mer*-[RhHBr$_2$(PMe$_3$)$_3$] and ethylene *via* *mer*-[Rh(=CH$_2$)(Br)(Me)(PMe$_3$)$_3$]Br and [Rh(Et)(Br)(PMe$_3$)$_3$]Br as proposed intermediates. It was also observed that [36] (L = PMe$_3$) in the presence of traces of [35] (L = PMe$_3$; S = MeCN) decomposed smoothly in deuterodichloromethane to yield methyl ethyl ether and methyl vinyl ether. The same organic products were observed in equal amounts when [35] (L = PMe$_3$; S = MeCN) was dissolved in deuterodichloromethane suggesting a common intermediate for their formation. This was proposed to be {RhH(CH(Me)OMe)(PMe$_3$)$_3$}$^+$ which was thought to form *via* α-hydrogen abstraction from the methoxymethyl group to first give [Rh(=CHOMe)(Me)(H)(PMe$_3$)$_3$]$^+$ in which migration of the methyl group to the carbene carbon atom then occurred. The proposed intermediate could then either undergo reductive elimination or β-hydride abstraction to yield the observed products (ref. 119). In related work, the carbomethoxy complex *mer*-[Rh(H)Cl(C(O)OMe)(PMe$_3$)$_3$] was prepared by oxidative addition of methyl formate to [RhCl(PMe$_3$)$_3$]. Both this and its hydroxyacetyl isomer, *mer*-[Rh(H)Cl(C(O)CH$_2$OH)(PMe$_3$)$_3$] were observed to decompose on heating to form methanol, formaldehyde, [RhCl(CO)(PMe$_3$)$_2$] and [RhH$_2$(PMe$_3$)$_4$]Cl but in significantly different amounts. Thus the first gave primarily methanol (93%) and [RhCl(CO)(PMe$_3$)$_2$] (96%) while the latter gave more formaldehyde (87%) and significant amounts of both rhodium products. The mechanism of

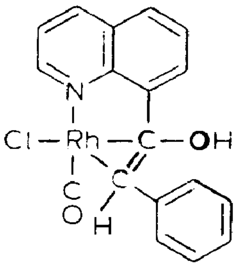
Scheme IV (L = PMe_3) was proposed with the predominance of path *c* over path



Scheme IV

a for methanol formation suggesting that reductive elimination from a cis-{M(H)(OMe)} species is preferred to that from a cis-{M(H)(CH_2OH)} moiety (ref. 120).

Further work on the reactions of 8-quinolinyl ketones with rhodium(I) complexes has been reported. With $[RhCl(CO)_2]_2$, 8-quinolinyl benzyl ketone and 8-quinolinyl phenyl ketone form [38] and [39] respectively while



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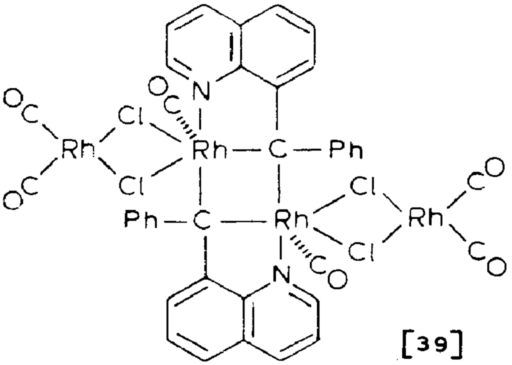
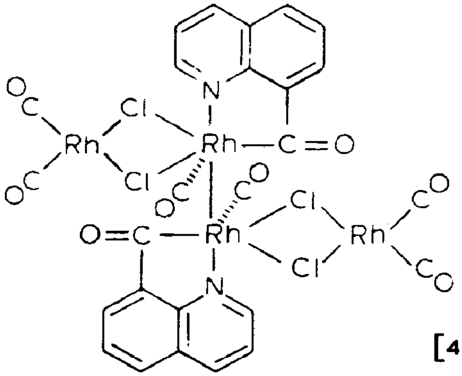


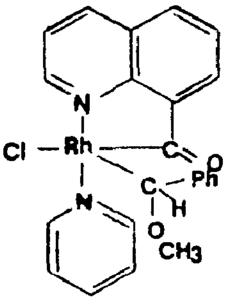
[39]

8-formylquinoline forms [40] which is proposed to contain an unsupported Rh(II)-Rh(II) single bond. Successive reaction of $[RhCl(C_2H_4)_2]_2$ with



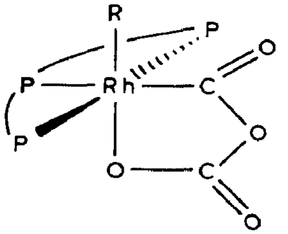
[40]

(S)-8-quinolinyl-α-methoxybenzyl ketone and pyridine forms [41] from which



[41]

the ketone can be recovered by treatment with trimethylphosphite. The essentially complete retention of optical rotation of the recovered ketone compared to that of the starting material suggested that both the carbon-carbon bond cleavage and formation reactions occurred with retention. Heating [41] at temperatures below 60°C causes racemization at the chiral carbon suggesting reversible homolysis of the rhodium-carbon bond is occurring. Some escape of the radicals from the cage can also occur as shown by a crossover experiment (refs. 121, 122). Orthometallation of one ligand occurs when $[Rh(P(OPh)_3)_4]ClO_4$ is treated with potassium hydroxide. The product, $[Rh(P(OC_6H_4)(OPh)_2)L_3]$ (L = $P(OPh)_3$) reacts with various acids to form $[RhXL_3]$ (X = Cl, SCN), $[RhL_4]X$ (X = ClO_4, F) or $[Rh(acac)L_2]$ (ref. 123). In addition to the previously reported $[Rh(Oq)_2(P(\underline{o}\text{-}C_6F_4)Ph_2)]$, the thermolysis of $[Rh(oq)(CO)(P(\underline{o}\text{-}BrC_6F_4)Ph_2)]$ in toluene also forms a species isolated as $[Rh(oq)Br(H_2O)(P(\underline{o}\text{-}C_6F_4)Ph_2)]$ following chromatography on alumina. An isomer of the latter with the water molecule <u>cis</u> to phosphorus is formed if the thermolysis is carried out in the presence of bromide ion. The first isomer exists as hydrogen-bonded dimers in the solid state but the latter does not because of steric hindrance from the neighboring phenyl groups on phosphorus. In both isomers the water can be replaced by various phosphorus ligands and for the <u>trans</u> isomers, $^2J_{P-P}$ is observed in the range 538-813 Hz (refs. 124, 125). Addition of $\underline{p}$-tolyllithium to $[RhCl(L_3)]$ (L_3 = $Bu^tP((CH_2)_3PPh_2)_2$) forms $[Rh(\underline{p}\text{-tolyl})(L_3)]$ which reacts with carbon dioxide in ethanol to produce $[Rh(OC(O)OEt)L_3]$. In toluene the reaction with carbon dioxide yields [42] while if oxygen is also present, [43] (R = $\underline{p}$-tolyl) is the product. Both of these react with pyridine to



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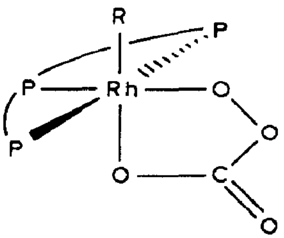
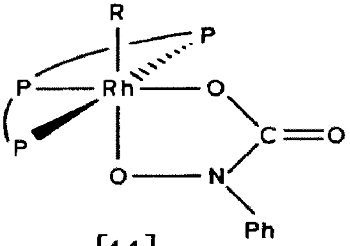


[43]

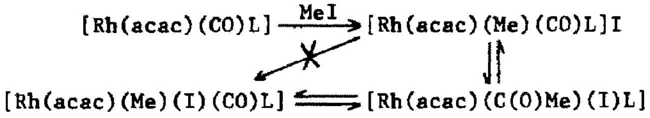
form [Rh(p-tolyl)$(O_2CO)(L_3)$] plus [Rh(p-tolyl)(py)(L_3)]. Coupling of carbon dioxide with nitrosobenzene occurs slowly in the presence of [Rh(p-tolyl)(L_3)] to yield [44] (R = p-tolyl) plus other isomeric forms. An



[44]

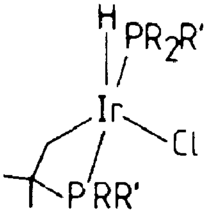
isolable 1:1 adduct of [Rh(p-tolyl)(L_3)] with nitrosobenzene can be formed that yields [44] when treated with carbon dioxide suggesting it is an intermediate but this has not yet been definitely established (refs. 126, 127).

Since earlier work had shown that the oxidative addition of methyl iodide to complexes of the type [RhCl(CO)L_2] (L = tertiary phosphine) (see 1981 Annual Survey Scheme IX (J. Organometal. Chem., 242(1983)241)) appeared more complex than initially thought, further studies were undertaken. Here, [RhBr(CO)L_2] (L = $(p\text{-EtC}_6H_4)_3P$) and n-propyl bromide form [$RhBr_2(C(O)Pr^n)L_2$] and as the rate was unaffected by added bromide ion it was concluded that [$RhBr_2(CO)L]^-$ is not a significant intermediate in this system. Also, reaction of methyl iodide with [$Rh_2(CO)_2(PPh_3)_2(\mu\text{-}X)_2$] (X = Cl, I) formed an equilibrium mixture of [$Rh_2(Me)_2(I)_2(CO)_2(PPh_3)_2(\mu\text{-}X)_2$] and [$Rh_2(C(O)Me)_2(I)_2(PPh_3)_2(\mu\text{-}X)_2$]. It was concluded that the alkyl and acyl complexes form by independent paths with the acyl complex requiring prior formation of the alkyl complex but the conclusions seem not to be well-supported by the results reported (ref. 128). In two papers on the oxidative addition of methyl iodide to [Rh(acac)(CO)L] (L = $P(OPh)_3$, PPh_3, $P(p\text{-anisyl})_3$, $P(p\text{-ClC}_6H_4)_3$), the first shows that both [Rh(acac)(C(O)Me)(I)$(P(OPh)_3)$] and [Rh(acac)(CO)(Me)(I)$(P(OPh)_3)$] formed with the rate being independent of the concentration of methyl iodide. At low concentrations, a 1:1 ratio of products was seen but at large concentrations the latter predominated (ref. 129). With the other ligands it was proposed that the reaction followed the course depicted in Scheme V (ref. 130).

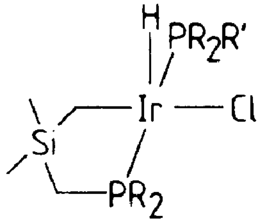


Scheme V

Cyclometallation occurs when $[IrCl(cyoct)_2]_2$ and $Bu^t_{3-n}P(CH_2SiMe_3)_n$ (n = 0-2) are heated at 70°C in toluene. The products are [45] (R = R' = Bu^t; R = Bu^t, R' = CH_2SiMe_3), [46] (R = Bu^t, R' = CH_2SiMe_3) and [47] (R = Bu^t, R' = CH_2SiMe_3) (ref. 131). Full details of the synthesis of trimethylenemethane complexes of iridium and rhodium have now appeared. Reaction of



[45]



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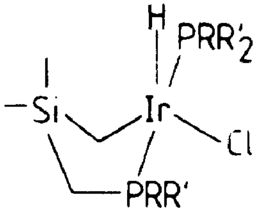
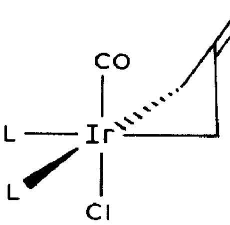


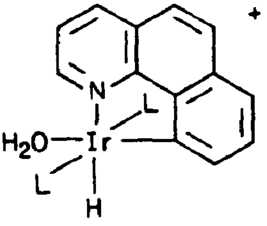
[47]

$[IrCl(CO)(PPh_3)_2]$ with 2-[(methylsulfonyloxy)methyl]-3-trimethylsilylprop-1-ene in hot toluene forms $[(\eta^4\text{-}C_4H_6)IrCl(CO)(PPh_3)]$. Reagents with acetate or chloride in place of the methylsulfonyloxy substituent also work but do not give as good yields. The same reaction with $[IrCl(CO)(PMe_2Ph)_2]$ in the presence of tetraphenylborate ion yields $[(\eta^3\text{-}2\text{-}MeC_3H_4)IrCl(CO)\text{-}(PMe_2Ph)_2]BPh_4$ while $[RhCl(CO)(PMe_2Ph)_2]$ under the same conditions gives $[(\eta^3\text{-}2\text{-}(Me_3SiCH_2)C_3H_4)RhCl(CO)(PMe_2Ph)_2]BPh_4$. This can be converted into $[(\eta^4\text{-}C_4H_6)Rh(CO)(PMe_2Ph)_2]BPh_4$ on treatment with fluoride ion. An attempt to synthesize $[(\eta^4\text{-}C_4H_6)Rh(CO)(PPh_3)_2]$ directly using the methylsulfonyloxy reagent and $[RhH(CO)(PPh_3)_3]$ gave only $[Rh(OSO_2Me)(CO)(PPh_3)_2]$. The difference between this reaction and that with iridium is attributed to the attack of the methylsulfonate ion generated in the earlier stages of the process occurring more rapidly on rhodium than on iridium so that in the latter it can preferentially displace the trimethylsilyl group (ref. 132). In related work, $[IrH(CO)(PPh_3)_3]$ or $[IrCl(CO)(PPh_3)_2]$ reacts with 1-trimethylsilyl-3-chloropropanone in hot toluene to form [48] (L = PPh_3)

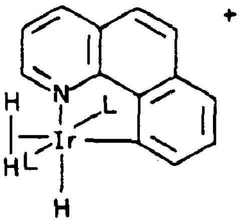


[48]

plus 2-trimethylsiloxy-3-chloroprop-1-ene. The organic product is proposed to form via a Brook rearrangement of the starting ketone in which the carbon-chlorine bond undergoes oxidative addition to the metal followed by migration of the trimethylsilyl group to oxygen and then reductive elimination to give the silylenol ether (ref. 133). Another full report now available concerns the characterization of molecular hydrogen complexes of iridium. Thus [49] (L = PPh_3, Pcy_3) reacts reversibly with molecular hydrogen to give not the anticipated classical trihydride but rather a species characterized as [50]. The relaxation time, T_1, for the dihydrogen



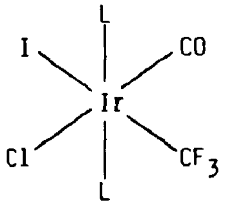
[49]



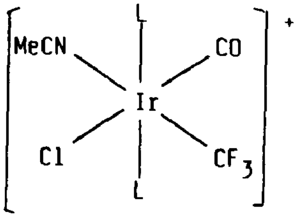
[50]

ligand was determined to be much shorter than that for the hydride ligand and it was suggested that ^{1}H NMR T_1 measurements can provide a criterion for detecting other such "non-classical" hydride complexes. This was used on the complex originally formulated as $[IrH_6(Pcy_3)_2]^+$ and the results suggested reformulation as $[IrH_2(H_2)_2(Pcy_3)_2]^+$. The water molecule in [49] can be replaced by a hydride ligand to give the neutral cis dihydride complex on reaction with lithium triethylborohydride. The same complex can be prepared by deprotonation of the dihydrogen ligand in [50] a process which is reversed by treatment with $PhCH(SO_2CF_3)_2$ (ref. 134).

Complex [51] (L = PPh_3) forms [52] on reaction with silver hexafluoroantimonate in acetonitrile. Addition of chloride ion to [52] forms [53]

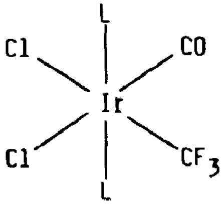


[51]

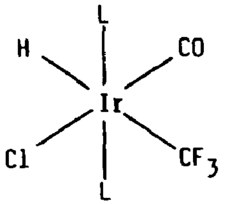


[52]

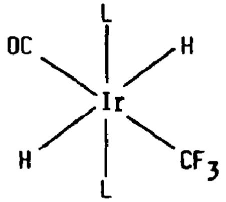
while with lithium triethylborohydride or an excess of sodium borohydride in ethanol the products are [54] and [55] respectively. In the last



[53]

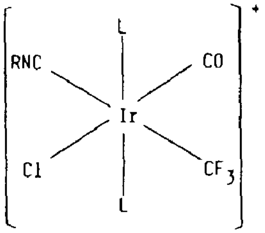


[54]

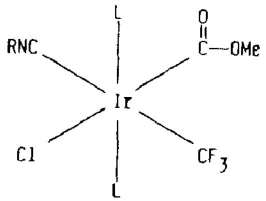


[55]

reaction some [54] is also formed. Complex [52] also reacts with p-tolylisocyanide to form [56] (R = p-tolyl) which on subsequent reaction with methoxide ion gives [57]. It was hoped that dehydrohalogenation of [54] would provide a synthesis of trans-[Ir(CF_3)(CO)(PPh_3)$_2$] but this could not

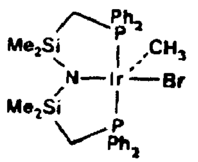


[56]

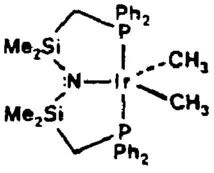


[57]

be achieved (ref. 135). The previously reported complexes [58] and [59] have been studied by ^1H NMR spectroscopy. The structure of [58] has been

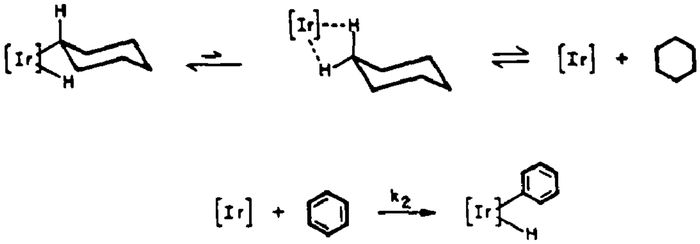


[58]

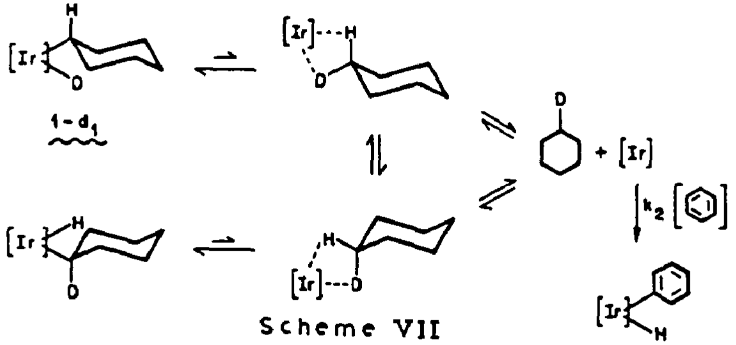


[59]

determined and is essentially square pyramidal as shown. Irradiation of the methylene protons of the ligand leads to a positive NOE for the methyl group. For [59], however, a single methyl resonance is seen and no NOE is detected when the methylene protons of the ligand are irradiated indicating a different structure which is presumed to be approximately trigonal bipyramidal. These results are in accord with theoretical calculations (Nouv. J. Chim., 3(1979)39) which predict a trigonal bipyramidal geometry if a single-faced π-donor ligand (e.g.-NR_2) is present. In this instance, strong σ-donor ligands should occupy equatorial sites (ref. 136). Two papers report reactions of [cp'Ir(H)(cy)(PMe_3)] with hydrocarbons. Thermolysis in the presence of ethylene forms a 2:1 ratio of [cp'Ir(H)(C_2H_3)(PMe_3)] and [cp'Ir(C_2H_4)(PMe_3)] plus cyclohexane. This is evidently a kinetically determined ratio since the isolated vinyl hydride complex converts to the ethylene complex at higher temperatures. Calculations modelling the formation of the two products from the presumed {cp'Ir(PMe_3)} intermediate were performed. The formation of the vinyl hydride complex is suggested to occur via an "end-on" approach of a carbon-hydrogen bond of the ethylene to the metal with the carbon-carbon double bond oriented in the perpendicular mode. While the ethylene complex would be expected to form by a simple addition to {cp'Ir(PMe_3)} the above results indicate that this does not occur. It is suggested that the intermediate, although presumably initially formed in a singlet state, rapidly converts to a triplet state which preferentially reacts to form the vinyl hydride. The conversion of the vinyl hydride to the ethylene complex is then proposed to involve a different transition state than that envisaged for the formation of the vinyl hydride. Some concern however was expressed about the adequacy of the EHMO method used for this particular problem. The same [cp'Ir(H)(cy)(PMe_3)] complex is converted to [cp'Ir(H)(Ph)(PMe_3)] on heating in benzene. The reaction is first order in starting complex and is inhibited by the presence of excess cyclohexane but not trimethylphosphine. Comparison of these data with those for the same reaction of [cp'Ir(D)-(C_6D_{11})(PMe_3)] shows an inverse isotope effect. Also while crossover experiments suggest that the reductive elimination of cyclohexane is an intramolecular process, studies with [cp'Ir(D)(cy)(PMe_3)] showed some deuterium incorporation into the α position of the cyclohexyl group of the unreacted starting complex after partial reaction. The overall reaction together with a proposal for the inverse isotope effect is given in Scheme VI while the deuterium scrambling is thought to occur as shown in Scheme VII ([Ir] = {cp'Ir(PMe_3)}). From related experiments with other alkyl



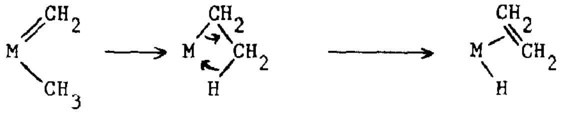
Scheme VI



Scheme VII

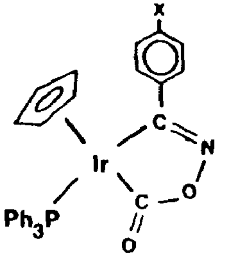
hydride complexes an estimate of bond dissociation energies for the iridium-alkyl bonds gave an ordering of Ph>>n-pentyl>2,3-dimethylbutyl>cyclopentyl>cyclohexyl>Np (refs. 137, 138).

In an interesting transformation, [cpIr$(Me)_2$(PPr^i_3)] and trityl hexafluorophosphate react at -78°C to form the ethylene hydride complex [cpIr-(H)(C_2H_4)(PPr^i_3)]. A related rhodium species, [cpRh(H)(C_2H_4)(PMe_3)], is formed by the reaction of [cpRh(I)(CHOMe)(PMe_3)] with methyllithium to first give [cpRh(Me)(CH_2OMe)(PMe_3)] which is then treated with tetrafluoroboric acid etherate. The ethylene hydride complex is proposed to form in

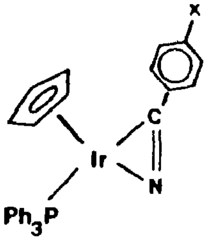


Scheme VIII

both instances as shown in Scheme VIII (ref. 139). Prolonged reflux of [60] (X = Cl, F) in toluene causes extrusion of carbon dioxide and the formation of [61]. A competition experiment indicated that the reaction was intramolecular and proceeded without the formation of free nitrile.

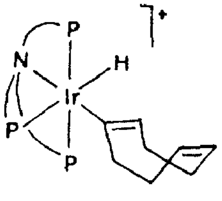


[60]

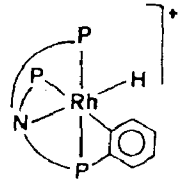


[61]

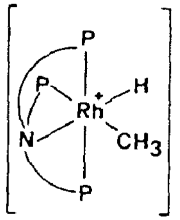
The authors believe that the nitrile ligand in [61] has undergone oxidative addition to the metal rather than being simply π-complexed (ref. 140). Addition of np_3 to $[IrCl(COD)]_2$ in THF simply forms $[Ir(np_3)Cl]$ but if this is treated with COD and sodium tetraphenylborate or if the original reaction is run in acetone in the presence of tetraphenylborate ion the product is [62]. Also, treatment of $[RhH(np_3)]$ with methyl triflate forms [63] which is proposed to form <u>via</u> [64] as an intermediate. In both instances,



[62]

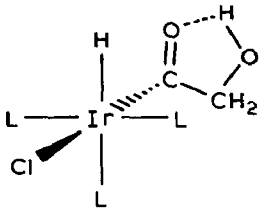


[63]



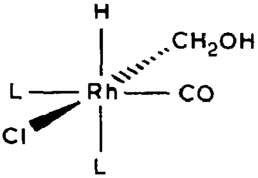
[64]

activation of an sp^2 carbon-hydrogen bond occurs under mild conditions (ref. 141). Reaction of $[Ir(DPPE)_2]Cl$ with lithium cyclopentadienide in THF results simply in metathesis to form $[Ir(DPPE)_2]cp{\cdot}THF$ but with methyllithium in benzene $[IrMe(DPPE)_2]$ is obtained. This adopts a distorted trigonal bipyramidal structure with an axial methyl group and is thus the second exception to the general trend that in $[IrX(L_2)_2]$ complexes the monodentate ligand is equatorial. $[IrMe(DPPE)_2]$ is fluxional, probably by reversible opening of one chelate ring and reacts with carbon monoxide and with tetrafluoroboric acid etherate to form $[Ir(Me)(CO)_2(DPPE)]$ and cis-$[Ir(H)(Me)(DPPE)_2]BF_4$ respectively. It also reacts with carbon dioxide although the product was not characterized and with silver ion to form what was thought to be $[Ir(Me)(DPPE)_2]^{2+}$ but did not react with dihydrogen (ref. 142). Combination of $[IrCl(cyoct)(PMe_3)_3]$ and the dimer of glycol aldehyde forms [65] (L = PMe_3). The rhodium analog was also synthesized and on



[65]

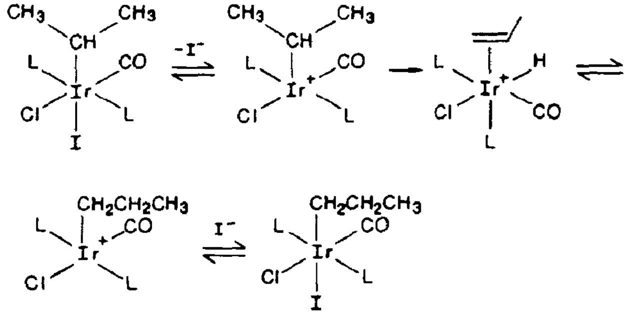
heating formed major amounts of $[RhH_2(PMe_3)_4]Cl$ plus formaldehyde and minor amounts of $[RhCl(CO)(PMe_3)_2]$ plus methanol via [66] (L = PMe_3) as a proposed intermediate. Oxidative addition of n-butyraldehyde to $[RhCl(PMe_3)_3]$



[66]

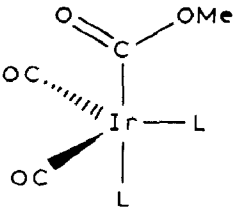
forms mer-$[Rh(H)(C(O)Pr^n)Cl(PMe_3)_3]$ which on heating partially reverts to reactants but also decomposes to yield $[RhCl(CO)(PMe_3)_2]$ plus propane (ref. 143).

Full details of rearrangements of alkyl complexes of iridium have now appeared. Oxidative addition of alkyl iodides to $[IrCl(CO)L_2]$ forms trans-$[Ir(R)(I)(Cl)(CO)L_2]$ (L = PMe_3, PMe_2Ph; R = Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, n-octyl. L = PMe_3; R = Np, 2-methylbutyl, 3-methylbutyl, 3-pentyl, 2-octyl, cy. L = PEt_3; R = Et, Pr^n). All the sec-alkyl complexes rearranged to the corresponding n-alkyl species in protic solvents and at elevated temperatures in non-polar solvents although in the latter instance halide scrambling also occurred. The rearrangement was inhibited by excess iodide ion and proceeded rapidly when coordinated iodide was abstracted by silver ion leading to the proposal of Scheme IX for the process. The major driving force for the rearrangement is attributed to a greater thermodynamic stability of the n-alkyl complex. Steric effects were thought to be minor. Also studied was the oxidative addition of alkyl halides to



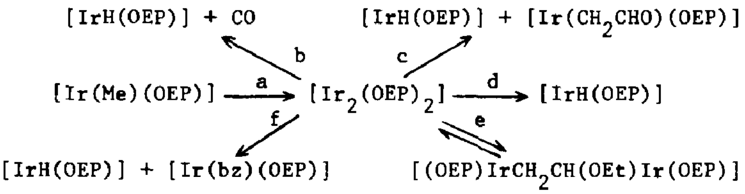
Scheme IX

trans-[Ir(R')(CO)(PMe$_3$)$_2$] to again give *trans*-[Ir(R)(X)(R')(CO)(PMe$_3$)$_2$] (R = Pr^n, Pr^i, Bu^n, Bu^i; R' = Me, Ph, CH$_2$SiMe$_3$; X = I. R = Pr^n, Pr^i, Bu^n, Bu^i, *n*-pentyl, *i*-pentyl; R' = Me; X = Br). Those with R' = Me also underwent the *i*-alkyl-to-*n*-alkyl rearrangement in methanol/benzene solution, presumably by the mechanism of Scheme IX but [Ir(Pr^i)(I)(CH$_2$SiMe$_3$)(CO)(PMe$_3$)$_2$] partially decomposed under these conditions to give [Ir(I)(CO)(PMe$_3$)$_2$], tetramethylsilane and propene in addition to the *n*-propyl isomer of the starting complex (refs. 144, 145). Slow conversion of [Ir(OMe)(CO)(PPh$_3$)$_2$] to [67] (L = PPh$_3$) occurs in the presence of carbon monoxide in



[67]

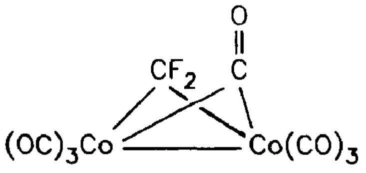
toluene solution (ref. 146) while some chemistry of iridium octaethylporphyrin complexes is outlined in Scheme X (ref. 147). The complex [Ir(2,2'-bipyrid-3-yl-C^3,N')(bipy)$_2$]$^{2+}$ in which one ring of one bipy ligand is metallated at carbon has been used as a sensitizer for the photoisomerization of NBD to quadricyclane. Initially its utility seemed surprising since the lowest excited state of the complex lies well below the reactive triplet state of the diene. Further work suggested that following encouter of the diene with the photoexcited iridium complex a partial charge transfer from the diene to the latter occurs which is thought to sufficiently distort the triplet state of the diene that its energy more closely matches that of the photoexcited state (ref. 148).



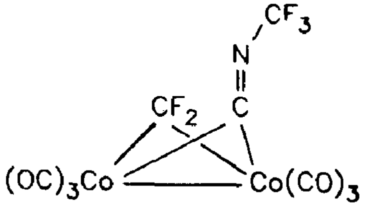
a) hν, C_6D_6. b) CH_2O. c) MeCHO. d) H_2. e) CH_2=CHOEt. f) Δ, toluene.

Scheme X

Interest in the chemistry of binuclear complexes remains high and among new complexes reported is [68] which is formed from Na[$Co(CO)_4$] and difluoromaleoyl dichloride in a reaction which proceeds <u>via</u> [$CF_2(C(O)Co(CO)_4)_2$] and [$(OC)_4CoC(O)CF_2Co(CO)_4$] as intermediates (detected only in solution) as the mixture is warmed to room temperature from the initial value of -30° C. Reaction of [68] with trifluoromethylisocyanide forms [69] (ref. 149). Addition of [$Co_2(CO)_8$] to [$Fe_2(CO)_6(\mu$-CO)(μ-CH=CHPh)]$^-$

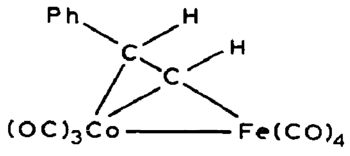


[68]



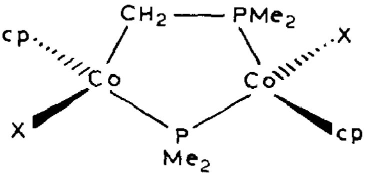
[69]

forms the heterobimetallic complex [70] (ref. 150). Addition of dihalomethanes to a benzene solution of [$cp_2Co_2(\mu\text{-}PMe_2)_2$] yields a mixture of

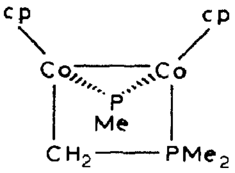


[70]

<u>trans</u>-[$cp_2Co_2X_2(\mu\text{-}PMe_3)_2$] (X = Br, I) and [71] (X = Br, I). When X = Br, [71] is obtained as a mixture of <u>cis</u> and <u>trans</u> isomers and is converted to [72] by sodium amalgam. Halogens also convert [$cp_2Co_2(\mu\text{-}PMe_2)_2$] to <u>trans</u>-[$cp_2Co_2X_2(\mu\text{-}PMe_2)_2$] (X = Cl, Br, I) and an analog with X = CN is formed from the same starting complex on treatment with hydrogen cyanide. The



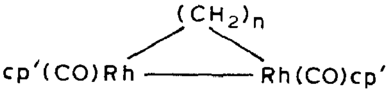
[71]



[72]

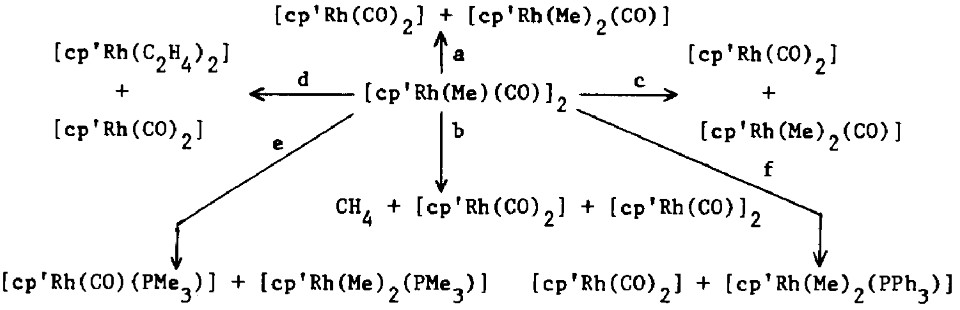
dihalide complexes react with one and two equivalents of silver hexafluorophosphate to yield $[cp_2Co_2(\mu\text{-}X)(\mu\text{-}PMe_2)_2]PF_6$ (X = Cl, Br, I) and $[cp_2Co_2(\mu\text{-}PMe_2)_2](PF_6)_2$ respectively. The latter on dissolution in acetonitrile gives $[cp_2Co_2(MeCN)_2(\mu\text{-}PMe_2)_2](PF_6)_2$. Finally, addition of methyl iodide to a benzene solution of $[cp_2Co_2(\mu\text{-}PMe_2)_2]$ forms a mixture of $[cpCo(Me)(PMe_3)_2]I$, $[cpCoI_2(PMe_3)]$ and $[cp_2Co_2(\mu\text{-}PMe_2)]$ (ref. 151). Carbonylation of $[Co_2(\mu\text{-}R)(\mu\text{-}R')(CO)_4(DPM)]$ in d_4-methanol yields $[Co_2(CO)_4(\mu\text{-}CO)_2(DPM)]$ and $R''CHDCO_2CD_3$ (R = CH_2; R' = CO, CH_2, $CHCO_2Et$; R" = H. R = R' = CHMe; R" = Me) indicating a coupling of carbon monoxide with the bridging alkylidene fragment to form the corresponding ketene (subsequently trapped by reaction with methanol). Some of the original alkylidene-bridged complexes also were reacted with sulfur dioxide to produce low yields of $[Co_2(CO)_4(\mu\text{-}SO_2)(DPM)]$ and ketene-derived products (ref. 152).

Like its cobalt analog, $[cp'_2Rh_2(\mu\text{-}CO)_2]$ can be reduced to the radical anion $[cp'_2Rh_2(\mu\text{-}CO)_2]^-$ with sodium/potassium alloy and here further reduction to $[cp'_2Rh_2(\mu\text{-}CO)_2]^{2-}$ is also observed. Both anions react with α,ω-diiodides or dioxytosylates to give the metallacycles [73] (n = 1, 3) plus $[cp'_2Rh_2(\mu\text{-}CO)_2]$ but when 1,2-di(tosyloxy)ethane was used the products



[73]

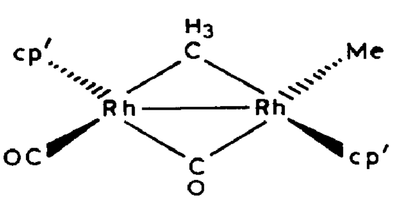
were ethylene plus $[cp'_2Rh_2(\mu\text{-}CO)_2]$. Low yields of <u>cis-trans</u> mixtures of $[cp'_2Rh_2(Me)_2(CO)_2]$ together with $[cp'_2Rh_2(\mu\text{-}CO)_2]$ were obtained when either anion was treated with methyl iodide. On the other hand, reaction of $[cp'_2Rh_2(\mu\text{-}CO)_2]$ itself with organolithium reagents gave $Li[cp'_2Rh_2(R)(\mu\text{-}CO)_2]$ (R = Me, Et, Ph) which underwent rapid reaction with alkyl tosylates to give good yields of cis-$[cp'(R)Rh(\mu\text{-}CO)_2Rh(R')cp']$ (R = Me, Et, Ph; R' = Me, Et). This slowly isomerized to give an equilibrium mixture of cis and trans isomers, a process which appears not to involve fragmentation of the binuclear complex. The course of the reaction with alkyl tosylates appears to be dominated by steric factors and an "early" transition state is proposed for this nucleophilic displacement. Attempts to form hydrides, <u>sec</u>-alkyl complexes and species containing rhodium-oxygen and rhodium-nitrogen bonds from $Li[cp'_2Rh_2(R)(\mu-CO)_2]$ failed. Further chemistry of $[cp'_2Rh_2(Me)_2(\mu-CO)_2]$ is outlined in Scheme XI. In reactions a) and b) various decomposition products were also seen while in the other four,



a) hν. b) H_2. c) CO. d) C_2H_4. e) PMe_3. f) PPh_3.

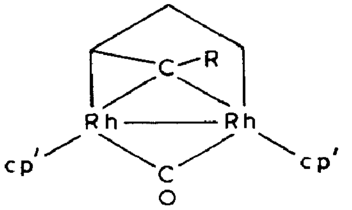
Scheme XI

initial formation of $[cp'Rh(CO)_2]$ and $[cp'Rh(Me)_2(L)]$ (L = CO, C_2H_4, PMe_3, PPh_3) was presumed with the differences in final products obtained being due to secondary reactions. Some insight into the nature of the initial process was obtained from a study of reaction f) which is irreversible and shows first order kinetics. This was interpreted as suggesting conversion of $[cp'_2Rh_2Me_2(\mu-CO)_2]$ to [74] followed by cleavage to $[cp'Rh(CO)_2]$ plus $\{cp'Rh(Me)_2\}$ and trapping of the latter by the phosphine (ref. 153). The

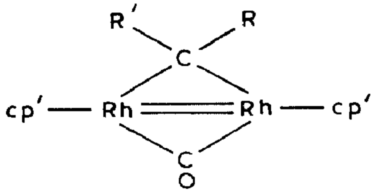


[74]

alkylidene-bridged complexes $[cp'_2Rh_2(CO)_2(\mu-CRR')]$ (R = <u>cyclo</u>-C_3H_5, Me; R' = <u>cyclo</u>-C_3H_5) prepared by standard routes from $[cp'_2Rh_2(\mu-CO)_2]$ and the appropriate diazoalkane undergo photolysis to form [75] (R = Me, <u>cyclo</u>-C_3H_5) <u>via</u> [76] as a proposed intermediate (ref. 154).

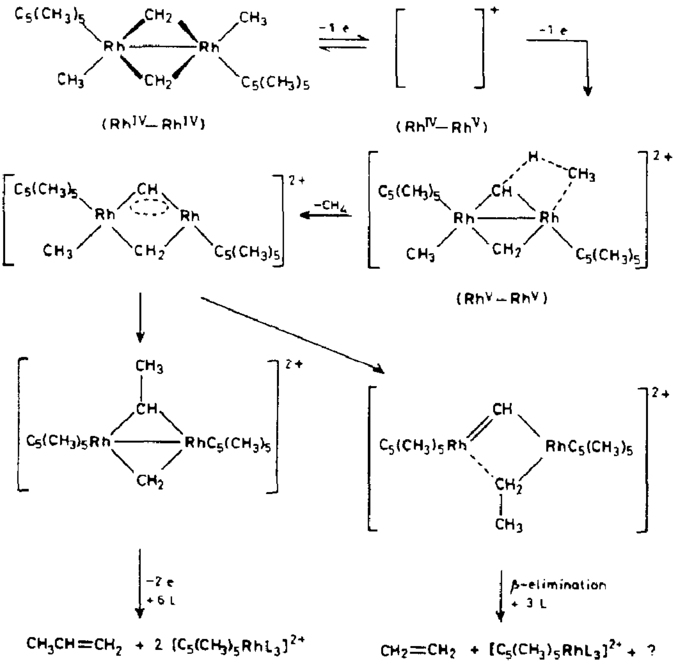


[75]

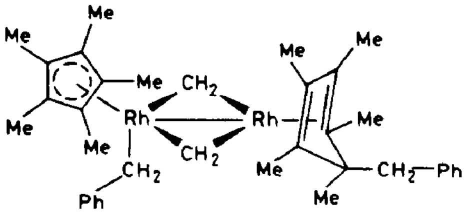


[76]

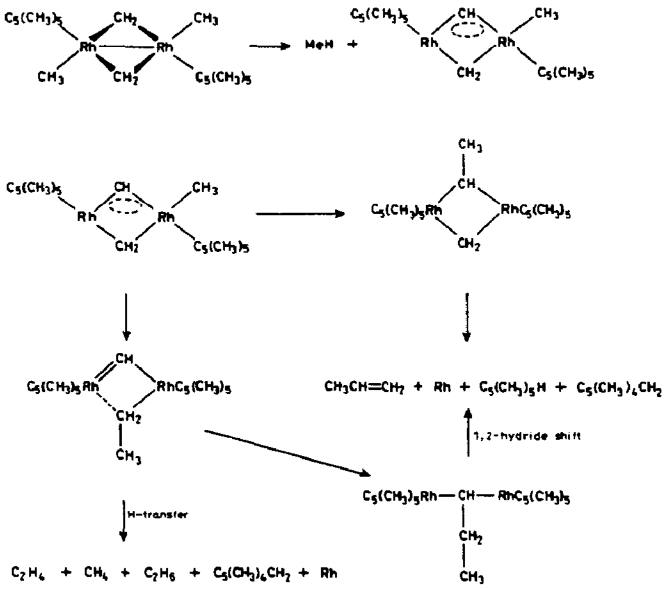
Both the oxidative and the thermal decomposition of $[cp'_2Rh_2(Me)_2(\mu-CH_2)_2]$ forms methane, ethylene, propene and some ethane. The former process using $[IrCl_6]^{2-}$ is cleaner and faster possibly because the migrations required are more facile in a cationic species. Labelling studies indicate that the gaseous products are formed intramolecularly and no involvement of the pentamethylcyclopentadienyl rings appears to occur. The C_2 products appear to arise from coupling of methyl and methylene groups and Schemes XII and XIII are proposed for the oxidative and thermal processes respectively (ref. 155). Simple metathesis occurs between trans-$[cp'_2Rh_2Cl_2(\mu-CH_2)_2]$ and alkynyl Grignard reagents with the formation of trans-$[cp'Rh_2(C_2R)_2(\mu-CH_2)_2]$ (R = Bu^t, Ph) but with benzylmagnesium chloride the product is [77] which is proposed to form according to Scheme XIV. Terminal acetylenes also react with trans-$[cp'_2Rh_2(MeCN)_2(\mu-CH_2)_2]^{2+}$ as depicted in Scheme XV but only that with R' = p-ClC_6H_4 provided a pure



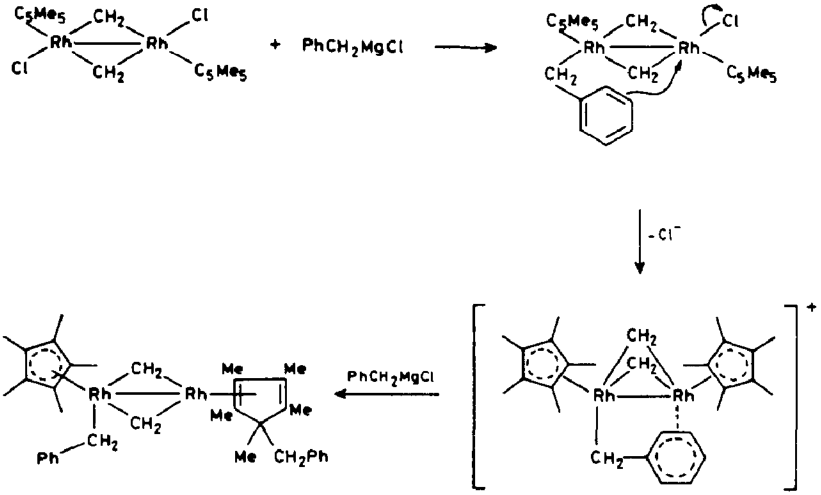
Scheme XII



[77]

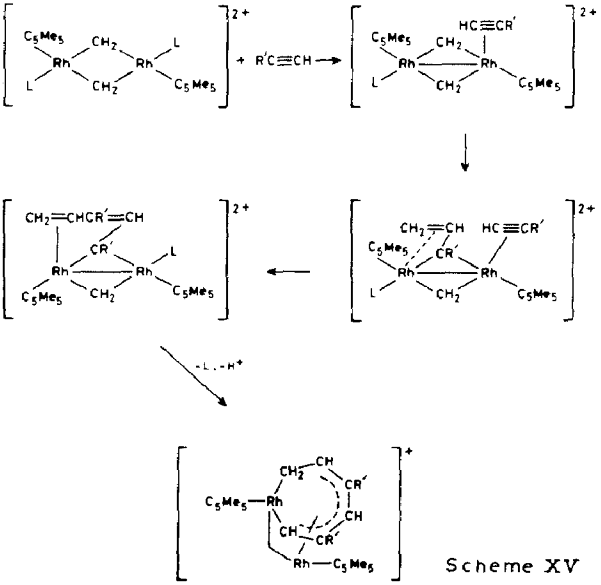


Scheme XIII

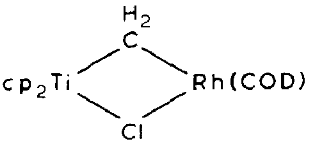


Scheme XIV

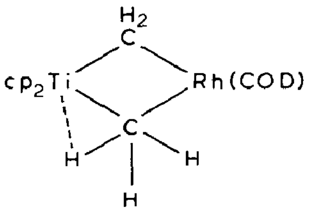
product (ref. 156). The metallacycle $[\mathrm{cp_2\overline{TiCH_2CMe_2CH_2}}]$ is cleaved by $[\mathrm{RhCl(COD)}]_2$ to form [78] and 2-methylpropene. Complex [78] reacts with methyllithium to yield [79] which contains an agostic hydrogen atom. Low temperature NMR studies gave the first recorded value of $^{1}J_{C-H}$ for an agostic hydrogen and it is significantly smaller than the other carbon-hydrogen couplings. A sample of [79] enriched with carbon-13 at the methyl group slowly rearranges to incorporate the label into the methylene group (ref. 157). The complex [cp'Zr(Me)$(OCH_2PPh_2)_2$], prepared from [cp'$ZrMe_3$]



Scheme XV

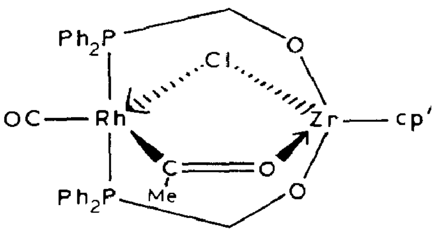


[78]

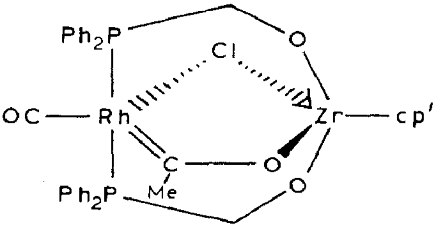


[79]

and hydroxymethyldiphenylphosphine in hexane, reacts with $[RhCl(CO)_2]_2$ in toluene to form a binuclear species thought to be best represented by the resonance hybrid [80a,b]. This reacts with hydrogen chloride or with

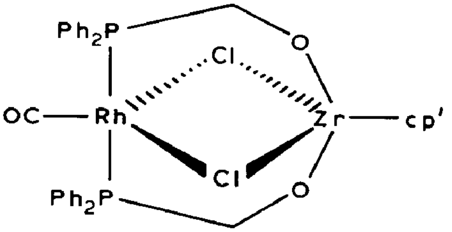


[80a]

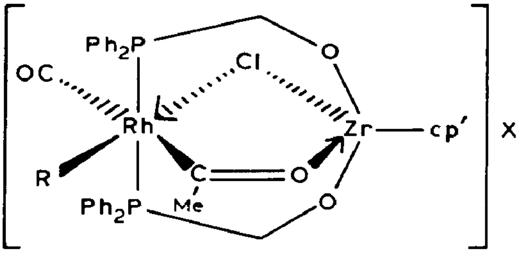


[80b]

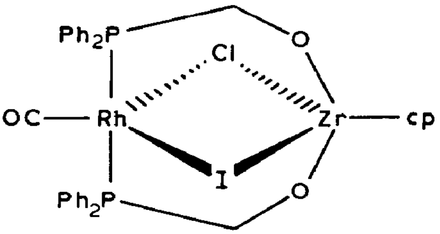
methyl iodide to form [81] plus acetaldehyde or [82] plus acetone respectively <u>via</u> [83] (R = H; X = Cl. R = Me; X = I) as the proposed intermediate (ref. 158).



[81]

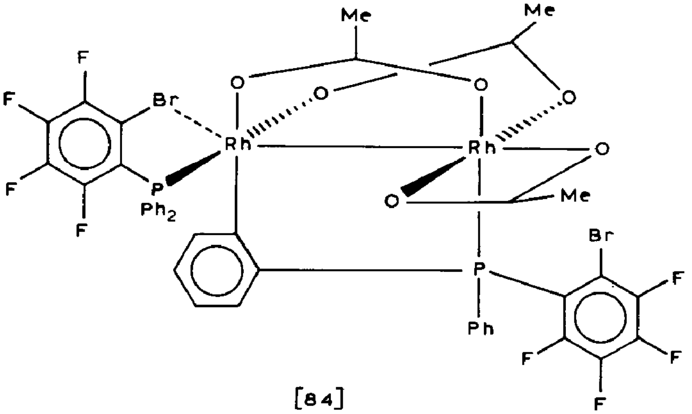


[83]



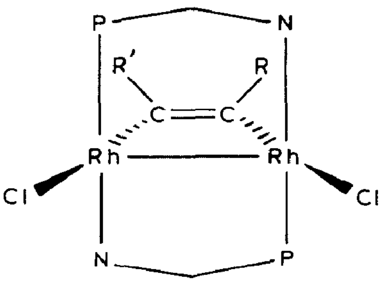
[82]

Addition of o-bromotetrafluorophenyldiphenylphosphine (L) to [Rh$_2$(O$_2$CMe)$_4$]·2MeOH forms [Rh$_2$(O$_2$CMe)$_4$]·2L which on refluxing in toluene forms [84]. Unlike the triphenylphosphine analog only one phosphine ligand

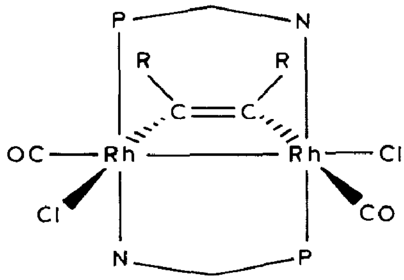


[84]

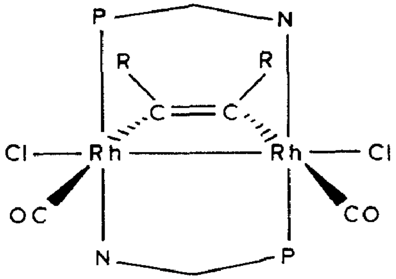
undergoes metallation (ref. 159). The bridging carbonyl ligand in [Rh$_2$Cl$_2$(μ-CO)(PPh$_2$py)$_2$] is replaced by certain acetylenes to give the dimetallated olefin complexes [85] (R = R' = CO$_2$Me, CF$_3$. R = H; R' = CO$_2$Me). These can be reversibly carbonylated to a mixture of [86] and [87] (R = CF$_3$, CO$_2$Me) with the former predominating. Chloride abstraction from [Rh$_2$Cl$_2$(μ-CO)(PPh$_2$py)$_2$] with silver perchlorate forms [Rh$_2$Cl(μ-CO)(PPh$_2$py)$_2$]ClO$_4$ which



[85]

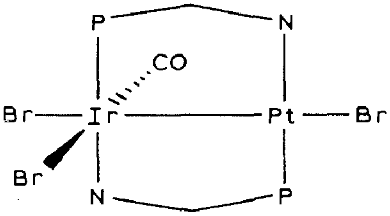


[86]



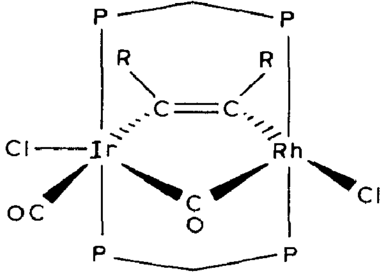
[87]

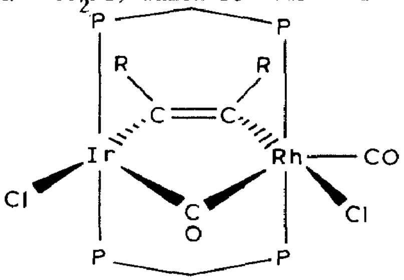
can be carbonylated to give the "A-frame" complex $[Rh_2(CO)_2(\mu\text{-}Cl)(PPh_2\text{-}py)_2]ClO_4$. In refluxing THF $[PtBr_2(PPh_2py)_2]$ and $Bu^n{}_4N[IrBr_2(CO)_2]$ yield [88]. Addition of DMAD to a dichloromethane solution of the "A-frame" complex $[IrRh(CO)_2(\mu\text{-}Cl)(DPM)_2]Cl$ forms [89] ($R = CO_2Me$) while the



[88]

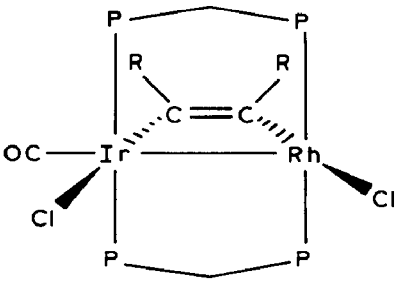
same reaction in the presence of carbon monoxide also forms a minor amount of [90] ($R = CO_2Me$). Both [89] and the mixture of [89] and [90] decarbonylate on refluxing in THF to yield [91] ($R = CO_2Me$) which reforms a mixture



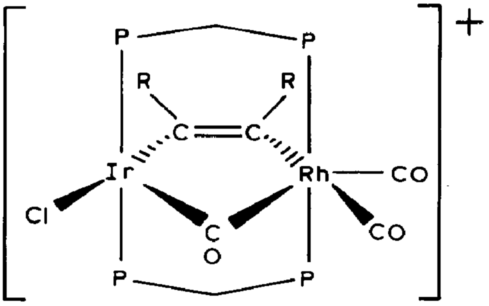


[89] [90]

of [89] and [90] with the latter now predominating on reaction with carbon monoxide via [92] as an intermediate. Complex [92], as its perchlorate

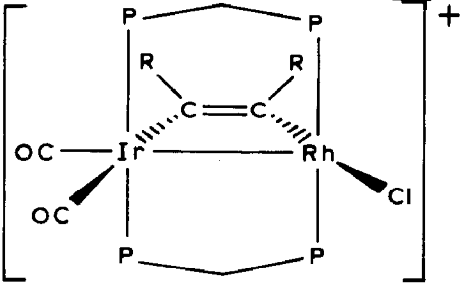


[91]

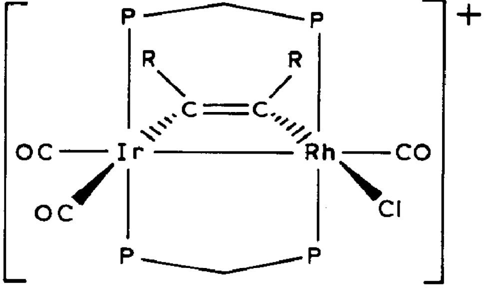


[92]

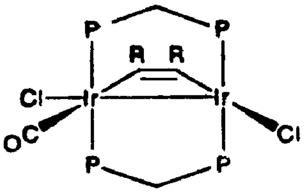
salt, can be prepared from [89] and silver perchlorate in the presence of carbon monoxide and is readily decarbonylated to [93] (R = CO$_2$Me). Recarbonylation also occurs easily *via* [94] as an intermediate. Attempts to prepare heterobinuclear rhodium-iridium complexes using 2-pyridyldiphenylphosphine were generally unsuccessful (ref. 160). While carbon monoxide adds to [95] to give [96] (R = CO$_2$Me) other ligands form [97] (L = P(OMe)$_3$, PMe$_3$, MeCN). The difference in the products formed is attributed to the significant π-acceptor character of carbon monoxide and the relatively greater σ-donor ability of the other ligands. Thus addition of the latter ligands to the electron-rich, coordinatively unsaturated metal center



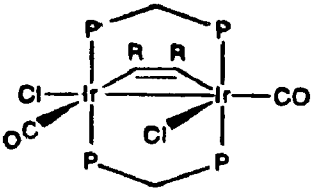
[93]



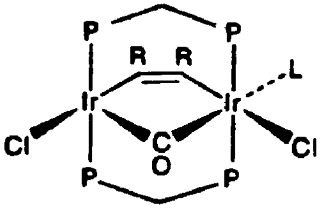
[94]



[95]



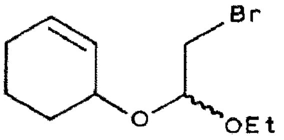
[96]



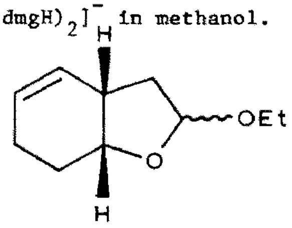
[97]

increases the electron density there even more and the original terminal carbonyl ligand moves to a bridging position in order to remove some of the excess electron density. This proposal is supported by the low value of ν_{CO} observed in [97] (ref. 161). Carbonylation of $[Ir_2(COD)_2(\mu\text{-}pz)_2]$ forms $[Ir_2(CO)_4(\mu\text{-}pz)_2]$ which reacts further with diiodomethane to give $[Ir_2(CO)_4(I)(CH_2I)(\mu\text{-}pz)_2]$, $[Ir_2(CO)_4I_2(\mu\text{-}CH_2)(\mu\text{-}pz)_2]$ and $[Ir_2(CO)_4I_2(\mu\text{-}pz)_2]$ in a 7:2:1 ratio. Heating the first complex converts it to the second plus some more if the third, a reaction which is claimed to be the first example of the formation of a methylene-bridged complex by ring closure at a dimetal center. An analogous series of complexes could also be formed with 1,1-diiodoethane but the ring closure reaction was not observed (ref. 162).

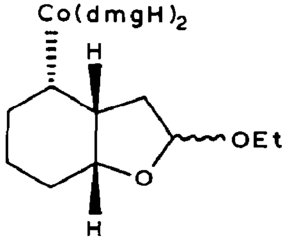
Although cobaloxime complexes continue to be studied, as was noted last year the majority of the work is in areas other than as models for vitamin B_{12}. Coupling of the alkyl group in $[RCo(dmgH)_2(H_2O)]$ (R = Me, Et, Pr^i, bz) with the added radical species $\{\cdot CMe_2OH\}$ and $\{\cdot CHMeOEt\}$ occurs at a rate which is relatively insensitive to the steric bulk about the α-carbon of the cobalt-bound alkyl group. This is interpreted to indicate that direct attack at this carbon is unlikely but rather the incoming radical attacks a nitrogen atom of the dimethylglyoximate ligand followed by reductive elimination of the coupling product (ref. 163). Oxidation of $[RCH_2Co(dmgH)_2(py)]$ (R = Ph, $\underline{p}\text{-}XC_6H_4$ (X = Cl, Br, NO_2, CHO, CN, Me), $\underline{m}\text{-}O_2NC_6H_4$, PhX ($X$ = O, S, NH), 2-naphthyl, 2-furyl) with manganese(III) acetate in an acetic acid/acetic anhydride solvent containing sodium acetate forms the appropriate benzyl ether of dimethylglyoxime. It is proposed that the starting complex is oxidized to the radical cation after which the benzyl group transfers to the dimethylglyoximate ligand (ref. 164). Hydrogenation of a mixture of S-vinylmonothiocarbamates and $[Co(dmgH)_2(py)]$ provides a synthesis of $[(RR'NC(O)SCH(Me))Co(dmgH)_2py]$ ($R = R' = Pr^n$. R = Et; $R' = Bu^n$, cy) (ref. 165). Conversion of [98] to [99] can be accomplished by reaction with $[Co(dmgH)_2]^-$ in methanol. It is proposed that [98] is converted to the corresponding radical by loss of a bromine atom followed by cyclization and trapping as [100], a species which could be isolated in a stoichiometric reaction. Elimination of a cobalt-hydride species completes the process (ref. 166). Further studies on the coupling of alkyl groups from alkyl cobaloximes with sulfonyl halides have shown



[98]



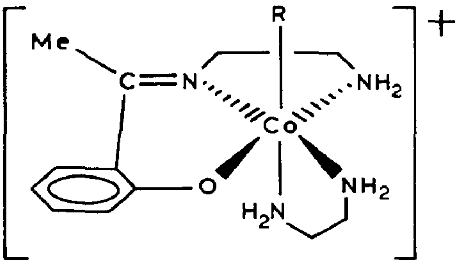
[99]



[100]

that photolysis of [(RR'C=C=CH)Co(dmgH)$_2$(py)] in the presence of sulfonyl halides forms RR'C=C=CHSO$_2$R" for R = R' = H and R" = *p*-XC$_6$H$_4$ (X = F, Cl, Br, Me) but HC≡CCRR'SO$_2$R" for R = R' = H and R" = Me and for R = R' = Me and R" = *p*-XC$_6$H$_4$ (X = F, Cl, Br, Me). When R = R' = H and R" = Ph a 50/50 mixture of both species is obtained (ref. 167). Activation parameters for the homolysis of certain cobalt-carbon bonds have been obtained from the kinetics of the thermal racemization of [RCo(dmgH)$_2$B] (R = (-)CHMeCO$_2$Me; B = 4-CNpy, 4-Mepy. R = (+)-CH(CH$_2$X)CO$_2$Me (X = H, CO$_2$Me); B = py). The data suggest that the stability of the cobalt-carbon bond is enhanced by increasing the electron density at cobalt and by decreasing it on the α-carbon atom (ref. 168).

Tested syntheses of [101] (R = Me, Et, Bu^n, Pr^i, cy) are now available (ref. 169). A species proposed to be a one-dimensional polymer containing

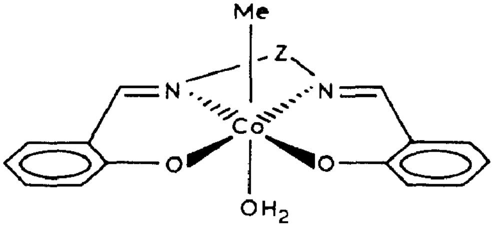


[101]

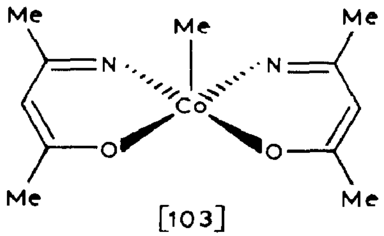
phthalocyanine radicals is formed when [Co(phthalocyanine)Cl] is treated with bis(bromomagnesio)acetylene (ref. 170).

An aqueous solution of vitamin B_{12s} can be converted to ethylcobalamin by triethyloxonium tetrafluoroborate suggesting the utility of the latter as an ethylating agent in aqueous solution (ref. 171). The enantioselective alkylation of [Co(PPD)$_2$]$^-$ by acrylonitrile and methyl acrylate occurs in the presence of chiral amines indicating that the nature of the axial ligand can be important in the formation of cobalt-carbon σ-bonds (ref. 172). Treatment of dichloromethane solutions of [Co(salen)] and monoalkyl hydrazines with oxygen or *tert*-butylhydroperoxide and then pyridine forms [RCo(salen)(py)] (R = Me, Pr^i, Bu^n, Bu^i, Bu^s, Ph, MeC(O)) although in the case of the isopropyl and *sec*-butyl reactions the yields were rather poor.

This procedure also works with the corresponding Me$_2$salen, saloph, acacen and bis(dimethylglyoximate) complexes but for the last two the yields were low. The process is proposed to involve initial formation of a cobalt(III)-dioxygen or -*tert*-butylperoxy complex which oxidizes the hydrazine to an alkyl diazine plus hydroxyl or *tert*-butyloxy radical. These radicals in turn generate an alkyl radical from the diazene which is then trapped by the cobalt complex (ref. 173). In related work, the rearrangement of [(5-hexenyl)Co(salen)(py)] to [(cyclopentylmethyl)Co(salen)(py)] has been studied. The process is inhibited by dioxygen, TEMPO, brief electrochemical reduction or [Co(salen)] and is accelerated by electrochemical oxidation or oxidation by ferricinium ion indicating the involvement of radicals. A radical chain process is proposed with the 5-hexenyl radical or its cyclopentylmethyl isomer as the chain carrier. Thus dioxygen and TEMPO inhibit the reaction by intercepting the chain carrier while reduction removes the small amount of the Co(IV) complex thought to be the initial source of the 5-hexenyl radical. The remaining step is then proposed to be a homolytic displacement of 5-hexenyl radical from the starting complex by the chain carrier (ref. 174). Other studies reported are those on the thermal decomposition of [102] (Z = (CH$_2$)$_3$) and [103] (ref. 175), the anaerobic thermal decomposition of adenosyl-cobalamin in aqueous solution where homolysis of the cobalt-carbon bond is dominant at pH 7 and heterolysis dominates at pH 4 (ref. 176) and the solid state racemization of [((R)-1-cyanoethyl)Co(dmgH)$_2$(3-Mepy)]. In the last study, the asymmetric unit contains two independent molecules. On exposure to x-rays, both cyanoethyl groups undergo inversion with the process being about twice as fast for one as for the other. Eventually, the slower one reverts to its original configuration while the other remains inverted leading to the formation of a racemic crystal (ref. 177).

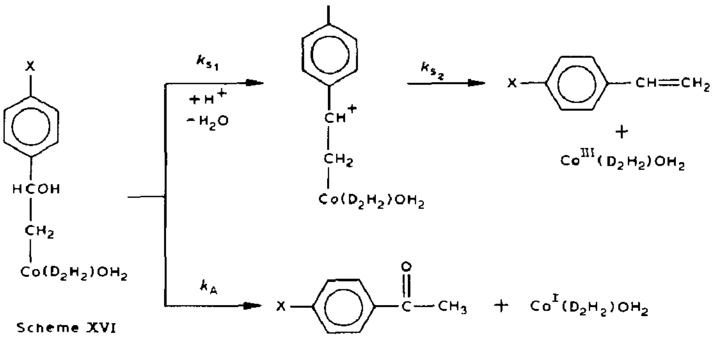


[102]

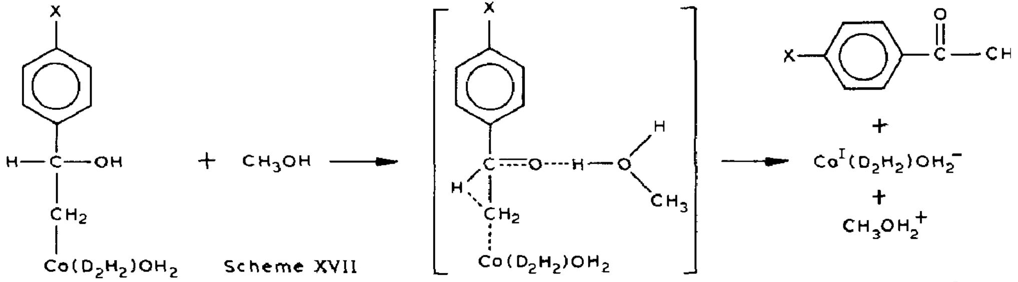


[103]

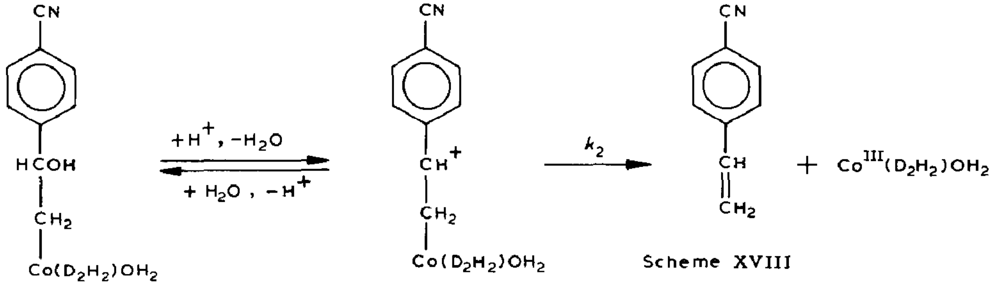
The decomposition of a variety of cobaloximes of the formula [RCo(dmgH)$_2$(H$_2$O)] has been studied. When R = XOCH$_2$CH$_2$ (X = Ph, CF$_3$CH$_2$, Me, Et, Pr^i) the decomposition in aqueous base gives stoichiometric quantities of ethylene and XOH when X is a good leaving group (X = Ph, CF$_3$CH$_2$). Here it is thought that the reaction proceeds *via* initial attack of hydroxide ion at a quaternary carbon of the dimethylglyoximate ligand followed by displacement of the alkyl group which then undergoes fragmentation. In the other complexes, the yield of ethylene is pH dependent and less than stoichiometric. The mechanism for these has not yet been established with certainty. When R = $\underline{\text{p}}\text{-XC}_6\text{H}_4\text{CH(OH)CH}_2$ (X = H, Me) the decomposition was studied in methanol and the organic products were observed to be styrene plus acetophenone and the methyl derivatives of these respectively. For X = H the reaction exhibited biphasic kinetics above 25°C but was first order below 15°C. However when X = Me the reaction was first order above 25°C and biphasic below this temperature. Scheme XVI (D_2H_2 = $(dmgH)_2$) was proposed with the acetophenone thought to form *via* Scheme XVII. In contrast to expectation, both paths of Scheme XVI appear to be ionic and solvent-assisted rather than concerted although it is noted that since the reaction is concerted when R = $CH(Ph)CH_2OH$, steric effects are evidently important in determining its course. When R = $\underline{\text{p}}\text{-NCC}_6\text{H}_4\text{CH(OH)CH}_2$, the complex is stable in methanol but decomposes in aqueous sulfuric acid to form primarily $\underline{\text{p}}$-cyanostyrene. Scheme XVIII is proposed here (refs. 178, 179).



Scheme XVI

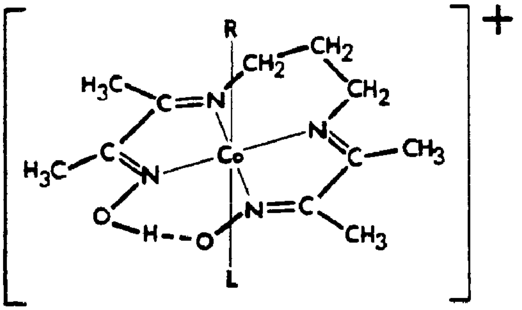


Scheme XVII



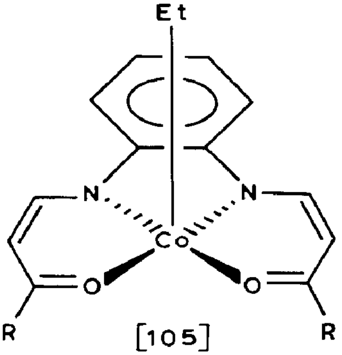
Scheme XVIII

The ^{31}P NMR spectra of a variety of alkyl cobalamins (alkyl = Me, Et, Pr^n, $(CH_2)_3CN$, CH_2CF_3, CH_2CN, CF_3) have been measured and the fact that in the base-off form J_{P-H} in the ribityl phosphate side chain is the same for all complexes was interpreted to mean that all had the same conformation. In the base-on form the measured values of J_{P-H} increased as the alkyl group was changed in approximately the order given above. This order generally parallels that of the strength of interaction with the axial base and suggests that the more strongly this coordinates, the more strain is induced in the ribityl phosphate side chain (ref. 180). Using an extensive series of complexes of the type $[RCo(dmgH)_2(L)]$ (R = alkyl; L = py, $P(OMe)_3$) a set of substituent constants for substituents on the α-carbon of the alkyl group has been derived using the observed ^{13}C NMR chemical shifts for the γ-carbon of the axial pyridine. A good correlation was found between the sum of these constants for each alkyl group and the cobalt-nitrogen (of pyridine) distance, the ^{13}C NMR chemical shift of the γ-carbon of an axial *tert*-butylpyridine ligand, the ^{31}P chemical shift of an axial trimethylphosphite ligand and the rate constant for the exchange of the axial ligand. The substituent parameters were thus interpreted as measuring primarily an electronic *trans* influence (ref. 181). The complexes [104] (R = Me; L = PPh_3, $PPh_2((CH_2)_2CN)$, PPh_2cy, PPh_2Pr^1, PPh_2vy,



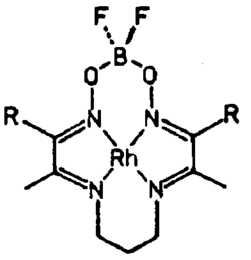
[104]

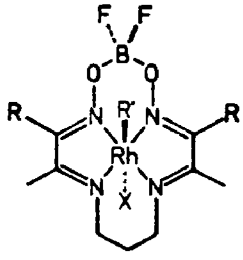
P(*p*-$Me_2NC_6H_4$)$_3$, $P(OMe)_3$, PPh_2Et, $PPh_2(OEt)$, $PPh(OMe)_2$) have been prepared as perchlorate salts and the rates of exchange of L with trimethylphosphite or N-methylimidazole measured. These rates decrease with L in the order shown. Also measured were the rates of exchange of L (= nitrogen donor ligand) with trimethylphosphite or ethyldiphenylphosphine. The structures of [104] (L = $P(OMe)_3$, PPh_3) were determined and found to be little different from those of the cobaloxime analogs. Thus these two model systems for vitamin B_{12} do not differ much in the Co(III) state although the present one shows a greater sensitivity to the bulk of L in the relative rates of loss of this ligand. Because of this and the greater ease of reduction to Co(II), [104] is considered to be a better model than the cobaloximes. However the data obtained in the second study suggest that the cobalt center in [104] is more electrophilic than that in the cobaloximes and since the electrophilicity of cobalt in cobalamins is low, this represents a deficiency in both models (refs. 182, 183). When 2-aminopyridine is used as an axial base with [RCo(dmgH)$_2$] (R = CH$_2$X (X = NO$_2$, CF$_3$, Br, H, Me, OMe), C(Me)(CO$_2$Me)$_2$, Bu^t, Pr^i, Np, adamantyl), an equilibrium, largely intramolecular, occurs between species where the base is bound _via_ the endocyclic nitrogen atom and _via_ the exocyclic nitrogen atom. The position of this equilibrium is affected by the identity of the alkyl group in a manner which suggests steric effects dominate. This is claimed to be the first clear indication of a steric _trans_ influence in solution (ref. 184). Proton and ^{13}C NMR data are available for [105] (R = Me, OEt) (ref. 185) as are the results of molecular orbital calculations on several cobalt porphine complexes (ref. 186).


[105]

The anation reactions of [RRh(dmgH)$_2$(H$_2$O)] (R = Me, Et, CH$_2$CF$_3$, CH$_2$Cl) are significantly faster than those of the cobalt analogs and an I$_d$ mechanism is proposed. Both the R group and the equatorial ligands are thought to make significant contributions to the labilization of the water molecule (ref. 187). Standard routes have been used to prepare [RRh(salen)] (R = Me, Et, Pr^i) whose luminescence spectra have been measured. The rhodium-carbon bond (R = Et) is cleaved homolytically in several aerated solvents including ethanol, chloroform and benzene (refs. 188, 189).

Complex [106] (R = Me, Et) has been characterized as a "supernucleophile" and oxidatively adds organic halides to form [107] (X = Br; R' = bz,


[106]


[107]

Bu^n, Pr^i, cy, adamantyl. X = Cl; R' = Bu^n, bz. X = I; R' = Me, Bu^n, cyclopropylmethyl. X = Ots; R' = Bu^n. X = SCN; R' = bz). Rapid halide exchange between various examples of [107] occurs presumably via initial loss of halide from one to give a five-coordinate cation to which halide from a second can transfer. The initial step is supported by the ready abstraction of halide by silver tetrafluoroborate. An extensive study of the formation of [107] from [106] indicates that the mechanism is sensitive to the steric bulk about the α-carbon of the potential alkyl group. With unhindered alkyl iodides, nucleophilic displacement of iodide by [106] is suggested while with more bulky ones radical paths appear important. Overall, the authors prefer a predominantly radical pair mechanism with possibly some short-lived chains in certain instances. It was also found that [106] (R = Me, Et) underwent facile alkyl transfer with [107] (R = Me, Et. R' = Me; X = I. R' = bz; X = Cl) as shown by crossover experiments. As the benzyl complex reacted faster than the methyl complex and those with bulkier alkyl groups were unreactive it was suggested that nucleophilic attack of [106] on the α-carbon atom of the alkyl group in [107] occurs. Reaction of [106] (R = Et) with 1,3-dihalopropanes forms [107] (R = Et. X = Br; R' = $(CH_2)_3Y$ (Y = Cl, Br, I). X = I; R' = $(CH_2)_3Y$ (Y = Cl, Br)) plus small amounts of the trimethylene-bridged binuclear complex derived from oxidative addition of [106] to both ends of the dihalopropane. Previous results showing formation of significant quantities of the binuclear species are attributed to incomplete dissolution of [106] in the solvent used and not to a neighboring group effect. The same reaction with 1,2-dibromoethane forms a 1:1 mixture of the corresponding dimethylene-bridged dimer and [107] (R' = X = Br) together with ethylene. Since the rates of reaction of the dihalopropanes and -ethanes are comparable it is felt that both proceed initially by a normal oxidative addition process. In contrast, [106] (R = Et) reacts much more rapidly with 1,2-dibromocyclohexane to form [107] (R' = X = Br) and cyclohexene and here a concerted elimination process is proposed (refs. 190-192).

The heterobimetallic complex [(OEP)RhIn(OEP)] is formed on reaction of Na[Rh(OEP)] with [In(OEP)Cl] but is unreactive towards syngas, phenylacetylene, acrylonitrile, triethylphosphite and tert-butylisocyanide under conditions where $[Rh_2(OEP)_2]$ does react. It does however react with methyl iodide to form [Rh(Me)(OEP)] and [In(OEP)I]. The lack of interaction in solution with water, triethylphosphite or tert-butylisocyanide as judged from proton NMR measurements was taken to suggest formulation of the bimetallic species as $[(OEP)Rh^{I}\rightarrow In^{III}(OEP)]$ (ref. 193). Under a syngas atmosphere (< 1 atm) $[Rh(OEP)]_2$ is partially converted to [RhH(OEP)] and [Rh(CHO)(OEP)]. Photolysis of this equilibrium mixture forms formaldehyde and $[Rh(OEP)]_2$ but if the system is kept closed, the original equilibrium is established on termination of the irradiation. Photolysis of the same system at 353 K causes catalytic formation of methanol for which the mechanism of Scheme XIX is proposed. In further work it was found that [RhH(OEP)] behaved as a weak acceptor towards pyridine, n-butylisocyanide

$$[Rh(OEP)]_2 \overset{H_2/CO}{\rightleftharpoons} [RhH(OEP)] + [Rh(CHO)(OEP)]$$

$$[Rh(CHO)(OEP)] \xrightarrow{h\nu} [\cdot Rh(OEP)] + \cdot CHO$$

$$[RhH(OEP)] + \cdot CHO \longrightarrow [\cdot Rh(OEP)] + H_2CO$$

$$2[\cdot Rh(OEP)] \longrightarrow [Rh(OEP)]_2$$

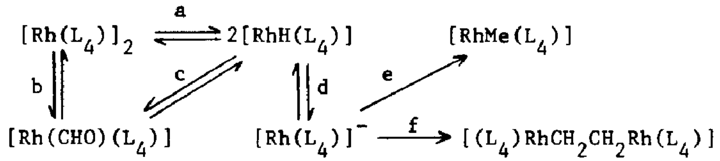
$$[RhH(OEP)] + H_2CO \rightleftharpoons [Rh(CH_2OH)(OEP)]$$

$$[Rh(CH_2OH)(OEP)] + [RhH(OEP)] \longrightarrow [Rh(OEP)]_2 + CH_3OH$$

Scheme XIX

and triphenylphosphine and did not add carbon monoxide trans to the hydride ligand but rather reacts differently to give [Rh(CHO)(OEP)]. The iridium analog proved to be a much better acceptor towards the first three ligands and did form trans-[IrH(CO)(OEP)]. A thermodynamic analysis of the formation of [Rh(CHO)(OEP)] from [RhH(OEP)] suggested that the rhodium-hydrogen and rhodium-carbon bond strengths were comparable so the success of this reaction appears to be due to the unusual strength of the latter. For the iridium analog, the iridium-hydrogen bond is stronger than its rhodium counterpart but apparently the desired iridium-carbon bond is not comparably stronger so that formation of [Ir(CHO)(OEP)] is not thermodynamically favored. Finally, $[Rh(OEP)]_2$ itself reacts with carbon monoxide with ultimate insertion into the metal-metal bond to yield [(OEP)Rh(μ-CO)Rh(OEP)] (refs. 194-196). Other workers have found that treatment of [RhCl(OEP)] with silver perchlorate or tetrafluoroborate in certain aromatic solvents at 50°C regioselectively forms $[Rh(p\text{-}RC_6H_4)(OEP)]$ (R = H, OMe, Me, Cl). The regioselectivity is presumed to be steric in origin and the fact that the silver salts plus [RhCl(OEP)] in non-aromatic solvents produces unstable [RhX(OEP)] ($X = ClO_4^-$, BF_4^-) which subsequently reacts with benzene to form [Rh(Ph)(OEP)] indicates that $[Rh(OEP)]^+$ is the reactive species in the original reaction. This appears to be an example of electrophilic aromatic metalation with the rhodium cation appearing approximately as electrophilic as NO_2^+. Reaction of [Rh(Ph)(OEP)] with iodine forms [RhI(OEP)] plus iodobenzene while photolysis yields biphenyl (ref. 197).

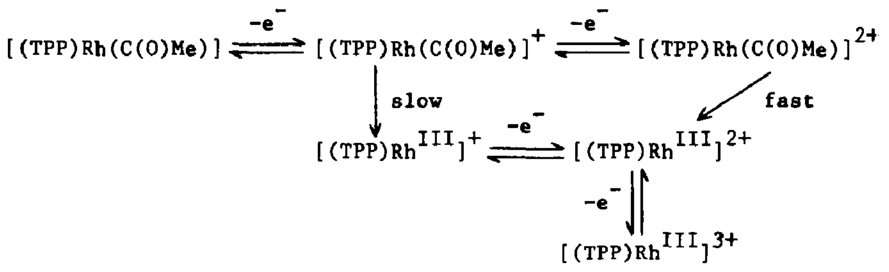
The Wayland group has also reported extensions of its work on octaethylporphyrin complexes of rhodium to the analogs $[Rh(L_4)]_2$ (L_4 = TPP, TTP). Some of these results are outlined in Scheme XX. Formaldehyde reacts with



a) H_2. b) H_2/CO (1:2). c) CO. d) OH^-. e) MeBr. f) CH_2BrCH_2Br.

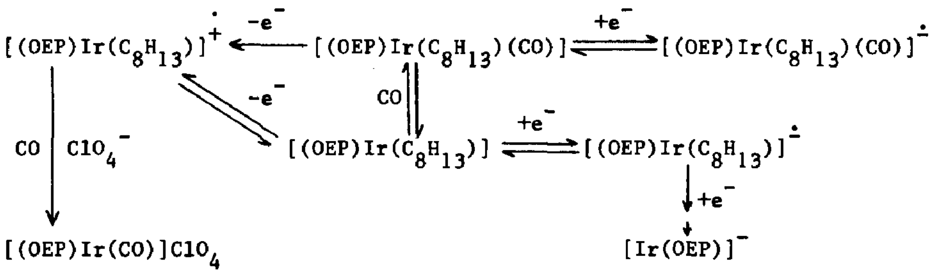
Scheme XX

[RhH(TPP)] to reversibly give [Rh(CH_2OH)(TPP)] which in turn undergoes reversible condensation to [(TPP)Rh($CH_2CH_2OCH_2CH_2$)Rh(TPP)]. Also while [RhMe(TPP)] is unreactive towards carbon monoxide under thermal conditions, [Rh(C(O)Me)(TPP)] can be formed upon photolysis. As the behavior of these systems is very comparable to that of the OEP analog, it appears that substituent effects on the porphyrin ring have little effect on the metal center (ref. 198). At -78°C in benzonitrile, THF or pyridine, [Rh(TPP)-($Me_2NH)_2$]Cl shows two reversible, one-electron reduction steps but at room temperature the first is irreversible due to the formation of $[Rh(TPP)]_2$. In dichloromethane solution, electrolytic reduction at the potential of the first wave yields [Rh(CH_2Cl)(TPP)] a species also formed by reaction of $[Rh(TPP)]_2$ with this solvent. The electrochemistry of [Rh(C(O)Me)(TPP)] has also been studied in benzonitrile solution. Two, one-electron reduction steps are noted but the second is only reversible on the cyclic voltammetric time scale and chemical reaction ensues. The first step appears to involve reduction of the TPP ligand rather than the metal. Three, one-electron oxidation steps are also observed but only the first is reversible and then only on the cyclic voltammetric time scale. The oxidation processes are thought to be those outlined in Scheme XXI (refs. 199, 200). The same group has determined the structure of [(OEP)Ir(C_8H_{13})] (C_8H_{13} = _cis_-bicyclo[3.3.0]oct-1-yl) and obtained its proton NMR spectrum. The significant upfield shift of the resonances of the alkyl group is attributed to the ring current of the porphyrin ligand. The complex



Scheme XXI

reversibly forms a carbonyl adduct and this system has been studied electrochemically with results as outlined in Scheme XXII (the perchlorate

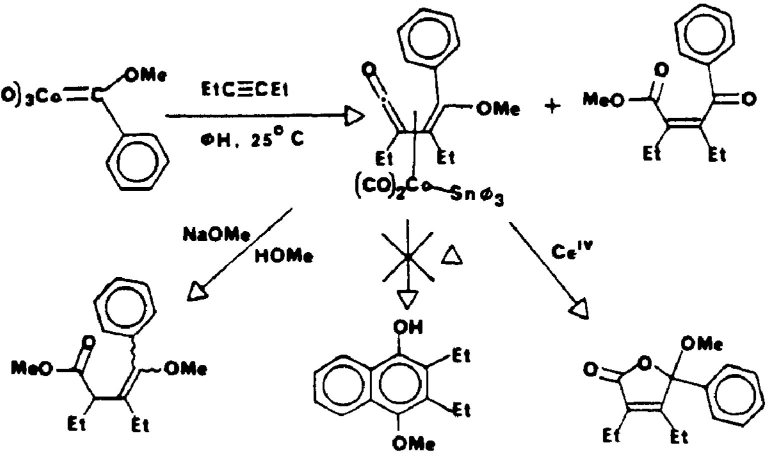


Scheme XXII

originates in the supporting electrolyte) (ref. 201).

Metal Carbene Complexes

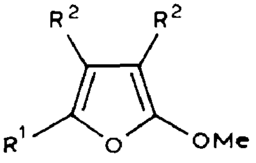
The complex $[Ph_3SnCo(=C(OMe)R_1)(CO)_3]$ (R_1 = Ph) reacts with hex-3-yne at room temperature as depicted in Scheme XXIII while at 50°C both it and



Scheme XXIII

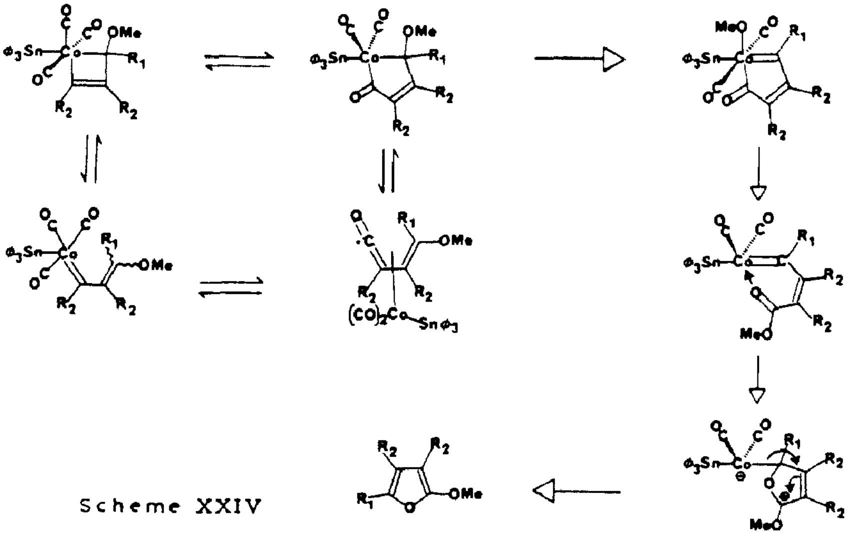
the analog with R_1 = Bu^n react with internal acetylenes to form [108] (R_1 =

Ph; R_2 = Me, Et, Ph. R_1 = Bu^n; R_2 = Ph). This is proposed to occur as



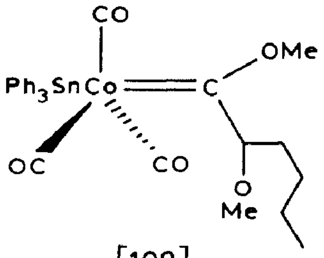
[108]

outlined in Scheme XXIV with the initial step being a [2+2] cycloaddition of the carbene complex to the acetylene to give the metallacycle shown at the upper left of Scheme XXIV. Successive reactions of $Bu^n_3SnCH(OMe)-(CH_2)_3Me$ with butyllithium, $[Ph_3SnCo(CO)_4]$ and trimethyloxonium tetrafluoroborate forms [109] which on reaction with but-2-yne at 50°C yields

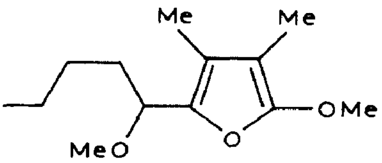


Scheme XXIV

[110] which is a precursor to bovolide (ref. 202). Addition of $[Co(CO)_4]^-$ to $[cpFe(=C(SR)_2)(CO)(MeCN)]^+$ (R = Me. R_2 = $(CH_2)_n$; n = 2,3) gives [111].

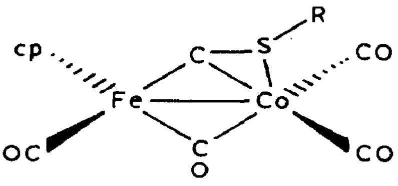


[109]



[110]

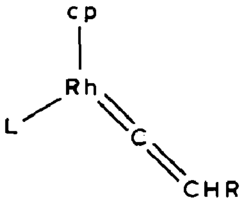
This was reacted with triethylphosphine in hopes of displacing the sulfur from cobalt but instead one carbonyl group on cobalt was replaced. Oxidation of [111] (R = Me) with iodine, bromine, trityl cation, ferricenium ion or tropylium ion generated $[cpFe(=C(SMe)_2)(CO)_2]^+$ but the cobalt-containing product was generally not isolated except where the oxidation with iodine



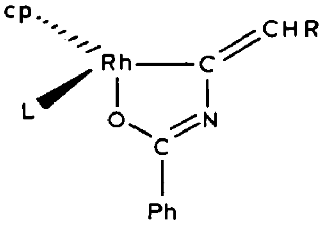
[111]

was performed in the presence of two equivalents of triphenylphosphine. Here [CoI(CO)$_2$(PPh$_3$)$_2$] was obtained (ref. 203).

The ketenylidene complex [112] (R = H, Ph; L = PPr^{i}_{3}) reacts with benzoyl azide to give [113] (R = H, Ph; L = PPr^{i}_{3}). Treatment of the

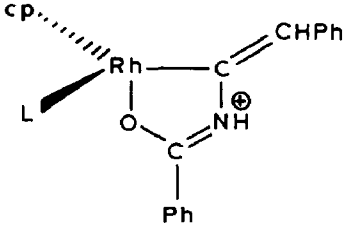


[112]

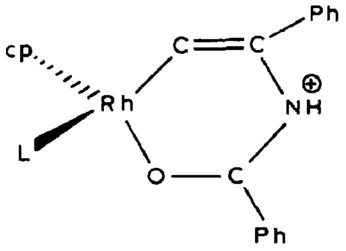


[113]

latter (R = Ph; L = PPr^{i}_{3}) with TFA gave an equilibrium mixture of [114] and [115] (ref. 204). Addition of bis(1,3-dimethylimidazolin-2-ylidene) to

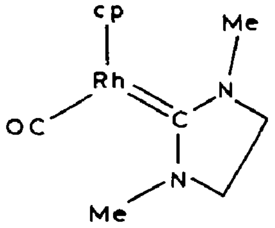


[114]



[115]

[cpRh(CO)$_2$] in refluxing methylcyclohexane forms [116] (ref. 205). Cyclopentanes can be formed by an intramolecular C-H insertion process mediated



[116]

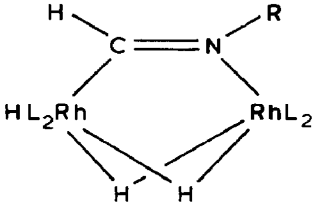
by $[Rh_2(O_2CMe)_4]$. Rhodium carbene species are thought to be involved as intermediates. The stereochemical course of these reactions as a function of steric effects suggests that the carbene intermediate approaches perpendicular to the carbon-hydrogen bond (ref. 206). Carbene intermediates are also proposed for the decomposition of methyllithium and methylmagnesium bromide induced by rhodium(III) chloride (ref. 207). Protonation of the ketenylidene complex $[Ir(=C=CHR)(Cl)L_2]$ (R = H, Me, Ph; L = PPr^i_3) with tetrafluoroboric acid etherate forms an equilibrium mixture of $[Ir(=C=CHR)(H)(Cl)L_2]BF_4$ and $[Ir(\equiv CCH_2R(Cl)L_2]BF_4$. Reconversion to the starting complex can be accomplished with a stoichiometric quantity of sodium hydride and further addition of this reagent gives $[IrH_5L_2]$ (ref. 208).

Metal Isocyanide Complexes

The complexes $[Co(CNBu^t)_4(H_2O)](ClO_4)_2$ are formed on treatment of $[Co(H_2O)_6](ClO_4)_2$ with the isocyanide in ethanol and are reduced to $[Co(CNBu^t)_3L_2]ClO_4$ (L = PPh_3, $P(\underline{p}\text{-anisyl})_3$, $P(\underline{p}\text{-ClC}_6H_4)_3$, $P(\underline{n}\text{-hexyl})_3$, $P(CH_2CH_2CN)_3$, $P(NMe_2)_3$) on addition of the appropriate ligand. Starting with $[Co(CNR)_5]A$ (R = 2,6-$Me_2C_6H_3$; A = ClO_4, BF_4) the complexes $[Co(CNR)_4L]A$ (L = $P(OPr^i)_3$, $P(OEt)_3$, $P(OMe)_3$) and $[Co(CNR)_3L_2]ClO_4$ (L = $P(OPr^i)_3$) have also been synthesized (refs. 209, 210). The acyl isocyanide complexes $[cpCo(CNC(O)R)_2]$ (R = Ph, 1-adamantyl) can be prepared by reaction of the corresponding isocyanide with $[cpCo(CO)_2]$. The complete replacement of both carbonyl ligands is exceptional and argues for significant π-acidity for the acyl isocyanides. Cyclic voltammetric studies of the benzoyl isocyanide complex show a reversible, two-electron reduction which is characterized as an ECE process (ref. 211). Thin films of poly(dimethylsiloxane) functionalized with 3-isocyanopropyl groups on silicon have been reacted with cobalt vapor by the metal vapor/fluid matrix techniques to form polymer-encapsulated $\{Co_2(CNR)_8\}$ moieties (ref. 212).

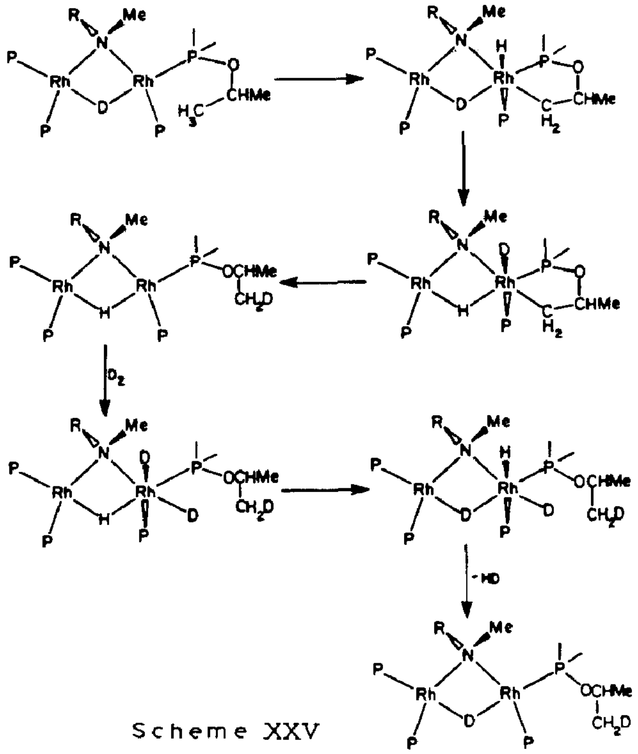
Both $[Rh_2br_4](BPh_4)_2$ and $[Rh_2(TMB)_4](OTf)_2$ have been studied by transient spectroscopic methods and assignments of the absorption made. In the latter, the lifetime of the $^1A_{2u}$ state has been determined to be 820 ps while that for the corresponding $^1B_2$ state of $[Ir_2(COD)_2(\mu\text{-pz})_2]$ is evidently less than 20 ps, a difference which was attributed to larger spin orbit coupling in the iridium complex. Although the luminescence of both the singlet and triplet states of the iridium complex is quenched by 1,2-dichloroethane and this molecule undergoes oxidative addition on continuous irradiation, using picosecond excitation the $^1B_2$ state appears unreactive. Thus the quenching of the luminescence is attributed to the chlorinated solvent enhancing the rate of intersystem crossing to the triplet relative to what occurs in cyclohexane (refs. 213, 214). The complexes $[Rh_2(L_2)_2(DPM)_2]^{2+}$ (L_2 = TMB, dimen) are synthesized from $[Rh_2(TMB)_4]^{2+}$ and DPM or from $[Rh_2Cl_2(CO)_2(DPM)_2]$ and dimen respectively. Both oxidatively add halogens to form the axial dihalo complexes $[Rh_2X_2(L_2)_2(DPM)_2]^{2+}$ (X = Cl; L_2 = TMB, dimen. X = Br, I; L_2 = TMB). Photochemical studies on $[Rh_2(TMB)_2(DPM)_2]^{2+}$ suggest that the $^3B_{1u}$ excited state is strongly reducing. Cyclic voltammetric studies of $[Rh_2(dimen)_2(DPM)_2]^{2+}$ show the presence of two, one-electron oxidation steps, the first of which is quasi-reversible. The EPR spectrum of the one-electron oxidation product suggests a delocalization of the unpaired electron over both metals. In contrast to $[Rh_2(br)_4]^{3+}$, $[Rh_2(dimen)_2(DPM)_2]^{3+}$ does not dimerize, presumably because of the bulk of the ligands, but if chloride ion is added disproportionation occurs to yield $[Rh_2Cl_2(dimen)_2(DPM)_2]^{2+}$ and $[Rh_2(dimen)_2(DPM)_2]^{2+}$. From this observation it is suggested that a similar radical disproportionation may take place in the net photolytic reduction of hydrogen ions to dihydrogen which occurs in the presence of $[Rh_2(br)_4]_2^{6+}$ (refs. 215, 216).

Hydrogenation of $[Rh_2(CNR)(\mu-H)_2L_4]$ (L = $P(OPr^i)_3$; R = bz, p-ClC_6H_4) yields $[Rh_2(\mu-H)(\mu-N(Me)R)L_4]$ and an intermediate proposed to be [117] has



[117]

been detected by NMR. The initial formation of $[Rh_2H_4L_4(CNR)]$ is suggested followed by transfer of one hydrogen to the isocyanide. Further hydrogenation of $[Rh_2(\mu-H)(\mu-N(Me)R)L_4]$ to give $[Rh_2H(\mu-H)_3L_4]$ and the corresponding secondary amine occurs but proceeds very slowly while reaction with other isocyanides gives a mixture of products including significant amounts of $[L_2Rh(\mu-H)(\mu-N(Me)R)Rh(L)(CNR')]$ (R = R' = Bu^n, Bu^t, bz, p-ClC_6H_4, 2,6-$Me_2C_6H_3$). To study the course of the original reaction in detail, $[Rh_2(CNR)(\mu-H)_2L_4]$ was reacted with deuterium and deuterium incorporation into the hydride positions as well as the methyl group on nitrogen and the ligand methyl groups was observed. The last was considered to arise as depicted in Scheme XXV (ref. 217). The complex $[RhCl(CO)_2(CNR)]$ (R = n-$C_9H_{19}OC_6H_4C_6H_5$) is mesogenic with liquid crystal properties (ref. 218) while $[Rh(CNXNC)_2Cl]_n$ (X = 1,4-C_6H_4, 4,4'-biphenylyl) which has a stacked layer structure shows semiconductor behavior (ref. 219).

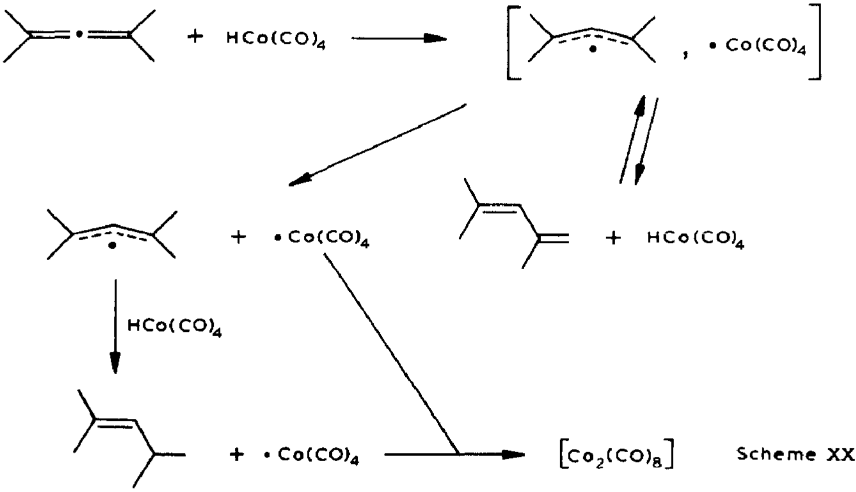


Scheme XXV

Metal Carbonyl Complexes and Related Compounds

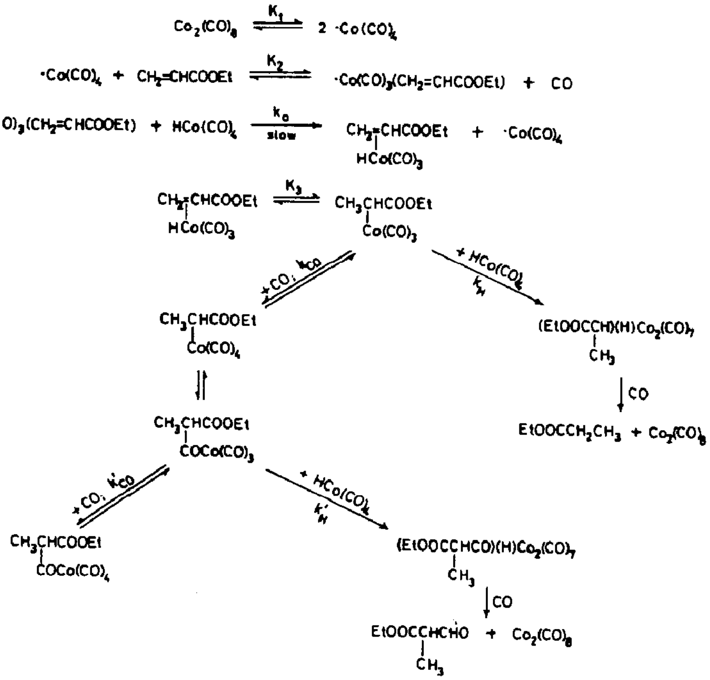
a) Homonuclear Carbonyl Compounds

Benzene solutions of tetramethylallene and [HCo(CO)$_4$] form a mixture 2,4-dimethylpenta-1,3-diene and 2,4-dimethylpent-2-ene indicating that both isomerization and hydrogenation of the allene occur. The diene can be hydrogenated to the monoolefin by [HCo(CO)$_4$] but at a rate which is slower than that at which the latter is formed from tetramethylallene. As CIDNP is observed when the reaction is monitored by proton NMR spectroscopy, the radical mechanism of Scheme XXVI is proposed (ref. 220). The reaction of



Scheme XXVI

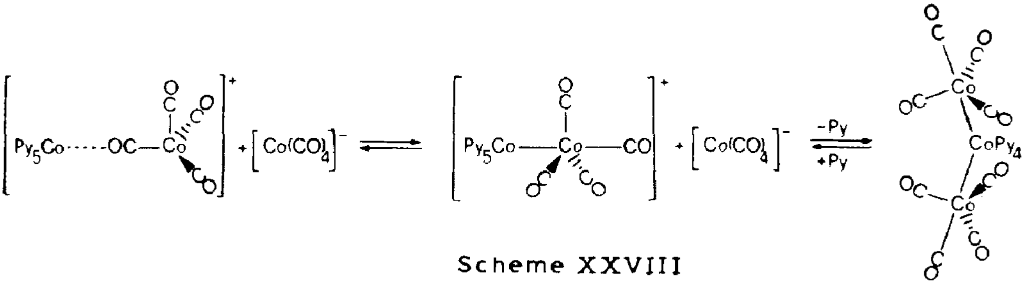
ethylacrylate with $[HCo(CO)_4]$ in the presence of $[Co_2(CO)_8]$ at 10° C forms ethylpropionate while the product is 2-ethoxycarbonylpropionaldehyde when carbon monoxide is also present. Analysis of the products of the latter reaction at the point that uptake of carbon monoxide ceases shows that a significant amount of $[(EtO_2CCH(Me))Co(CO)_4]$ is present. Addition of triphenylphosphine at temperatures below 10°C causes carbonyl "insertion" to occur and $[(EtO_2CCH(Me)C(O))Co(CO)_3(PPh_3)]$ forms. However on warming to room temperature carbon monoxide is lost yielding $[(EtO_2CCH(Me))Co(CO)_3(PPh_3)]$. If the original reaction (carbon monoxide present) is warmed to room temperature after 0.25 mol of carbon monoxide is absorbed, a greater amount is then taken up and $[(EtO_2CCH_2CH_2C(O))Co(CO)_4]$ is detected in solution. The results have been interpreted according to Scheme XXVII



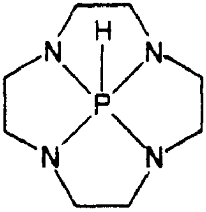
Scheme XXVII

(ref. 221). The pK_a values of several transition metal hydrides have been determined in acetonitrile solution from measurements of the equilibrium constants for their reactions with bases of known base strength. The systems $[HCo(CO)_4]/p\text{-}F_3CC_6H_4NMe_2$, $[HCo(CO)_3(P(OPh)_3)]$/anisidine and $[HCo(CO)_3(PPh_3)]$/morpholine gave values increasing from 8.3 to 15.4 in the order given. From this work, $[HCo(CO)_4]$ appears to have comparable strength to hydrogen chloride in acetonitrile but is much weaker than perchloric acid (ref. 222). Studies of the inhibition by Bronsted bases of the olefin hydrogenation reaction catalyzed by cobalt carbonyls correlates quantitatively with the degree of deprotonation of $[HCo(CO)_4]$ but the extent of deprotonation proved to be quite temperature dependent (ref. 223). Kinetic data on the reaction of $[HCo(CO)_4]$ with olefins to give alkyl cobalt tetracarbonyls have been obtained at -80°C. The data are interpreted in terms of an initial formation of $[HCo(CO)_2(olefin)_2]$ which subsequently loses one olefin and then rearranges to yield the final product (ref. 224). An ab initio CI calculation of the potential energy surface for the photolytic cleavage (homolytic) of the cobalt-hydrogen bond in $[HCo(CO)_4]$ suggests that the initially formed singlet state undergoes intersystem crossing to a triplet state from which dissociation occurs (ref. 225).

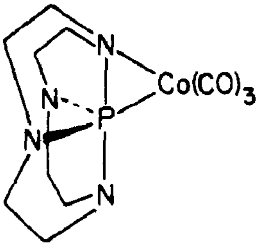
A variable temperature infrared spectroscopic study of $[Co(py)_6][Co(CO)_4]_2$ in THF under nitrogen suggested equilibria between several ion pairs such as those shown in Scheme XXVIII. Several of these same species were seen when a THF solution of $[Co_2(CO)_8]$ was treated with pyridine and the equilibrium composition of the system as a function of the pyridine and/or carbon monoxide concentration was identical to that produced on addition of carbon monoxide to the THF solution of $[Co(py)_6][Co(CO)_4]_2$. These results led the authors to suggest that to describe the reaction of pyridine with $[Co_2(CO)_8]$ as simply a disproportionation (as would be implied if one only considered the final product) is too restrictive (ref. 226). The cyclic phosphorane [118] reacts with $[Co_2(CO)_8]$ to form a mixture of [119] and [120] (ref. 227) while diphenylphosphine yields $[Co(CO)_3(\mu\text{-}PPh_2)]_n$. More bulky ligands however give the dimers $[Co_2(CO)_6(PR_2H)_2]$ (R = Bu^t, cy). Reduction of the polymer with sodium in THF forms



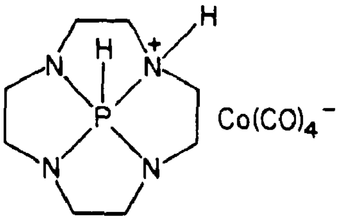
Scheme XXVIII



[118]



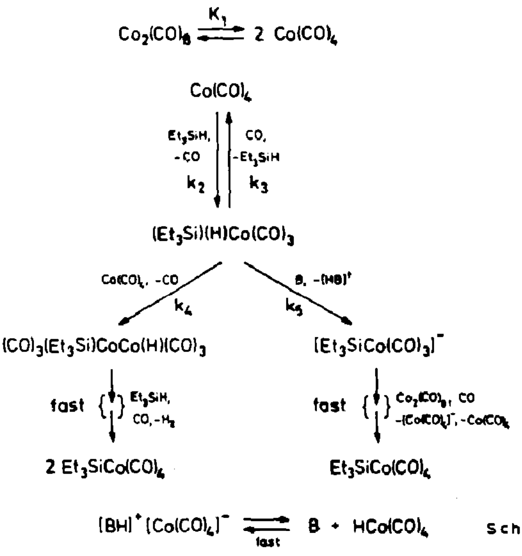
[119]



[120]

$Na_2[Co(CO)_3(PPh_2)]$ which reacts with dimethylsulfate, dichloromethane or butyllithium to yield $[Co(Me)(CO)_3(PMePh_2)]$, $[(OC)_3\overline{CoPPh_2CH_2}]$ and $Li_2[Co(CO)_3(PPh_2)]$ respectively. The dimers when similarly reduced form $Na[Co(CO)_3(PR_2H)]$ ($R = Bu^t$, cy) which reacts with diiodomethane or dimethyl sulfate to give $[(OC)_3\overline{CoPR_2CH_2}]$ and $[Co(Me)(CO)_3(PR_2H)]$ respectively (ref. 228). A low yield of the air- and heat-sensitive complex $[Co_3(CO)_9(\mu_3\text{-}PNPr^i{}_2)]$ is obtained from the prolonged reaction of $[Co_2(CO)_8]$ and bis(diisopropylamino)phosphine at room temperature. Several other unstable species were detected spectroscopically during the course of the reaction (ref. 229).

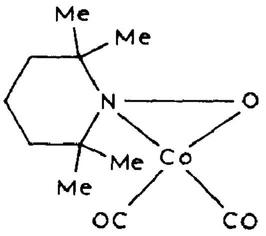
The reaction of $[Co_2(CO)_8]$ with triethylsilane to yield hydrogen and $[Et_3SiCo(CO)_4]$ has been reinvestigated and in contrast to previous reports no $[HCo(CO)_4]$ was detected. In fact the rate of formation $[Et_3SiCo(CO)_4]$ was unaffected by deliberate addition of $[HCo(CO)_4]$. On the other hand, a definite acceleration was noted upon irradiation but addition of galvanoxyl produced only a slight retardation. Despite the latter, the mechanism on the left of Scheme XXIX was proposed. The explanation for the small effect



Scheme XXIX

of added galvanoxyl is that even though radicals are involved this is not a radical chain reaction. Addition of base (B = py, PBu^n_3) accelerates the reaction and alters its course as shown on the right of Scheme XXIX (ref. 230). The same group has also shown that $[Co_2(CO)_8]$ reacts with [M(crypt)]-OR (M = Na, K; crypt = various cryptands; R = Me, Et, Pr^i, cy, bz) and carbon monoxide in THF to form $[(ROC(O))Co(CO)_4]$ plus $[M(crypt)][Co(CO)_4]$ (ref. 231) and that addition of pyridine to solutions of $[Co_2(CO)_8]$ significantly accelerates the rate of hydrogenation to $[HCo(CO)_4]$ by syngas mixtures and the rate of conversion to $[Co_4(CO)_{12}]$ under carbon monoxide alone. Kinetic data for the syngas reaction suggest a radical path (ref. 231a). Benzene solutions of $[Co_2(CO)_8]$ subjected to γ-irradiation generate several complexes including $[Co_2(CO)_6(C_2H_2)]$ (0.1%), $[Co_4(CO)_{12}]$ (0.3%), $[Co_2(CO_6)(C_6H_8)]$ (0.1%) and $[RCCo_3(CO)_9]$ (R = cyclopent-1-en-2-yl). The last can be formed in better yield by γ-irradiation of $[Co_4(CO)_{12}]$ in benzene and here the two dicobalt complexes are not detected (ref. 232).

A high pressure infrared study of the reaction of $[Co_2(CO)_8]$ with methanol in the presence of various additives under carbon monoxide shows the equilibrium is shifted towards product ($[Co(MeOH)_6][Co(CO)_4]_2$) by addition of pyridine or potassium iodide but towards reactants by olefins. The forward reaction is thought to involve associative attack on $[Co_2(CO)_8]$ while in the reverse reaction an electron transfer from Co(-1) to Co(II) is considered to be the rate-determining step. From these results the hydroesterification of oct-1-ene by the above system is thought to involve addition of $[Co(CO)_4]^-$ and hydrogen ion to the olefin with the latter being derived from methanol (ref. 233). Pentane solutions of $[Co_2(CO)_8]$ and TEMPO form [121] which has been characterized as a Co(I) complex by ^{59}Co

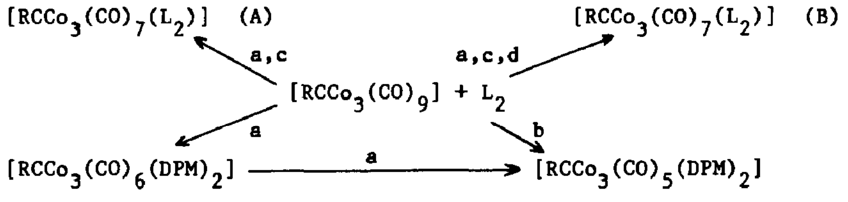


[121]

NMR (ref. 234) while several bidentate phosphines react with $[Co_2(CO)_8]$ to yield $[Co_2(CO)_4(\mu-L_2)]$ (L_2 = DPM, dmpm, $Ph_2PCH_2PMe_2$). The intermediate $[Co(CO)_3(dmpm)][Co(CO)_4]$ has been isolated but converts to $[Co(CO)_4(\mu-CO)_2(\mu-dmpm)]$ even in the solid state. Heating $[Co_2(CO)_4(\mu-CO)_2(\mu-DPM)]$ in solution forms $[Co_4(CO)_8(DPM)_2]$ in which each metal has one phosphorus coordinated to it. The same complex can also be obtained directly from $[Co_4(CO)_{12}]$. All the complexes are fluxional but the slow exchange limit could not be attained for the dimers. For the tetramer all carbonyl groups undergo a concerted polytopal rearrangement which is proposed to involve icosahedral-cuboctahedral interconversions of the ligand polyhedron (ref. 235).

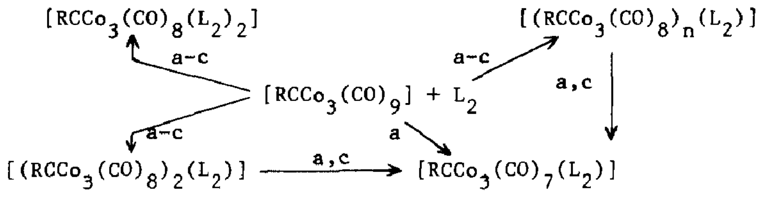
In THF solution $[CoH(N_2)(PPh_3)_3]$ reacts with excess paraformaldehyde to yield a mixture of $[Co(CO)(PPh_3)_3]_n$ (n = 1, 2) and substantial quantities of methyl formate (ref. 236) while good yields of $[Co_2(CO)_6(PBu^n{}_3)_2]$ can be obtained from cobalt(II) carbonate and the phosphine under 4 atm of syngas in benzene (ref. 237). Full details of EPR studies on $[Co_2(CO)_2(MeN(PF_2)_2)_3]^-$ have been published. The unpaired electron appears to occupy a σ^* orbital which is delocalized over both metals. ENDOR experiments allowed determination of the hyperfine coupling constants for the fluorine atoms and the methyl hydrogen atoms. The spectroscopic data could be adequately explained by EHMO calculations (ref. 238).

Reaction of $[MeCCo_3(CO)_9]$ with $Ph_2PCH_2PMe_2(L_2)$ formed a racemic mixture of $[MeCCo_3(CO)_7(L_2)]$. In attempts to resolve this mixture, it was reacted with chiral phosphines to give $[MeCCo_3(CO)_6(L_2)L]$ (L = PAMP, CAMP). The two resulting diastereoisomers detected by NMR could be separated by HPLC but on reaction with carbon monoxide to reform $[MeCCo_3(CO)_7(L_2)]$, each racemized (ref. 239). The reactions of $[RCCo_3(CO)_9]$ (R = Me, Ph) with bidentate phosphines under a variety of conditions are shown in Schemes XXX (L_2 = DPM) and XXXI (L_2 = DPPE). In Scheme XXX two isomers of $[RCCo_3(CO)_7(DPM)]$ were seen in reactions a) and c) (designated (A) and (B)) and (B) was the major form while in Scheme XXXI $[RCCo_3(CO)_8(DPPE)_2]$ was a minor product. The electrochemistry of the complexes described above was studied. The substituted complexes were thermodynamically more difficult to reduce but the resulting radical anions proved kinetically more stable



a) Δ, THF. b) Δ, ϕMe. c) BPK, THF. d) bulk electrolysis, acetone or MeCN or CH_2Cl_2

Scheme XXX

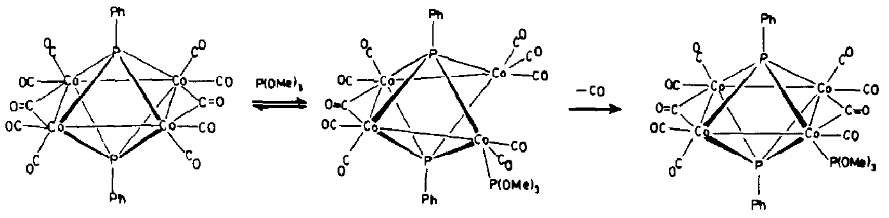


a) Δ, THF. b) BPK, THF. c) bulk electrolysis, acetone or MeCN or CH_2Cl_2, n = 1, 2.

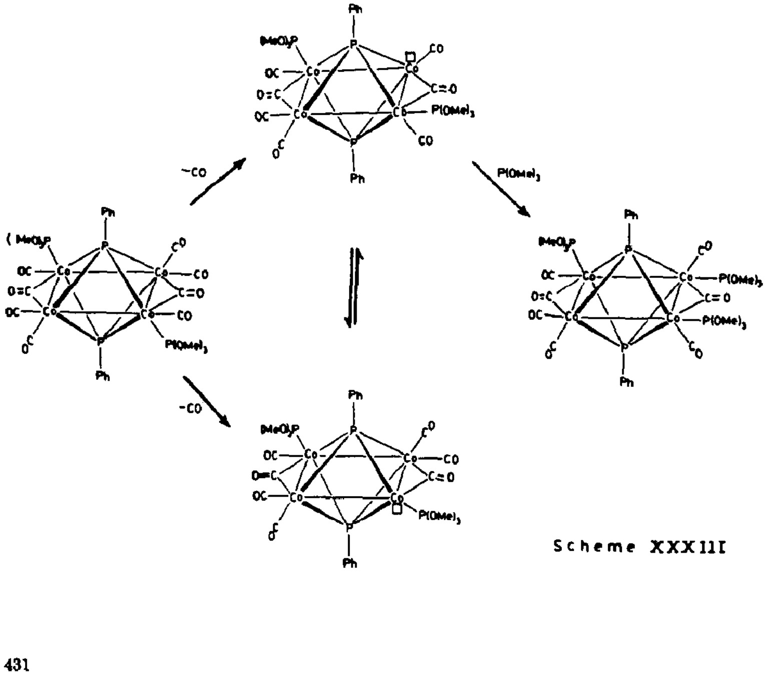
Scheme XXXI

than the parent complexes. In those complexes with monodentate DPM or DPPE (and also PPh_3 analogs) the primary reduction is a one-electron step but a fast ECE process causes the primary wave to exhibit two-electron diffusion currents. From all of these studies it is proposed that the substitution of the first carbonyl group in $[RCCo_3(CO)_9]$ by DPM or DPPE can be effected by a very efficient electron-transfer chain catalysis but that the subsequent steps may very well be thermal processes (refs. 240-242). Inelastic neutron scattering spectra have been used to obtain force constants for the normal vibrations of $[MeCCo_3(CO)_9]$ (ref. 243) while further evidence for the $[\cdot CCo_3(CO)_9]$ radical has been obtained from a study of the reaction of $[Co_2(CO)_8]$ with CX_4 (X = Cl, Br) or $[BrCCo_3(CO)_9]$ (ref. 244). A variable temperature ^{13}C NMR study of $[C(O)CCo_3(CO)_9]^+$ together with molecular orbital calculations suggest that the ketenylidene moiety is tilted as has been established in $[C(O)CFe_3(CO)_9]^{2-}$ although the results are not completely conclusive (ref. 245). The complex $[MeO_2CCCo_3(CO)_9]$ is stable in dichloromethane, diethyl ether and hydrocarbon solvents but in THF it decomposes to form $[Co_4(CO)_{12}]$, $[Co(CO)_4]^-$ and a third product which was not identified. If PPN$[Co(CO)_4]$ is added to the THF solution, PPN$[Co_4(CO)_{11}(C(O)Me)]$ is now obtained in addition to the two previously identified products. The acetyl cluster can also be formed from $[Co_4(CO)_{12}]$ and methyllithium in diethyl ether. The unidentified product from the original decomposition is thought to react with the excess $[Co(CO)_4]^-$ used in the second reaction to form the acetyl cluster (ref. 246).

Low yields of $[(Co_4(CO)_{11})_2(\mu\text{-DPPE})]$, $[Co_4(CO)_{10}(DPPE)]$ and $\{[(DPPE)Co_4(CO)_{10}](\mu\text{-DPPE})[Co_4(CO)_{10}](\mu\text{-DPPE})[Co_4(CO)_{10}(DPPE)]\}$ can be obtained from $[Co_4(CO)_{12}]$ and two equivalents of the ligand in hexane (ref. 247). The structures of $[Co_4(CO)_8(PMe_3)(TPM)]$, $[Co_4(CO)_7(DPM)(TPM)]$ and $[Co_4(CO)_7(PMe_3)_2(TPM)]$ have been determined and the results used with ^{31}P and ^{13}C NMR data to determine the site of ligand dissociation which is considered to be the first step in substitution reactions of these clusters. It was concluded that an apical carbonyl ligand is the one which is lost and the incoming ligand can enter here or a basal carbonyl ligand can first migrate to this site <u>via</u> a carbonyl-bridged intermediate followed by addition of the incoming ligand to the vacated basal site (ref. 248). A synthesis of $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ which gives higher yields than those previously reported involves the reduction of $[Co_2(CO)_8]$ with sodium amalgam followed by reaction with phenyldichlorophosphine. In refluxing acetonitrile one carbonyl group can be replaced to give $[Co_4(CO)_7(MeCN)(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ which is a convenient precursor to other monosubstituted derivatives such as $[Co_4(CO)_7(L)(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ (L = PPh_3, PEt_3, $P(OMe)_3$). In refluxing toluene further substitution can occur to yield $[Co_4(CO)_{8-n}(L)_n(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ (L = PPh_3, $P(OMe)_3$; n = 2. L = $P(OMe)_3$; n = 3, 4) in which each phosphorus ligand is on a different metal atom. A detailed study of the formation of the trimethylphosphite complexes showed that the mono- and disubstituted complexes arise <u>via</u> both ligand-dependent and -independent paths with the former predominating while the tri- and tetrasubstituted species arise by a ligand-independent path. The ligand-dependent path is proposed to be that of Scheme XXXII while the change in stereochemistry which accompanies the formation of the trisubstituted complex is proposed

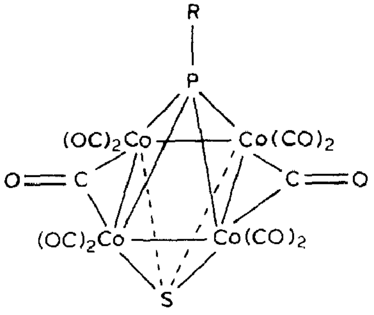


Scheme XXXII



Scheme XXXIII

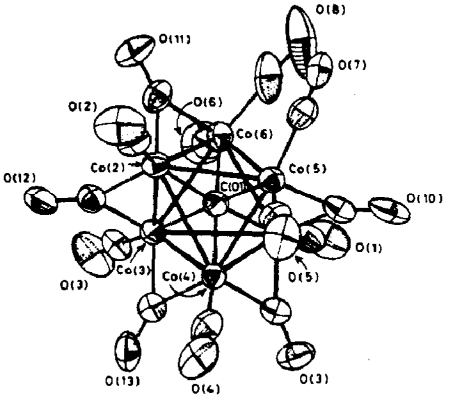
to occur as shown in Scheme XXXIII. Cyclic voltammetric studies on these complexes show that $[Co_4(CO)_8(\mu\text{-}CO)(\mu_4\text{-}PPh)_2]$ exhibits three reduction waves, the first of which is reversible. These waves shift to more negative potentials with increasing degrees of phosphine substitution and tend to be irreversible at room temperature although at lower temperatures the degree of reversibility increases. Because of the shifts of the reduction waves, the more highly substituted complexes cannot be reduced as far as the parent complex but now greater degrees of oxidation become accessible and in some instances tripositive cations can be formed. Bulk electrolysis of both $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ and $[Co_4(CO)_7(PPh_3)(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ yields radical anions which have been studied by EPR spectroscopy. Also, $[Co_4(CO)_6(PPh_3)(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ can be oxidized to a radical cation by silver ion but no EPR spectrum could be observed. As with $[RCCo_3(CO)_9]$ electrocatalytic substitution reactions of $[Co_2(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ and its derivatives can be performed but these show rather low current efficiencies (refs. 249, 250). A related complex, [122] (R = Me, p-anisyl) has been synthesized from $Na[Co(CO)_4]$ and the appropriate organodichlorophosphine sulfide (ref. 251).



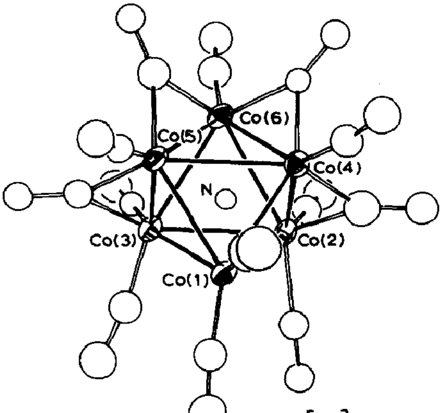
[122]

The ^{13}C and ^{59}Co NMR spectra of $[Co_4(CO)_{12}]$ in solution have been measured and the latter found to be consistent with earlier ^{17}O NMR data which indicated the presence of two different metal environments in the ratio 1:3 (apical:basal). Also identified in the ^{13}C NMR spectrum was a fourth resonance which has not previously been seen and which is assigned to the apical carbonyl ligands. The breadth of this resonance is attributed to $^{59}Co\text{-}^{13}C$ scalar coupling and a relaxation of the ^{59}Co nucleus which occurs more rapidly for the apical metal atom than for the basal atoms (ref. 252). The same complex has also been studied in the solid state by MAS ^{13}C NMR spectroscopy. At 63°C all carbonyls are equivalent while at 24°C three signals are observed. On further cooling four resonances are discerned which presumably indicates attainment of the low-temperature-limiting spectrum and is consistent with the results of the preceeding paper. However the observed chemical shifts were not those expected and no adequate explanation could be advanced (ref. 253). Another ^{13}C NMR study explored the fluxional behavior of $[(\eta^6\text{-L})Co_4(CO)_9]$ (L = mesitylene, triptycene) and showed that in the triptycene complex the rotation of the arene ligand occurs at a faster rate than that for the process which equilibrates all the carbonyl ligands. The relative rates of exchange of carbonyl ligands between bridging, axial and equatorial sites are very dependent on temperature. In the mesitylene complex the bridging-equatorial exchange is slowest at 178 K and the axial-equatorial exchange is fastest but at 308 K the reverse is seen (ref. 254).

Decarbonylation of $[Co_6(C)(CO)_{15}]^{2-}$ occurs in refluxing THF to form air-sensitive $[Co_6(C)(CO)_{13}]^{2-}$ ([123]). The observed structure supports a previous proposal that the disposition of ligands about such clusters is determined primarily by the requirement of providing an even distribution of the electrons donated to the cluster so long as this does not occasion severe steric interactions. Similar treatment of $PPN[Co_6(N)(CO)_{15}]$ forms $PPN[Co_6(N)(CO)_{13}]$ ([124]) which has a structure very similar to that of



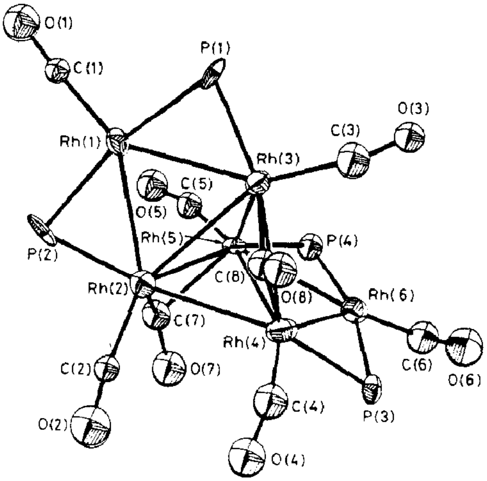
[123]



[124]

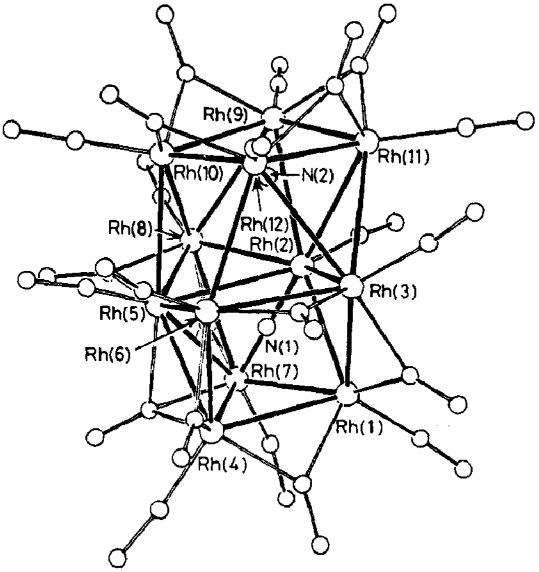
[123] and is claimed to be the first example of an octahedral cluster with an interstitial nitride (the parent cluster is trigonal prismatic) (refs. 255, 256). Electrochemical studies of $[Co_8(C)(CO)_{18}]^{2-}$, $[Co_6(C)(CO)_{15}]^{2-}$ and $[Rh_6(C)(CO)_{15}]^{2-}$ reveal that the first undergoes two reversible, one-electron reductions and two one-electron oxidations, only the first of which is reversible. The second shows two closely spaced one-electron oxidations and an irreversible two-electron reduction while the third could only be oxidized in an irreversible, two-electron process. Electrolysis of the rhodium cluster did however form $[Rh_{12}(C)_2(CO)_{24}]^{2-}$. The reversibility of the redox processes for the first is thought to be due to the more closely-packed metal cluster which provides more basic metal sites for localization of charge (ref. 257).

If $[Rh_4(CO)_{12}]$ and di-tert-butylphosphine (Rh:P = 3:2) are refluxed in toluene, good yields of $[Rh_6(CO)_6(\mu\text{-}PBu^t_2)_4(\mu\text{-}CO)_2(\mu\text{-}H)_2]$ ([125] (Bu^t groups omitted)) are obtained but if the rhodium:phosphine ratio is 2:3 the product is $[Rh_2(CO)_2(PBu^t_2H)_2(\mu\text{-}H)(\mu\text{-}PBu^t_2)]$. The hydride ligands in [125] were not located crystallographically but are thought to be located on the Rh(3)-Rh(5) and Rh(2)-Rh(4) edges. The formation of an open cluster rather than a capped closo or capped trigonal bipyramidal species as predicted by Wade's rules is attributed to the bulk of the di-tert-butylphosphido groups (ref. 258). A kinetic study of the conversion of $[Rh_4(CO)_{12}]$ to $[Rh_6(CO)_{16}]$ in heptane indicates it proceeds by a two-path process. Each path is first order in $[Rh_4(CO)_{12}]$ and one is proposed to involve initial loss of two carbonyl ligands from the starting cluster (ref. 259). A new method of determining ^{17}O quadrupole coupling constants in carbonyl ligands which involves measuring the T_1's for the ^{13}C and ^{17}O nuclei at 6.3 and 9.4 T has been proposed and applied to $[Rh_6(CO)_{16}]$. Because of anisotropies in the



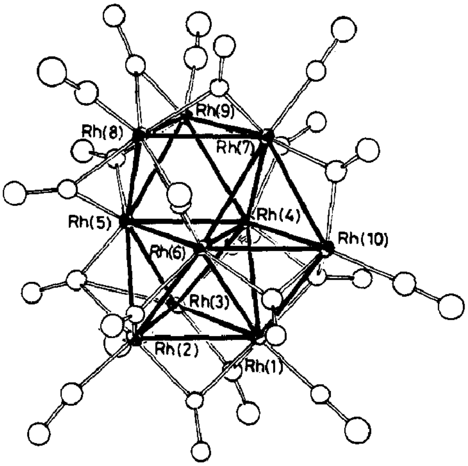
[125]

^{13}C shieldings, the T_1's decrease significantly on going to the higher field. The coupling constants determined in this manner agree well with earlier estimates (ref. 260). In refluxing methanol containing sodium hydroxide and potassium bicarbonate, $K[Rh_6(N)(CO)_{16}]$ is converted to $[Rh_{12}(H)(N)_2(CO)_{23}]^{3-}$, which was isolated as the benzyltrimethylammonium salt, among other products. The structure was determined to be [126] and



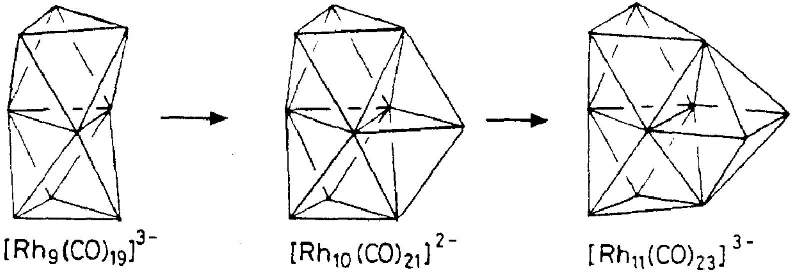
[126]

although the hydride was not located directly, consideration of the geometry of the rest of the cluster suggested it could be located on either the Rh(2), Rh(3), Rh(11) or the Rh(2), Rh(8), Rh(9) face (ref. 261). The mononuclear fragment, $[Rh(CO)_2(MeCN)_2]^+$ adds to $[Rh_9(CO)_{19}]^{3-}$ to form $[Rh_{10}(CO)_7(\mu\text{-}CO)_{12}(\mu_3\text{-}CO)_2]^{2-}$ ([127]) which is thought to be a possible



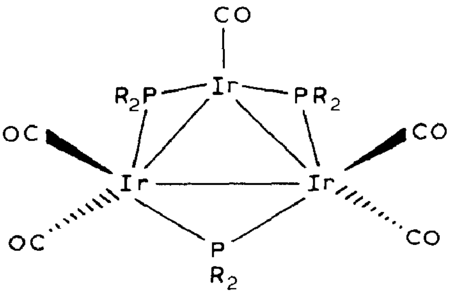
[127]

intermediate in the conversion of $[Rh_9(CO)_{19}]^{3-}$ to $[Rh_{11}(CO)_{23}]^{3-}$. Assuming this to be the case, the conversion could proceed as shown in Scheme XXXIV (ref. 262). The core of $[Rh_9(CO)_{19}]^{3-}$ can be considered as two fused trigonal antiprisms while that of the closely related $[Ni_9(CO)_{18}]^{2-}$ is a fusion of a trigonal prism with a trigonal antiprism. The difference is attributed to electronic factors and can be explained using current models for cluster bonding (ref. 263). The clusters $[Rh_{13}(CO)_{24}H_n]^{(5-n)-}$ (n = 1-4) and $[Rh_{14}(CO)_{25}H_n]^{(4-n)-}$ (n = 0, 1) have been studied by variable temperature proton, ^{13}C, ^{103}Rh, $^{1}H\{^{103}Rh\}$ and $^{13}C\{^{103}Rh\}$ NMR spectroscopy to attempt to establish migration processes for the hydride and carbonyl ligands. The metal polyhedra appear to be non-fluxional while the hydride ligands undergo migrations inside the clusters. At room temperature the first set of complexes shows complete randomization of all carbonyl ligands but in the second set only some of the carbonyl ligands are equilibrating (ref. 264).

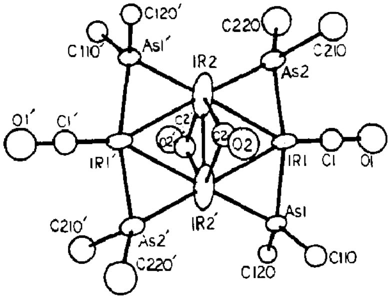


Scheme XXXIV

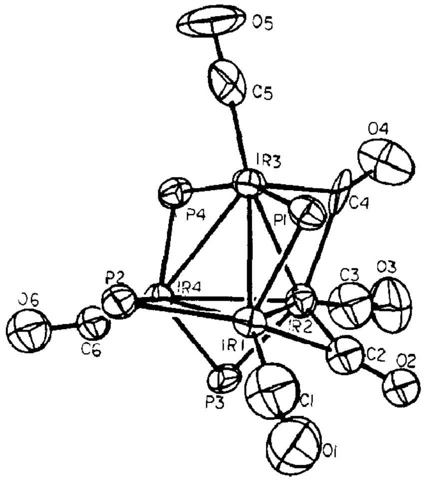
In work related to that described above for $[Rh_4(CO)_{12}]$ (see ref. 258), $[Ir_4(CO)_{12}]$ was reacted with di-*tert*-butylphosphine (Ir:P = 1:1) in refluxing toluene to afford a mixture of [128] (R = Bu^t) and $[Ir_2(CO)_2(PBu^t{}_2H)_2(\mu\text{-}H)(\mu\text{-}PBu^t{}_2)]$. Under the same conditions dicyclohexylphosphine and di-*tert*-butyl-arsine form [129] (cyclohexyl groups omitted) and [130] (α-carbons of *tert*-butyl groups only) plus $[Ir_2(CO)_4(\mu\text{-}AsBu^t{}_2)_2]$ respectively. Complex [130] is proposed to contain an iridium-iridium double bond (ref. 265). The kinetics of the reaction of $[Ir_4(CO)_{12}]$ with various



[128]



[129]

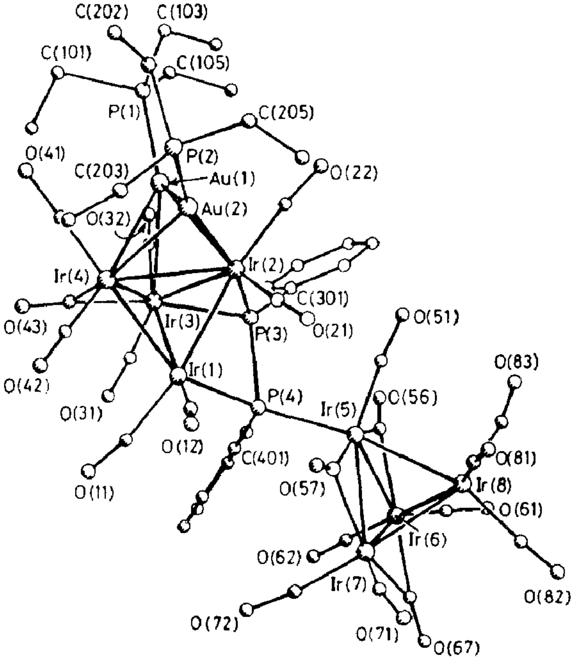


[130]

phosphorus ligands have been measured. With tri-n-butylphosphine the observed product is $[Ir_4(CO)_{10}(PBu^n{}_3)_2]$ while with tricyclohexylphosphine it is $[Ir_4(CO)_9(Pcy_3)_3]$ and no intermediates were detected. With triethylphosphite and $P(OCH_2)_3CEt$ mixtures of isomers appeared to form and in the latter case a monosubstituted species was tentatively identified. All reactions showed first order dependence on ligand concentration suggesting an associative process. Linear free energy relationships were derived which could be used to determine the intrinsic susceptibility of $[Ir_4(CO)_{12}]$ to nucleophilic attack. The high susceptibility thus determined is attributed to the strength of the iridium-phosphorus bonds which are formed and to the ability of the cluster to readily decrease the number of electrons used in cluster bonding. It is not clear however whether this latter feature involves the cleavage of a specific metal-metal bond as suggested by Darensbourg or whether it is a rearrangement of electrons in delocalized cluster orbitals (ref. 266). A water-soluble derivative of $[Ir_4(CO)_{12}]$ having the formula $[Ir_4(CO)_9L_3]$ (L = ($\underline{m}$-$NaO_3SC_6H_4)_3P$) can be prepared by direct reaction in refluxing methanol (ref. 267).

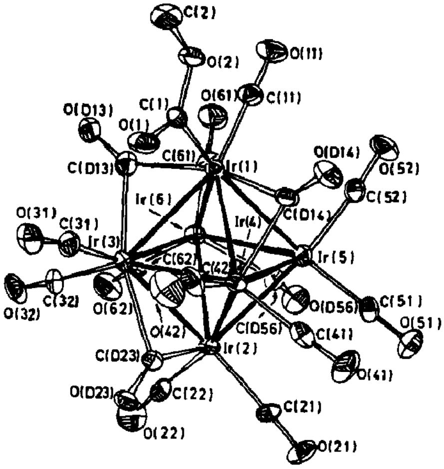
The anionic cluster $[Ir_4(CO)_{11}Br]^-$ has proven to be a useful precursor to a variety of tetrairidium clusters which are often not accessible from $[Ir_4(CO)_{12}]$. Direct reaction with phosphines at -10°C in dichloromethane forms $[Ir_4(CO)_{11}L]$ (L = PPh_3, PPh_2Me, $PPhMe_2$, $AsPh_3$). All have the ligand in the basal plane with bridging carbonyl ligands present here also. With triphenylphosphine only the axial isomer is formed while with the other two phosphines a mixture of interconverting axial and radial isomers is seen. Addition of diphosphine ligands forms $[Ir_4(CO)_{11}(L_2)]$ (L_2 = trans-vdiphos) in which the uncoordinated end can be oxidized with hydrogen peroxide, $[(OC)_{11}Ir_4(\mu\text{-}L_2)Ir_4(CO)_{11}]$ (L_2 = trans-vdiphos, DPPP, DPPB) or $[Ir_4(CO)_{10}(L_2)]$ (L_2 = DPM, DPPE, dmpe, cis-vdiphos, DPPP, DPPB, 1,2-$(Ph_2PCH_2)C_6H_4$)

(ref. 268). Abstraction of halide from $[Ir_4(CO)_{11}Br]^-$ with silver ion at -30°C in the presence of ligands also forms $[Ir_4(CO)_{11}L]$ (L = C_2H_4, cyclopropene, norbornene, 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene, NBD, PPh_2H, $PPhH_2$). The ethylene complex is formed in dichloromethane, the other olefin complexes in dimethyl ether and the phosphine complexes in THF. The olefins can be displaced by carbon monoxide and sulfur dioxide to yield $[Ir_4(CO)_{12}]$ and $[Ir_4(CO)_9(\mu\text{-}CO)_2(\mu\text{-}SO_2)]$ respectively. The NBD complex on warming forms a mixture of $[Ir_4(CO)_{12}]$ and $[Ir_4(CO)_7(\mu\text{-}CO)_3\text{-}(NBD)]$. The phosphine complexes (L = PPh_2H, $PPhH_2$) react with DBU to form $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ and an unidentified anion respectively. The former can be reversibly protonated by tetrafluoroboric acid to yield $[Ir_4(H)\text{-}(CO)_{10}(\mu\text{-}PPh_2)]$ and reacts with $[Au(L)]ClO_4$ to give $[Ir_4(AuL)(CO)_{10}\text{-}(\mu\text{-}PPh_2)]$ (L = PEt_3, PPh_3). The latter on protonation forms $[Ir_4H(CO)_{10}\text{-}(\mu\text{-}PPhH)]$ among other products but on reaction with $[Au(PEt_3)]ClO_4$ and silver perchlorate the product is $[(OC)_{11}Ir_4(\mu\text{-}PhPPPh)Ir_4(CO)_9(Au(PEt_3))]$ ([131]). The bridging moiety is considered to be a diphosphane with a phosphorus-phosphorus single bond (refs. 269, 270). Both $[Ir_4(CO)_{12}]$ and $[Ir_6(CO)_{16}]$ are converted to $[Ir_3(CO)_6(\mu_3\text{-}S)_2]^-$ on refluxing with potassium thiocyanate in THF. Intermediates in these reactions are $[Ir_4(CO)_{11}(SCN)]^-$ and $[Ir_6(CO)_{14}(SCN)]^-$ respectively. Selenium analogs of all three can be prepared similarly from potassium selenocyanate. $[Ir_4(CO)_6(\mu_3\text{-}S)_2]^-$ can be obtained in better yields from the same starting clusters and potassium



[131]

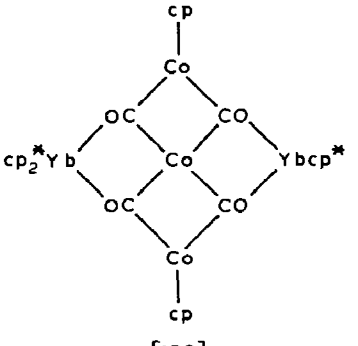
polysulfides (K_2S_x (x = 1-8)) in methanol at room temperature, from $[Ir_6(CO)_{15}]^{2-}$ and the stoichiometric quantity of sulfur or from $[IrCl_2(CO)_2]^-$ and the stoichiometric quantity of sulfide ion (ref. 271). The red form of $[Ir_6(CO)_{16}]$ is attacked by alkoxides in the corresponding alcohol under carbon monoxide with the formation of $[Ir_6(CO)_{15}(CO_2R)]^-$ (R = Me, Et) ([132] (R = Me)). Use of an excess of sodium methoxide carries the reaction further to $[Ir_6(CO)_{14}(CO_2Me)_2]^{2-}$. All three products revert to



[132]

$[Ir_6(CO)_{16}]$ on treatment with sulfuric acid or a large excess of acetic acid and although they are more stable towards moisture than their rhodium analogs, there is rapid exchange of alkoxy groups (ref. 272).

Among several relevant theoretical papers are ones on the electronic structures of $[P_n(Co(CO)_3)_{4-n}]$ (n = 1-4) (CNDO/2 method) (ref. 273) and the $\{cp^*_2Co_3(CO)_4\}^{2-}$ core of [133] (cp^* = $C_5H_4SiMe_3$). In the latter some direct

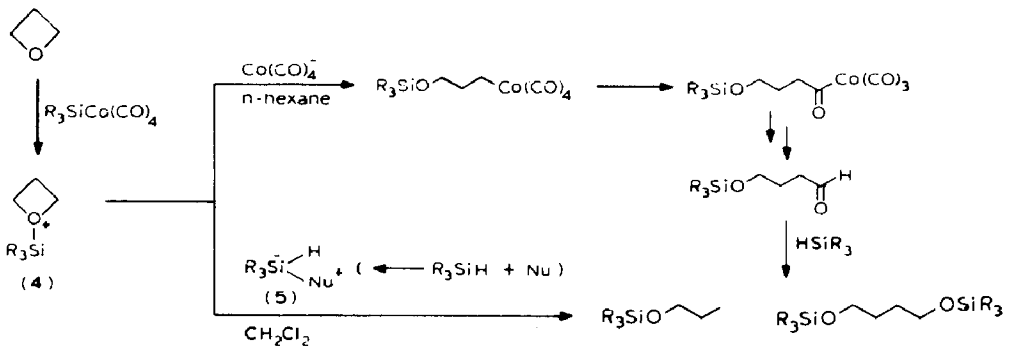


[133]

carbon-carbon interactions between the carbonyl groups is indicated and the unpaired electron is predicted to occupy a cobalt-cobalt π^* orbital (ref. 274). A molecular mechanics approach to determining preferred arrangements of the ligands in carbonyl clusters has been applied to $[Co_2(CO)_8]$ and

$[M_4(CO)_{12}]$ (M = Co, Rh, Ir) among others. The results indicate a definite correlation between high steric energy and long metal-metal bonds (ref. 275). Other papers describe the application of previously proposed topological models to anionic rhodium carbonyl clusters (ref. 276), further specific applications of another recently proposed method for determining the numbers and types of atoms in close-packed clusters (ref. 277) and a notation for unequivocally describing the spatial distribution of metal atoms and ligands in clusters (ref. 278). Finally a description is given of spectroelectrochemical techniques applied to iridium carbonyls in molten sodium tetrachloroaluminate (ref. 279).

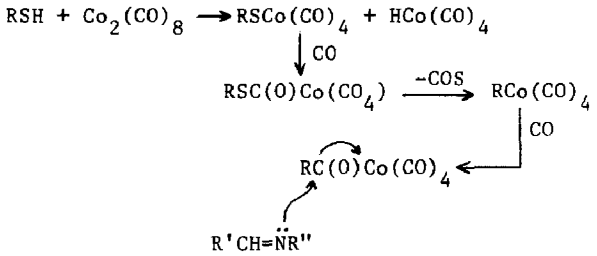
As has been the case for several years, there is a substantial number of reports on the use of cobalt-group carbonyl complexes and derivatives thereof in various catalytic applications. One of these describes the use of $Me(MeO)Si(CH_2CH_2PBu^n{}_2)_2$ and $Bu^n{}_2PCH_2CH_2CH_2P(Bu^n)(CH_2CH_2SiMe_2(OMe))$ as ligands with $[HCo(CO)_4]$ or $[Co_2(CO)_8]$ for olefin hydroformylation. The former provides a good selectivity to straight chain aldehydes (ref. 280). Successive reactions of $[Co_2(CO)_8]$ with 2-dimethylaminoethyldiphenylphosphine in benzene and methyl iodide in diethyl ether followed by metathesis with sodium hexafluorophosphate forms $[Co(CO)_3(Ph_2PCH_2CH_2NMe_3)]_2(PF_6)_2$ which can be used in a two-phase liquid system (aqueous phosphate buffer (pH 5-7)/benzene) to catalyze olefin hydroformylation. When supported on a microreticular cation exchange resin, hydroformylation activity is destroyed although both hydrogenation and isomerization of the olefin are seen. Better results were obtained using a macroreticular resin but the selectivity was poor (ref. 281). Reduction of $[CoCl_2L_2]$ (L = PPh_2H, PPh_2Me, PPh_2Et, PPh_2Pr, PPh_3, PBu_3; L_2 = DPPE) with zinc in THF under carbon monoxide forms clusters of unspecified composition which catalyze the conversion of tetradec-1-ene to pentadecanol. High activity is seen when L is PPh_3 or DPPE but the selectivity is low (ref. 282). A catalyst for the reductive carbonylation of dimethyl ether to acetaldehyde and ethanol is formed from $[Co_2(CO)_8]$, DPPE and iodine. The best solvent appears to be sulfolane and the activity is enhanced by the presence of Lewis acids (ref. 283). Dicobalt octacarbonyl is a catalyst precursor for the hydrosilylation/carbonylation of oxetan and various esters and lactones. With oxetan in dichloromethane the primary product from methyldiethylsilane is _n_-propoxymethyldiethylsilane but in hexane the sole product is 1,3-bis(methyldiethylsiloxy)butane which arises from incorporation of carbon monoxide. Scheme XXXV (R_3 = $MeEt_2$) is proposed in which the nucleophile (Nu) may be oxetan (ref. 284). With secondary alkyl acetates or the lactones of secondary alkyl esters good yields of enol silyl ethers are obtained but tertiary alkyl acetates fail to give carbonylation products unless the



Scheme XXXV

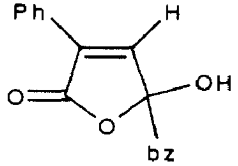
acetate moiety is situated at a bridgehead carbon (ref. 285). Aryl halides can be carbonylated to mixtures of α-keto acids and aryl carboxylic acids in alcohols in the presence of dicobalt octacarbonyl, calcium hydroxide and stoichiometric quantities of methyl iodide or dimethyl sulfate (ref. 286) while aliphatic α-keto acids can be formed from primary or secondary alkyl halides in a similar system but using sodium hydroxide (ref. 287). Reasonable yields of 2-ethylnaphthalene can be obtained from 2-vinylnaphthalene in a two-phase system consisting of benzene and aqueous tetrafluoroboric acid containing dicobalt octacarbonyl and sodium p-dodecylbenzenesulfonate (ref. 288). The rate of hydrogenation of benzylideneaniline in the presence of dicobalt octacarbonyl appears identical to the rate of formation of $[HCo(CO)_4]$ suggesting that the latter is the species which effects the hydrogenation (ref. 289). Pent-1-ene can be hydrocarboxymethylated in methanol containing dicobalt octacarbonyl and γ-picoline in a 1:1 ratio (ref. 290).

Under rather strenuous conditions (170-180°C, 850 psi) dicobalt octacarbonyl catalyzes the reaction of p-methylthiophenol, carbon monoxide and various Schiff bases (R'CH=NR" (R' = Ph; R" = Me, bz. R' = Pr^i; R" = Bu^n, Bu^t)) in benzene/water to form p-tolylC(O)NHR" and smaller amounts of p-tolylC(O)N(R")CH_2R' plus R'CH=CHR'. The initial stages of the reaction are proposed to be those of Scheme XXXVI (R = p-tolyl) (ref. 291). In related work, the $[Co_2(CO)_8]$-catalyzed conversion of benzylic thiols to thiocarboxylic acid esters in aqueous alcohol or to the corresponding hydrocarbons in benzene was found to be markedly affected by the presence of dienes. The best diene found was 2,3-dimethoxybuta-1,3-diene and although the role of the diene was not firmly established it was suggested that formation of $[(\eta^4\text{-diene})_2Co_2(CO)_2(\mu\text{-}CO)_2]$ as an active intermediate



Scheme XXXVI

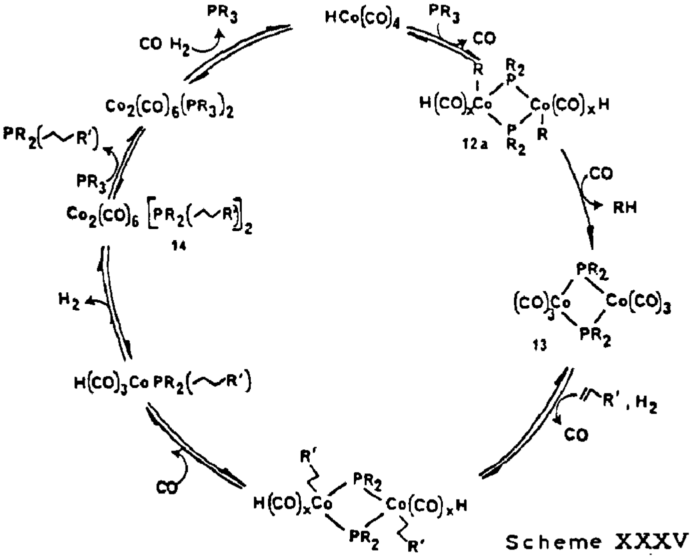
might occur since an example of this species (diene = 2,3-dimethylbuta-1,3-diene) reacted with benzenethiol to give esters of thiobenzoic acid (ref. 292). Under phase transfer conditions the system $[Co_2(CO)_8]$/CTAB/-$NaOH/H_2O/C_6H_6/CO$ catalyzes the formation of aryl carboxylic acids and aryl methyl ketones from aryl bromides and excess methyl iodide (ref. 293) while in aqueous sodium hydroxide under photolytic conditions $[Co_2(CO)_8]$ catalyzes the conversion of aryl halides to sodium aryl carboxylates. Use of sodium methoxide in methanol allows conversion of dihalobenzenes to the methyl esters of the corresponding dicarboxylic acids (refs. 294-296). Finally, TDA functions effectively as a solid/liquid phase transfer agent in the system $[Co_2(CO)_8]/NaOH/TDA/CO/C_6H_6$ for the conversion of benzyl bromide and phenylacetylene to [134] (ref. 297).



[134]

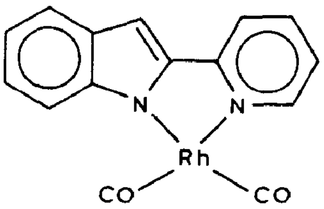
Under an atmosphere of syngas, both $[RhCl(PPh_3)_3]$ and $[Co_2(CO)_8]$ mediate a partial reduction of vanadyl porphyrins to vanadyl chlorins (ref. 298) while a mixture of $[Co_2(CO)_8]$ and $[RhH(CO)(PPh_3)_3]$ has been used in an attempt to effect the isomerization/amidocarbonylation of 3-methylbut-2-en-1-ol by acetamide to N-acetylleucine. In contrast to earlier results which indicated a good selectivity to this product, a mixture of acetylamino acids was obtained (ref. 299). Two other mixed-metal catalyst systems are those based on $[Co_2(CO)_8]$ plus $[Ru_3(CO)_{12}]$ which in alcohol solvents are much more active for the hydroformylation of cyclohexene, hex-1-ene and styrene than either carbonyl complex alone (ref. 300) and which are effective for the homologation of the alkoxy moiety of carboxylic esters if iodine is also present (ref. 301).

Under commercial hydroformylation conditions (190°C, 2000 psi) triarylphosphines undergo phosphorus-carbon bond cleavage in the presence of $[Co_2(CO)_8]$, a process which is slowed significantly when olefin is also present. The cleavage reaction is accelerated by electron-withdrawing substituents on the aryl groups and when a mixture of two different phosphines is used, significant scrambling of the aryl groups occurs at a rate which is comparable to that observed for the appearance of ligand-derived degradation products. Both radical and o-metallation processes were ruled out and Scheme XXXVII (R = Ph, R' = Bu^n) was proposed for the hex-1-ene hydroformylation system using triphenylphosphine (ref. 302). The polyphosphazine $[NP(OPh)_{1.7}(OC_6H_4PPh_2)_{0.3}]_n$ and the cyclic trimer $[N_3P_3(OPh)_5(OC_6H_4PPh_2)]$ react with $[Co_2(CO)_8]$ to form the supported species $[Co_2(CO)_7P]$, $[Co_2(CO)_6P_2]$ and $[Co(CO)_3P_2][Co(CO)_4]$ (P = pendant PPh_2 group on the phosphazine). As hydroformylation catalysts these show activities comparable to those for homogeneous $[Co_2(CO)_8]/PPh_3$ systems as well as for those formed from $[Co_2(CO)_8]$ and phosphinated polystyrene/divinylbenzene copolymers. The activity declines with time as a result of cobalt-mediated phosphorus-carbon bond cleavage (ref. 303).



Scheme XXXVIII

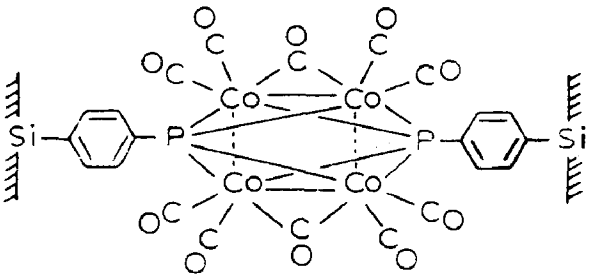
Among the applications of $[Rh_4(CO)_{12}]$ as a catalyst precursor are the arylation of methyl acrylate by various mono- and disubstituted benzenes to give isomeric mixtures of methyl cinnamates (ref. 304), the hydroformylation and hydrocarbonylation of enynes to form cyclopentenones and 2-formyl-1,3-dienes (ref. 305) and, when supported on dimethylaminomethyl-functionalized Amberlite or Amberlyst resins, the hydrogenation of α,β-unsaturated aldehydes, ketones, acids and amides. Selective hydrogenation occurred for all of these except the aldehydes which were reduced to the alcohols. The last system is considered to be more effective in these reactions than homogeneous counterparts (ref. 306). In studies of the catalysis by $[Rh_4(CO)_{12}]$ of ethylene glycol synthesis from syngas in NMP it is reported that the rate is significantly increased on raising the reaction temperature from 230°C to 300°C and at elevated temperatures a species thought to be $[RhH(CO)_3(NMP)]$ is detected by in situ infrared monitoring. The analogous species $[RhH(CO)_3(PPr^i_3)]$ is proposed from similar data on the same catalyst system to which the phosphine had been added. In this last study, the presence of bulky phosphines enhances the stability and activity of the catalyst but with phosphines of low cone angle, ligand decomposition occurs leading to the formation of inactive clusters such as $[Rh_9P(CO)_{21}]^{2-}$. While $[Ir_4(CO)_{12}]$ also serves as a catalyst precursor for the hydrogenation of carbon monoxide in NMP, it is much less active than the rhodium analog. Addition of triarylphosphines improves the reactivity and selectivity to ethylene glycol while trialkylphosphines improve the selectivity towards methanol and phosphites inhibit both reactions. In one instance, $[Ir_2(CO)_6(PPh_3)_2]$ could be isolated from the reaction mixture and it proved to be an effective catalyst precursor (refs. 307-310). Both $[Rh_4(CO)_{10}(DIOP)]$ and $[Rh_6(CO)_{10}(L_2)_3]$ (L_2 = DIOP, (S,S)-CHIRAPHOS) have been investigated as catalysts for asymmetric hydrogenation but only with the DIOP complexes is enantioselectivity observed (optical yields up to 60%). Addition of three equivalents of DIOP to $[Rh_4(CO)_{10}(DIOP)]$ forms a mixture of $[Rh_4(CO)_8(L_2)_2]$ and $[Rh_2(CO)_2(\mu\text{-}CO)_2(L_2)_2]$ (L_2 = DIOP). The latter complex adds dihydrogen to form $[RhH(CO)_2(DIOP)]$ which is thought to be the active species. All the results indicate that irrespective of the starting species, catalysis occurs with a mononuclear complex (ref. 311). Carbonylation of a mixture of allyl phosphites and various amines in the presence of $[Rh_6(CO)_{16}]$ and tetra-n-butylammonium chloride forms β,γ-unsaturated amides (ref. 312) while the same cluster under carbon monoxide catalyzes the deoxygenation of o-nitrostyrenes to indoles in moderate yields. With trans-β-(2-pyridyl)-o-nitrostyrene [135] could be isolated but it proved to be a very poor



[135]

catalyst precursor (ref. 313). Other uses of $[Rh_6(CO)_{16}]$ are as a highly active WGSR catalyst when combined with ethylenediamine, as a good catalyst for aldehyde hydrogenation when combined with TMEDA (ref. 314) and as a catalyst for the reduction of dialdehydes to the corresponding diols in aqueous ethanol or 2-methoxyethanol under carbon monoxide (ref. 315).

Interest in cobalt-group carbonyls on solid supports continued to be high. Adsorption of $[Co_2(CO)_8]$ from pentane solution onto NaX and NaY zeolites is quantitative but the amount of carbon monoxide evolved is very sensitive to reaction conditions. Species detected include $[Co(CO)_4]^-$, $[Co_4(CO)_{12}]$ and $[Co(CO)_3L_2]^+$ (L = oxygen atom of support) with the first being more favored on the NaX zeolite. On the other hand, $[Co_4(CO)_{12}]$ is incompletely adsorbed from pentane and very little carbon monoxide is evolved leading to the conclusion that $[Co_2(CO)_8]$ enters the zeolite cages but $[Co_4(CO)_{12}]$ remains on the surface outside (ref. 316). A wider range of Y-type zeolites with H^+, Ca^{2+}, La^{+3} and Na^+ as the cation has been used by a second group to support $[Co_2(CO)_8]$. In all instances formation of $[Co_4(CO)_{12}]$ within the supercages is seen and this is proposed to be hydrogen bonded to hydroxyl groups on the inner surface of the cavity through the oxygen atoms of the bridging carbonyl groups. On heating decomposition occurs to give only cobalt(II) for the first support but with the second and third systems tentative evidence for the formation of formate and/or carbonate was obtained (ref. 317). Both $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ adsorb on Al_2O_3, SiO_2, TiO_2 and MgO to give similar coordinatively unsaturated carbonyl species on the surface which are active catalysts for olefin hydrogenation but in order to catalyze benzene hydrogenation it is necessary to completely decarbonylate the surface cobalt atoms. Because of the greater basicity of magnesium oxide as compared with the others, the thermal decarbonylation of the species initially formed on this support is more reversible. These also react with syngas to form methane but not higher hydrocarbons (refs. 318, 319). The decarbonylation of $[Co_2(CO)_6(PBu^n{}_3)_2]$ on ZrO_2 and $Zr(OH)_4$ surfaces occurs only partially at temperatures below 300°C (ref. 320) while the silica-supported cluster [136] is thermally more stable and more active for hex-1-ene hydroformylation than its unsupported counterpart (ref. 321).

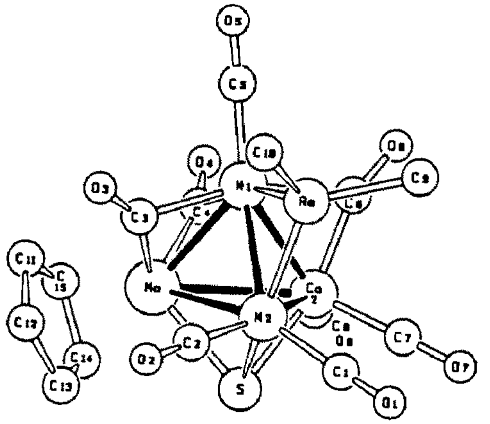


[136]

Decarbonylation of $[Rh_4(CO)_{12}]$ on Al_2O_3, ZrO_2 and TiO_2 supports gives a higher dispersion of rhodium and a stronger interaction with the support than when the rhodium is introduced as Rh(III). Only the cluster-derived rhodium is able to fix dioxygen and the species formed initially is thought to be a Rh(III) superoxide (refs. 322, 323). On La_2O_3 $[Rh_4(CO)_{12}]$ initially forms species resembling $[Rh_6(CO)_{16}]$ but on heating these form dispersed $\{Rh(CO)_2\}$ moieties which are considered to be the active species for carbon monoxide hydrogenation (ref. 324). A variety of rhodium and iridium salts when impregnated into zeolite supports form $[Rh_6(CO)_{16}]$ and $[Ir_4(CO)_{12}]$ respectively when treated with syngas or a mixture of carbon monoxide and water vapor. These appear to resist further aggregation and maintain their structural integrity over a wide temperature range (ref. 325). A second group however reports that Rh(III)-impregnated Y-type zeolites initially from two different types of $\{Rh^I(CO)_2\}$ moieties on carbonylation and reversible formation of $\{Rh^I(CO)_3\}$ species is seen whose formation constants depend on the valence of the cations present. When treated with syngas these do condense to form $[Rh_4(CO)_{12}]$ and then $[Rh_6(CO)_{16}]$ within the cages. Analogous behavior was noted for iridium-impregnated zeolites. The cage-enclosed rhodium clusters catalyze olefin hydroformylation and on treatment with dihydrogen at 120°C decarbonylation occurs to give a catalyst which displays shape selectivity for olefin hydrogenation (refs. 326-330). An EXAFS study of $[Rh_6(CO)_{16}]$ supported on alumina suggests retention of the cluster structure but on treatment with moist dioxygen most degrade to surface-bound $\{Rh^I(CO)_2\}$ moieties. The cluster can be completely regenerated however on reaction with carbon monoxide plus water vapor (ref. 331). TPD studies of $[Rh_4(CO)_{12}]$ in flowing dihydrogen show initial formation of $[Rh_6(CO)_{16}]$ rather than $[Rh_4(CO)_9]$ as previously proposed. The clusters $[Co_{4-n}Rh_n(CO)_{12}]$ (n = 0-2) were also studied. Most of the carbonyl groups were lost as carbon monoxide but some conversion to methane was detected (ref. 332).

b) Heteronuclear Metal-Metal Bonded Compounds

The Vahrenkamp group remains active in the synthesis of clusters containing several different metal atoms. The complexes [137] (M_1 = Co; M_2 = Fe (major isomer). M_1 = Fe; M_2 = Co (minor isomer)) and [138] (two isomers as for [137]) together with their tungsten analogs have been fully characterized and all isomeric mixtures separated. No isomerization of these occurs in solution under "clean" conditions but with the onset of decomposition at elevated temperature this does occur. Reaction of [138] and its tungsten analog with carbon monoxide gives [139] (M = Mo, W) and then [140] plus $[cpM(CO)_3AsMe_2]$ (M = Mo, W) however under the same conditions [137]



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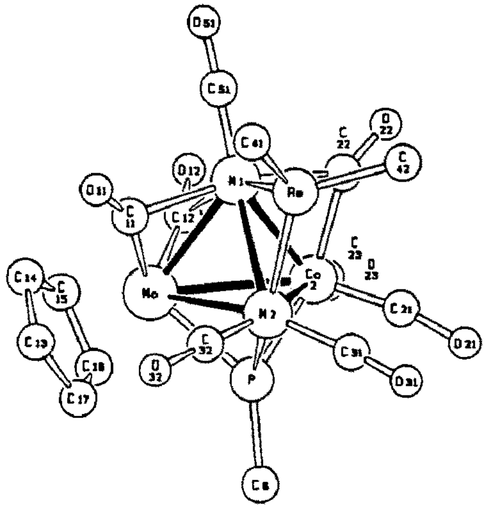
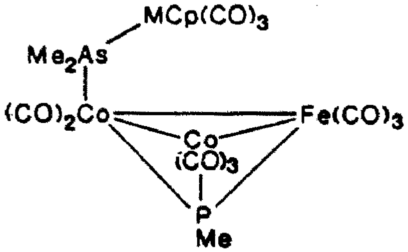


[138]

and its tungsten analog yield [141] (ref. 333). Replacement of a $\{Co(CO)_3\}$ vertex in [142] occurs on reaction with $Na[cpW(CO)_3]$ in THF to form [143]



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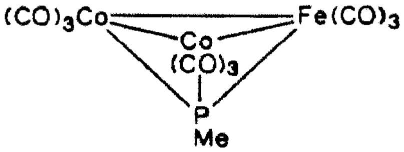

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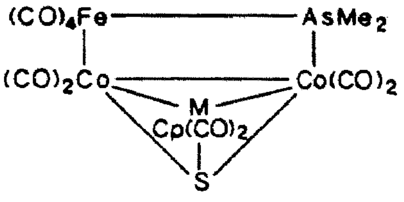

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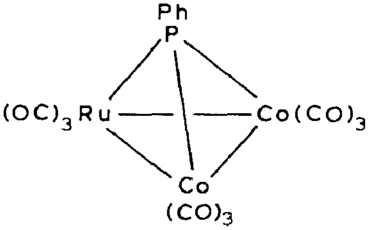

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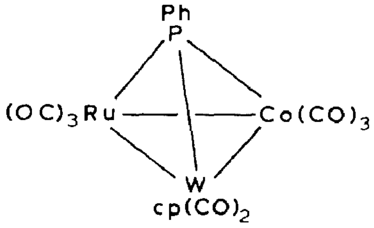
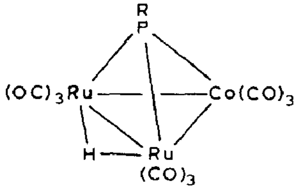


[143]

while $[Ru_3(CO)_{12}]$ and $[(OC)_4\overline{Fe(\mu\text{-}PRH)Co}(CO)_3]$ (R = Me, Bu^t) in refluxing hexane yield a mixture of [144] and [145] (R = Me) or [144] - [148] (R = Bu^t). Reaction of [148] (R = Me) with $[Ru(CO)_5]$ is incomplete but some



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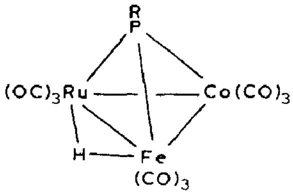

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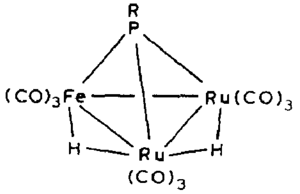

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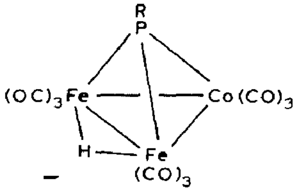

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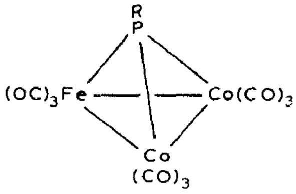
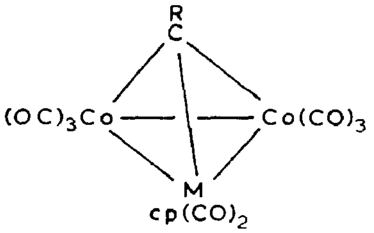
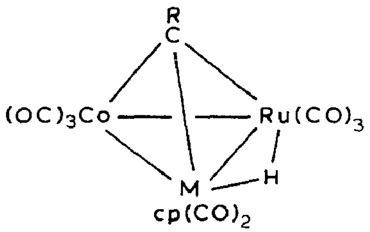


[148]

conversion to [144] and [145] (R = Me) occurs. Better yields of these are obtained using $[Ru(CO)_4]^{2-}$ but when R = Bu^t this latter route gives only a 50% yield of [144] (R = Bu^t). With $[Ru_3(CO)_{12}]$, [148] (R = Ph) gives both [144] and [145] (R = Ph) while [149] (R = Me; M = Mo, W) and $[Ru(CO)_4]^{2-}$ form [150] (R = Me; M = Mo, W) (ref. 334). Metal exchange reactions also



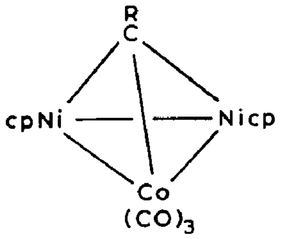
[149]



[150]

occur in $[RCCo_3(CO)_9]$ (R = Me, Ph, CO_2Me, CO_2Ph, C(O)Ph) on reaction with

$[cpNiCo]_2$ and $[cpM(CO)_3]_2$ (M = Mo, W) to yield [151] (R = Me, CO_2Me) and [152] (R = Me; M = Mo, W. R = Ph, CO_2Me, C(O)Ph; M = W). In some



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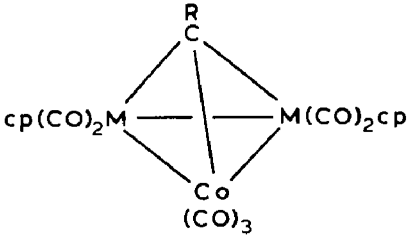
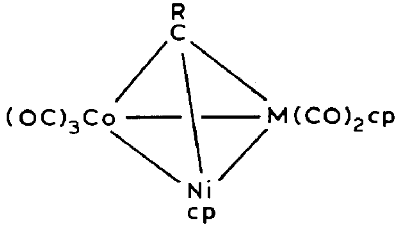


[152]

instances previously reported monosubstituted clusters were also obtained as were $[MeO_2CCNi_3cp_3]$ and $[RCMo_3(CO)_6cp_3]$ (R = Me, Ph, CO_2Me). Another complication in some instances was transfer of cyclopentadienyl groups to cobalt (ref. 335). In a related study, [149] (M = Mo, R = Me, Ph, CO_2Me, CO_2Ph, C(O)Ph. M = W; R = Me, Ph, CO_2Ph) reacts with $[cpNi(CO)]_2$ to give [153] and in certain instances with $[Fe(CO)_4]^{2-}$ to form [154] (R = Me; M =



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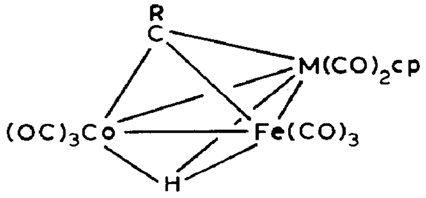
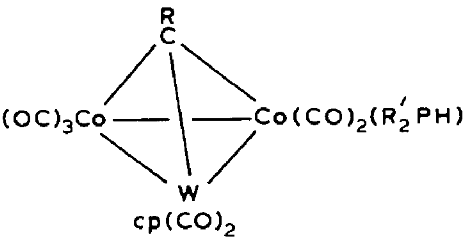
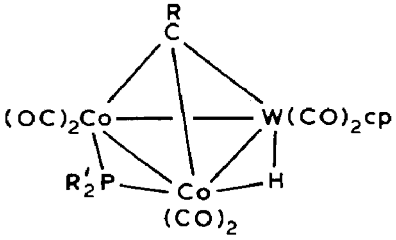


[154]

Mo, W. R = Ph; M = Mo). In some of these systems pure enantiomers of these optically active clusters could be obtained (ref. 336). Other workers have found that [153] (R = p-tolyl; M = W) reacts with secondary phosphines to form [155] (R = p-tolyl; R' = Et, Ph) which on refluxing in dichloromethane converts to [156]. Reaction with further phosphine at

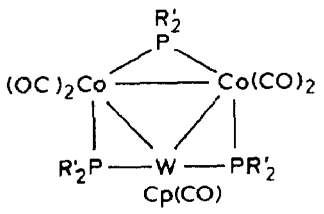


[155]



[156]

reflux yields [157] (R' = Et, Ph) while with acetylenes the product is [158] (R = p-tolyl; R' = Ph; R" = Me, Et) which converts to [159] (R = p-tolyl; R" = Me, Et; X = OH, OMe) on treatment with tetrafluoroboric acid etherate or with trimethyloxonium tetrafluoroborate respectively (ref.



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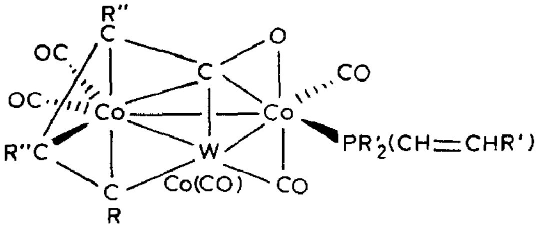

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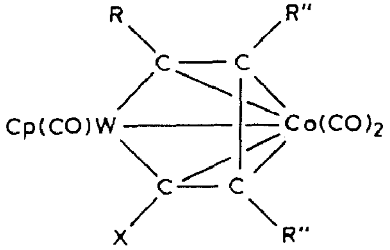
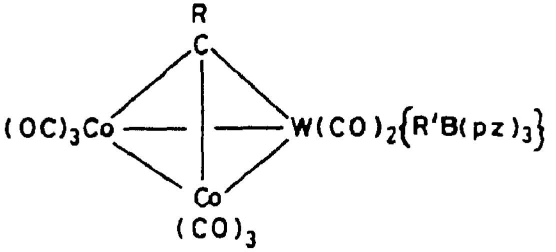


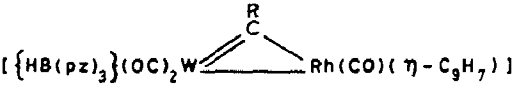
[159]

337). The carbyne complexes $[(R'B(pz)_3)W(\equiv CR)(CO)_4]$ (R = Me, *p*-tolyl; R' = H. R = *p*-tolyl; R' = pz) prepared from $[W(\equiv CR)(CO)_4Br]$ and the appropriate polypyrazolylborate react with $[Co_2(CO)_8]$ to form [160] (R = Me, *p*-tolyl;

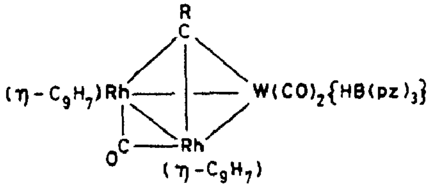


[160]

R' = H. R = *p*-tolyl; R' = pz) and with $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ (R' = H) to give a mixture of [161] and [162] when R = *p*-tolyl and only the latter when R = Me. In [162] the carbonyl groups on tungsten appear to be semi-bridging

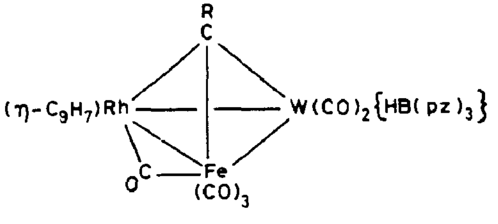


[161]

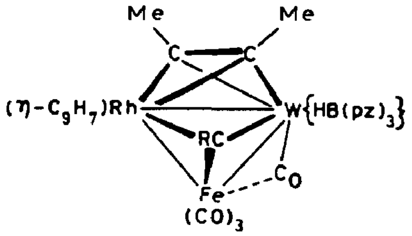


[162]

towards the rhodium atoms. The analog of [161] with an $\{Fe(CO)_3\}$ moiety in place of the $\{Rh(CO)(\eta^5\text{-}C_9H_7)\}$ unit reacts with $[(\eta^5\text{-}C_9H_7)Rh(CO)_2]$ in diethyl ether to yield [163] (R = Me, p-tolyl) which reacts further with but-2-yne in refluxing toluene with the formation of [164] (R = Me, p-tolyl). In general these polypyrazolylborate complexes appear to be more reactive than their cyclopentadienyl analogs (ref. 338). Transfer of the carbyne fragment from tungsten in $[(OC)_4CoW(\equiv CR)(CO)_4]$ (R = p-tolyl) occurs on reaction with $[Fe_2(CO)_9]$ and the products are [165] (L = CO), $[W(CO)_6]$, $[Fe(CO)_5]$ and $[Fe_3(CO)_{12}]$. The analog with L = PPh_3 is formed by reaction with this ligand while with one and two equivalents of DPM the products are [166] and [167] respectively. Protonation of [167] with tetrafluoroboric acid etherate is thought to occur across a cobalt-iron bond (ref. 339). Addition of a mixture of propionic anhydride and hexafluorophosphoric acid to [149] ($R = CO_2Pr^i$) generates the acylium ion ($R = C(O)^+$) which reacts with a variety of nucleophiles to produce other derivatives of [149] (R = $C(O)NEt_2$, $C(O)C_6H_4NMe_2$, CO_2R' (R' = alkyl)) (ref. 340).



[163]



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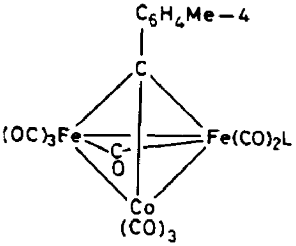
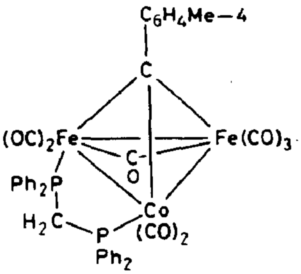
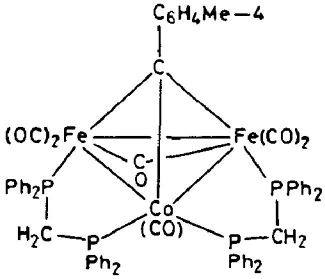


[165]

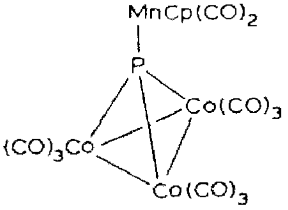


[166]

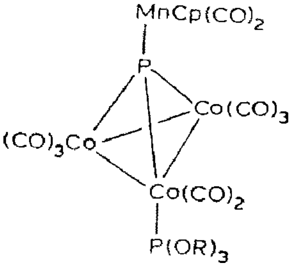


[167]

In THF, $[Mn(CO)_4(PPh_2)]^{2-}$ displaces iodide from $[cpCo(CO)I_2]$ with the formation of $[cp(CO)\overline{Co(\mu\text{-}PPh_2)Mn}(CO)_4]$ (ref. 341). Among the products of the reaction of $[Co_2(CO)_8]$ with $[cpMn(CO)_2(PBr_3)]$ is [168] which reacts with phosphites to form mixtures of [169] (R = Pr^i), [170] (R = Me, Pr^i, Ph) and [171] (R = Me, Ph). With phosphines however only the monosubstituted species are formed. Addition of $Na[Co(CO)_4]$ to $[(cpMe)Mn(CO)_2\text{-}(PPhBr_2)]$ yields a mixture of $[(cpMe)(CO)_2\overline{Mn(\mu\text{-}PPhH)Co}(CO)_3]$, $[Co_4(CO)_8\text{-}(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ and other unidentified species while the same reaction with $[L_nM(PR_2Cl)]$ forms $[L_n\overline{M(\mu\text{-}PR_2)Co}(CO)_3]$ (R = Pr^i; L_nM = $cpMn(CO)_2$. R = Ph; L_nM = $(cpMe)Mn(CO)_2$). Low yields of [172] and [173] can be obtained together with a variety of other species from the reaction of $[((OC)_5Cr)_2\text{-}AsCl]$ and one or three equivalents of $Na[Co(CO)_4]$ respectively (ref. 342). The heterometallic ketenylidene complex [174] can be prepared together with $[Mn(CO)_5Br]$ and cobalt(II) bromide from the reaction of $[Mn(CO)_5(CBr_3)]$ and



[168]



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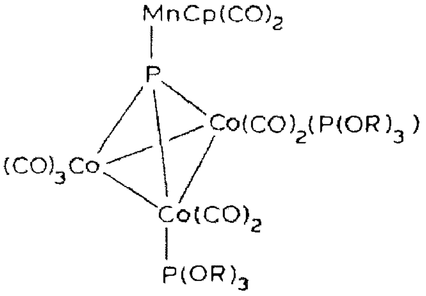
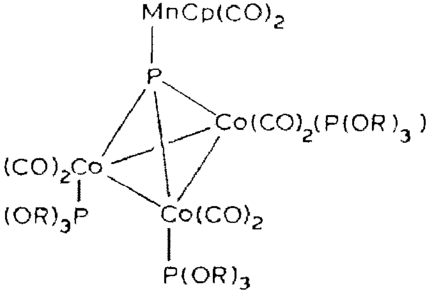


[170]



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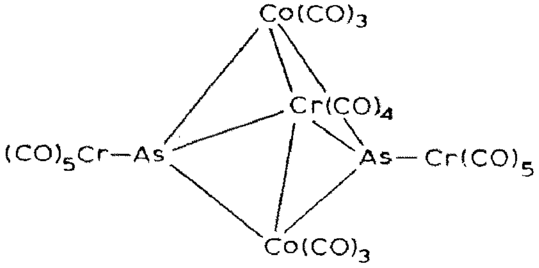

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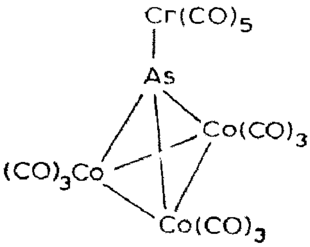

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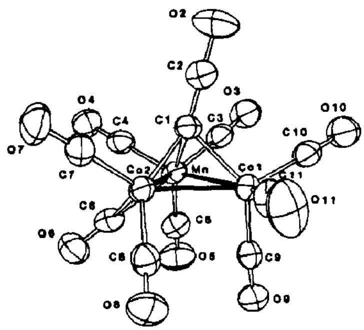
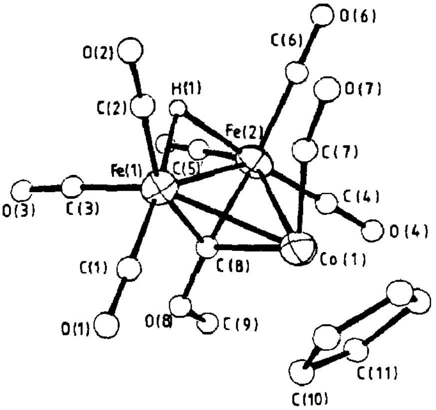


[174]

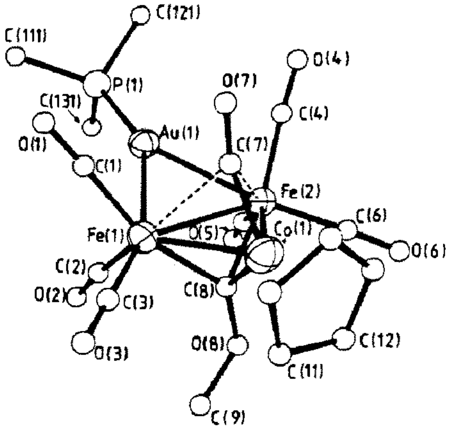
1.7 equivalents of PPN[$Co(CO)_4$] at -78°C in THF. It is thought that [$(OC)_5MnCCo_3(CO)_9$] forms initially and is subsequently reduced by [$Co(CO)_4$]$^-$. The reaction is, however, quite dependent on the halide in the starting manganese complex, the solvent and the counterion for [$Co(CO)_4$]$^-$. Protonation of [174] with triflic acid forms [$MnCo_2(CO)_{10}(\mu_3$-CH)] (ref. 343).

Replacement of one iron vertex in [$Fe_3(CO)_{10}(\mu$-H)(μ-COMe)] occurs on reaction with [$cpCo(CO)_2$] and [175] is obtained in which the bridging



[175]

hydride can be replaced by a {$AuPPh_3$} moiety when [Au(Me)(PPh_3)] is added to give [176] (α-carbons of phenyl groups shown only). In [175] the distance from the cobalt to the triply-bridging carbon atom is longer than the corresponding iron-carbon distance in the parent triiron compound while in [176] the μ_3-COMe group is more symmetrically attached. Also in [175] the carbonyl ligand on cobalt is thought to have a weak semi-bridging interaction with the iron atoms while in [176] this interaction is noticeably stronger (ref. 344). Another example of vertex replacement occurs when [$Bi_2Fe_3(CO)_9$] reacts with [$Co(CO)_4$]$^-$ in THF and [177] is the product (ref. 345). Further work on germanium-cobalt clusters has appeared this year. Reaction of [Ge_3H_8] with four moles of [$Co_2(CO)_8$] yields a mixture



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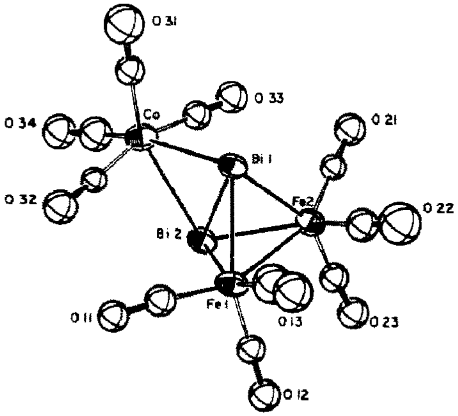
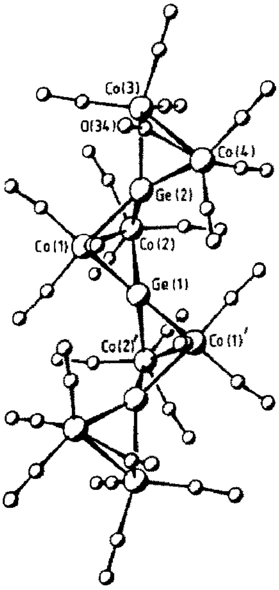


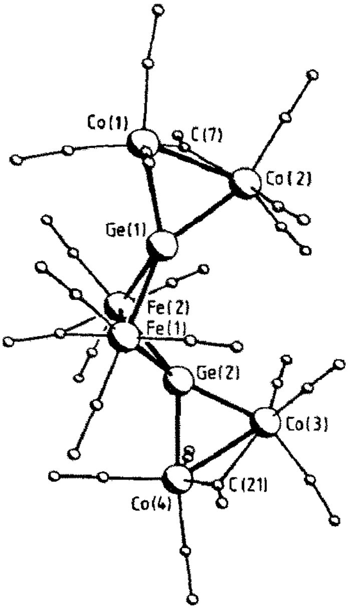
[177]

of the previously reported clusters $[Ge(Co_2(CO)_7)_2]$, $[Ge_2Co_6(CO)_{20}]$ and the new complex $[Ge_3Co_8(CO)_{26}]$ ([178]). Although mixtures of these three clusters can be obtained in this manner from all accessible germanes, the



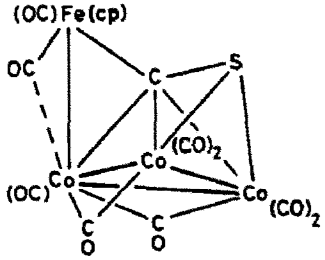
[178]

one just mentioned gives the cleanest route to [178]. Also explored was the reaction of $[Fe(CO)_4GeH_2]_2$ with two moles of $[Co_2(CO)_8]$ which ultimately formed [179] *via* an intermediate of unknown composition (ref. 346).



[179]

Addition of $[Co_2(CO)_8]$ to $[cp(CO)_2Fe(\mu\text{-}C(S)S)Fe(CO)_2cp]$ forms the known complexes $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)_2]$ and $[cp(CO)Fe(\mu\text{-}CO)_2Co(CO)_3]$ plus the new complex [180] in which the thiocarbonyl moiety is considered to function as a six-electron donor (ref. 347). Carbonylation of benzene solutions of nitrobenzene containing $[M_3(CO)_{12}]$ (M = Fe, Ru) at reflux forms



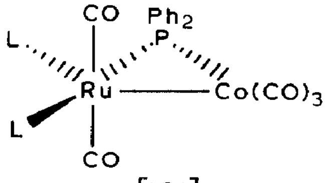
[180]

iron oxides or $[Ru_3(CO)_{10}(NPh)]$ plus $[Ru_3(CO)_9(NPh)_2]$ respectively. However if $[Co_2(CO)_8]$ is also present, the products are $[Fe_3(CO)_9(NPh)_2]$ plus $[FeCo_2(CO)_9(NPh)]$ or $[(\eta^6\text{-}C_6H_6)Ru_3(CO)_7(\mu_3\text{-}NPh)]$ plus $[Ru_3(CO)_9(NPh)_2]$ and $[(\eta^6\text{-}C_6H_6)Co_4(CO)_9]$ respectively (ref. 348). In a mixture of THF and methanol, $[Ni(COD)_2]$ reacts with $Et_4N[Fe_4M(C)(CO)_{14}]$ (M = Co, Rh) to form

$Et_4N[Fe_4MNi(C)(CO)_{15}]$. The same product together with $Et_4N[Fe_3M_3(C)(CO)_{15}]$ is formed if the original complex is reacted with nickel(II) chloride (ref. 349).

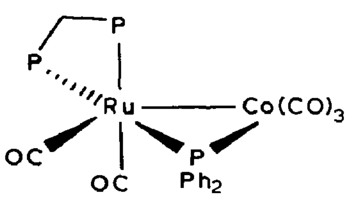
The clusters $[FeCo_3(CO)_{12}]^-$, $[Fe_3Co(CO)_{13}]^-$, $[FeCo(CO)_8]^-$ and $[HFeCo_3(CO)_{12}]$ as well as $[Co(CO)_4]^-$ and $[Co_2(CO)_8]$ have been used as sources for metal catalysts supported on high surface area carbon. Those derived from $[Co_2(CO)_8]$ give only paraffins in Fischer-Tropsch applications and seem fairly active but those derived from the heterometallic clusters are less active and also produce some olefins (ref. 350). Adsorption of $[HFeCo_3(CO)_{12}]$ on partially hydroxylated magnesium oxide from dichloromethane solution rapidly forms supported $[FeCo_3(CO)_{12}]^-$ clusters which decompose above 50°C. Some $[Co(CO)_4]^-$ also forms. Treatment of the system with dihydrogen at 400°C forms small bimetallic particles with the same composition as the original cluster (refs. 351, 352).

Reaction of $[(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3]$ with one or two equivalents of monodentate phosphines in refluxing THF forms $[L(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_3]$ (L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, $Ph_2PC{\equiv}CR$ (R = Bu^t, Ph)) or $[L_2(OC)_2Ru(\mu\text{-}PPh_2)Co(CO)_3]$ (L = PPh_2Me, $PPhMe_2$, PPh_2H, $Ph_2PC{\equiv}CR$ (R = Bu^t, Ph)) respectively although particularly in the second reaction both mono- and disubstituted products form. These are easily separated. In the monosubstituted products, two isomers are seen in which the phosphine ligand is either <u>cis</u> or <u>trans</u> to the bridging phosphide while in the disubstituted complexes all four possible isomers are found. The same reaction with excess trimethylphosphite at 45°C forms a mixture of both isomers of $[L(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_3]$ (L = $P(OMe)_3$) plus the diequatorial isomer of $[L_2(OC)_2Ru(\mu\text{-}PPh_2)Co(CO)_3]$ while at reflux [181] (L = $P(OMe)_3$) is the

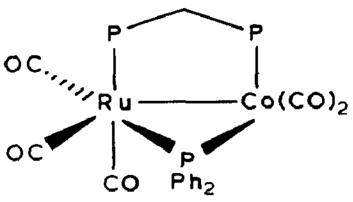


[181]

product. At 45°C in THF $[(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3]$ reacts with DPM to yield [182] while at reflux the product is [183]. Conversion of [182] to [183] occurs at reflux in the presence of DPM but does not occur under these conditions if free ligand is absent (refs. 353-355). Addition of $PPN[Co(CO)_4]$ to $[M_3(CO)_{10}(MeCN)_2]$ in THF forms $PPN[M_3Co(CO)_{13}]$ (M = Ru, Os) which can be protonated by sulfuric acid in dichloromethane to yield $[HM_3Co(CO)_{13}]$ (ref. 356). Other capping reactions reported involve the addition

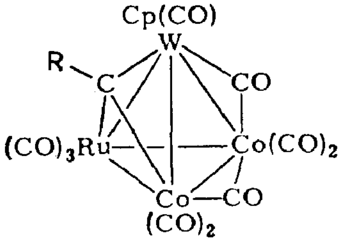


[182]



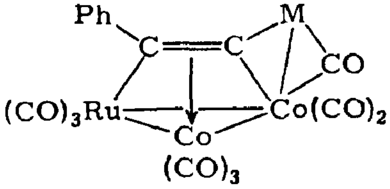
[183]

of $[Co(CO)_4]^-$, primary phosphines, methyl arsine, thiols or elemental sulfur and diphenyl diselenide to $[RuCo_2(CO)_{11}]$ which form $[RuCo_2(CO)_{12}]^-$, $[RuCo_3(CO)_9(\mu_3\text{-PR})]$ (R = Me, Ph, p-tolyl), $[RuCo_2(CO)_9(\mu_3\text{-AsMe})]$, $[RuCo_2(CO)_9(\mu_3\text{-S})]$ and $[RuCo_2(CO)_9(\mu_3\text{-Se})]$ respectively. The same complex with $[cpW(\equiv CR)(CO)_2]$ (R = p-tolyl) yields [184] while with $[L_nMC\equiv CPh]$ (L_nM =

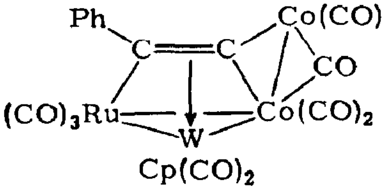


[184]

$cpFe(CO)_2$, $cpRu(CO)_2$, $cpW(CO)_3$) the products are [185] (M = Fe, Ru) and [186] (ref. 357). Addition of one fourth mol of $[CuCl(PPh_3)]_4$ to $K[MCo_3(CO)_{12}]$ in toluene yields [187] (M = Fe, Ru) which reacts with triphenylphosphine to form $[Cu(PPh_3)_2][MCo_3(CO)_{12}]$ among other products. With

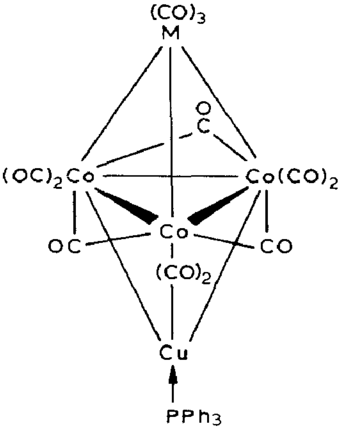


[185]

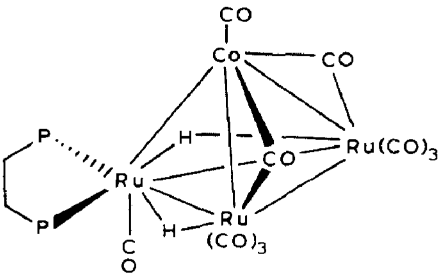


[186]

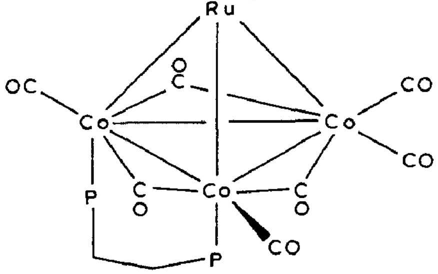
triphenylarsine, [187] (M = Fe) forms a mixture of [187] (M = Fe) in which the triphenylphosphine on copper has been replaced by the arsine and $[Cu(AsPh_3)_2][FeCo_3(CO)_{12}]$. EHMO calculations on some of the clusters were also performed (ref. 358). Substitution of DPPE into $[H_3Ru_3Co(CO)_{12}]$ and $[HRuCo_3(CO)_{12}]$ occurs in THF in the presence of catalytic amounts of BPK with the formation of [188] and [189] respectively while the latter with trimethylamine N-oxide, triethylamine or triphenylphosphine in the absence of BPK forms $[HRuCo_3(CO)_{11}(L)]$ (L = Me_3N, Et_3N, PPh_3). TMEDA under analogous conditions yields $[HRuCo_3(CO)_{10}(TMEDA)]$. The ^{59}Co NMR spectra of the



[187]



[188]

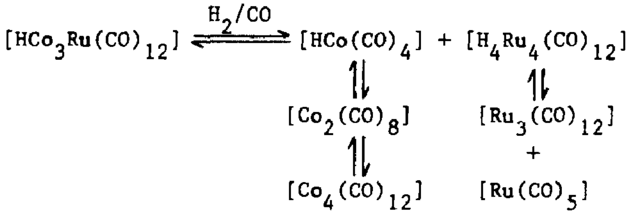


[189]

products indicate substitution at ruthenium for the amine ligands but the phosphine ligand appears to be bound to cobalt. In all instances the hydride ligand is presumed to be coordinated in a μ_3-fashion to the tri-cobalt face (refs. 359, 360). Reversible cluster formation and degradation processes have been studied by high pressure infrared studies. From these, thermodynamic quantities associated with the equilibria of Scheme XXXVIII

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

$$[M_4(CO_{12}] + 4CO \rightleftharpoons 2[M_2(CO)_8] \quad (M = Co, Rh)$$

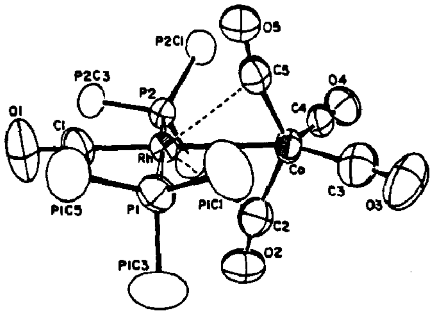


$$\begin{array}{ccccc} [HCo_3Ru(CO)_{12}] & \overset{H_2/CO}{\rightleftharpoons} & [HCo(CO)_4] & + & [H_4Ru_4(CO)_{12}] \\ & & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\ & & [Co_2(CO)_8] & & [Ru_3(CO)_{12}] \\ & & \upharpoonleft\downharpoonright & & + \\ & & [Co_4(CO)_{12}] & & [Ru(CO)_5] \end{array}$$

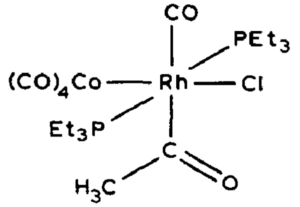
Scheme XXXVIII

have been determined. Also formed in the third system are traces of $[H_3CoRu_3(CO)_{12}]$ and $[H_2Co_2Ru_2(CO)_{12}]$ (ref. 361).

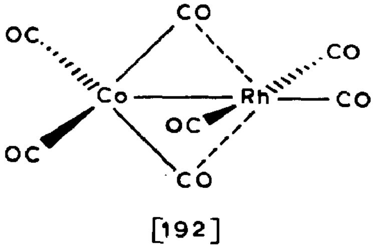
Full details of the preparation of trans-$[Rh(CO)(Co(CO)_4)L_2]$ (L = PEt_3) and its chemistry have now appeared. The structure is [190] (α-carbons of ethyl groups shown only) and the rhodium-cobalt distance is interpreted as indicating the presence of a Co(-1)→Rh(I) single bond. Addition of chloride ion regenerates $[RhCl(CO)(PEt_3)_2]$ plus $[Co(CO)_4]^-$ while with DMA•HCl, $[HCo(CO)_4]$ and the same rhodium complex form. No reaction occurs between [190] and phenyl- or diphenylacetylene but with DMAD an adduct tentatively identified as $[Rh(CO)(DMAD)L_2][Co(CO)_4]$ can be isolated. A very rapid equilibration between [190] and $[Rh(CO)(MeCN)L_2]^+$ plus $[Co(CO)_4]^-$ corresponding to ca 13,000 turnovers per second occurs when [190] is dissolved in acetonitrile. It also reacts with acetyl chloride to form [191] but is unreactive towards dihydrogen (ref. 362). The related species $[(OC)_3RhCo(CO)_4]$ which is now thought to have the structure [192]



[190]



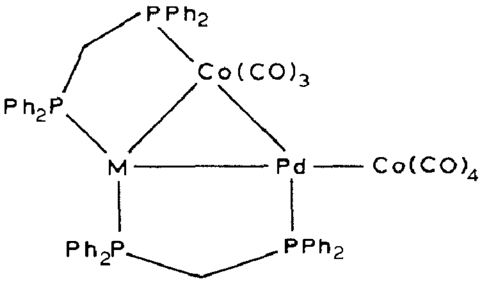
[191]



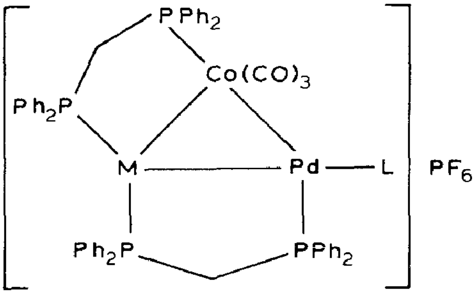
[192]

rather than the unabridged one proposed earlier (J. Organometal. Chem., 213 (1981) 303) can be prepared from $[Co(CO)_4]^-$ and $[RhCl(CO)_2]_2$ under carbon monoxide at -78°C. It is reversibly converted to $[Co_2Rh_2(CO)_{12}]$ under 2.5 atm of carbon monoxide at 0°C, to $[CoRh(CO)_8]$ under 13 atm of carbon monoxide at the same temperature and at room temperature to $[Co_2(CO)_8]$ plus $[Rh_4(CO)_{12}]$ (ref. 363). Addition of four mols of triethylphosphine to $[Co_2Rh_2(CO)_{12}]$ forms the previously characterized derivative of [192], $[CoRh(CO)_5(PEt_3)_2]$ while with one or two equivalents of this ligand the substituted tetrahedral clusters $[Co_2Rh_2(CO)_{9-n}(\mu\text{-}CO)_3L_n]$ (n = 1,2; L = PEt_3) are formed in which the phosphine occupies an axial or axial plus radial sites on the rhodium atoms. Both are fluxional with no indication of site selectivity in the rearrangements of the carbonyl ligands. The monosubstituted complex is partially and reversibly converted to [192] and its derivative $[CoRh(CO)_6(PEt_3)]$ by carbon monoxide while the disubstituted cluster gives only the latter which in this instance only slowly reconverts to the cluster. Further reaction of $[CoRh(CO)_6(PEt_3)]$ with carbon monoxide forms $[CoRh(CO)_7(PEt_3)]$ which is thought to have a structure analogous to that of $[Co_2(CO)_7(PEt_3)]$. The fragmentation of $[Co_2Rh_2(CO)_{12}]$ on reaction with triethylphosphine contrasts with simple substitution by trimethylphosphite (J. Organometal. Chem., 186(1980)101) and is attributed to the higher basicity of the phosphine ligand (ref. 364). The products of reaction of $[Rh_xCo_{4-x}(CO)_{12}]$ (x = 0-2, 4) with tertiary amines or resins functionalized with tertiary amine groups are catalysts for the hydroformylation of dicyclopentadiene. The results of a detailed study of the systems indicate the formation after several hours of operation of a common active species regardless of the composition of the cluster added initially (ref. 365).

Displacement of $[Co(CO)_4]^-$ from [193] (M = Pd, Pt) can be effected by phosphines in the presence of hexafluorophosphate ion to form [194] (M = Pd; L = $PPhMe_2$. M = Pt; L = PPh_3). These four complexes plus the analog



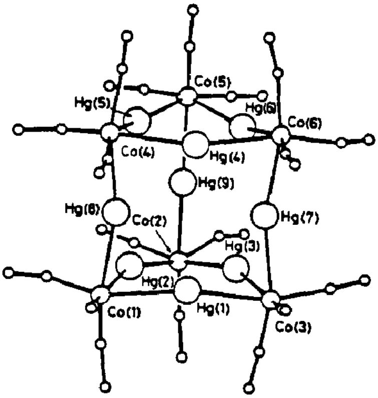
[193]



[194]

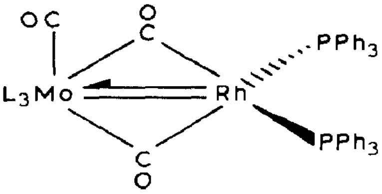
of [193] with iodide in place of the $\{Co(CO)_4\}$ moiety were studied electrochemically. The neutral complexes decompose in dichloroethane while in

DMSO the iodide and $[Co(CO)_4]^-$ ions dissociate. All complexes show several irreversible oxidation processes while those with M = Pd show two reversible one-electron reduction steps and when M = Pt a single reversible two-electron reduction could be observed (ref. 366). Declusterification of [195] occurs on reaction with nine equivalents of mercury(II) halides in THF with the formation of fac-$[Co(CO)_3(HgX)_3]$ (X = Cl, I, CF_3CO_2) from which a virtually quantitative reassemblage of the parent cluster can be achieved by treatment with triphenylphosphine. Reaction of fac-$[Co(CO)_3(HgI)_3]$ with tetrabutylammonium iodide, phenyllithium or silver p-toluenesulfonate yields $Bu_4N[CoI(CO)_3(HgI)_3]$, $[Co(CO)_3(HgPh)_3]$ and $[Co(CO)_3(HgOS(O)_2$-p-tolyl$)_3]$ respectively (ref. 367). Toluene solutions of $Hg[Co(CO)_4]_2$ and $Hg[Pt(C_6Cl_5)(PPh_3)_2]$ form the linear trimetallic complex $[(OC)_4CoHgPt(C_6Cl_5)(PPh_3)_2]$ (ref. 368) while the former with rare earth metal amalgams in a 3:2 ratio in THF form $M[Co(CO)_4]_3 \cdot nTHF$ (M = Sm, La, Eu, Tm, Yb; n = 4-5). Reduction of some of these with the corresponding rare earth metal or with sodium naphthalenide in THF forms $M[Co(CO)_4]_2 \cdot nTHF$ (M = Sm, Yb; n = 4-5). These can also be prepared from $[Co_2(CO)_8]$ and an excess of the appropriate metal amalgam (refs. 369-371).



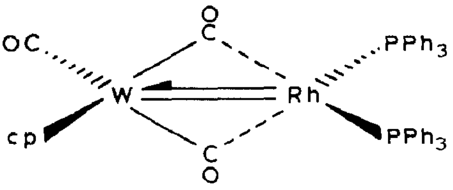
[195]

In work related to that described earlier (see refs. 193-196), $[Rh(OEP)]_2$ reacts with $[Mn_2(CO)_{10}]$, $[cp_2Mo_2(CO)_6]$ and $[cp'_2Ru_2(CO)_4]$ in benzene to form $[(OEP)RhML_n]$ (ML_n = $Mn(CO)_5$, $cpMo(CO)_3$, $cp'Ru(CO)_2$ respectively) in which the metal-metal bond can be cleaved by dihydrogen to give [RhH(OEP)] and $[HML_n]$. In the molybdenum and ruthenium complexes the magnetic anisotropy of the porphyrin ring causes a significant upfield shift of the proton resonances of the cyclopentadienyl and pentamethylcyclopentadienyl ligands respectively (ref. 372). The complexes $Na[Mo(CO)_3L_3]$ (L_3 = $MeGapz_3$, $Me_2Ga(pz)OCH_2CH_2NMe_2$, $HBpz_3$), prepared from $[Mo(CO)_3(MeCN)_3]$ and the sodium salt of the appropriate ligand react with $[RhCl(PPh_3)_3]$ to form [196] (ref. 373). The closely related complexes [197] and [198] are formed

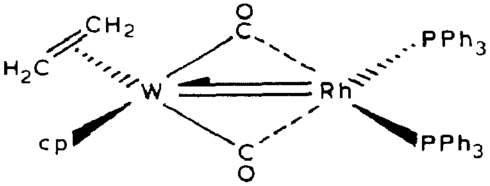


[196]

as a mixture from the reaction of $[cpW(\equiv CMe)(CO)_2]$ with either $[RhH(CO)(PPh_3)_3]$ or $[RhH(PPh_3)_4]$. Complex [198] is thought to be a precursor of [197] (ref. 374).

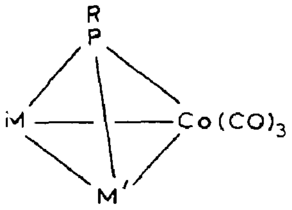


[197]

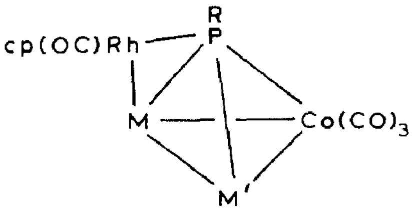


[198]

Addition of a {cpRh(CO)} fragment to the clusters [199] occurs on refluxing with $[cpRh(CO)_2]$ in benzene and [200] (R = Me, Ph; M = $Ru(CO)_3$; M' = $Co(CO)_3$. M = $Ru(CO)_3$; R = Ph; M' = $cpW(CO)_3$; R = Me; M' = $Ru(CO)_3(\mu\text{-}H)$; $Fe(CO)_3(\mu\text{-}H)$. M = $Fe(CO)_3$; R = Me; M' = $Co(CO)_3$, $Fe(CO)_3(\mu\text{-}H)$) is the product.

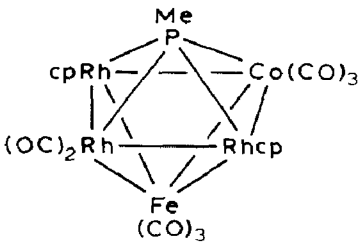


[199]



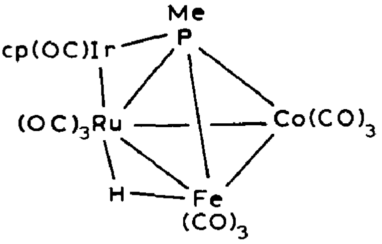
[200]

The same reaction with $[(OC)_4\overline{Fe(\mu\text{-}PMeH)Co}(CO)_3]$ forms [201] while [200] (R = Me; M = $Ru(CO)_3$; M' = $Fe(CO)_3(\mu\text{-}H)$) and

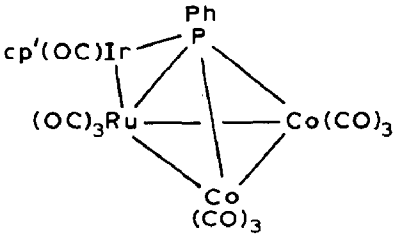


[201]

$[cpIr(CO)_2]$ react to form a mixture of four isomeric complexes of which [202] is one. By contrast [200] (R = Ph; M = $Ru(CO)_3$, M' = $Co(CO)_3$) and $[cp'Ir(CO)_2]$ form the single compound [203] (ref. 375).



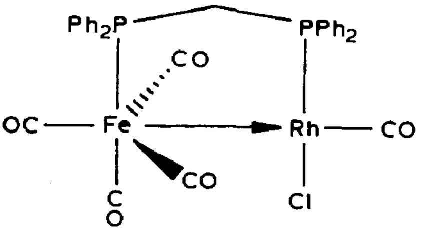
[202]



[203]

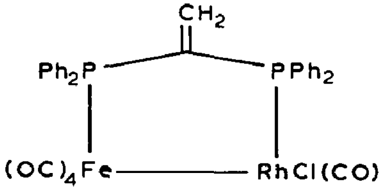
The rhodium analog of [175] has been prepared in similar fashion and here also the {MeOC} moiety is asymmetrically bound to the trimetal unit with the rhodium-carbon bond being longer than those to iron. Molecular orbital calculations were also performed (ref. 376).

Reaction of $[Fe(CO)_4(DPM)]$, in which the phosphine ligand is monodentate, with $[RhCl(CO)_2]_2$ forms [204] in which two of the carbonyl ligands on

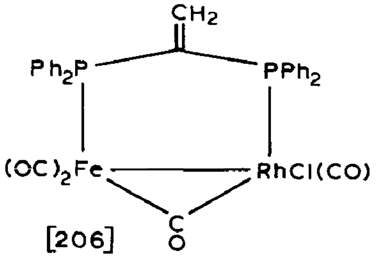


[204]

iron show weak semi-bridging behavior and there is proposed to be an iron-rhodium donor bond (ref. 377). The apparently closely related complex [205] is prepared from $[Fe(CO)_3((Ph_2P)_2C{=}CH_2)]$ and $[RhCl(CO)_2]_2$ and on treatment with trimethylamine N-oxide forms a product thought to be [206].



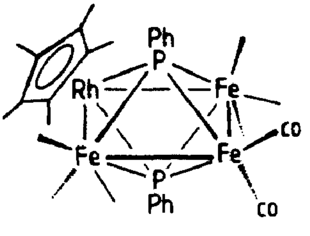
[205]



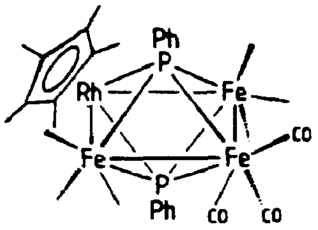
[206]

Neither has been structurally characterized however (ref. 378). Reduction of $[Fe_3(CO)_9(\mu_3\text{-}PPh)_2]$ with sodium naphthalenide forms $Na_2[Fe_3(CO)_9(\mu_3\text{-}PPh)_2]$ which subsequently reacts with $[cp'RhCl_2]_2$ at -78°C to provide a modest yield of [207]. This reversibly adds carbon monoxide to form [208].

Complex [207] exhibits two reversible, one-electron reduction waves and most of the resulting dianion can be reoxidized by Rh(III) to produce

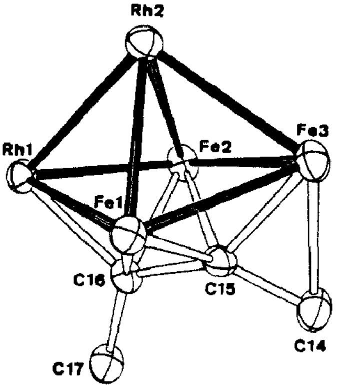


[207]



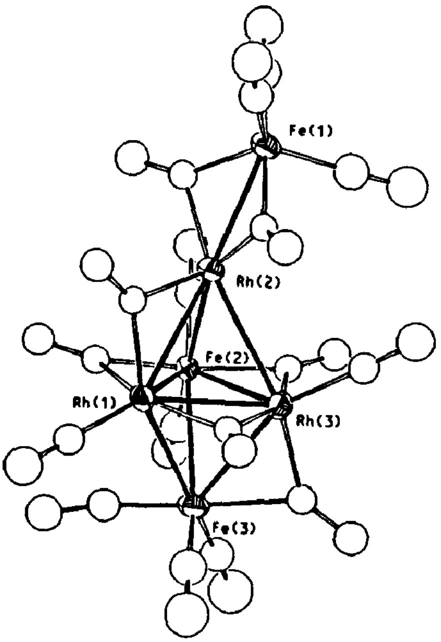
[208]

$[Fe_3(CO)_9(\mu_3\text{-}PPh)_2]$. Two reversible, one-electron oxidation steps are seen for [208] and on reduction one carbonyl ligand is lost to form $[cp'RhFe_3(CO)_8(\mu_3\text{-}PPh)_2]^-$ (ref. 379). Addition of thallium(I) tetrafluoroborate to a mixture of the vinylidene complex $Ph_4P[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]$ and $[RhCl(CO)_2]_2$ results in the assemblage of a pentametallic cluster formulated as $Ph_4P[Fe_3Rh_2(CO)_{10}(\mu\text{-}CO)_3(\mu_4\text{-}MeC{=}C{=}CH_2)]$ and containing an allenyl ligand which evidently arises from the coupling and rearrangement of two of the original vinylidene moieties. The structure of the core of the complex is shown as [209] and the full complex contains two terminal carbonyl



[209]

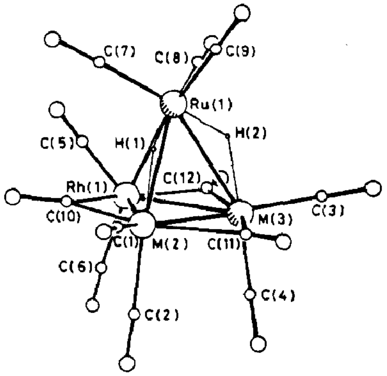
ligands on each metal plus bridging carbonyls along the Rh(1)-Fe(1), Rh(1)-Fe(2) and Rh(2)-Fe(3) edges (ref. 380). Among the several products of the reaction of $[Fe_2Rh(CO)_{10}]^-$ with $[Fe_3(CO)_{11}]^{2-}$ or $[Fe_2(CO)_8]^{2-}$ is $[Fe_3Rh_3(CO)_{10}(\mu\text{-}CO)_7]^{3-}$ whose structure is shown as [210]. It is better prepared by sodium reduction of $[Fe_2Rh(CO)_{10}]^-$ however (ref. 381). Both $(Et_4N)_2[Fe_6C(CO)_{16}]$ and $(Et_4N)_2[Fe_5C(CO)_{14}]$ react with $[Ni(H_2O)_6]Cl_2$ to form $(Et_4N)_2[Fe_5NiC(CO)_{15}]$ but attempts to produce a derivative with three different metal atoms by reaction of the last with $[RhCl(CO)_2]_2$ were unsuccessful; instead the nickel is replaced to yield $Et_4N[Fe_5RhC(CO)_{16}]$. Assignments of metal-carbon (carbide) vibrational frequencies in this and



[210]

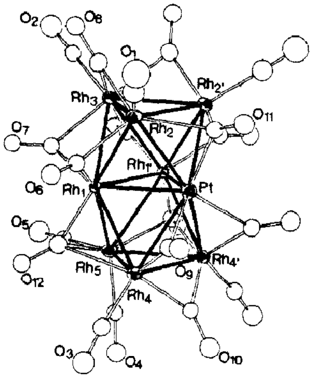
the related complexes $[Fe_4MC(CO)_{14}]^-$ (M = Co, Rh) and $[Fe_4Rh_2C(CO)_{16}]$ have also been made (ref. 382, 383).

Reaction of a mixture of hydrated rhodium(III) chloride and potassium hydroxide with carbon monoxide in DMSO forms $K[Rh(CO)_4]$ which can be extracted into THF and reacted with $[Ru_3(CO)_{12}]$ to form a heterometallic anionic cluster which has not yet been fully characterized. Acidification of the anion with phosphoric acid yields a mixture of $[Ru_2Rh_2H_2(CO)_{12}]$ and $[RuRh_5(CO)_{16}]^-$. The structure of the former is shown as [211] in which



[211]

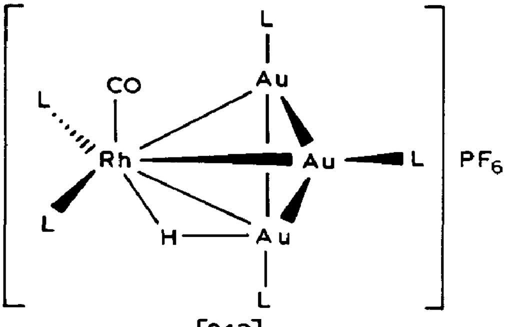
there is nearly 1:1 disorder of rhodium and ruthenium between the M(2) and M(3) sites. The molecule is fluxional with the hydrides exchanging between the Ru(1)-Rh edges and then between the Ru-Ru edges. The carbonyl ligands first undergo bridge-terminal exchange and then all equilibrate. Triphenylphosphine substitutes for one carbonyl group on rhodium but at least two other products, one of which is $[H_4Ru_4(CO)_{12}]$, also form (refs. 384, 385). While synergistic effects on the catalysis of methanol homologation by syngas are noted when mixtures of rhodium(III) and ruthenium(III) chlorides are used with methyl iodide, cluster catalysis does not seem to be occurring since use of $[H_2Rh_2Ru_2(CO)_{12}]$, $[HRuRh_3(CO)_{12}]$, $[HRuRh_3(CO)_{10}(PPh_3)_2]$ or $PPN[RuRh_5(CO)_{16}]$ as catalyst precursors did not increase the production of ethanol (ref. 386). Addition of $[RhCl(CO)_2]_2$ to $(Ph_3MeP)_2[Ni_6(CO)_{12}]$ in DMSO followed by addition of water forms a paramagnetic cluster formulated as $(Ph_3MeP)_3[Rh_5Ni_6(CO)_6(\mu\text{-}CO)_{12}(\mu_3\text{-}CO)_3H]$ although the number of hydrides present could not be determined with certainty. The structure is considered to best be described as a trigonal bipyramid of rhodium atoms interpenetrating a trigonal prism of nickel atoms. The terminal carbonyl ligands reside on the nickel atoms, the doubly bridging ones on the rhodium-nickel edges and the triply bridging ones on the $RhNi_2$ faces (ref. 387). Four clusters can be isolated from the reaction of $(Et_4N)_2[PtRh_4(CO)_{12}]$ with $[Rh_4(CO)_{12}]$ in acetonitrile or THF. Three of these have been characterized as $(Et_4N)_2[PtRh_8(CO)_{19}]$ ([212]), $Et_4N[PtRh_5(CO)_{15}]$ and $(Et_4N)_2[Rh_{12}(CO)_{30}]$ while the fourth is of unknown composition.



[212]

Both the $PtRh_5$ and Rh_{12} clusters appear to form at early stages of the reaction and the latter precipitates. However if the reaction is run in acetone the Rh_{12} cluster remains in solution and reacts further to give a higher yield of [212]. The platinum atom in [212] resides at the site of higher metal-metal connectivity as seems to be preferred in related clusters. The carbonyl ligands are fluxional and the rhodium framework may be as well. Treatment of [212] with carbon monoxide forms $[Rh_5(CO)_{15}]^-$, $[PtRh_5(CO)_{15}]^-$ and $[PtRh_4(CO)_{14}]^{2-}$ (ref. 388). Based on the observation that gold clusters can be generated by borohydride reduction of $\{Au(PR_3)\}^+$

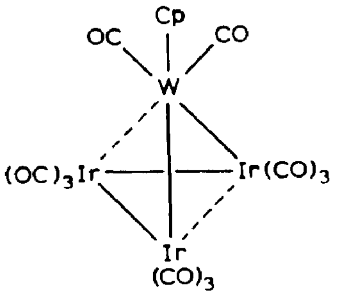
moieties it has been suggested that transition metal hydride complexes should also be effective and possibly also form heterometallic clusters. In at least one instance this has proven successful and [213] (L = PPh_3)



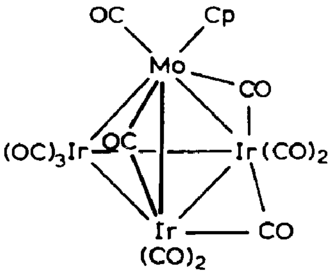
[213]

was synthesized from $[RhH(CO)(PPh_3)]$ and $[Au(NO_3)(PPh_3)]$ in toluene followed by metathesis with potassium hexafluorophosphate in methanol (ref. 389).

The reaction of $[cpWH(CO)_3]$ and $[IrCl(CO)_2$(p-toluidine)] with zinc anc carbon monoxide in dichloromethane at 60°C forms [214] plus a trace of $[cp_2W_2Ir_2(CO)_{10}]$. The molybdenum analog, [215], was prepared similarly but

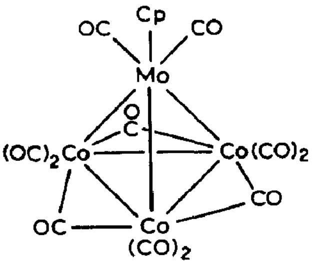


[214]



[215]

found to have a different arrangement of carbonyl ligands. Treatment of $[cpMoH(CO)_3]$ and $[Co_4(CO)_{12}]$ with trimethylamine N-oxide in dichloromethane forms [216] (ref. 390). In refluxing toluene $[cp'Ir(CO)_2]$ reacts with



[216]

$[RhClL_2]$ ($L = P(OPr^i)_3$) to form $[cp'Ir(CO)(L)RhCl(CO)(L)]$ which contains an unsupported metal-metal bond. The complex does not dissociate in solution nor is there site exchange of the carbonyl ligands. The metal-metal bond is readily cleaved by various ligands, however, with the formation in each case of $[cp'Ir(CO)(P(OPr^i)_3)]$ plus the several rhodium complexes shown in Scheme XXXIX ($L = P(OPr^i)_3$). No reaction occurs with dihydrogen but

$$\begin{tikzcd}
 & \underline{\text{trans}}\text{-}[RhCl(CO)(L)(PPr^i_3)] & \\
{[cpRh(CO)(L)]} & {[cp'Ir(CO)(L)RhCl(CO)(L)]} \arrow[l, "a"'] \arrow[u, "b"'] \arrow[r, "c"] \arrow[d, "d"] & {[Rh(CO)(L)(\mu\text{-}I)]_2} \\
 & \underline{\text{trans}}\text{-}[RhCl(L)(CNBu^t)_2] &
\end{tikzcd}$$

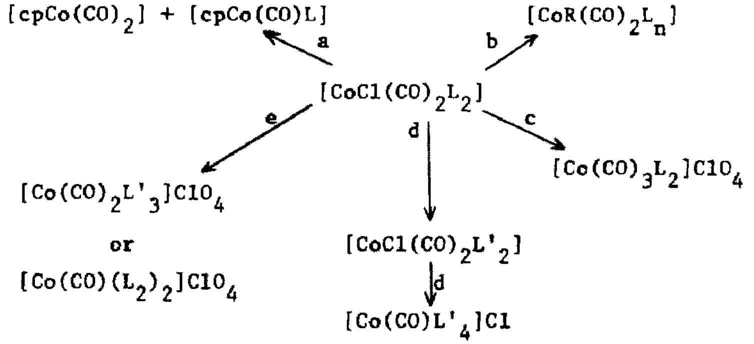
a) Tlcp. b) PPr^i_3. c) KI. d) $CNBu^t$.

Scheme XXXIX

potassium triisopropoxyborohydride cleaves off $[cp'Ir(CO)L]$ and forms rhodium metal (ref. 391). In related work, an attempt to prepare $[cp'(CO)_2IrRe(CO)_4Br]$ by reaction of $[cp'Ir(CO)_2]$ with $[Re(CO)_4Br]_2$ in hot dichloromethane failed and instead, slow formation of $[cp'Ir(CO)_2(CH_2Cl)][Re_2(CO)_6(\mu\text{-}Cl)_x(\mu\text{-}Br)_{3-x}]$ ($x \sim 1.5$) occurred. The same reaction with $[Re(CO)_5Cl]$ proceeds much more rapidly and the product is $[cp'Ir(CO)_2(CH_2Cl)][Re_2(CO)_6(\mu\text{-}Cl)_3]$ (ref. 392).

c) Metal(I), -(II) and -(III) Compounds

In liquid sulfur dioxide, arsenic pentafluoride oxidizes $[Co_2(CO)_8]$ to $[Co(CO)_4(SO_2)]AsF_6$ (ref. 393). Borohydride reduction of $[Co(H_2O)_6]Cl_2$ in ethanol containing triphenylphosphine and phosphonium salts under carbon monoxide yields $PPh_3R[CoX_2(CO)_2(PPh_3)]$ (R = bz; X = Cl. R = Et; X = Br). With phosphonium iodides however the product is $[CoI(CO)_2(PPh_3)_2]$. The same complex as well as its chloro and bromo analogs can be prepared by reaction of $[CoX(PPh_3)_2]_n$ (X = Cl, Br, I) with carbon monoxide in ethanol and further chemistry of $[CoCl(CO)_2(PPh_3)_2]$ is outlined in Scheme XL ($L = PPh_3$) (ref. 394). Carbonylation of $[Co(P\text{-}SR)_2](BF_4)_2$ ($P\text{-}SR = Ph_2PCH_2CH_2SR$ (R = Me, Et)) forms $[Co(CO)_2(P\text{-}SR)_2]BF_4$ which can also be prepared from $[Co(H_2O)_6](BF_4)_2$ and the appropriate ligand in isopropanol under carbon monoxide. The latter route also affords the complex with R = Ph. The products are proposed to be five-coordinate with approximately trigonal bipyramidal geometry and containing one chelate and one monodentate P-SR ligand (ref. 395).

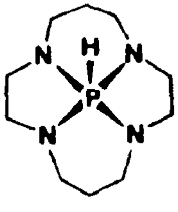


a) Nacp. b) RMgBr (R = C_6F_5; n = 2. R = allyl; n = 1). c) $AgClO_4$.
d) $P(OMe)_3$ (=L'). e) $TlClO_4$, L' or L_2 (L' = PPh_2Me; L_2 = DPM, DPPE).

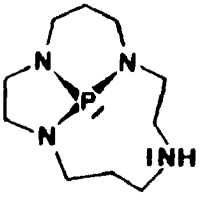
Scheme XL

An attempt to add [cpFe(CO)$_2$Me] to [cp'$_2$Co$_2$(μ-CO)$_2$] was unsuccessful and only a small quantity of [cp'$_3$Co$_3$(μ_3-CO)$_2$] could be isolated. This could also be formed in low yield by the photolysis of [cp'Co(CO)$_2$], a reaction which also produces a low yield of [cp'$_3$Co$_3$(μ_3-CO)(μ_3-O)]. The latter undergoes a reversible, one-electron oxidation while [cp'$_3$Co$_3$(μ_3-CO)$_2$] undergoes a reversible, one-electron reduction. A variable temperature ^{1}H NMR study of the dicarbonyl provides evidence for an equilibrium between singlet and triplet electronic states which was unexpected since the structural study indicates three-fold symmetry which should lead to the observation of two unpaired electrons. The low paramagnetism is suggested to be the result of a rapid deformation of the bonding of one pentamethylcyclopentadienyl ring from five-fold symmetry which would lead to nonequivalence of the cobalt atoms and a raising of the degeneracy of the HOMO. In related work, heating a mixture of [(cpMe)Co(CO)$_2$] and trimethylsilylazide in hexane forms a modest amount of [(cpMe)$_3$Co$_3$(μ_3-CO)(μ_3-NSiMe$_3$)] together with ca 5% [(cpMe)$_3$Co$_3$(μ_3-CO)(μ_3-NC(O)NH$_2$)] and a trace of [(cpMe)$_3$Co$_3$-(μ_3-CO)(μ_3-NH)]. The same reaction with [cp'Co(CO)$_2$] gives mainly [cp'$_2$-Co$_2$(μ-CO)$_2$] but ca 10% of [cp'$_3$Co$_3$(μ_3-CO)(μ_3-NH)] is also formed. Treatment of [R$_3$Co$_3$(μ_3-CO)(μ_3-NSiMe$_3$)] (R = cp, cpMe) with either hydrated tetrabutylammonium fluoride or rigorously dried cesium fluoride in THF provides a higher yield synthesis of [R$_3$Co$_3$(μ_3-CO)(μ_3-NH)]. No reaction of [R$_3$Co$_3$(μ_3-CO)(μ_3-NX)] (X = H; R = cp) occurs with trityl radical, butyllithium or methyl iodide but this complex and the analogs with X = SiMe$_3$ and R = cp or cpMe react with nitrosyl tetrafluoroborate to produce [R$_3$Co$_3$-(μ_3-NO)(μ_3-NH)]BF$_4$. The structures of many of these complexes have been determined and as the metal-metal distances do not vary much with the bulk of the ligand R it is concluded that the cluster bonding is quite strong. Electrochemical studies on $[R_3Co_3(\mu_3\text{-}L)(\mu_3\text{-}NX)]$ (R = cp, cpMe; L = CO; X = $SiMe_3$, H. R = cpMe; L = CO; X = $C(O)NH_2$) show reversible, two-electron oxidation and reduction processes for all except when R = cpMe and X = H in which case they are quasi-reversible. On the other hand, $[cp'_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]$ shows two reversible, one-electron oxidation processes and one reversible one-electron reduction, a difference which is attributed to the greater electron-donating power and the greater bulk of the pentamethylcyclopentadienyl ligand which change the relative stabilities of the HOMO's of the oxidized and reduced products. The complexes with R = cp, cpMe; L = NO; X = H show only two reversible, one-electron reduction processes (see also ref. 496). Although the nitrogen atom in the neutral species $[cp_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]$ cannot be deprotonated as noted above, the cation $[cp_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]^{2+}$, generated electrochemically, does appear to react with triethylamine to give $[cp_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}N)]^+$ (refs. 396-398). Molecular orbital calculations have been performed on $[cp'_2Co_2(\mu\text{-}CO)_{2-m}(\mu\text{-}PH_2)_m]^n$ (m = 0, 1; n = 0, ±1) which are models for known dialkyl- or diarylphosphide-bridged complexes (ref. 399) while photolysis of $[cp_2M_2(CO)_2(\mu\text{-}CO)]$ (M = Co, Rh) in methylcyclohexane matrices provides data suggesting that the lowest excited state has significant M-CO σ^* character (ref. 400).

As in the past, $[RhCl(CO)_2]_2$ has been used extensively as a source of rhodium(I) carbonyl complexes. Its reaction with the tautomeric mixture of phosphoranes [217a,b] forms [218] in which $^1J_{Rh\text{-}P}$ is 200 Hz (ref. 401). In

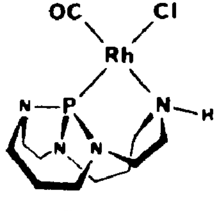


[217a]



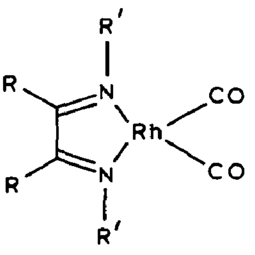
[217b]

refluxing hexane $[RhCl(CO)_2]_2$ reacts with diazadienes to form [219] (R = H; R' = Bu^t, Pr^i, p-tolyl, o-tolyl, 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$. R = Me; R' =



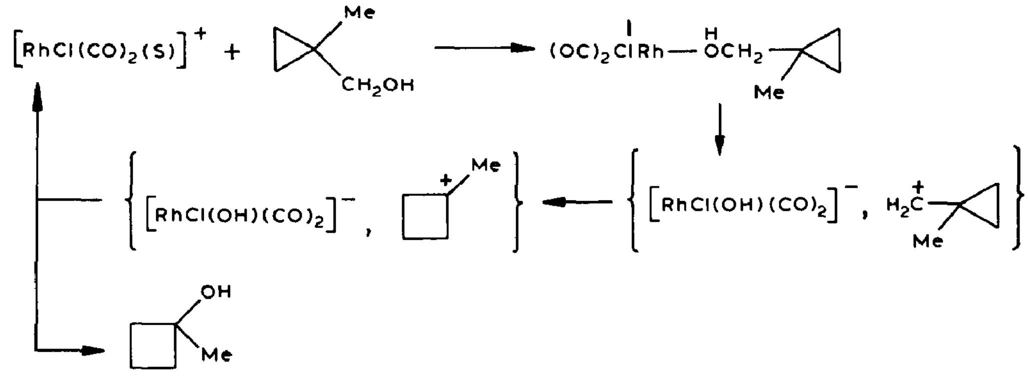
[218]

Ph, p-tolyl, p-anisyl, 2,6-$Me_2C_6H_4$, 2,6-$Pr^i_2C_6H_3$) but at room temperature in ethanol the product is $[RhCl(R'N{=}CRCR{=}NR')(\mu\text{-}CO)]_2$ (R = H; R' = Bu^t, R



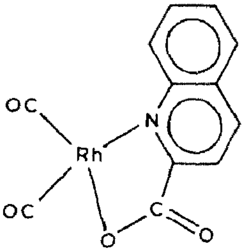
[219]

= Me; R' = Ph, *p*-tolyl, *p*-anisyl). With an excess of monoazadienes the familiar complexes *trans*-$[RhCl(CO)L_2]$ (L = *trans*-*trans*-PhCH=CHCH=NR' (R = Pr^i, PhMeHC, Ph, *p*-tolyl)) are formed. Both these and several examples of [219] are catalyst precursors for alkene and alkyne hydrosilylation (refs. 402, 402a). In acetone, $[RhCl(CO)_2]_2$ reacts with 2-cyclopropyl-2-propyl-*p*-nitrobenzoate to form $[Rh_2(CO)_4(\mu-O_2CR)_2]$ (R = *p*-$O_2NC_6H_4$) and 2-methyl-5-chloropent-2-ene but with 1-methyl-1-hydroxymethylcyclopropane, a rhodium-catalyzed ring expansion occurs rather than the ring-opening observed in the former case. An equilibrium mixture (*ca* 20:1) of 1-methylcyclobutanol and the starting cyclopropane results with the rhodium proposed to function as a Lewis acid catalyst as shown in Scheme XLI (S =

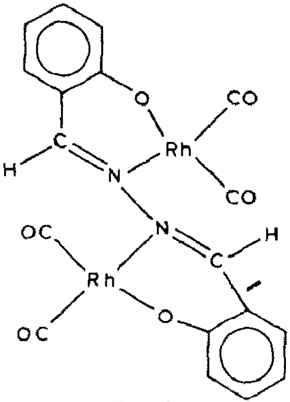


Scheme XLI

acetone) (ref. 403). With quinaldic acid in aqueous DMF $[RhCl(CO)_2]_2$ forms [220] in which the carbonyl ligands can be replaced by triphenylphosphite (ref. 404) while in refluxing benzene reaction with disodium salicylaldizinate gives [221]. Here, one carbonyl group on each metal can be replaced by triphenylphosphine (ref. 405). The Schiff bases RR'C=NN(Me)C(S)SMe (R = Me; R' = $MeC(O)CH_2$, $PhC(O)CH_2$, 1-thienyl$C(O)CH_2$, *o*-C_6H_4OH. R = H; R' =

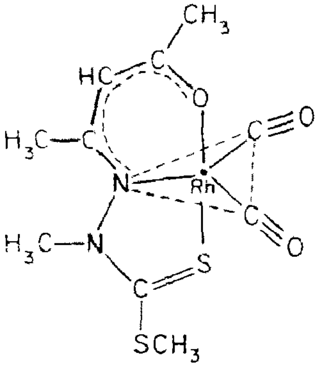


[220]

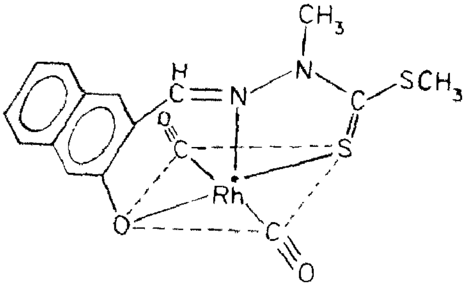


[221]

$\underline{o}$-C_6H_4OH, 2-hydroxy-1-naphthyl) react with $[RhCl(CO)_2]_2$ to form five-coordinate dicarbonyl complexes which are thought to be trigonal bipyramidal, e.g. [222], for alkyl substituents and square pyramidal, e.g. [223], for



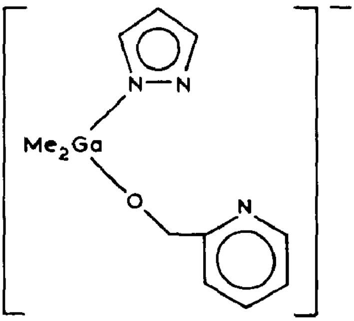
[222]



[223]

aromatic substituents (ref. 406).

The pyrazolylgallate derivative [224] (L), as its sodium salt, reacts with $[RhCl(CO)_2]_2$ at -78°C to form [225] which was isolated by removal of solvent and extraction of the residue with benzene. It is weakly associated in the solid $\underline{via}$ rhodium-rhodium interactions. Also formed was an analog in which one methyl group on gallium was replaced by chlorine.



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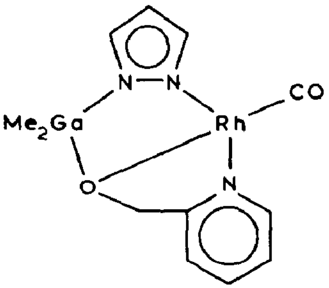
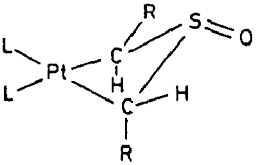


[225]

Complex [225] adds methyl iodide to yield [Rh(C(O)Me)I(L)] which has a square pyramidal structure (ref. 407). Other reactions of $[RhCl(CO)_2]_2$ are with [226] (L = PPh_3; R = PhC(O)) to give [227] (ref. 408), with [228] (L) to form [RhCl(CO)L] which is thought to involve trans chelation of the ligand and to possibly be dimeric in solution (ref. 409) and with [229] (m = n = 0, 1; m = 1, n = 0) to yield [230] which are monocations and were isolated as triflate salts. A variety of mono-, di- and tripositive metal



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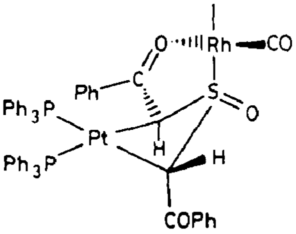

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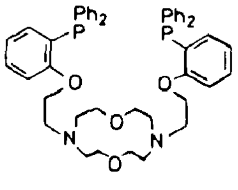

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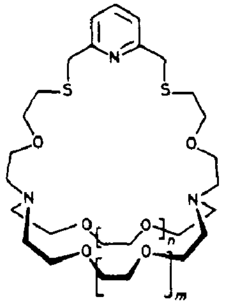

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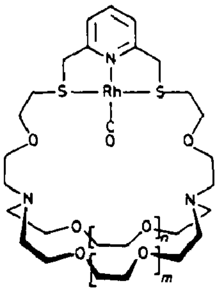
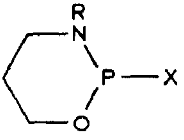


[230]

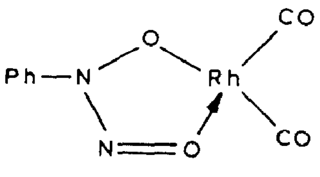
cations can be bound at the site in the lower portion of the macrocycle (ref. 410). The metallophosphines $[O(cp_2MCH_2PPh_2)_2]$ (L_2; M = Ti, Zr) and $[(HB(Me_2pz)_3)M(NO)(X)(NH(CH_2)_3PPh_2)]$ (L; M = Mo; X = I. M = W; X = Cl) both react with $[RhCl(CO)_2]_2$. The first gives $[RhCl(CO)(L_2)]$ in which the ligands span *trans* positions and when M = Zr, several rotameric conformations are seen in solution (ref. 411). The second gives simple *trans*-$[RhCl(CO)(L)_2]$ complexes (ref. 412).

The oxazaphosphorinanes [231] (R = H, Pr^i; X = OEt. R = Me, bz, Pr^i; X = NMe_2, NEt_2. R = Pr^i; X = $O(CH_2)_3NR'R''$ (R' = R'' = H, Me)) replace one



[231]

carbonyl group in $[Rh(acac)(CO)_2]$ and in some instances these products react with $[RhCl(CO)_2]_2$ to transfer the phosphorus ligand to the dimeric rhodium complex (refs. 413, 414). Addition of two mols of tricyclohexylphosphine to $[Rh(acac)(CO)_2]$ in cyclohexane forms $[Rh(acac)(CO)(Pcy_3)]$. If this mixture is heated to 80°C under syngas, a mixture of $[RhH(CO)(Pcy_3)_2]$ and $[(Pcy_3)_2Rh(\mu\text{-}CO)_2Rh(CO)(Pcy_3)]$ forms. The latter has tetrahedral coordination about the left hand rhodium and square planar coordination about the other. The dimer converts to the monomer on reaction with dihydrogen alone in the presence of excess phosphine and the mixture of the two complexes can be converted to $[Rh_2(CO)_4(Pcy_3)_2(\mu\text{-}CO)_2]$ by carbon monoxide but this is stable only if carbon monoxide is present (ref. 415). Addition of triphenylphosphine to $[Rh(TFTMAA)(CO)_2]$ forms $[Rh(TFTMAA)(CO)(PPh_3)]$ in which the phosphine resides *trans* to the oxygen atom of TFTMAA that is adjacent to the carbon bearing the trifluoromethyl substituent. This is contrary to the prediction of the established *trans* effect series in these compounds and is attributed to the bulk of the *tert*-butyl group hindering substitution at the expected site (ref. 416). In related work, the observation that reaction of triphenylphosphine with [232] forms [233]



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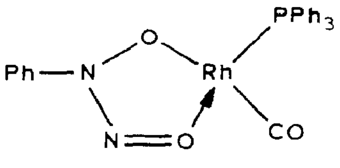
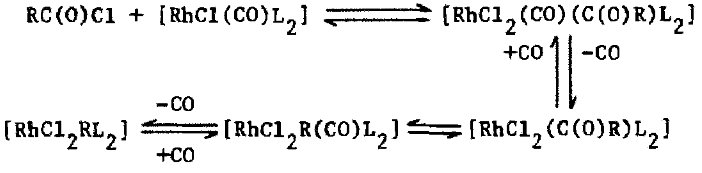


[233]

is interpreted to indicate that the oxygen of the nitroso group exerts the greater trans effect (ref. 417). Reaction of Na_2dahd with $[RhCl(CO)_2]_2$ forms $[(OC)_2Rh(\mu\text{-dahd})Rh(CO)_2]$ which subsequently reacts with triphenylphosphine to form a species of composition $[Rh_2(CO)_2(PPh_3)_2(dahd)]$. This is proposed to be polymeric on the basis of its insolubility but confirmation of this proposal has not been obtained (ref. 418).

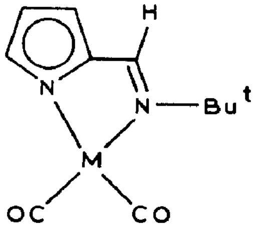
The complex $[RhCl(CO)(PPh_3)_2]$ catalyzes the labelling of acid chlorides with carbon-13 at the acyl carbon as depicted in Scheme XLII (L = PPh_3; R = Me, Pr^n, Pr^i, n-heptyl, bz, PhMeHC, cyclopentyl, cyclohexyl) when placed under an atmosphere of ^{13}CO. The lack of significant formation of alkyl chlorides or olefins except when benzylic substituents are used indicates that reductive elimination and/or β-hydride abstraction processes involving the alkylrhodium species proposed in this Scheme must generally occur more slowly than the equilibrations shown (ref. 419). The rate and equilibrium constants for the formation of complexes between $[RhCl(CO)(PPh_3)_2]$ and cumyl or tert-butyl hydroperoxides have been determined as part of a study of rhodium-catalyzed olefin oxidation processes. Formation of short-lived 1:1 complexes which then coordinate the olefin is proposed (ref. 420). Addition of succinimide, its tetrafluoro analog or phthalimide (LH) to $[MCl(CO)(PPh_3)_2]$ (M = Rh, Ir) in the presence of triethylamine forms trans-$[M(L)(CO)(PPh_3)_2]$ (ref. 421) while $[MCl(CO)(PEt_3)_2]$ (M = Rh, Ir) and chlorodifluoroamine react at 190 K in dichloromethane to yield $[MCl_2(NF_2)(CO)(PEt_3)_2]$. Also detected in the reaction mixture is $[MCl_3(CO)(PEt_3)_2]$ and N_2F_4. The difluoroamido complexes decompose above 240 K with the formation of N_2F_4 (ref. 422). Halide abstraction from $[MX(CO)(PPh_3)_2]$ (M = Rh, Ir; X = Cl, Br) with silver perrhenate forms $[M(OReO_3)(CO)(PPh_3)_2]$ and perrhenate also displaces tetrafluoroborate from $[IrHCl(FBF_3)(CO)(PPh_3)_2]$ yielding $[IrHCl(OReO_3)(CO)(PPh_3)_2]$. From these studies it was concluded that perrhenate is a better ligand than perchlorate, tetrafluoroborate or triflate (ref. 423). In a related study, the nitrile complexes $[Rh(NCR)(CO)(PPh_3)_2]ClO_4$ (R = Me, Pr^n, Ph) are obtained by displacement of perchlorate from $[Rh(OClO_3)(CO)(PPh_3)_2]$ in benzene (ref. 424). Borohydride



Scheme XLII

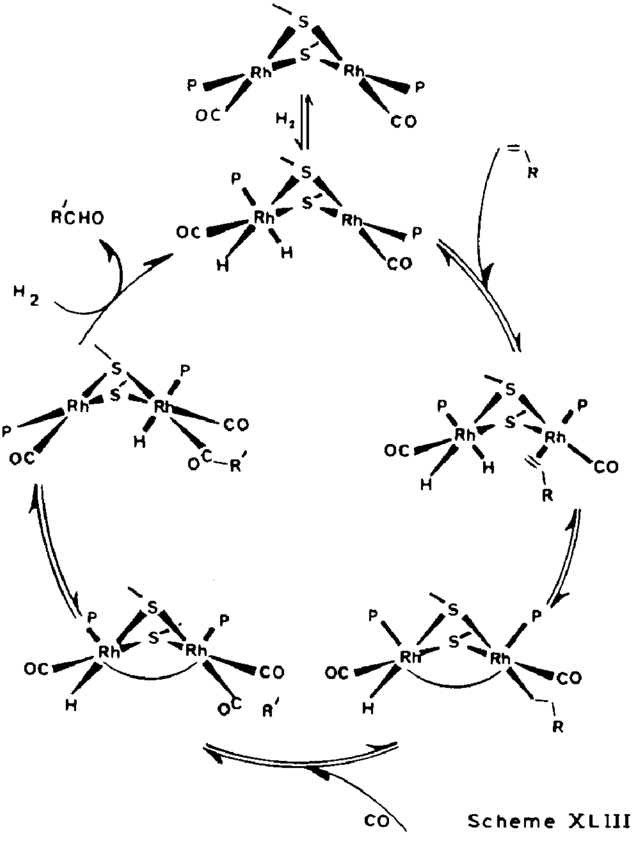
ion reacts with $[\mathrm{Rh(CO)_2(triphos)}]^+$ in THF at -60°C to form [Rh(CHO)-(CO)(triphos)] which converts to [RhH(CO)(triphos)] on warming. With methyllithium $[\mathrm{Rh(CO)_2(triphos)}]^+$ forms [Rh(C(O)Me)(CO)(triphos)] which reversibly decarbonylates to [Rh(Me)(CO)(triphos)] and reacts further with methyllithium to yield $[\mathrm{Rh(CO)(triphos)}]^-$ and acetone. The last reaction is interesting in that the methyllithium undergoes nucleophilic addition to the acyl carbon atom rather than functioning as a strong base to deprotonate the complex (ref. 425). In the reaction of $[\mathrm{RhCl(CO)_2(BTD)}]$ with piperidine in halocarbon solvents, including even carbon tetrachloride, significant amounts of piperidine hydrochloride are formed. It appears that the rhodium complex catalyzes the formation of the hydrochloride by presumably generating chlorine radicals from reaction with the solvent which then abstract hydrogen from some source in the system to generate hydrogen chloride. The same result is observed with $[\mathrm{RhCl(CO)_2}]_2$ and, to a lesser extent with $[\mathrm{RhCl(CO)(PPh_3)_2}]$ (ref. 426).

Binding constants for the addition of carbon monoxide to $[\mathrm{Rh_2(O_2CMe)_n}$-$\mathrm{(HN(O)CMe)_{4-n}}]$ (n = 0-2, 4) have been measured. Both mono- and dicarbonyl adducts were detected and the extent of π-backbonding to the carbonyl ligand was found to increase with decreasing values of n (ref. 427). In related work, an E and C analysis has been made of the variations in ν_{CO} with changes in ligands B in $[\mathrm{(OC)Rh(\mu\text{-}O_2CC_3F_7)_4Rh(B)}]$. The results suggest that for ligands which are σ-donors the metal-metal bond transmits the effects of coordination of B at one metal to the other thereby influencing the Lewis acidity of the latter (ref. 428). Electronic absorbance and emission spectra of $[\mathrm{M_2Cl_2(CO)_2(L_2)_2}]$ and $[\mathrm{Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2}]\mathrm{BPh_4}$ (M = Rh, Ir; L_2 = DPM, DAM) have been measured. In all complexes both fluorescence and phosphorescence were observed with the former occurring at higher energy. In the last complex a metal-metal bond was proposed to exist in the excited state (refs. 429, 430). Photoelectron spectra of [234] (M = Rh, Ir) confirm molecular orbital calculations which predict



[234]

very little π-backbonding occurs to the pyrrole portion of the ligand (ref. 431) while variable temperature ^{13}C and ^{31}P NMR spectra have been used to unravel the dynamic processes involving rotations of and within the ligands in trans-[MX(CO)(PBu$^t_2$R)$_2$] (M = Rh, Ir; X = Cl, Br, I; R = Me, H. M = Rh, Ir; X = Cl; R = Pr^i). Generally three rotamers were observed with the major one having R syn to X (refs. 432, 432a). Of two papers reporting EHMO calculations, the first concerns addition to cis-[RhCl(CO)(PH$_3$)$_2$] (as a model for known complexes) and to [RhX$_2$(CO)$_2$]$^-$ (X = H, Cl, CN). The results suggest that addition of dihydrogen should occur parallel to the Rh-CO bond irrespective of the nature of the ligand trans to carbonyl and that the two-electron interactions responsible for electron transfer from the metal to the incoming dihydrogen ligand and from it to the metal play a minor role at best in determining the direction of addition. The significant factor appears to be a four-electron repulsion between the metal d$_{z^2}$ and dihydrogen σ-bonding orbitals which is less when the hydrogen-hydrogen bond is in the plane of the strongest π-acceptor ligand (ref. 433). The second paper also includes chemical studies on [Rh$_2$(CO)$_2$L$_2$(μ-SR)$_2$] as olefin hydroformylation catalysts. Those with R = Bu^t and L = P(OMe)$_3$, P(OPh$_3$), PPh$_3$ are particularly active and show good selectivity. The results suggest retention of the binuclear structure throughout the process as shown in Scheme XLIII (ref. 434). Specific applications to hydroformylation of propenylbenzenes were also reported (ref. 435).



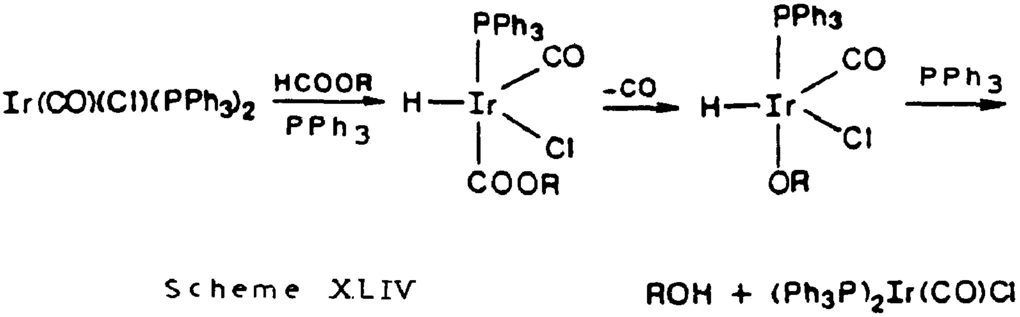
Scheme XLIII

Among the applications of rhodium(I) complexes as catalysts or catalyst precursors is the use of $[RhClL_2]_2$ (L = CO; L_2 = COD) with a large excess of a trialkylphosphine for the conversions of syngas to methanol and ethylene glycol, of formaldehyde to methanol and of glycolaldehyde to ethylene glycol (ref. 436). Other catalyst systems based on $[RhCl(CO)_2]_2$ are those with iodide sources for the hydrocarbonylation of lactones to acids (ref. 437), with $MoOCl_n$ (n = 3, 4) for the carbonylation of nitromesitylene to mesityl isocyanate (ref. 438) and without co-catalysts for the stereospecific desulfurization of thiiranes (ref. 439). In DMSO, DMF or HMPA containing a small amount of water and potassium or tetramethylammonium hydroxide, $[RhCl(CO)_2]_2$ forms a catalyst for the reduction of nitrous and nitric oxides to dinitrogen by carbon monoxide at 100°C. The major component of the active system appears to be $[Rh(CO)_4]^-$ but $[Rh_4(CO)_{11}]^-$ was also detected (ref. 440). Polyimides formed from aliphatic diamines and terephthaloyl chloride have been used as is or after partial phosphination with chlorodiphenylphosphine to support rhodium species derived from $[RhCl(CO)_2]_2$ for the catalysis of hex-1-ene hydroformylation (ref. 441).

Also popular as a catalyst precursor is $[Rh(acac)(CO_2)]$. In 1,3-dimethylimidazolidinone solvent containing phosphines (e.g. $PBu^n{}_3$, $PBu^n{}_2Bu^t$, $PBu^nBu^t{}_2$, $PBu^t{}_3$, $PPr^i{}_3$, $PPr^n{}_3$) it forms a catalyst for the conversion of syngas to methanol and ethylene glycol. The course of the reaction is sensitive to both steric and electronic effects but these do not always parallel one another and their importance also depends on the ratio of phosphine to rhodium. For example, much less triisopropylphosphine than tri-n-propylphosphine is required for maximum activity. In one instance $[(OC)_3(PPr^i{}_3)RhRh(CO)_3(PPr^i{}_3)]$ was isolated (ref. 442). In another study $[Rh(acac)(CO)_2]$ formed a catalyst for the hydrosilylation of acetylene and terminal alkynes (refs. 443, 444).

Various rhodium phosphine complexes catalyze the hydroformylation of allyl alcohol but extensive hydrogenation and isomerization also occurs and the activity and selectivity rapidly diminish due to the formation of 2-methylacrolein. Under carbon monoxide alone, $[Rh(H)(CO)(PPh_3)_3]$ reacts with allyl alcohol to form $[Rh(OC(O)Et)(CO)(PPh_3)_2]$ (ref. 445). In work related to that described in refs. 434 and 435 a mixture of $[RhH(CO)(PPh_3)_3]$ and one equivalent of tert-butyl thiol was tested for olefin hydroformylation activity and after 30 min this was higher than in the absence of thiol. The results were interpreted as indicating the formation of $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}SBu^t)_2]$ and since excess phosphine is ultimately present this study further confirms the mechanism proposed in Scheme XLIII (ref. 446).

Further details have been reported on iodide-promoted rhodium catalysts for homologation of methanol to acetic acid (see also Inorg. Chim. Acta, 101(1985)L47). The original report of a greater rate enhancement by added lithium iodide than by lithium acetate appears in error as both seem to be about as effective and the rate enhancement is attributed to anion coordination favoring the carbonyl insertion step (ref. 447). Another paper reports the stability of the same catalyst system is improved by added tin(II) chloride (ref. 448) while a system containing hydrated rhodium(III) chloride, zinc acetate, methyl iodide and methyl acetate forms acetic anhydride when heated in the presence of carbon monoxide. Here it is proposed that the rhodium is converted to $[RhI_2(CO)_2]^-$ which reacts with methyl iodide to form acetyl iodide. This in turn reacts with zinc acetate to give acetic anhydride and the zinc-containing product then reacts with methyl acetate to regenerate zinc acetate and methyl iodide (ref. 449). The carbonylation of phenylacetylene to the methyl esters of cinnamic and atropic acids occurs in the system $[RhCl(CO)(PPh_3)_2]/MeOH/CHCl_3/HCl/H_2O/KI$ but no mechanistic details were provided (ref. 450). The isomerization of fumaronitrile to an equilibrium mixture with malonitrile is catalyzed by chlorobenzene solutions of $[Rh(OClO_3)(CO)(PPh_3)_2]$ under dihydrogen. A small amount of reduction to succinonitrile was also seen and $[RhCl(PPh_3)_2L]$ (L = CO, PPh_3) showed no catalytic activity (ref. 451). At 180°C in an open system $[IrCl(CO)(PPh_3)_2]$ catalyzes the formation of n-octanol from n-octyl formate in 64% yield in the absence of solvent. In a closed system, higher conversions can be obtained but now the yield of alcohol is lower and more side-products are formed. The reaction is inhibited by excess triphenylphosphine, added p-toluenesulfonic acid, and by the use of iridium complexes of more basic phosphines. Scheme XLIV (R = n-octyl) is



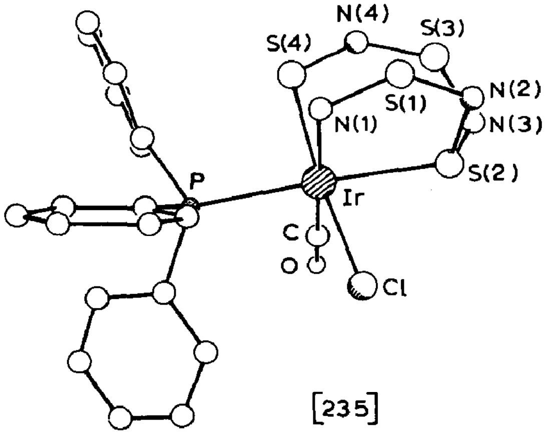
Scheme XLIV

proposed with loss of phosphine from the starting iridium complex being the likely rate-determining step. The same system works with other n-alkyl formates except methyl formate, giving 25-65% yields of alcohol, but the analogous rhodium complex is inactive (ref. 452).

A comparison of the surface species formed on alumina from the deposition of $[RhCl(CO)_2]_2$ from hexane with those formed by carbonylation of rhodium(III)impregnated alumina which has been prereduced with dihydrogen indicates that both seem to be $\{Rh^I(CO)_2\}$ but the former are isolated and noninteracting while the latter cluster around residual paramagnetic rhodium sites (ref. 453). Vapor deposition of $[RhCl(CO)_2]_2$ on silica, on the other hand, results in little if any change of the structure of the complex and ready absorption of carbon monoxide occurs to form species proposed to be supported $\{RhCl(CO)_3\}$ moieties (ref. 454). Carbonylation of Rh(III)- and Ir(III)-impregnated NaX and NaY zeolites also forms supported $\{M^I(CO)_2\}$ (M = Rh, Ir) moieties which undergo substitution reactions with other ligands and oxidative addition of methyl iodide. The methyl iodide adduct of the iridium system can be converted to an acetyl species (ref. 455). Fourier-transform infrared spectroscopy of the $\{Rh^I(CO)_2\}$ moieties adsorbed on NaX, NaY, Al_2O_3, TiO_2 and related oxide supports shows the order of π-backbonding increases in the order NaX < Al_2O_3 < NaY < TiO_2 and correlates well with the ease of desorption of carbon monoxide (ref. 456). Finally, $[RhCl(CO)_2]_2$ supported on macroporous styrene/divinylbenzene copolymers functionalized with various phosphorus, nitrogen and oxygen donor groups forms an effective catalyst for the hydroformylation of diisobutylene (refs. 457, 458).

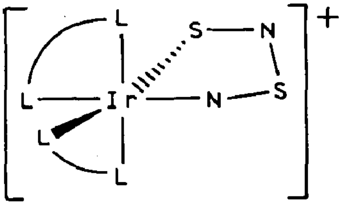
A new, general route to Vaska-type complexes has been proposed which involves treating $[IrCl(COD)]_2$ with the appropriate ligand in hexane and then reacting the product with carbon monoxide. With trimethylphosphine the carbonylation product is $[IrCl(CO)_2(PMe_3)_2]$ but this could be converted to $[IrCl(CO)(PMe_3)_2]$ on vacuum drying (ref. 459). Reaction of $[IrCl(CO)(PPh_3)_2]$ with sodium pentafluorophenolate in THF forms $[Ir(OC_6F_5)(CO)(PPh_3)_2]$ which is converted into a mixture of $[Ir(CO)_3(PPh_3)_2](OC_6F_5)$ and $[Ir(OC_6F_5)(CO)_2(PPh_3)_2]$ by carbon monoxide in benzene. No insertion of carbon monoxide into the iridium-oxygen bond was detected. When <u>trans</u>-$[Ir(OR)(CO)(PPh_3)_2]$ is reacted with triphenylphosphine in hot toluene $[IrH(CO)(PPh_3)_3]$ forms when R = Me, Pr^n, Pr^i but not when R = H, Bu^t, Ph suggesting that the reaction involves a β-hydride abstraction process. In support of this it was noted that the n-propoxy and i-propoxy complexes also formed propionaldehyde and acetone respectively. Initially puzzling was the observation of isopropanol in the latter reaction but since it was found that $[Ir(OPr^i)(CO)(PPh_3)_2]$ reacts with $[IrH(CO)(PPh_3)_3]$ to form isopropanol and an unidentified, air-sensitive iridium complex it was felt that the alcohol in the original reaction resulted from reaction of the $[IrH(CO)(PPh_3)_3]$ formed initially with the starting complex (refs. 460, 461). Photolysis of $[IrH(CO)_2(DPPE)]$ in hot benzene in the presence of carbon monoxide generates small quantities of benzeldehyde presumably by activation of a carbon-hydrogen bond in benzene at iridium followed by carbonyl insertion and reductive elimination. Comparable results are seen under the same conditions with [IrH$_3$(CO)(DPPP)], [IrBr(CO)(DPPE)], [RhH(CO)(PPh$_3$)$_3$] and [MCl(CO)(PPh$_3$)$_2$] (M = Rh, Ir). The amount of benzaldehyde formed corresponds to about three turnovers in forty eight hours and the low activity is attributed to unfavorable thermodynamics. Use of ^{13}CO in the reaction results in considerable fraction of the product containing carbon-13 which indicates the occurrence of multiple carbonylation/decarbonylation steps in the course of the reaction (ref. 462).

The reaction of [Ir(CO$_2$Me)(CO)$_2$(PPh$_3$)$_2$] with [PdI$_2$(NCPh)$_2$] forms a complex formulated as [(Ph$_3$P)$_2$Ir(CO)$_2$PdI$_2$]. Its reaction with triphenylphosphine, dihydrogen, carbon monoxide or carbon tetrachloride caused loss of the {PdI$_2$} moiety (ref. 463). Association of the square planar anion [Ir(CO)$_2$(Tcbiim)]$^-$, presumably via weak metal-metal interactions, occurs in acetonitrile with a significant concentration of dimers being seen at concentrations above 10^{-3} M and what appear to be higher oligomers above 10^{-2} M (ref. 464). With [IrX(CO)(PPh$_3$)$_2$] (X = Cl, Br, I) tetrasulfur tetranitride forms [235] (X = Cl) presumably via oxidative addition of a



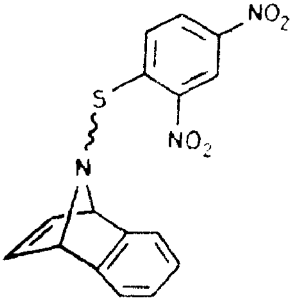
[235]

sulfur-nitrogen bond to the metal (ref. 465) but with [Ir(CO)(L$_2$)$_2$]BPh$_4$ (L$_2$ = DPM, cis-vdiphos) fragmentation occurs and the product is [236]. This is



[236]

a full report on the synthesis and chemistry of [236] and no further resolution of the disorder problem noted in the preliminary report could be achieved so the details of the bonding within the $\{IrN_2S_2\}$ moiety remain uncertain. Photolysis of a mixture of [236] and $[W(CO)_6]$ in dichloromethane affords a derivative with a $\{W(CO)_5\}$ moiety bound to the uncoordinated nitrogen (ref. 466). Since [237] is reported to form 2,4-dinitrobenzenesulfenyl nitrene on heating this was reacted with $[IrCl(CO)(PPh_3)_2]$ in hot toluene in an attempt to form an iridium nitrene complex. This did not occur and instead [238] was obtained suggesting that some dissociation of triphenylphosphine occurred under reaction conditions and the nitrene preferentially attacked the free ligand (ref. 467). Carbonylation of $[IrCl(SO_2)L_2]$ (L = PPr^i_3, Pcy_3) formed the unstable $[IrCl(CO)(SO_2)L_2]$ which readily lost the sulfur dioxide ligand. Reaction with dihydrogen on the other hand formed $[IrH_2Cl(SO_2)L_2]$ (ref. 468). Reaction of mer-$[IrH_3(PPh_3)_3]$ with p-toluenesulfonic acid in refluxing ethanol forms $[IrH_2(OSO_2R)(PPh_3)_3]$ (R = p-tolyl). With $[IrH(CO)(PPh_3)_3]$ in refluxing benzene this and other sulfonic acids form $[IrH_2(CO)(PPh_3)_3](O_3SR)$ while in refluxing toluene the product is $[IrH(OSO_2R)_2(CO)(PPh_3)_2]$ (R = Me, CF_3, p-tolyl, d-camphoryl). The same acids with $[IrCl(CO)(PPh_3)_2]$ in refluxing benzene yield $[IrHCl(OSO_2R)(CO)(PPh_3)_2]$ (ref. 469).



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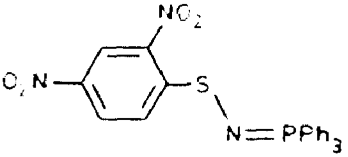
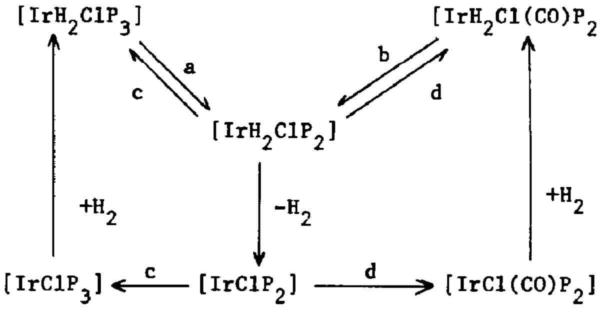


[238]

Flash photolysis of $[MCl(CO)(PPh_3)_2]$ (M = Rh, Ir) in benzene is proposed to form $[MCl(PPh_3)_2]$ which recombines very rapidly with the liberated carbon monoxide ($k \approx 10^8\ M^{-1}\text{-sec}^{-1}$) and reacts at comparable rates with ethylene and triphenylphosphine when photolyzed in the presence of these ligands. The reaction of the photoproduct with dihydrogen is noticeably slower although still quite fast ($k \approx 10^5\ M^{-1}\text{-sec}^{-1}$). Full details of the flash photolysis of $[IrH_2Cl(L)(PPh_3)_2]$ (L = CO, PPh_3) are now available and the results are explained as shown in Scheme XLV (P = PPh_3). In this instance, loss of dihydrogen from $[IrH_2ClP_2]$ appears to occur within the time of the flash (refs. 470, 471). The ^{17}O NMR chemical shifts of the dioxygen ligand in $[IrX(O_2)(CO)(PPh_3)_2]$ (X = Cl, I) have been determined using an 11.7 T spectrometer and found to be the same for both complexes. This is somewhat surprising since the binding of dioxygen to the chloro

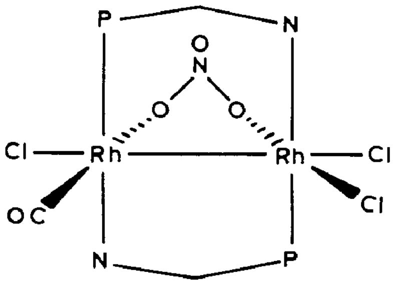


a) hν, -P. b) hν, -CO. c) +P. d) +CO

Scheme XLV

complex appears to be weaker than it is to the iodo complex based on the fact that the dioxygen ligand can be readily removed from the former but not from the latter. From the data obtained this ligand appears to be best described as a coordinated peroxide. Because the observed linewidths of the ^{17}O signals are about 10 KHz considerable care must be used with the acquisition parameters to obtain satisfactory spectra (ref. 472).

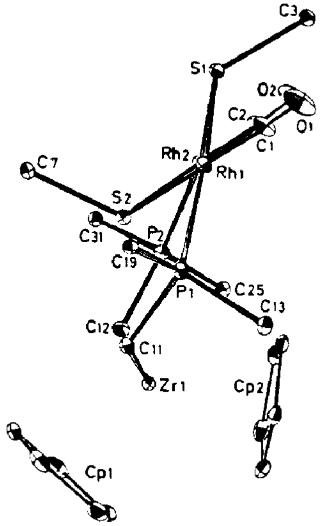
Interest in binuclear A-frame and related complexes remains high. Electrolytic oxidation of [$Rh_2Cl_2(\mu-CO)(PPh_2py)_2$] in the presence of tetrabutylammonium nitrate and tetrabutylammonium chloride forms [239]



[239]

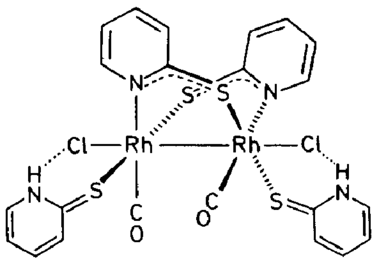
which has a very short metal-metal distance of 2.589 Å (ref. 473). Treatment of the A-frame complexes [$Rh_2(CO)_2(\mu-Cl)(L_2)_2$]$PF_6$ (L_2 = DPM, DAM, DAPM) with lithium pyrazolates forms [$Rh_2(CO)_2(\mu-X)(L_2)_2$]PF_6 (X = pz, tz, 4-Mepz, 3,5-Me_2pz) which react with one or two equivalents of tert-butylisocyanide to yield [$Rh_2(CO)(CNBu^t)(\mu-X)(L_2)_2$]$PF_6$ and [$Rh_2(CNBu^t)_2(\mu-X)(L_2)_2$]$PF_6$ respectively. Addition of iodine to [$Rh_2(CO)_2(\mu-X)(DPM)_2$]PF_6

forms $[Rh_2I_2(CO)_2(\mu\text{-}X)(DPM)_2]PF_6$ with axial iodo ligands. Analogous reactions occur with chlorine and bromine but when X = pz or 3,5-Me_2pz, halogenation of the pyrazolate ligand at the 4-position also occurs (ref. 474). Addition of silver salts to $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}DPM)]$ forms $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}DPM)(\mu\text{-}AgX)]$ (X = O_2CMe, O_2CCF_3, S_2CNEt_2) while with silver malonate the product is $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}DPM)(\mu\text{-}AgO_2CCH_2CO_2Ag\text{-}\mu)(\mu\text{-}DPM)(\mu\text{-}CO)Rh_2cp_2]$ (ref. 475). The complex [240] (α-carbons only shown) is

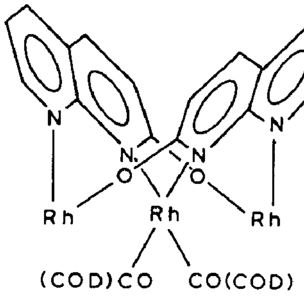


[240]

prepared from $[Rh_2(CO)_4(\mu\text{-}SBu^t)_2]$ and $[cp_2Zr(CH_2PPh_2)_2]$. The relatively close approach of S_2 to the zirconium suggests an interaction of its lone pair with this metal and this is used to explain the stereorigidity of [240]. Complex [240] is a better hydroformylation catalyst than its DPPB analog and a possible explanation is that the zirconium atom could act as an electron buffer but this is not yet certain (ref. 476). Reaction of $[RhCl(CO)_2]_2$ with two moles of pyridine-2-thiol forms a species proposed to be cis-$[RhCl(CO)_2(py\text{-}SH)]$ from in situ spectroscopic data but on attempted isolation only a dark, uncharacterizable solid could be obtained. Use of larger ratios of the ligand gave a mixture of mono- and dicarbonyl complexes which were not characterized. However if a mixture of $[RhCl(CO)_2]_2$ and py-SH (1:4) in chloroform allowed to stand under dinitrogen for several days crystals of [241] formed. Air-oxidation of a similar solution in which py-SH:Rh > 6 formed an orange compound which on chromatography on alumina yielded the red complex $[Rh(py\text{-}SH)(py\text{-}S)_3]$ (ref. 477). Addition of $[Rh(CO)_2(acetone)_x]ClO_4$ to two mols of [Rh(Onapy)(COD)] forms $[Rh_2(COD)_2(\mu\text{-}Onapy)_2Rh(CO)_2]$ ([242]) (ref. 478).

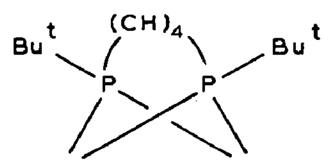


[241]



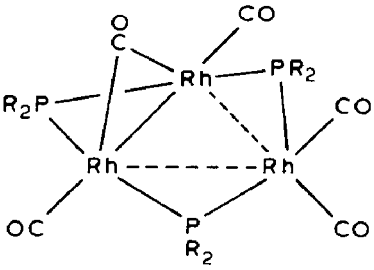
[242]

Refluxing a mixture of $[Rh_4(CO)_{12}]$ and di-*tert*-butylphosphine in toluene forms *cis*-$[Rh_2(CO)_2(PBu^t{}_2H)_2(\mu\text{-}PBu^t{}_2)(\mu\text{-}H)]$ while $[RhCl(COD)]_2$ and lithium di-*tert*-butylphosphide in refluxing THF yield $[Rh_2(COD)_2(\mu\text{-}PBu^t{}_2)(\mu\text{-}Cl)]$. The former contains a metal-metal bond and is planar while the latter does not and is folded along the phosphorus-chlorine axis. At -78°C in THF lithium di-*tert*-butylarsenide and $[RhCl(COD)]_2$ form planar $[Rh_2(CO)_4(\mu\text{-}AsBu^t{}_2)_2]$ which contains no metal-metal bond and $[Rh_6(CO)_{11}(\mu\text{-}AsBu^t{}_2)_2(\mu_4\text{-}AsBu^t)]$ whose structure was reported last year (J. Organometal. Chem., 324(1987)57 [104]). In contrast to the results of the reaction noted above, the reaction of $[RhCl(COD)]_2$ with 1,4-bis(lithio-*tert*-butylphosphino)butane at -78° in THF forms [243] which is thought to have tetrahedral coordination about each metal and a rhodium-rhodium double bond.



[243]

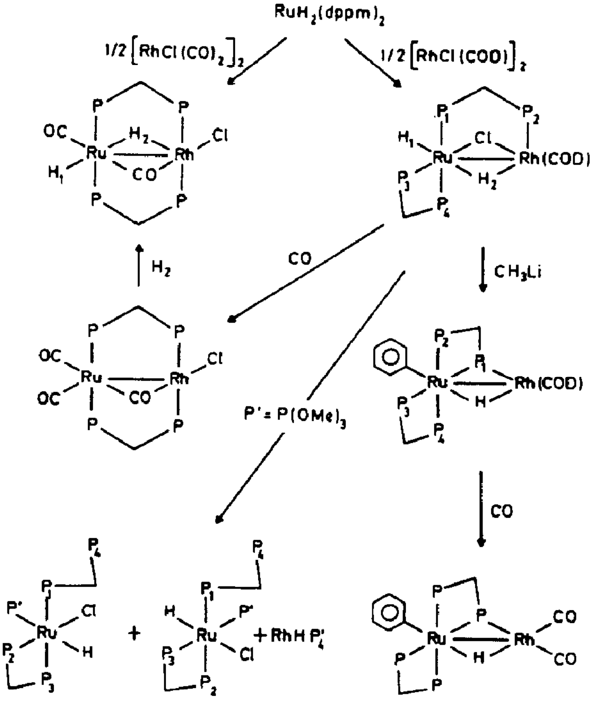
Carbon monoxide adds reversibly to $[Rh_3(CO)_3(\mu\text{-}PBu^t{}_2)_3]$ to form [244] (R = Bu^t) in which the rhodium-rhodium interactions indicated by dotted lines



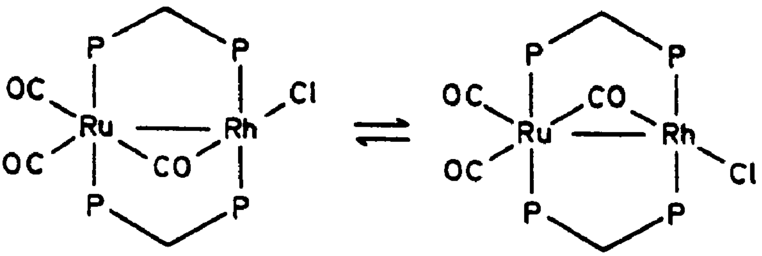
[244]

are significantly longer than in the parent complex but are still within bonding distances (ref. 479, 480).

The addition of sulfur dioxide to $[(OC)_3Mo(\mu\text{-DPM})_2RhCl(CO)]$ forms $[(OC)_2Mo(\mu\text{-DPM})_2(\mu\text{-CO})(\mu\text{-SO}_2)RhCl]$ (ref. 481). A full report on heterobinuclear ruthenium-rhodium complexes of DPM has now appeared and the results are outlined in Scheme XLVI. The tricarbonyl complex is fluxional as shown in Scheme XLVII (see also ref. 558) (ref. 482). Reaction of $[RhCl(CO)_2]_2$ with *dl*-*trans*-1,2-bis(diphenylphosphino)cyclopropane(L_2) forms the face-to-face dimer $[Rh_2Cl_2(CO)_2(\mu\text{-}L_2)_2]$ while with $[Ag_2(\mu\text{-}L_2)_2](BF_4)_2$ the product is [245]. The face-to-face iridium dimer $[Ir_2Cl_2(CO)_2(\mu\text{-}L_2)_2]$ is formed from the ligand and $[IrCl(CO)(PPh_3)_2]$ or $[IrCl(CO)_2(p\text{-toluidine})]$

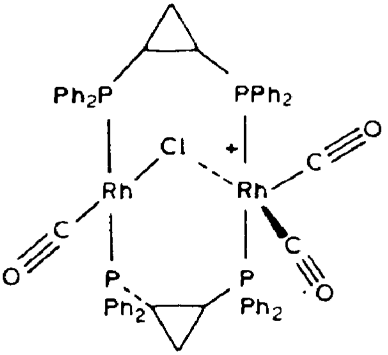


Scheme XLVI

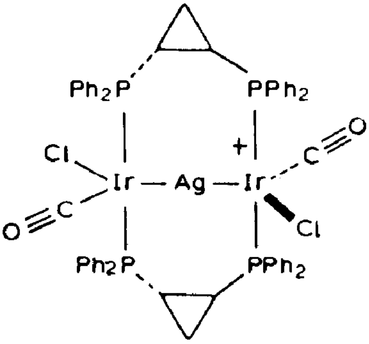


Scheme XLVII

and on treatment with silver tetrafluoroborate gives [246] (ref. 483). Addition of dmmm to $[RhCl(CO)_2]_2$ in methanol/dichloromethane followed by

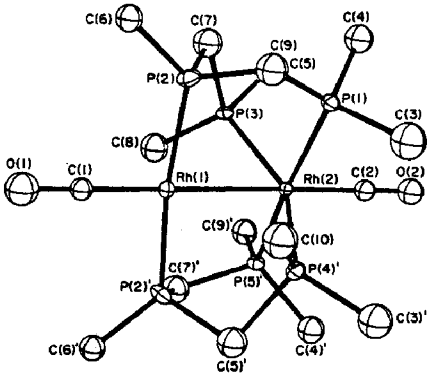


[245]



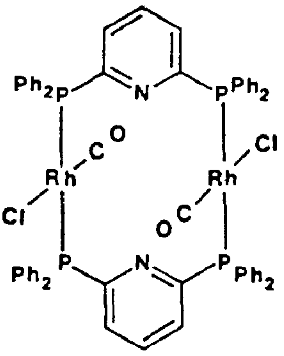
[246]

metathesis with sodium tetraphenylborate forms $[Rh_2(CO)_2(dmmm)_2](BPh_4)_2$ whose cation is shown as [247] plus smaller amounts of $[Rh_3Cl(CO)_3(dmmm)_2$-(μ-Cl)]BPh_4. The cation [247] shows considerable congestion about Rh(2),

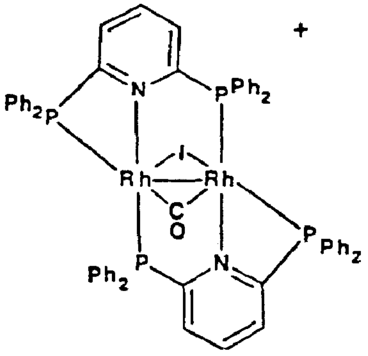


[247]

is fluxional, possible via a twisting about the metal-metal axis, and is considered to contain a donor (Rh(2)→Rh(1)) metal-metal bond (ref. 484). Metathesis of [248] with sodium iodide in methanol/dichloromethane causes a rearrangement of the attachment of the diphosphine ligand to form the cation [249] which was isolated as the tetraphenylborate salt (ref. 485).

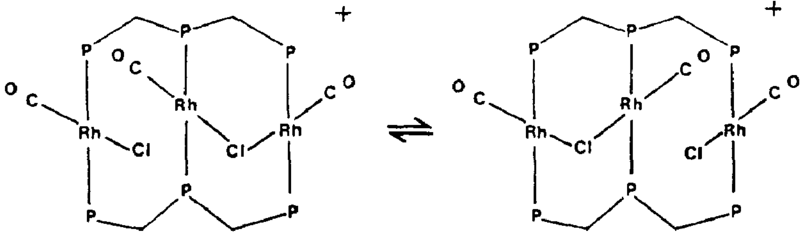


[248]

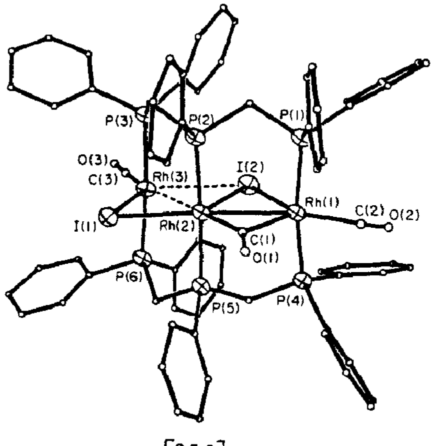


[249]

The trimetallic complexes $[Rh_3Cl(CO)_3(\mu\text{-}Cl)(L_3)_2]BPh_4$ (L_3 = dpmp, dpma) are formed from $[RhCl(CO)_2]_2$ and the ligand in chloroform/ethanol followed by metathesis with sodium tetraphenylborate. They are fluxional as shown in Scheme XLVIII for the dpmp complex. Metathesis of $[Rh_3Cl(CO)_3(\mu\text{-}Cl(L_3)_2]BPh_4$ with sodium halides or pseudohalides in methanol forms $[Rh_3X(CO)_3(\mu\text{-}X)(L_3)_2]BPh_4$ (L_3 = dpmp; X = N_3, NCO. L_3 = dpma; X = Br) which have the same structure as the parent complex and are also fluxional by the process of Scheme XLVIII. With sodium iodide (L_3 = dpmp) the previously characterized monocation [250] which is non-fluxional forms

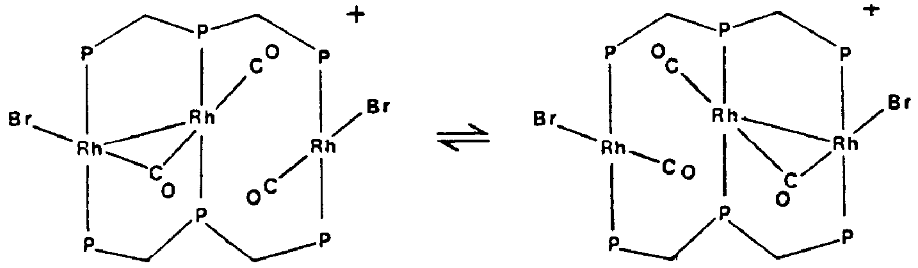


Scheme XLVIII



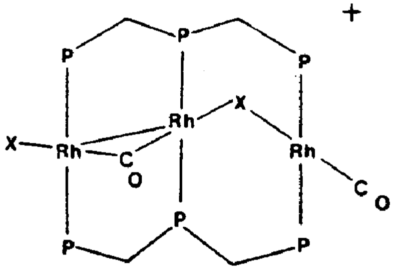
[250]

while with sodium bromide (L_3 = dpmp) the product can adopt two different structures depending on the solvent used for recrystallization. When obtained from acetone/diethyl ether it has the same structure as the parent chloro complex (see Scheme XLVIII) but when obtained from dichloromethane/methanol it has the structure shown in Scheme XLIX which also shows the

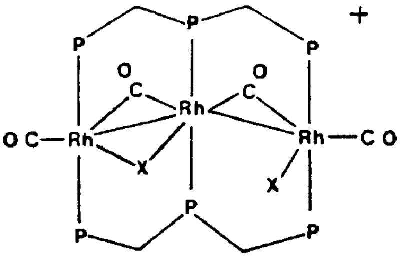


Scheme XLIX

fluxional process observed in solution. The cations $[Rh_3X_2(CO)_3(dpmp)_2]^+$ (X = Cl, Br, I) lose carbon monoxide to form [251] and add carbon monoxide to give [252]. Additional chemistry of [251] (X = Cl) is shown in Scheme L

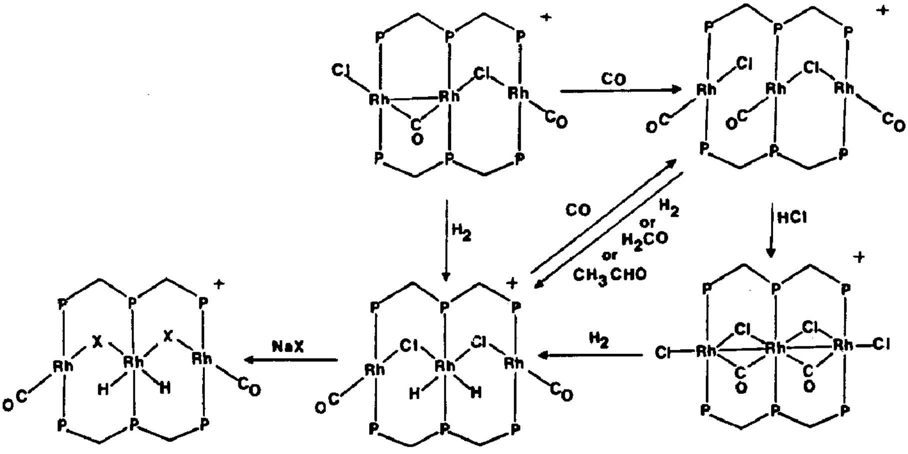


[251]



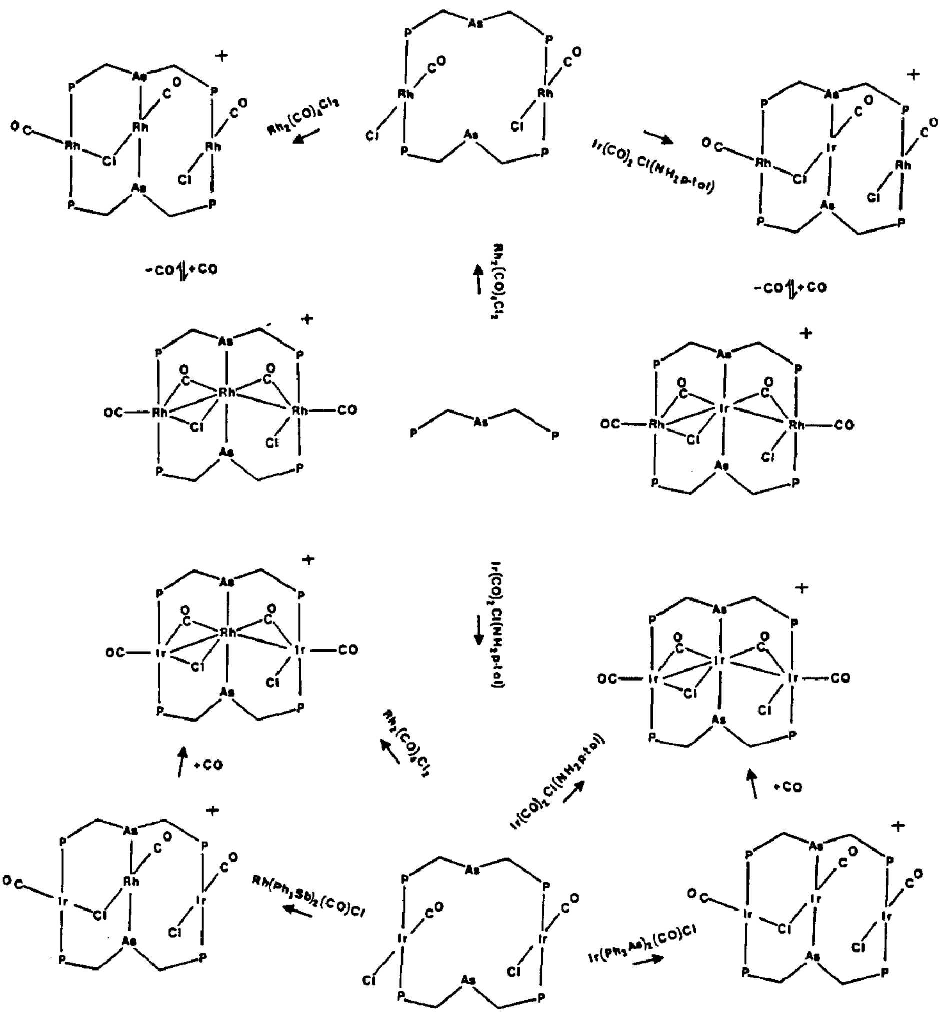
[252]

and when the tricarbonyl is treated with a mixture of hydrogen and deuterium a significant amount of HD is seen in the gas phase indicating the



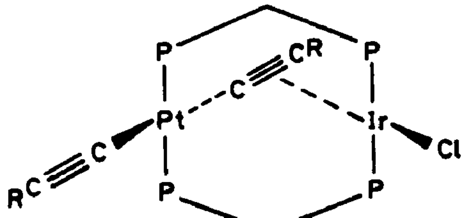
Scheme L

presence of multiple sites for hydrogen activation. The reaction with formaldehyde is thought to involve formation of an {Rh(H)CHO} moiety but this has not been detected. Reaction of DMAD with $[Rh_3Cl(CO)_3(\mu\text{-}Cl)(dpmp)_2]BPh_4$ forms $[Rh_3Cl_2(CO)_2(DMAD)(dpmp)_2]BPh_4$ as a mixture of two isomers of unknown structure but with DEAD a single product is obtained which appears to be the same as the major isomer formed in the previous reaction. The major isomer of $[Rh_3Cl_2(CO)_2(DMAD)(dpmp)_2]BPh_4$ reacts in a stepwise fashion with iodide ion to replace the chloride ligands without apparently altering the structure but is unreactive towards carbon monoxide. The minor isomer, on the other hand, reversibly adds carbon monoxide and reacts with iodine to form $[Rh_3Cl(I)(CO)_2(DMAD)(dpmp)_2]I$. Reaction of appropriate quantities of dpma and $[IrCl(CO)_2(\underline{p}\text{-toluidine})]$ followed by metathesis with sodium tetraphenylborate forms $[Ir_3Cl(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)_2(dpma)_2]BPh_4$ whose structure is essentially the same as [252] but unlike the latter does not tend to lose carbon monoxide. The complex is fluxional, presumably <u>via</u> bridge-terminal interchange of the chloride ligands and can be converted to bromo and iodo analogs of the same structure by metathesis with sodium halides in methanol. If dpma and $[RhCl(CO)_2]_2$ or $[IrCl(CO)_2(\underline{p}\text{-toluidine})]$ are combined with a metal:ligand ratio of 1:1, the face-to-face dimers $[M_2Cl_2(CO)_2(dpma)_2]$ shown in the center column of Scheme LI are formed. From these a variety of cationic heterotrimetallic derivatives as well as the previously described trirhodium complex can be prepared as shown in Scheme LI. The two tetracarbonyl complexes in the second row from the top and the triiridium complex at the bottom right were identified in solution but could not be isolated. The stability of the tetracarbonyl complexes towards loss of carbon monoxide increases in the order $Rh_3 < Rh_2Ir < Ir_2Rh < Ir_3$ and all these plus the tricarbonyl complexes are fluxional presumably by interchanges of bridging and terminal ligands (refs. 486-490).

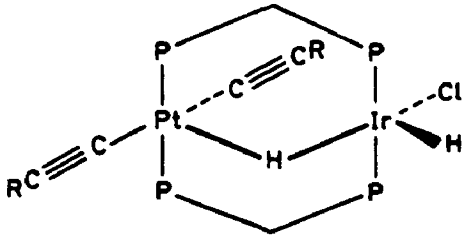


Scheme LI

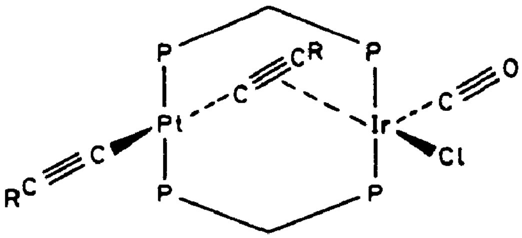
Reaction of $[Pt(C{\equiv}CR)_2(DPM)_2]$ (R = Ph, *p*-tolyl) with $[IrCl(cyoct)_2]_2$ forms a mixture of $[Pt_2(C{\equiv}CR)_4(DPM)_2]$ and [253]. The latter adds dihydrogen to yield [254]. Refluxing a benzene solution of $[Pt(C{\equiv}CR)_2(DPM)_2]$ and $[IrCl(CO)(PPh_3)_2]$ gives [255] (R = Me, Ph, *p*-tolyl) which on metathesis



[253]

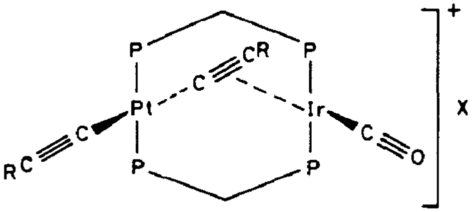


[254]

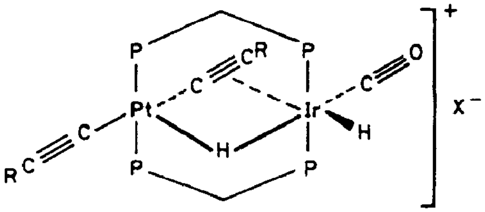


[255]

with salts of non-coordinating anions yields [256] (X = BPh_4, R = Me, Ph, p-tolyl. X = PF_6; R = Me, p-tolyl). Complexes [256] reversibly add dihydrogen to form [257] (R = Ph; X = BPh_4. R = Me, p-tolyl; X = PF_6)



[256]



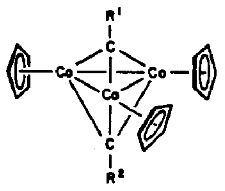
[257]

(ref. 491). The structure of $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}H)(DPM)_2]BF_4$ appears to be quite similar to that of its rhodium analog except that in the solid the four phenyl groups on the side of the bridging hydride obstruct the adjacent metal sites more than is the case in the rhodium complex (ref. 492).

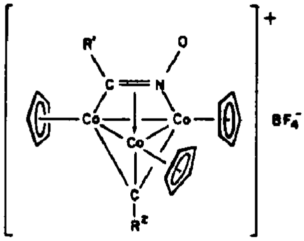
Metal Nitrosyl and Aryldiazo Complexes

In refluxing toluene, benzyl bromide reacts with $[Co(NO)(P(OEt)_3)_3]$ under carbon monoxide to give low yields of benzamide, benzaldehyde, benzyl alcohol and 1,2-diphenylethane while $[RhCl_2(NO)(PPh_3)_2]$ forms the first three plus benzonitrile and $[Rh(NO)(PPh_3)_2]$ yields benzonitrile, benzaldehyde and benzyl alcohol. In all cases most of the benzyl bromide was recovered at the end of the reaction (ref. 493). The complexes $[CoX_2(NO)(PMe_3)_2]$ (X = Cl, Br, I, NO_2) can be prepared from $[CoX_2(PMe_3)_2]$ (X = halide) or $[Co(NO_2)_2(PMe_3)_3]$ and nitric oxide in methanol. The iodide complex has a trigonal bipyramidal structure with axial phosphine ligands and an equatorial, linear nitrosyl ligand. The chloride complex has the same structure with possibly a bent nitrosyl ligand but a disorder problem hampered definite determination of its geometry. The nitrite complex is proposed to have a square pyramidal structure with a bent nitrosyl ligand. The structural differences are attributed to electronic factors (ref. 494).

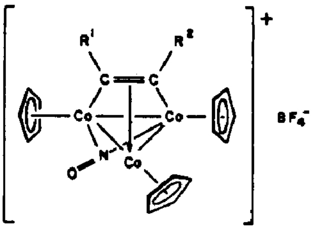
The first example of insertion of nitric oxide into a metal-carbon bond in a cluster has been reported in the reaction of [258] with nitrosyl tetrafluoroborate in dichloromethane/nitromethane which yields [259] (R^1 = R^2 = Bu^n, Ph. R^2 = H; R^1 = Pr^n, Bu^n. R^1 = Me; R^2 = CO$_2$Me). Complex [259] (R^1 = Bu^n; R^2 = Bu^n, H) reacts with butyllithium or sodium methoxide to form [260] and with carbon monoxide to give [261]. Comparison of the structures of [259] and [258] when R^1 ≠ R^2 indicates that the insertion is regiospecific and occurs at the more electron-rich metal-carbon bond (ref. 495).



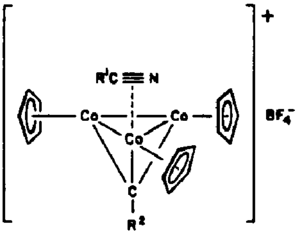
[258]



[259]



[260]



[261]

The complexes $[R_3Co_3(\mu_3\text{-NO})(\mu_3\text{-NH})]^+$ (R = cp, cpMe) (see refs. 397, 398) can be chemically reduced to $[R_3Co_3(\mu_3\text{-NO})(\mu_3\text{-NH})]$ by cobaltocene. The structure of the neutral product shows that the metal framework has become distorted to an isosceles triangle suggesting that the added electron occupies a HOMO of <u>e</u> symmetry. The distortion is attributed to a vibronic Jahn-Teller effect and since the cobalt-nitrogen distances are not significantly different from those in the parent cation, this orbital is proposed to be largely cobalt-cobalt antibonding and to be localized primarily between the two cobalt atoms whose separation increases (ref. 496). Reaction of $Na_2[Fe_2(\mu\text{-S})_2(NO)_4]\cdot 8H_2O$ (Roussin's Red Salt) with [cp'Co(CO)I$_2$] forms $[cp'_2Co_2Fe(NO)_2(\mu_3\text{-S})_2]$ in low yield (ref. 497).

The gas phase, ion-molecule chemistry of [Co(NO)(CO)$_3$] has been studied by FTMS techniques. Stepwise reactions of bare and ligated cobalt ions with this molecule occur as outlined in Scheme LII (each step involves reaction with another molecule of [Co(NO)(CO)$_3$]). Significant ligand effects on the reactivity of the cluster ions were noted and appear to be determined by the number of vacant cluster valence molecular orbitals. In

$$\begin{tikzcd}
Co^{+} \arrow[r] & Co_2(CO)_x(NO)^{+} \arrow[r] & Co_3(CO)_2(NO)_2^{+} \arrow[r] & Co_4(CO)_{x+2}(NO)_3^{+} \arrow[d] \\
 & Co_6(CO)_{x+4}(NO)_5^{+} & Co_5(CO)_{x+3}(NO)_4^{+} \arrow[l] & \arrow[l]
\end{tikzcd}$$

(x = 1, 2)

$$\begin{tikzcd}
Co(CO)^{+} \arrow[r] & Co_2(CO)_x(NO)^{+} \arrow[r] & Co_3(CO)_2(NO)_2^{+} \arrow[d] \\
Co_5(CO)_4(NO)_4^{+} & Co_4(CO)_{x+1}(NO)_3^{+} \arrow[l] & \arrow[l]
\end{tikzcd}$$

(x = 2-4)

$$Co(NO)^{+} \longrightarrow Co_2(CO)_3(NO)_2^{+}$$

$$\begin{tikzcd}
Co(CO)_2^{+} \arrow[r] & Co_2(CO)_x(NO)^{+} \arrow[r] & Co_3(CO)_4(NO)_2^{+} \arrow[d] \\
Co_5(CO)_4(NO)^{+} & Co_4(CO)_{x+1}(NO)^{+} \arrow[l] & \arrow[l]
\end{tikzcd}$$

(x = 3, 4)

$$Co(CO)(NO)^{+} \longrightarrow Co_2(CO)_x(NO)_2^{+}$$

(x = 2, 3)

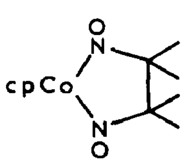
$$\begin{tikzcd}
Co(CO)_2(NO)^{+} \arrow[r] & Co_2(CO)_x(NO)_2^{+} \arrow[r] & Co_3(CO)_{x+1}(NO)_y^{+} \arrow[d] \\
 & Co_4(CO)_4(NO)_3^{+} & \arrow[l]
\end{tikzcd}$$

(x = 3, 4; y = 2, 3)

Scheme LII

general it appears that a fragment reacts with the neutral species in such a way as to add fourteen electrons to the cluster (ref. 498). Other work on $[Co(NO)(CO)_3]$ include a molecular beam study of the dynamics of photofragmentation using 193 nm radiation (ref. 499) and a laser-based time-resolved infrared study of the photolysis using 248 nm radiation. In this work, a sequence of ligand losses is proposed to occur following the initial excitation which ends with the formation of {Co(CO)}. This then reacts with undissociated $[Co(NO)(CO)_3]$ to form $[Co_2(NO)(CO)_4]$ whose structure is unknown (ref. 500). The ultraviolet photolysis of $[Co(NO)(CO)_3]$ in liquid xenon containing dihydrogen or deuterium forms a species formulated as a molecular hydrogen (or deuterium) adduct $[Co(NO)(CO)_2(X_2)]$ (X = H, D). No significant oxidation of the metal is apparent and the species rapidly disappears when dihydrogen is vented. No cobalt-hydrogen stretching vibrations were seen but ν_{H-H} and low frequency vibrations due to the $\{Co(H_2)\}$ moiety could be detected (ref. 501). In related work, photolysis of $[Co(NO)(CO)_3]$ and but-1-ene in liquid xenon is proposed to form $[Co(NO)(CO)_2(\eta^2\text{-}C_4H_8)]$ (ref. 502).

Fenske-Hall molecular orbital calculations have been performed on the isoelectronic species $[cp_2Co_2(CO)(NO)]$ and $[cp_2Co_2(CO)_2]^-$ in an effort to determine why they are more stable than $[cp_2Co_2(CO)_2]$. In $[cp_2Co_2(CO)_2]^-$, the odd electron appears to occupy an orbital which is metal-metal antibonding but its presence also raises the energies of the other metal d orbitals relative to those of the π-acceptor orbitals on the ligands. Thus π-backbonding is enhanced and leads to increased stability. The situation is similar for $[cp_2Co_2(CO)(NO)]$. Also since the HOMO does not mix with orbitals involved in the bonding to the bridging ligands it is predicted that removal of the electron from the HOMO will decrease the amount of π-backbonding which is consistent with the observed irreversibility of the electrochemical oxidation of this complex. From these calculations it is also predicted that $[cp_2Co_2(NO)(CO)]$ should have a net metal-metal bond order of one while $[cp_2Co_2(CO)_2]$ has a bond order of two (refs. 503, 504). Hoffmann has used his fragment molecular orbital approach to explore details of the reaction of $[cp_2Co_2(NO)_2]$ with alkenes which has been shown to form [262]. In this study the species [263] has frontier orbitals which



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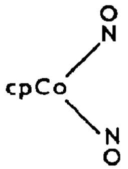
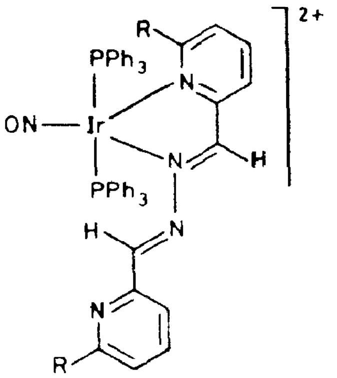


[263]

are well-suited for interaction with the π-bond of the olefin (ref. 505). The solid-state MAS ^{13}C NMR spectrum of $[Co(NO)(CO)_3]$ encapsulated in the cages of an NaY zeolite shows a much narrower signal than is observed for the complex itself in chloroform solution. This is proposed to be the result of a more rapid scalar quadrupolar relaxation of the cobalt in the former case. Reduction of the zeolite-encapsulated species with dihydrogen forms a catalyst showing Fischer-Tropsch activity which does not give products higher than C_8. This is presumed to indicate that the catalyst exhibits a shape selectivity (ref. 506).

Reaction of $[Rh(NO)(NO_3)(PPh_3)_2]$ with iodosobenzene in refluxing chloroform yields $[Rh(NO_3)_2(PPh_3)_2]$ while with $[Rh(NO)_2(PPh_3)_2]ClO_4$ in the presence of pyridine the product is $[Rh(NO_2)_2py_4]ClO_4$ (ref. 507). In a related study, $[Rh(NO)_2(PPh_3)_2]^+$ is shown to undergo exchange with free nitric oxide in contrast to a previous report. The exchange is enhanced by free triphenylphosphine and an associative mechanism is proposed (ref. 508). A convenient synthesis of $[MCl_2(NO)(PPh_3)_2]$ (M = Rh, Ir) involves reaction of the hydrated metal trichloride and triphenylphosphine with N-nitroso-N-methylaniline (M = Rh) or N-nitrosodibenzylamine (M = Ir) in refluxing 2-methoxyethanol under an atmosphere of hydrogen chloride (ref. 509). Addition of 2-pyridinecarbaldehyde azine and its 6-methyl analog to $[Ir(NO)(MeCN)_3(PPh_3)_2](PF_6)_2$ forms a complex proposed to be [264] (R = H, Me). The monocationic carbonyl analog is prepared from $[Ir(CO)(MeCN)(PPh_3)_2]^+$ and reacts with a second equivalent of $[Ir(CO)(MeCN)(PPh_3)_2]^+$ to form [265] (R = H, Me) (ref. 510).



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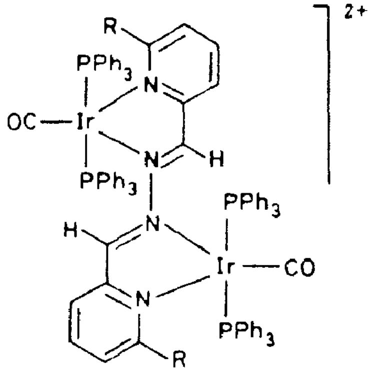


[265]

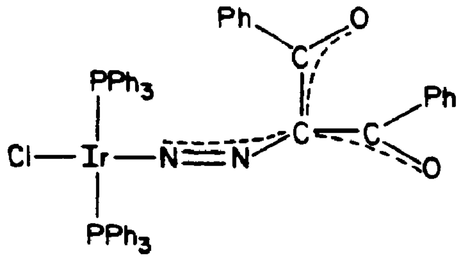
The aryldiazo complexes $[Co(N_2R)L_4]^{2+}$ (L = $P(OEt)_3$, $PPh(OEt)_2$; R = *o*-tolyl, *m*-tolyl, *p*-tolyl, *p*-anisyl, Ph) can be obtained by reaction of the appropriate aryldiazonium cation with $[Co(CO)L_4]^+$. This route was not successful when L = $P(OMe)_3$ and with this ligand it was necessary to start with $[Co(P(OMe)_3)_5]^+$. The complexes are proposed to have a trigonal bipyramidal structure with an equatorial, bent aryldiazo ligand and are fluxional *via* an intramolecular process. Displacement of the aryldiazo ligand by π-acceptor ligands occurs as shown in Scheme LIII (L and R as above) (ref. 511). Addition of dibenzoyldiazomethane to $[IrCl(N_2)(PPh_3)_2]$ forms [266] which adds dimethylphenylphosphine, *tert*-butylisocyanide or nitrosyl cation to give five-coordinate adducts. With carbon monoxide however simple replacement of the diazoalkane occurs. Reaction of [266]

$$\begin{tikzcd}
& {[\mathrm{CoL}_5]^+} & {[\mathrm{Co(CO)}_2\mathrm{L}_2]^+} \\
{[\mathrm{Co(NO)}_2\mathrm{L}_2]^+} & {[\mathrm{Co(N}_2\mathrm{R)L}_4]^{2+}} \arrow[l, "d"'] \arrow[u, "a"'] \arrow[r, "b"] \arrow[d, "c"] & {[\mathrm{Co(CO)L}_4]^+} \arrow[u, "b"'] \\
& {[\mathrm{Co(CNR')L}_4]^+ + [\mathrm{Co(CNR')}_2\mathrm{L}_3]^+} &
\end{tikzcd}$$

a) L, Δ. b) CO. c) CNR' (R' = p-tolyl). d) NO.

Scheme LIII

with hydrogen chloride in toluene forms an equilibrium mixture of [267] and [268] in which the former predominates. Use of an excess of hydrogen chloride forms an insoluble material thought to possibly be an analog of [268] with a chloride ligand in place of the hydride. Complex [266] is stable at room temperature in non-halogenated solvents in the absence of air but on heating or dissolution in dichloromethane it forms a mixture of [267] and [269]. Only [269] is formed if $[\mathrm{IrCl(N_2)(PPh_3)_2}]$ is refluxed with dibenzoyldiazomethane in toluene while in THF [269] and a minor amount of an isomer of this form. Starting with $[\mathrm{IrCl(PPh_3)_3}]$ this last reaction gives the second isomer of [269] as the major product together with minor amounts of [270] (refs. 512, 513).



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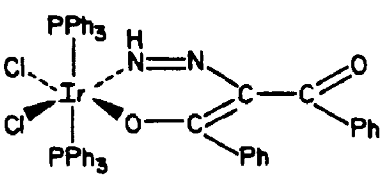

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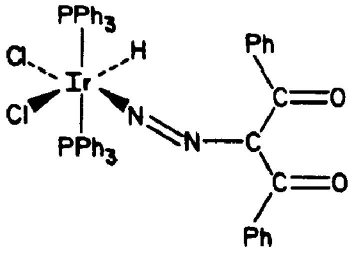

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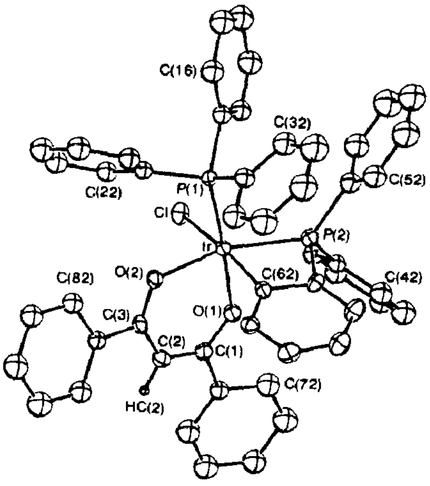

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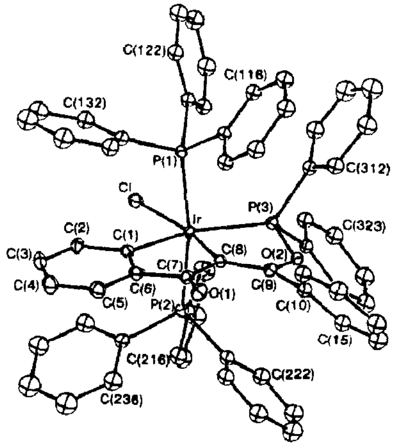
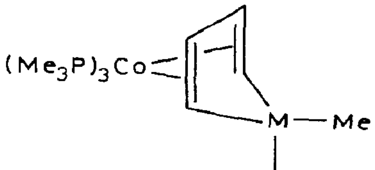


[270]

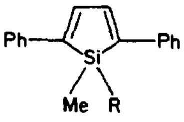
Metal Alkene Complexes

Reaction of 1,1,3,4-tetramethylsilacyclopenta-2,4-diene and its germanium analog with [CoBr(PMe$_3$)$_3$] and sodium tetraphenylborate in acetone forms [271] (M = Si, Ge). The structures of both have been determined and the

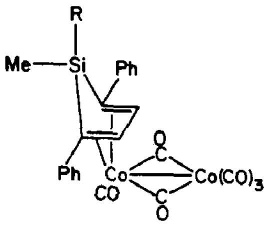


[271]

coordination geometry about cobalt is considered to be approximately square pyramidal with the cyclic ligand bonded as an η^4-diene. The complexes are

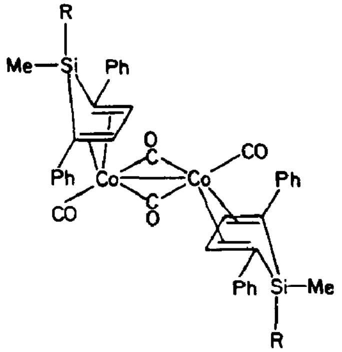


[272]

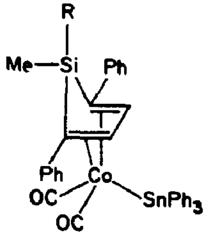


[273]

fluxional even at the lowest temperature attainable on the instrument used (ref. 514). With dicobaltoctacarbonyl the silacyclopentadienes [272] form [273] (R = $SiMe_3$, CH_2=$CHCH_2$) or [274] (R = Me). Addition of more of the corresponding [272] to [273] forms other examples of [274] (R = $SiMe_3$, CH_2=$CHCH_2$) while reduction of [273] (R = $SiMe_3$, CH=$CHCH_2$) and [274] (R = Me) with sodium amalgam in the presence of triphenyltin chloride yields [275] (R = Me, $SiMe_3$, CH_2=$CHCH_2$). In the reactions of [273], [$Ph_3SnCo(CO)_4$] is also formed (ref. 515). Treatment of [$CoBr(PMe_3)_3$] with olefins

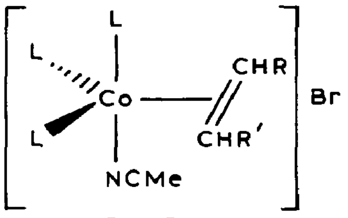


[274]



[275]

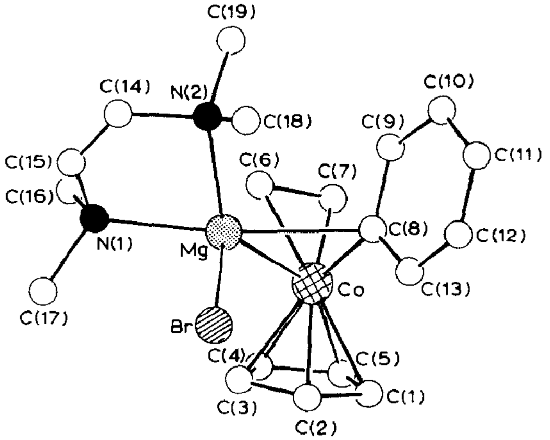
in acetonitrile/acetone at -80°C forms [276] (L = PMe_3, R = R' = H, R = H; R' = CN, Ph. R = Me, R' = CN) which was identified in solution. Attempted



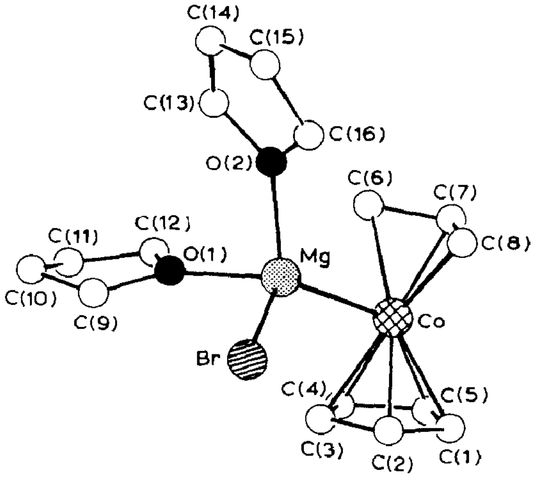
[276]

isolation of the styrene complex by addition of tetraphenylborate ion formed [$Co(H_2C$=$CHPh)(PMe_3)_3$]BPh_4 which is tetrahedral and the first example of a paramagnetic alkene complex of cobalt(I) (ref. 516). Addition of TCNE to [(cpMe)Co(CO)(L)] in benzene forms [(cpMe)Co(TCNE)L] (L = $P(OMe)_3$, CO, PPh_3, py) which is paramagnetic with the unpaired electron localized on the TCNE ligand (ref. 517).

Addition of diphenylmagnesium to a THF solution of $[cpCo(C_2H_4)_2]$ forms the adduct $[cpCo(C_2H_4)(C_6H_5)Mg(C_6H_5)(THF)_2]$ while with diallylmagnesium the product is $[cpCo(\pi-C_3H_5)Mg(\sigma-C_3H_5)(THF)_2]$. No reaction occurs between $[cpCo(C_2H_4)_2]$ and methyl or phenyl magnesium bromide in diethyl ether but if THF is also present $[cpCo(C_2H_4)(R)MgBr(THF)_2]$ (R = Me, Ph) forms. When R = Ph this product reacts with TMEDA to yield [277] which is considered to be a Lewis acid base adduct between $[Mg(tmeda)Br]^+$ and $[cpCo(C_2H_4)Ph]^-$. Finally, allyl magnesium bromide and $[cpCo(C_2H_4)_2]$ react in THF to form [278] (ref. 518). In an attempt to prepare $[cpCo(\eta^5-CH_2C(CF_3)CHC(CF_3)-CH_2)]^+$, $[cpCo(C_2H_4)_2]$ was treated successively with 2,4-bis(trifluoromethyl)penta-1,3-diene to give [279] and then with trityl cation but the

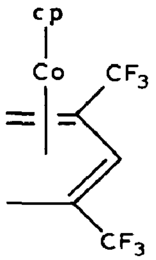


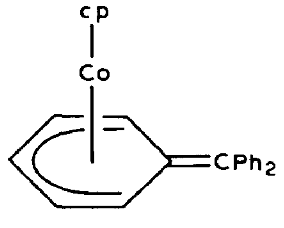
[277]



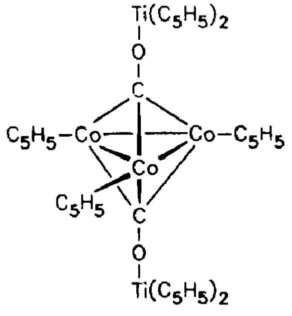
[278]

isolated product was [280]. This could also be prepared directly from [cpCo(C_2H_4)$_2$] and trityl cation (ref. 519). Reaction of [cp$_2$Ti(CO)$_2$] and

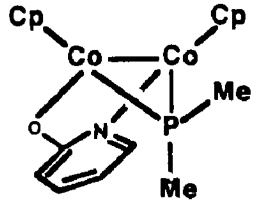

[279]


[280]

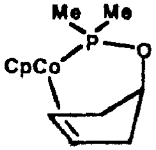
[cpCo(C_2H_4)$_2$] (2:3 ratio) in warm toluene forms the cluster [281] in which a carbonyl ligand on each titanium has been effectively reduced (ref. 520).


[281]

No isolable products could be obtained from the reaction of 2-pyridyldimethylphosphinite with [cpCoL$_2$] (L = CO. L$_2$ = NBD, COD) but with [cpCo(C_2H_4)$_2$] cleavage of the phosphorus-oxygen bond occurs to form [282]. On


[282]

the other hand no cleavage occurs when p-*tert*-butylphenyldimethylphosphinite (L) is used and the simple substitution product [cpCo(C_2H_4)(L)] is obtained. The *tert*-butylphenoxy substituent can be replaced in the coordinated ligand by the alkoxide of cyclopent-3-en-1-ol on reaction with its potassium salt. Photolysis of the resulting cobalt complex then yields [283] and the analogs [284] and [285] (R = H, Me, Pr^i) could be prepared in similar fashion. The samples of [285] with R = Me, Pr^i were obtained as



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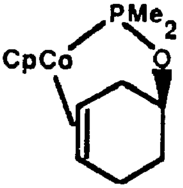
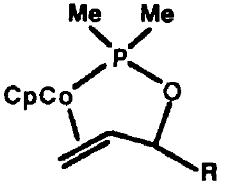
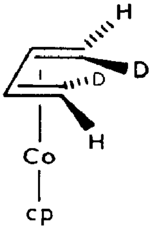


[284]



[285]

mixtures of diastereoisomers (ref. 521). Thermolysis of [286] leads to stereorandomization but photolysis at -96°C forms [287] and this is proposed to form <u>via</u> [288] as an intermediate. To further elucidate the



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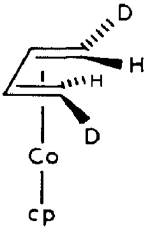

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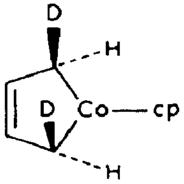

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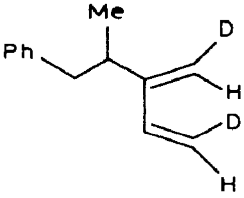
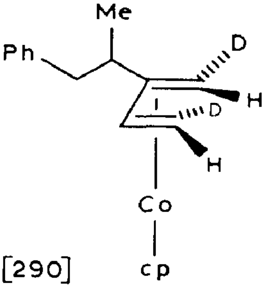
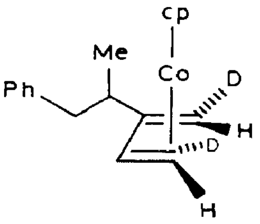


[289]

details of the reaction, $[cpCo(C_2H_4)_2]$ was reacted with [289] to form [290] and [291] in a 1:5 ratio. Irradiation of this mixture forms [292] and

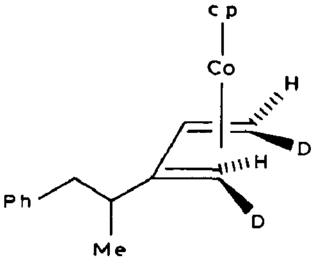


[290]



[291]

[293] in equal amounts which indicates that the isotopomerization is synchronous with diastereoisomerization and no ligand crossover occurs. The results are taken to support the "envelope" inversion mechanism (<u>via</u> intermediates like [288]) for the fluxional behavior of η^4-diene complexes (ref. 522). Refluxing hexane solutions of OFCOT and $[cp'ML_2]$ (M = Co; L = CO. M = Rh; L = C_2H_4) yield [294] which on photolysis equilibrates with



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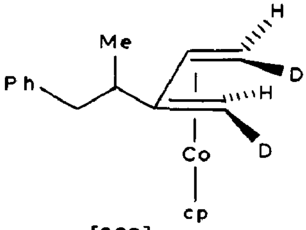

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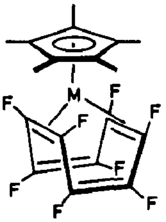
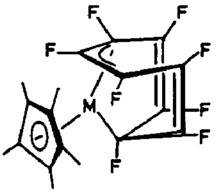
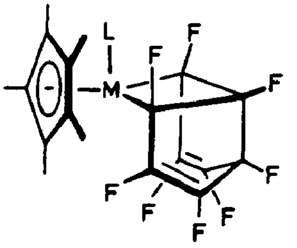


[294]



[295]

[295] (M = Co, Rh). From this equilibrium [295] reacts thermally with ligands to form [296] (M = Co, Rh; L = Bu^{t}NC. M = Rh; L = PMe$_3$) via [297] as an intermediate which could be isolated (M = Rh; L = PMe$_3$) at low



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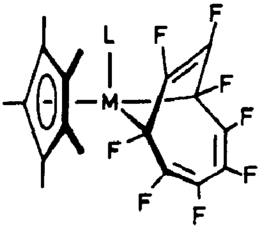
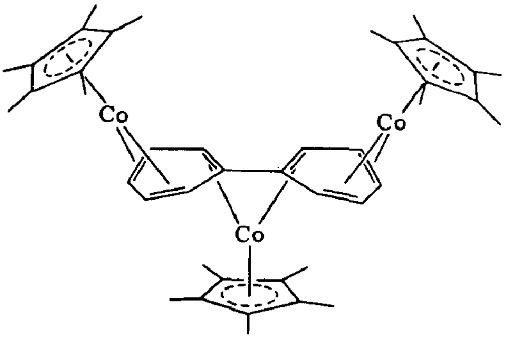


[297]

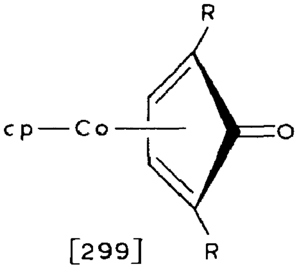
temperature (ref. 523). One carbonyl group in [cpCo(CO)$_2$] can be replaced by 3-tert-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene when a mixture of the two is photolyzed (ref. 524) while reaction of [cp'$_2$Co$_2$(μ-Cl)$_2$] with phenyllithium in diethyl ether at -80°C followed by warming to room temperature forms [298]. The coordination of the metal atoms to the biphenyl in a



[298]

manner which involves localized carbon-carbon double bonds is proposed on the basis of the NMR spectrum (ref. 525). $[(\eta^5\text{-}C_5H_4CO_2Me)Co(L_2)]$ (L_2 = COT, COD) is a catalyst precursor for the cocyclotrimerization of acetylenes with nitriles to form substituted pyridines. It appears to have a greater resistance to deactivation by dioxygen than its cyclopentadienyl analog (ref. 526).

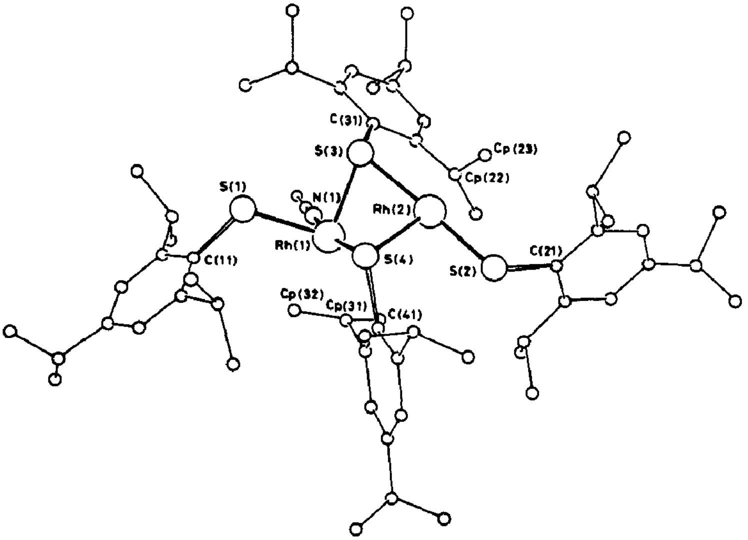
As part of a study to probe why $\{M(CO)_3\}$ and $\{CoL_3\}^+$ (L = tertiary phosphine) fragments prefer to bind to conjugated diolefins but the isolobal {cpM} (M = Co, Rh, Ir) fragments prefer non-conjugated diolefins, the complexes [cpCo(COT)] and [cp'Co(COT)] were examined and the rates of isomerization between the isomer with the COT bonded as a 1,3-diene (conjugated form) and that where it is bonded as a 1,5-diene (non-conjugated form) were determined. In both instances the non-conjugated form is preferred and while the rate of conversion of the pentamethylcyclopentadienyl complex to the conjugated form is an order of magnitude slower than that for the cyclopentadienyl analog those for the monoanions of both complexes are approximately equal and six orders of magnitude larger. This difference is attributed to a raising of the symmetry restriction for the least motion pathway when the complexes are reduced (ref. 527). Cotton-Kraihanzel force constants for carbon-oxygen stretching motions in carbonyl ligands have been used to predict the reactivity of $\eta^2\text{-}C_2H_4$ and $\eta^6\text{-}C_6H_6$ ligands towards nucleophilic attack. Thus carbonyl force constants in $[L_nM(CO)]$ were used to assess the electron-withdrawing ability of the $\{L_nM\}$ fragment in complexes such as $[L_nM(C_2H_4)]$ or $[L_nM(\eta^6\text{-}C_6H_6)]$. Unfortunately in the case of the ethylene complexes, it proved impossible to predict by this method whether replacement of coordinated ethylene by a nucleophile such as a tertiary phosphine would be faster or slower than addition to it (ref. 528). A variety of ^{103}Rh NMR data on [cpRh(diene)] complexes and ^{59}Co NMR data on [cpCo(diene)] and $[(\eta^5\text{-}C_9H_7)Co(diene)]$ complexes has been reported (ref. 529) as has the structure of and EHMO calculations on [299]



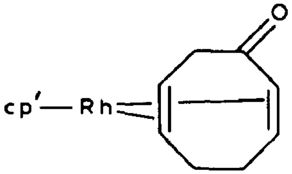
[299]

(R = H, $SiMe_3$) (ref. 530).

The cumulenes $R_2C{=}C{=}C{=}C{=}CR'_2$ (R = Me; R' = Me, Ph) replace the triphenylphosphine ligand trans to chloride in $[RhCl(PPh_3)_3]$ (ref. 531) while hydrated rhodium(III) chloride reacts with 2,4,6-triisopropylbenzene thiol in acetonitrile to form [300]. In [300] one o-isopropyl group on each of the bridging thiolate ligands has been dehydrogenated to an isopropenyl moiety which also coordinates to the adjacent metal (ref. 532). Lithium tert-butylperoxide converts [cp'Rh(1-3:5-6-η-C_8H_{11})]BF_4 to [301] but

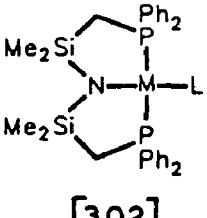


[300]



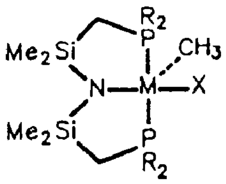
[301]

potassium tert-butylperoxide and [Rh(COD)$_2$]BF_4 form [Rh(O_2Bu^t)(COD)]·KBF_4 (ref. 533). The full paper on complexes of the bis(diphenylphosphinomethyldimethylsilyl)amide ligand has now appeared. Reaction of the lithium salt of the ligand with [RhClL$_2$]$_2$ (L = CO, C_2H_4, cyoct) in toluene at 0°C forms [302] (M = Rh; L = CO, C_2H_4, cyoct) and analogs with L = PPh_3 and



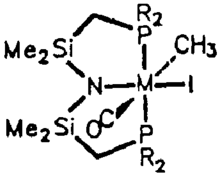
[302]

PMe_3 can be obtained under the same conditions from $[RhCl(PPh_3)_3]$ and $[RhCl(PMe_3)_4]$ respectively. The iridium analog of [302] (L = cyoct) can be prepared similarly from $[IrCl(cyoct)_2]_2$. Addition of ligands to [302] (M = Rh, Ir; L = cyoct) forms further analogs (M = Rh, Ir; L = C_2H_4, CO, PPh_3, PMe_3) while methyl halides undergo oxidative addition to form [303] (M =

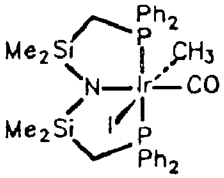


[303]

Rh, Ir; X = Br, I; R = Ph). An analog of [302] (M = Rh, Ir; L = cyoct) with isopropyl substituents on phosphorus can be prepared from $[MCl(cyoct)_2]_2$ and the corresponding ligand and also forms examples of [303] (M = Rh, Ir; X = I; R = Pr^i). Addition of carbon monoxide to [303] (M = Rh, Ir; X = I; R = Pr^i, Ph) forms [304] but oxidative addition of methyl iodide to [302] (M = Ir; L = CO) forms [305] (ref. 534).

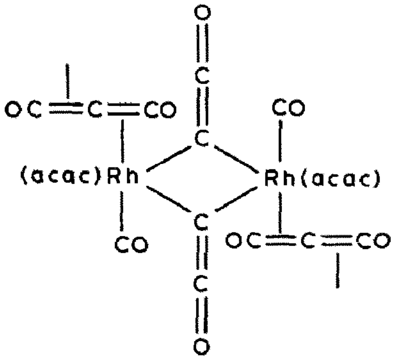


[304]

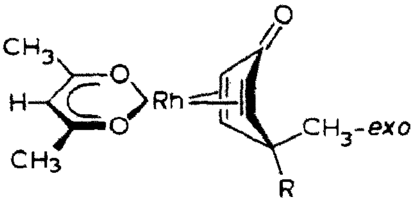


[305]

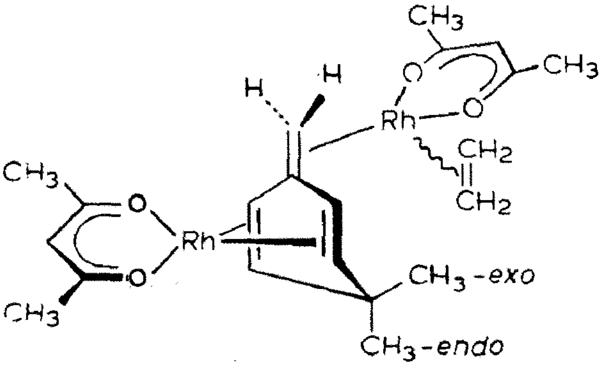
Five-coordinate intermediates are suggested to form during the reaction of COD with $[RhCl(C_2H_4)_2]_2$ and $[RhCl(BDN)]_2$ (ref. 535). Addition of carbon dioxide to a mixture of $[RhCl(C_2H_4)_2]_2$ and tertiary phosphines forms $[RhCl(CO_2)L_3]$ (L = PPh_2Et, $PPhEt_2$) while a mixture of dioxygen and carbon dioxide converts $[RhCl(PPhEt_2)_3]$ to the peroxycarbonate complex $[RhCl(O_2(O)CO)(PPhEt_2)_3]$. Photolysis of a solution of $[RhCl(PPhMe_2)_3]$ in cyclopropane under carbon dioxide forms butyrolactone and dimethylphenylphosphine oxide (ref. 536). Addition of carbon suboxide to a diethyl ether solution of $[Rh(acac)(C_2H_4)_2]$ forms an insoluble product which is proposed from its infrared spectrum to be a polymer of [306] associated *via* bridging C_3O_2 ligands as shown. No reaction occurred between carbon suboxide and $[cpRhL_2]$ (L = CO, C_2H_4) (ref. 537). Cyclohexadienones replace both ethylene ligands in $[Rh(acac)(C_2H_4)_2]$ to form [307] (R = Me, $CHCl_2$, Bu^n) and with R ≠ Me, both *exo* and *endo* isomers are obtained. On the other hand, reaction of 1-*exo*-methylene-4,4-dimethylcyclohexadiene with two equivalents of [Rh(acac)$(C_2H_4)_2$] in refluxing pentane yields the bimetallic complex [308] which appears to be isomerically pure. With one of the methyl groups replaced by a different alkyl group, mixtures of diastereoisomers are formed but the metals still adopt the *anti* arrangement. The same reaction in refluxing heptane with a metal:diene ratio of 2:3 forms [309] stereospecifically (refs. 538, 539). Another application of [Rh(acac)$(C_2H_4)_2$] is as a "phosphite sponge" for the removal of a triphenylphosphite ligand from [310] (P = $P(OPh)_3$) while at the same time providing a source of ethylene for the formation of [311]. The last is proposed to be an intermediate in



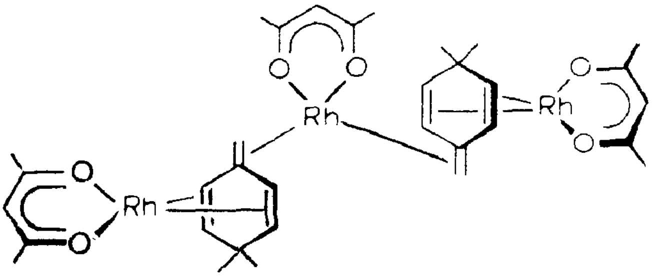
[306]



[307]

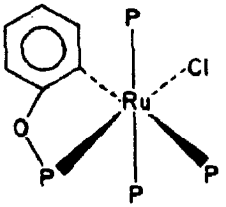


[308]

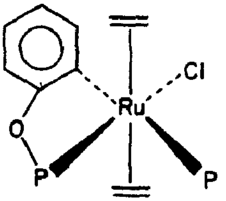


[309]

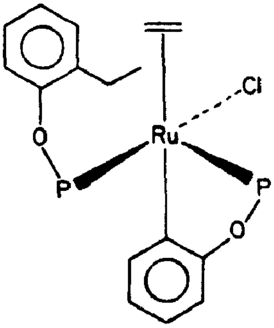
the formation of [312] via [313] which occurs when the reaction mixture is refluxed in deuterobenzene (ref. 540).



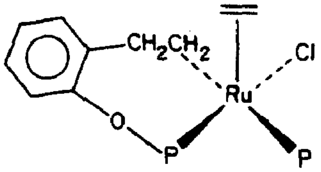
[310]



[311]



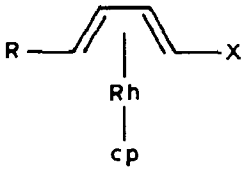
[312]



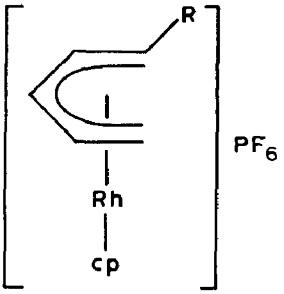
[313]

Photolysis of $[Rh(acac)(\eta^2-CH_2=CHCl)_2]$ in a 5%CO/95%CH_4 matrix forms both $[Rh(acac)(CO)(\eta^2-CH_2=CHCl)]$ and $[Rh(acac)(CO)_2]$. Because of the unsymmetrical nature of the olefin it was possible to detect the presence of free olefin in the matrix by the appearance of a band assigned to $\nu_{C=C}$ (ref. 541). In related work, photolysis of $[cpRh(C_2H_4)_2]$ at 229 nm in a 10%CO/90%CH_4 matrix forms $[cpRh(CO)(C_2H_4)]$, $[cpRh(CO)_2]$ and $[cpRh(C_2H_4)]$. Further photolysis of this mixture at wavelengths greater than 290 nm led to the formation of more $[cpRh(CO)(C_2H_4)]$ and the complete loss of $[cpRh(C_2H_4)]$ while photolysis of $[cpRh(CO)(C_2H_4)]$ at 229 nm in an argon matrix formed both $[cpRh(CO)]$ and $[cpRh(C_2H_4)]$. The last experiment indicates the competitive loss of carbon monoxide and ethylene occurs. In liquid xenon containing dinitrogen $[cpRh(C_2H_4)_2]$ forms $[cpRh(C_2H_4)(N_2)]$ upon photolysis and if this is irradiated with carbon monoxide present, $[cpRh(CO)(C_2H_4)]$ forms (refs. 542, 543).

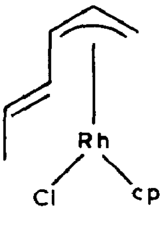
Further chemistry of [314] (X = CHO; R = Ph, *m*-tolyl, *m*-anisyl, *p*-FC_6H_4) includes reduction to the alcohol (X = CH_2OH) by borohydride and conversion to the Schiff base (R = Ph; X = CH=NR' (R' = Ph, *p*-tolyl, *p*-anisyl)) by reaction with the appropriate aniline derivative. Protonation of [314] (X = CH_2OH; R = Ph, *m*-tolyl, *m*-anisyl, *p*-FC_6H_4) with hexafluorophosphoric acid etherate forms [315] which converts to [316] on addition of chloride ion in acetone (ref. 544). The complex prepared by the action of excess trimethylphosphite on $[cpRh(C_2H_4)_2]$ or its indenyl analog and originally proposed to be $[Rh_2(P(OMe)_3)_8]$ (J. Chem. Soc., Chem. Commun., (1974)147) has now been shown to be $[Rh(P(OMe)_3)_4(P(O)(OMe)_2)]$ on the basis of an extensive NMR study. The fluxionality observed in solution is proposed to involve a ligand rearrangement by a tetrahedral edge traverse which is close to being the usual Berry pseudorotation. Also reported are the syntheses of $[(\eta^5\text{-}C_9H_7)IrL_2]$ (L = C_2H_4, cyoct) and $[(\eta^5\text{-}C_9H_7)Rh(1,5\text{-}HD)]$ by reaction of indenyllithium with the appropriate chloro-bridged dimeric olefin complex. Reaction of $[(\eta^5\text{-}C_9H_7)ML_2]$ or $[M_2Cl_2L_4]$ (M = Rh, Ir; L = C_2H_4, cyoct) with excess trimethylphosphite in chlorinated solvents forms $[M(P(OMe)_3)_5]Cl$ (M = Rh, Ir) which on dissolution in THF quantitatively converts to $[M(P(OMe)_3)_4(P(O)(OMe)_2)]$ presumably *via* the Arbusov reaction



[314]



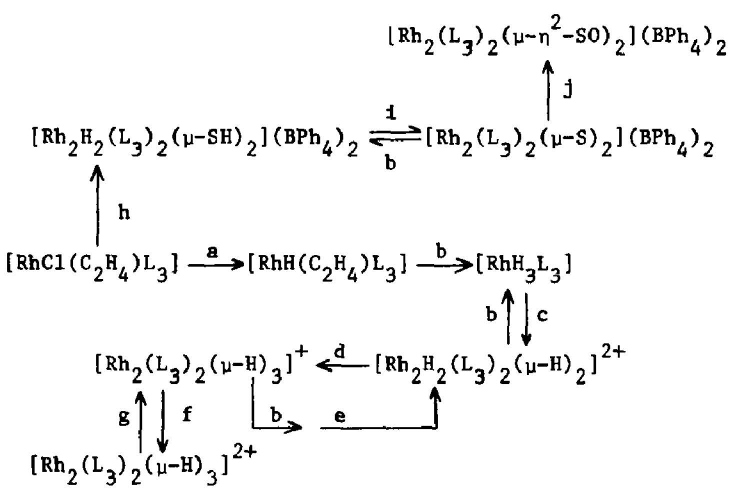
[315]



[316]

(chloride attack on coordinated trimethylphosphite). Reaction with dihydrogen forms $[RhH(P(OMe)_3)_4]$ or cis-fac-$[IrH_2(P(OMe)_3)_3(P(O)(OMe)_2)]$ while with methyl iodide the product is $[M(P(OMe)_3)_5]I$ (M = Rh, Ir). In the hydrogenation of $[Rh(P(OMe)_3)_4(P(O)(OMe)_2)]$, dimethylphosphite is also detected suggesting the reaction may proceed via initial dissociation of trimethylphosphite followed by oxidative addition of dihydrogen and reductive elimination of dimethylphosphite. Addition of DMAD to $[M(P(OMe)_3)_5]X$ (X = Cl, BPh_4) forms $[M(P(OMe)_3)_4(DMAD)]X$ (M = Rh, Ir) (refs. 545, 546). The structure of $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ has been determined and the results suggest the possibility of a contribution of the η^3-bonding mode of the indenyl ligand. The proton NMR spectra of this complex and its 1-methyl analog suggest that the lowest energy fluxional process observed is a rotation of the indenyl ligand and that olefin rotation occurs with a higher energy of activation (ref. 547). Addition of $[cp_2M(PR_2)_2]$ (M = Zr, Hf; R = Et, Ph) to $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ in hexane forms $[cp_2M(\mu\text{-}PR_2)_2Rh(\eta^5\text{-}C_9H_7)]$. The structure of the zirconium complex was determined and shows pronounced slip-fold distortion of the indenyl ligand (towards η^3-coordination). This distortion appears to persist in solution but it is uncertain whether this is the origin of the observed barrier to rotation of the indenyl moiety. When R = Et, oxidative addition of methyl iodide occurs at rhodium without affecting the bridging ligands and no reaction is observed with dihydrogen, carbon monoxide or acetyl chloride. By contrast, reaction with acetyl bromide and ammonium hexafluorophosphate is said to occur in a manner which alters but does not completely disrupt the bridging system. The results were not described in detail however (ref. 548).

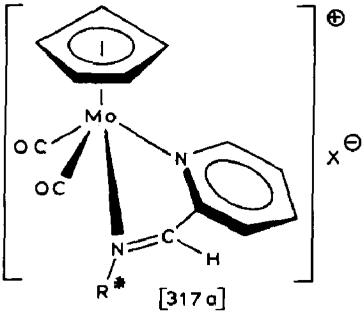
The square planar complex $[Rh(L_2)_2]BF_4$ (L_2 = (S,S)-CHIRAPHOS), which can be prepared by standard routes from $[RhCl(cyoct)_2]_2$, is unreactive towards dihydrogen, dioxygen and carbon monoxide. It does oxidatively add hydrogen halides to yield trans-$[RhHX(L_2)_2]BF_4$ (X = Cl, Br). The ^{31}P NMR spectrum of the bromo complex shows two non-equivalent pairs of phosphorus atoms indicating a distortion in the $\{RhP_4\}$ moiety (ref. 549). $[RhCl(cyoct)_2]_2$ also reacts with octaethylporphyrin in refluxing mesitylene under carbon monoxide. Addition of triphenylphosphine to the reaction mixture followed by purging with dinitrogen finally affords $[RhCl(PPh_3)(OEP)]$ as the product. This can be converted to $[Rh(OEP)(PPh_3)_2]Cl$ by triphenylphosphine in dichloromethane and to $[RhCl(CO)(OEP)]$ when photolyzed in THF solution containing carbon monoxide (ref. 550). Some chemistry of $[RhCl(C_2H_4)(triphos)]$ is outlined in Scheme LIV (L_3 = triphos) (refs. 551, 552).



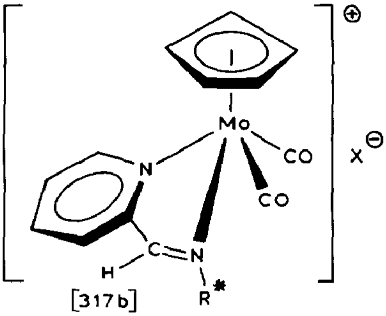
a) $LiBHEt_3$, THF. b) H_2, THF. c) HOTf, THF. d) $EtOH/CH_2Cl_2$. e) air. f) DMF/air. g) Sodium naphthalenide. h) H_2S, CH_2Cl_2/DMF then $NaBPh_4$. i) N_2, CH_2Cl_2. j) O_2.

Scheme LIV

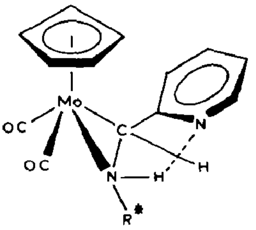
Reduction of the isomeric mixture [317a,b] (R^* = (R)-1-phenylethyl) with sodium amalgam forms a mixture of the interconverting pairs of isomers [318a,b] and [319a,b]. The first pair was separated from the second by column chromatography and from the separate fractions [318a] and [319a] could be obtained as crystalline solids. Regardless of whether one adds [318a] or [319a] to a solution of $[RhCl(NBD)]_2$, the same product, [320] is



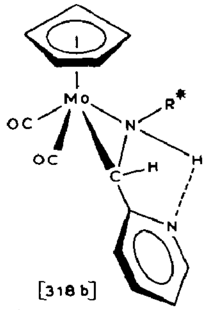
[317a]



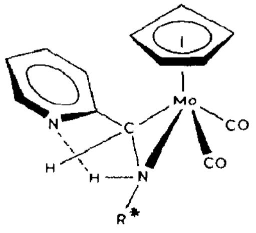
[317b]



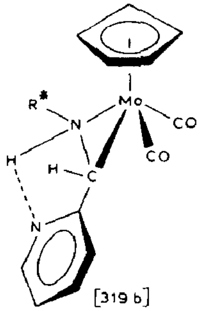
[318a]



[318b]

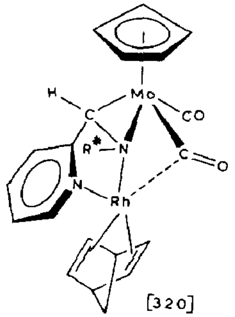


[319a]



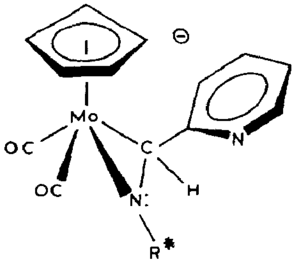
[319b]

obtained. This is explained by the proposal that [318a,b] and [319a,b] equilibrate in solution via [321a-c] and [321a] is the species reacting

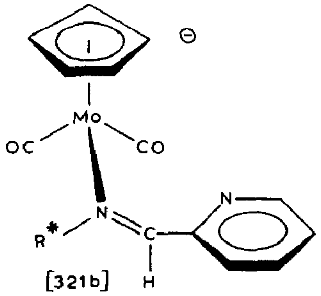


[320]

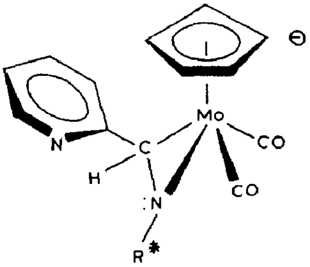
with the rhodium complex. This equilibration is also used to explain the formation of the [318a,b]-[319a,b] mixture described earlier with the initial product of reduction of [317a,b] being [321b] which then rearranges to either [321a] or [321c]. Complex [320] and analogs with other chiral



[321a]

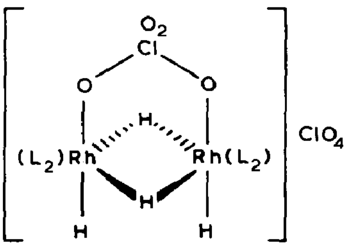


[321b]



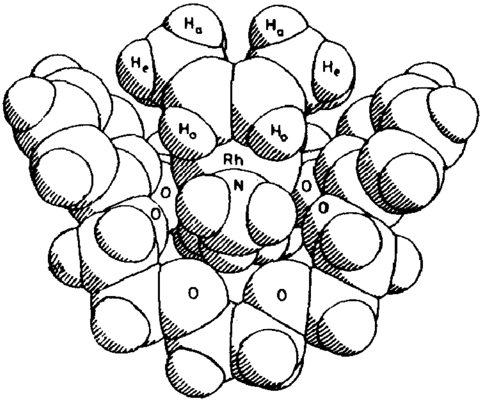
[321c]

substituents at R* were tested as catalysts for the asymmetric hydrosilylation of acetophenone but very poor chemical and optical yields were obtained (refs. 553, 553a). Hydrogenation of $[\mathrm{Rh(NBD)(L_2)]ClO_4}$ ($\mathrm{L_2}$ = dippp, dippb, cydiop) in methanol initially forms $[\mathrm{Rh(L_2)(MeOH)_2]ClO_4}$ and eventually [322] is isolated. It is proposed that [322] forms via $[\mathrm{RhH_2(L_2)(MeOH)_2]ClO_4}$ but this was not detected. Complex [322] is not a good catalyst because of the strong coordination of the perchlorate ion (ref. 534). A full report is now available on crown ether adducts of $[\mathrm{Rh(L_2)(NH_3)_2]^+}$ ($\mathrm{L_2}$ = NBD, COD) which have been studied to explore second coordination sphere interactions. The crown ethers employed were the dibenzo-3n-crown-n



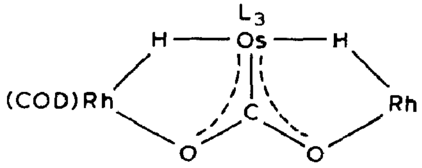
[322]

(n = 6-12) family. With n = 6-11 $[Rh(L_2)(NH_3)_2(crown)]PF_6$ can be isolated with the rhodium moiety situated in the V-shaped cavity of the crown as illustrated in [323] (n = 7). In general, four N-H---O hydrogen bonds are formed to the crown ether. For the adducts with n = 7-10 a significant upfield shift of the proton NMR resonances for the COD and NBD ligands are seen indicating that they lie in the anistropic shielding regions of the aromatic rings of the crown ether. It is also suggested that there may be specific interactions of the arene moieties with some of the hydrogen atoms of the dienes which contribute to the stability of the adducts. In the instance where n = 12, the isolated product is $[(Rh(COD)(NH_3)_2)_2(crown)]$-$(PF_6)_2$ in which the crown ether is in an open conformation and forms three long N-H---O hydrogen bonds to each rhodium moiety. Here there does not appear to be any interaction of the aromatic rings with ligands on the metal (ref. 555). Addition of solid $[RhCl(L_2)]_2$ (L_2 = COD, NBD) to an aqueous solution of β-cyclodextrin forms the inclusion complexes [(β-cyclodextrin)$_2$(RhCl(L$_2$)$_2$)$_2$]. The COD complex forms a low yield of an analogous complex with α-cyclodextrin but the NBD complex does not. It is proposed that the cyclodextrin surrounds the diolefin ligand but structural proof is lacking at present (ref. 556).



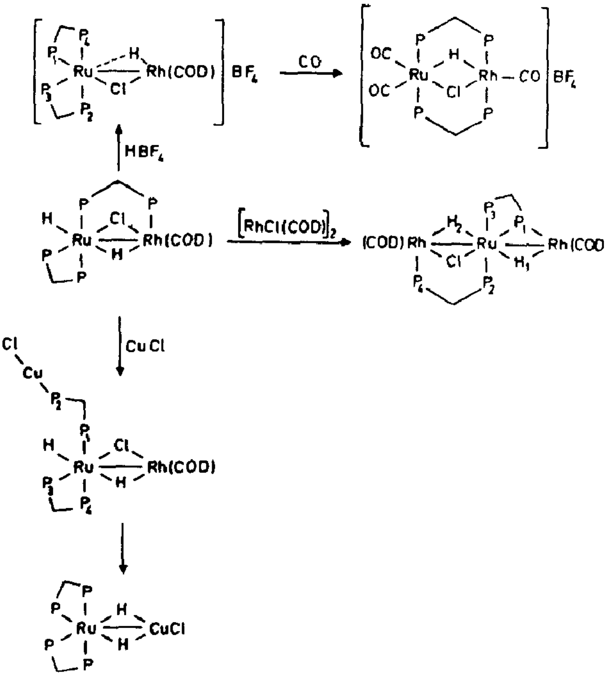
[323]

As is the case with $[RhCl(CO)_2]_2$, $[RhCl(COD)]_2$ and related diolefin complexes continue to be popular starting points for the synthesis of low-valent rhodium complexes. Reaction of the COD complex with $K[OsH_3(PPhMe_2)_3]$ in THF forms $[(COD)Rh(\mu\text{-}H)_3Os(PPhMe_2)_3]$ which reacts further



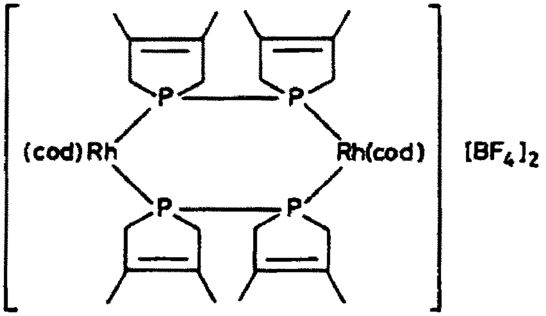
[324]

with carbon dioxide to yield [324] (L = $PPhMe_2$), water and $[OsH_2(CO)(PPhMe_2)_2]$. A labelling study with $^{13}CO_2$ indicates that the carbonyl ligand in $[OsH_2(CO)(PPhMe_2)_2]$ is derived from carbon dioxide (ref. 557). Work related to that described in ref. 482, is outlined in Scheme LV in



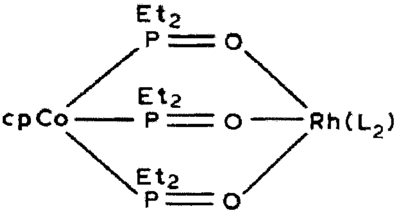
Scheme LV

which the ligand used is DPM (ref. 558). Addition of bis(3-dimethylphosphinopropyl)tert-butylphosphine (L_3) to $[RhCl(COD)]_2$ forms $[RhCl(L_3)]$ which causes the disproportionation of carbon dioxide with formation of mer-$[RhCl(O_2CO)(L_3)]$ and carbon monoxide (ref. 559) while $[Rh(COD)_2]BF_4$ and 2,2'5,5'-tetrahydro-3,3',4,4'-tetramethyl-1,1'-biphosphole form [325]. The structure determination showed the $\{Rh_2P_4\}$ skeleton adopts a chair conformation and the observed fluxionality was interpreted to result from a chair-to-chair inversion process (ref. 560).

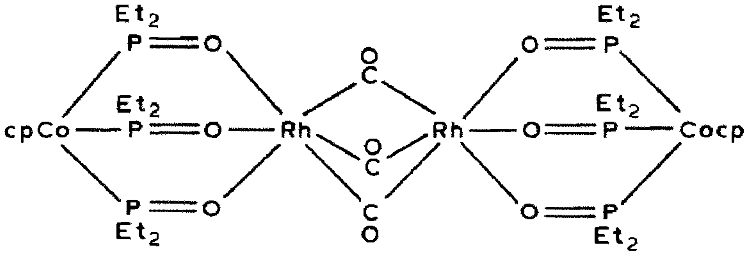


[325]

Reaction of $[RhCl(L_2)]_2$ (L_2 = COD, NBD, TFB, Me_3TFB, duroquinone) with $[cpCo(P(O)Et_2)_3]^-$ in refluxing hexane forms [326] and the analog with L_2 = $(C_2H_4)_2$ can be prepared similarly at room temperature. When L_2 = COD, NBD, TFB, Me_3TFB, the diolefin can be replaced by two carbonyl ligands and the reaction can be reversed on addition of the appropriate diolefin. On standing in solution, the dicarbonyl complex loses one carbonyl ligand with the formation of [327] (ref. 561). In acetonitrile $(Ph_4P)_2[WS_4]$ reacts with $[RhCl(COD)]_2$ to form $[(COD)Rh(\mu\text{-}S_2WS_2)Rh(COD)]$. This reacts further with $(Ph_4P)_2[WS_4]$ to give $(Ph_4P)[Rh(WS_4)(COD)]$ and with phosphine ligands to yield $[L_2Rh(\mu\text{-}S_2WS_2)RhL_2]$ (L = PPh_3; L_2 = DPPE). In the triphenylphosphine complex one phosphine on each rhodium can be replaced by carbon

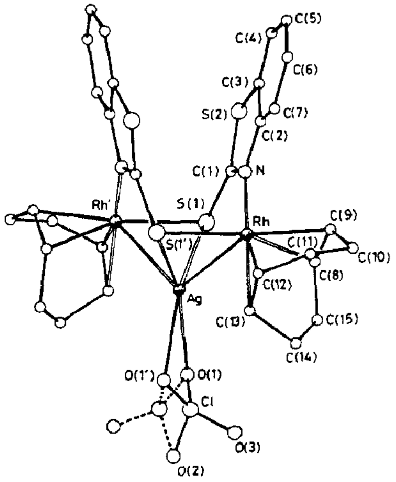


[326]



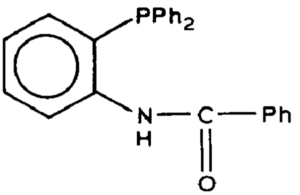
[327]

monoxide while addition of bis(diphenylphosphino)acetylene to $[(COD)Rh(\mu\text{-}S_2WS_2)Rh(COD)]$ forms $[(COD)Rh(\mu\text{-}S_2WS_2)Rh(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2Rh(\mu\text{-}S_2WS_2)Rh(COD)]$. The complexes $[(COD)Ir(\mu\text{-}S_2WS_2)Ir(COD)]$ and $[(COD)Rh(\mu\text{-}S_2MoS_2)Rh(COD)]$ were also prepared but the latter proved to be rather unstable (refs. 562, 562a). Dithiophosphate complexes of rhodium formulated as $[Rh(S_2P(OR)_2)(COD)]$ can be synthesized from $[RhCl(COD)]_2$ and two equivalents of $M[S_2P(OR)_2]$ (M = Na; R = Et, Pr^n. $M = NH_4^+$; R = Pr^i; $(OR)_2$ = $OCH_2CMe_2CH_2O$, $OCHMeCH_2CMe_2O$, $OCMe_2CMe_2O$) (ref. 563). Lithium benzothiazole-2-thiolate reacts in diethyl ether with $[RhCl(COD)]_2$ to form a fluxional species formulated as $[Rh_2(COD)_2(\mu\text{-}C_7H_4NS_2)]$. This adds silver perchlorate with the formation of [328] in which the perchlorate on silver can be replaced by triphenylphosphine. Analogs of [328] formulated as $[Rh_2(COD)_2(\mu\text{-}C_7H_4NS_2)_2(MCl)]$ (M = Cu, Ag) with presumably the same structure can be prepared in similar fashion (ref. 564). While 1-diphenylphosphino-2-methylthioethane (L_2) displaces both COD ligands from $[Rh(COD)_2]BF_4$ to give $[Rh(L_2)_2]BF_4{\cdot}H_2O$, 2-thienyldiphenylphosphine (L) coordinates only through phosphorus and the product is $[Rh(COD)(L)_2]BF_4$. The source of the water in the former complex is unknown (ref. 565).

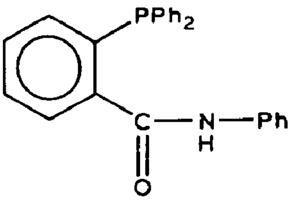


[328]

The complexes $[MCl(L)(COD)]$ and $[M(COD)L_2]^+$ (M = Rh, Ir; L = $P(\underline{o}\text{-anisyl})_3$, $P(\underline{o}\text{-anisyl})Me_2$, $P(\underline{o}\text{-anisyl})_2Me$, $P(\underline{o}\text{-anisyl})Ph_2$, $P(\underline{o}\text{-}Me_2NC_6H_4)Ph_2$, $P(\underline{o}\text{-}Pr^iOC_6H_4)Ph_2$) have been prepared by standard routes but only in the case of $P(\underline{o}\text{-}Me_2NC_6H_4)Ph_2$ is chelation of the ligand observed. The COD ligand could be displaced by carbon monoxide but not by other phosphines (ref. 566). The ligands [329] and [330] have been studied in an effort to cause oxidative addition of a nitrogen-hydrogen bond to a metal. When reacted with $[MCl(COD)]_2$ (M = Rh, Ir) they coordinate only through phosphorus and form $[MCl(COD)L]$. No oxidative addition occurred but the

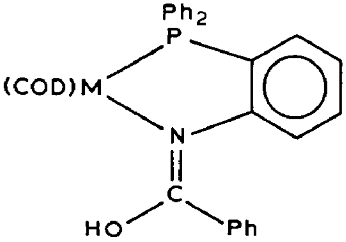


[329]

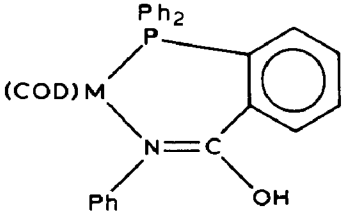


[330]

nitrogen could be deprotonated by a mixture of DABCO and sodium carbonate whereby the resulting amido group displaced chloride to form chelate complexes. With [M(COD)(THF)$_2$]ClO$_4$ (M = Rh, Ir) [329] and [330] formed [331] and [332] respectively in which the ligands have tautomerized to the iminol

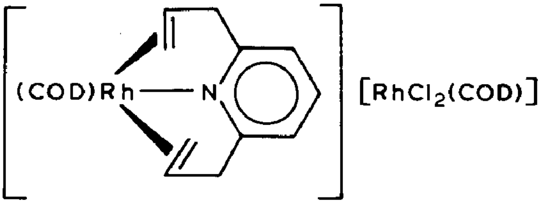


[331]



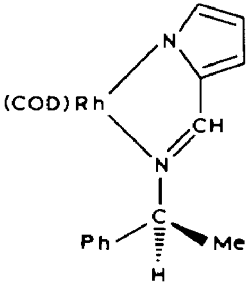
[332]

form. Again no oxidative addition was seen. For M = Rh, the coordinated nitrogen in [331] and [332] can be displaced from the metal by acetonitrile. The only instance in which oxidative addition of the nitrogen-hydrogen bond appeared to occur was when [329] was reacted with [IrClL$_2$] (L = PPh$_3$, AsPh$_3$; L$_2$ = DPPE) which was prepared <u>in situ</u> from [IrCl(cyoct)$_2$]$_2$. The product was formulated as [IrHClL$_2$($\widehat{PN}$)] and two isomers of uncertain stereochemistry were obtained (ref. 567). Benzene solutions of [RhCl(COD)]$_2$ react with 2,6-diallylpyridine to form [333] in which the counterion can be replaced by [CuCl$_2$]$^-$ on reaction with [CuCl(SMe$_2$)]. The same



[333]

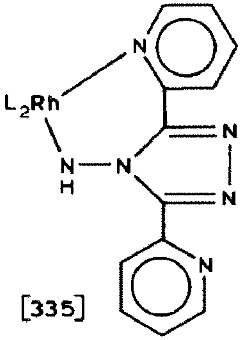
cation as its perchlorate salt can be prepared from [Rh(COD)S$_x$]ClO$_4$ (S = acetone) while reaction of the diallylpyridine with [RhCl(cyoct)$_2$]$_2$ forms a species of empirical formula [RhCl(DAP)] whose degree of association is unknown. This can be converted to [RhCl(L)(DAP)] (L = CO, PPh$_3$) on reaction with the appropriate ligand (ref. 568). Successive reaction of [RhCl-(COD)]$_2$ with diazadienes and sodium perchlorate or hexafluorophosphate in methanol forms [Rh(COD)(RN=CR'CR'=NR)]X (R = cy, Ph; R' = H. R = NH$_2$; R' = Me. X = ClO$_4$, PF$_6$) from which [RhH$_2$(RN=CR'CR'=NR)L$_2$]X (X = ClO$_4$, PF$_6$. L = PPh$_3$; R = cy, H; R' = H. R = NH$_2$; R' = Me. L = PPh$_2$Me, PEt$_3$; R = cy, R' = H) can be obtained on successive reaction with the phosphine and dihydrogen (ref. 569). The absolute configuration of [334], prepared from [RhCl-(COD)]$_2$ and the sodium salt of the ligand, has been determined by x-ray



[334]

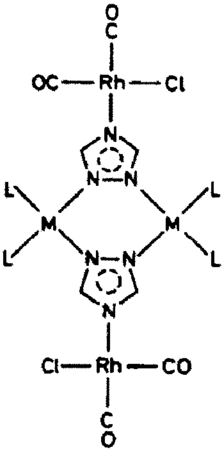
crystallography. The complex forms a catalyst for the asymmetric hydrosilylation of acetophenone (ref. 570).

The 3,4,5,6,7,8-hexamethyl and 4,7-dichloro derivatives of ophen (L$_2$) react with [MCl(COD)]$_2$ (M = Rh, Ir) to form [M(COD)(L$_2$)]Cl in which the COD can be replaced by two carbonyl ligands. With the 2,9-dimethyl and 2,9-dimethyl-4,7-diphenyl derivatives of ophen however the products are [MCl(COD)(L$_2$)] (ref. 571). Complexes of the same formula (M = Rh) are also formed with ethylenediamine, 1,3- and 1,2-diaminopropane and 1,2-diphenyl-1,2-diaminoethane but with N,N'-dimethyl- or N,N-dimethylethylenediamine or TMEDA the products are [Rh(COD)(L$_2$)][Rh(COD)Cl$_2$] (ref. 572). Addition of Hdipy to [M(L$_2$)(acetone)$_x$]ClO$_4$ (M = Rh; L$_2$ = COD, NBD, TFB. M = Ir; L$_2$ = COD) forms [M(L$_2$)(Hdipy)]ClO$_4$ in which the ligand coordinates via the pyridyl nitrogen atoms and in which the diolefin can be replaced by two carbonyl ligands (M = Rh; L$_2$ = NBD. M = Ir; L$_2$ = COD). Deprotonation of the amine nitrogen atom in [M(L$_2$)(Hdipy)]ClO$_4$ occurs on reaction with potassium hydroxide in methanol to form [M(L$_2$)(dipy)] and the starting cation can be regenerated with tetrafluoroboric acid. Direct formation of [M(L$_2$)(dipy)] (M = Rh; L$_2$ = COD, TFB, NBD. M = Ir; L$_2$ = COD, TFB) occurs on reaction of [MCl(L$_2$)]$_2$ with the lithium salt of the ligand (ref. 573). A mixture of [RhCl(L$_2$)]$_2$ (L$_2$ = COD, NBD, TFB) and NH$_2$bpt in methanol/dichloromethane containing potassium hydroxide forms [Rh(NHbpt)(L$_2$)] ([335]) which can be protonated with perchloric acid to yield [Rh(NH$_2$bpt)-(L$_2$)]ClO$_4$. The last can also be obtained directly from the neutral ligand and [Rh(L$_2$)(acetone)$_x$]ClO$_4$ (ref. 574). The complexes [M$_2$(L$_2$)$_2$(μ-tz)$_2$]



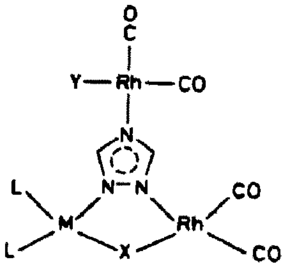
[335]

(M = Rh; L_2 = COD, NBD, TFB, Me_3TFB. M = Ir; L_2 = COD) are formed from $[MCl(L_2)]_2$ and the triazole in methanol containing triethylamine (M = Rh) or potassium hydroxide (M = Ir). Conversion of $[M_2(CO)_4(\mu\text{-tz})_2]$ occurs on reaction with carbon monoxide. Addition of one mol of $[RhCl(CO)_2]_2$ to $[M_2(L_2)_2(\mu\text{-tz})_2]$ (M = Rh; L_2 = COD, $(CO)_2$. M = Pd; L_2 = η^3-allyl) forms [336] and analogs with {M'Cl(COD)} (M ' = Rh, Ir) in place of the $\{RhCl(CO)_2\}$



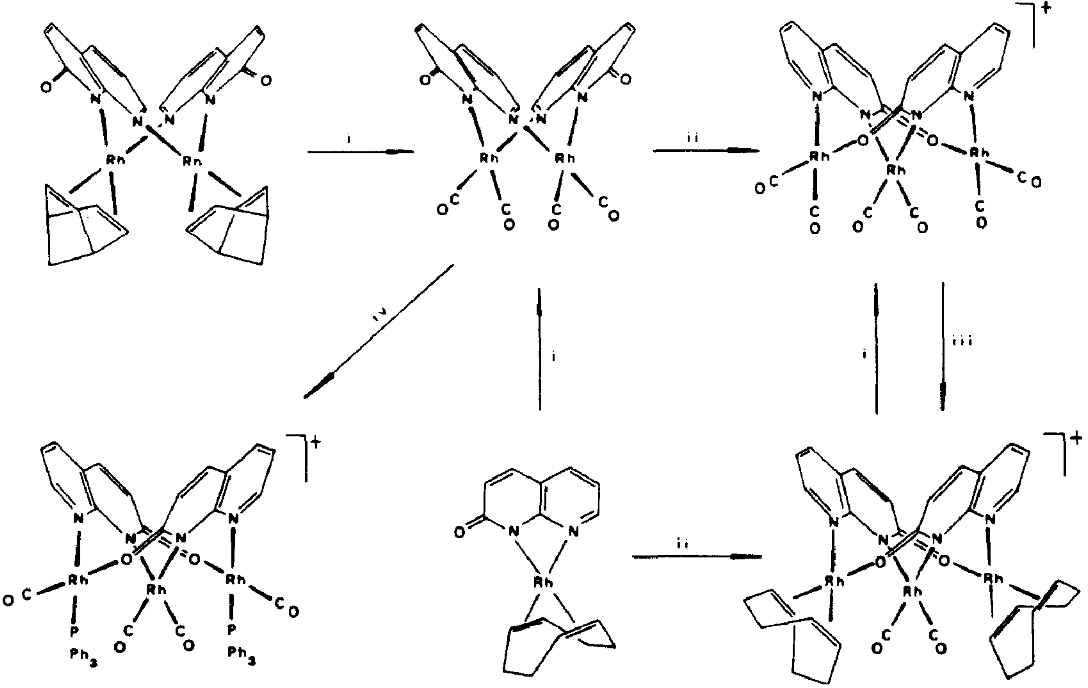
[336]

moieties can be prepared similarly (M = Rh; L_2 = COD, $(CO)_2$). With two mols of $[RhCl(CO)_2]_2$ in this reaction [337] (Y = Cl. M = Rh; L_2 = COD,



[337]

NBD, TFB, $(CO)_2$. M = Ir; L_2 = COD. M = Pd; L_2 = η^3-allyl) is formed (ref. 575). Formation of $[Rh(Onapy)(L_2)]_n$ (n = 1; L_2 = COD. n = 2; L_2 = NBD, TFB) occurs on reaction of $[RhCl(L_2)]_2$ with HOnapy and potassium hydroxide in methanol. The structure of the dimeric NBD complex is shown at the upper left of Scheme LVI and further chemistry of this complex is shown



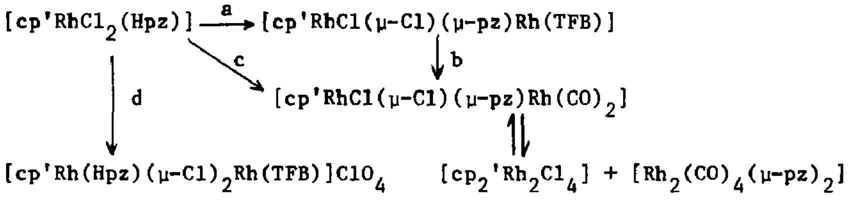
i) CO. ii) $[Rh(CO)_2(acetone)_x]^+$. iii) COD. iv) $[Rh(CO)(PPh_3)_2$-$(acetone)]^+$.

Scheme LVI

here also (ref. 576).

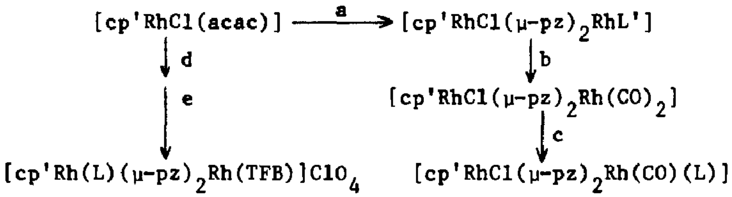
The metallophosphine $[cpFe(\eta^6$-$C_6Me_5CH_2PPh_2)]PF_6(L')$ cleaves the bridge in $[RhCl(L_2)]_2$ (L_2 = COD, Me_3TFB) to form $[RhCl(L_2)(L')]PF_6$ in which the diolefin can be replaced with carbon monoxide giving <u>cis</u>-$[RhCl(CO)_2(L')]$-PF_6. Electrochemical studies on these complexes indicate that the initial one-electron reduction occurs at iron and is followed by electron transfer from iron to rhodium. Rhodium hydride species are possibly formed here too (ref. 577). The complexes [Rh(COD)(L)] (L = various halogenated 8-oxoquinolinates) have been prepared by standard routes and the COD ligand replaced by two carbonyl or triphenylphosphite ligands. Oxidative addition reactions with halogens and methyl iodide were also performed (ref. 578). Tested syntheses of $[M(OMe)(L_2)]_2$ (M = Rh, Ir; L_2 = COD. M = Rh; L_2 = TFB,

Me_3TFB) and $[Rh(OH)(COD)]_2$ are now available (ref. 579). Some chemistry of rhodium pyrazole and pyrazolate complexes is outlined in Schemes LVII and LVIII. Analogs of some of the products with 3,5-Me_2pzH were also prepared



a) $[Rh(acac)(TFB)]$, acetone. b) CO. c) $[RhCl(CO)_2]_2$, acetone.
d) $[Rh(TFB)(acetone)_x]ClO_4$.

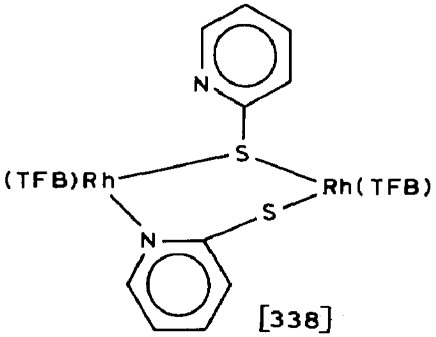
Scheme LVII



a) $[Rh(L')(Hpz)]ClO_4$ (L' = TFB, COD), KOH, acetone. b) CO.
c) L(= Bu^tNC, PPh_3). d) $AgClO_4$ (L' = TFB). e) L(= py, MeCN, Hpz).

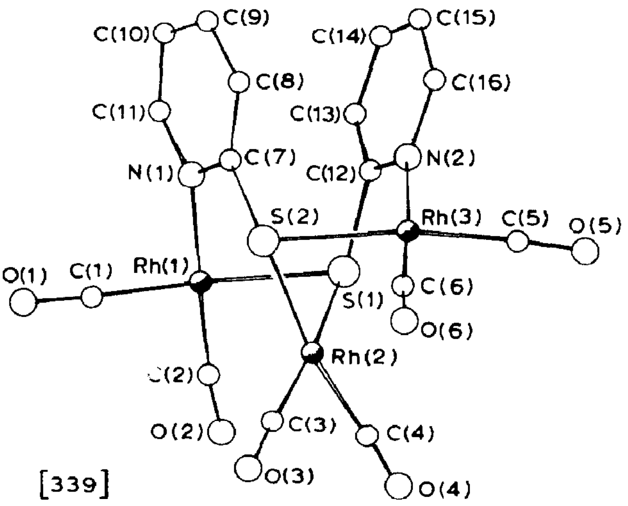
Scheme LVIII

(ref. 580). Lithium pyridine-2-thiolate and $[RhCl(TFB)]_2$ in diethyl ether form [338] which on successive reaction with $[Rh(TFB)(acetone)_x]ClO_4$ and



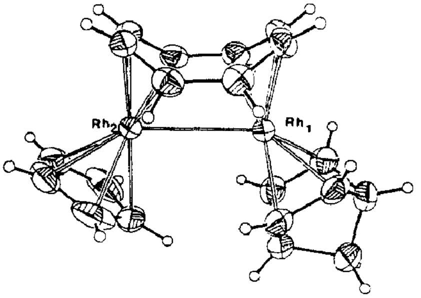
[338]

then carbon monoxide forms $[Rh_3(CO)_6(\mu-SC_5H_4N)_2]ClO_4$ whose cation has the structure [339] (ref. 581).

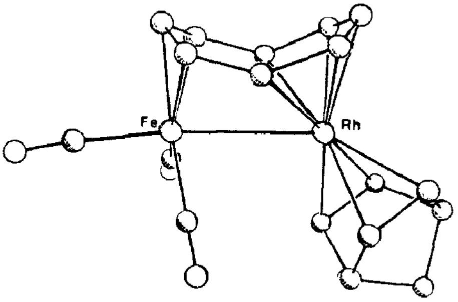


[339]

In a prodigous paper the synthesis and properties of a variety of homo- and heterobimetallic, COT-bridged complexes are described. The previously prepared complexes $[cpRh(\mu-\eta^4,\eta^4-COT)Rh(NBD)]BF_4$ and $[(OC)_3Fe(\mu-\eta^3,\eta^5-COT)Rh(NBD)]BF_4$ have been shown to have the structures [340] and [341] respectively. In the former, the {cpRh} moiety is considered to form a donor electron pair bond to the other metal and this is supported by the ^{103}Rh NMR spectrum. Addition of $[cp'M(acetone)_3](BF_4)_2$ (M = Rh, Ir) to [cpM'(COT)] (M' = Co, Rh) forms $[cp'M(\mu-COT)M'cp](BF_4)_2$ (M = Rh; M' = Co, Rh. M = Ir; M' = Rh) in which the COT ligand is fluxional. Reduction of

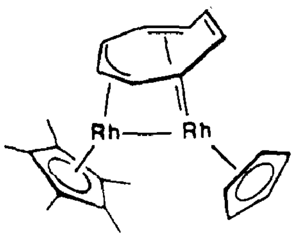


[340]

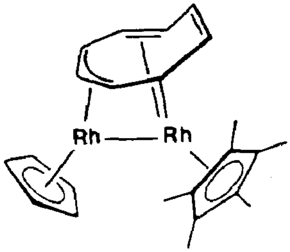


[341]

the dirhodium complex with sodium amalgam forms the neutral species as a mixture of noninterconverting diastereomers ([342a,b]) each of which is

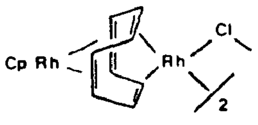


[342 a]

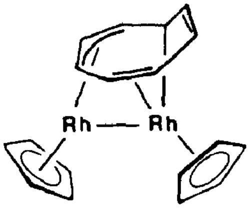


[342 b]

fluxional by interconversion to its enantiomer. In the dicationic complexes the ^{103}Rh chemical shifts are at quite high field possibly due to a delocalization of the positive charge onto the COT ligand. Also in the dirhodium complex there is a large chemical shift difference between the non-equivalent rhodium atoms although it is not as large as in [340]. The explanation for this is as yet uncertain. In similar fashion, [cpRu-$(MeCN)_3]^+$ and [cpM(COT)] react to form [cpRu(μ-COT)Mcp]$^+$ (M = Co, Rh) while [cpRh(COT)] and $[RhCl(C_2H_4)_2]_2$ in pentane yield [343] which is converted to [344] by thallium cyclopentadienide at -80°C in dichloromethane. Like



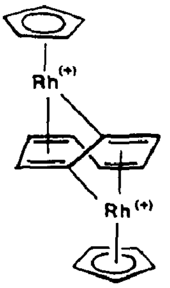
[343]



[344]

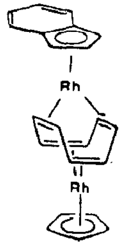
[342], [344] is fluxional via interconversion between enantiomers. It can be oxidized to $[cp_2Rh_2(\mu\text{-}COT)](BF_4)_2$ with silver tetrafluoroborate and regeneration of [344] from the latter can be achieved with sodium amalgam. If the reaction of [343] with thallium cyclopentadienide is performed at room temperature, the product is [345] which can be oxidized to [346] by

[345]



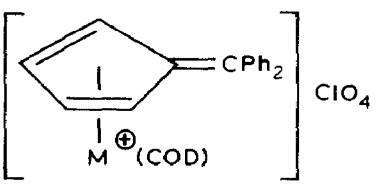
[346]

silver tetrafluoroborate. Other reactions of [343] include conversion to [340] by reaction with silver tetrafluoroborate and NBD, to [347] by

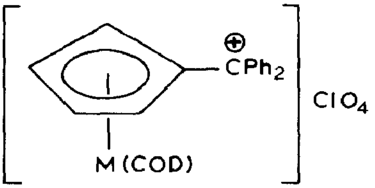


[347]

bis(indenyl)magnesium, to [cpRh(μ-η^4,η^4-COT)Rh(acac)] by potassium carbonate and acetylacetone and to [(η^6-C_6Me_6)Rh(μ-η^4,η^4-COT)Rhcp]BF_4 by hexamethylbenzene and triphenylmethyl tetrafluoroborate. The structures of the last two species are presumed to be analogous to that of [347] (ref. 582). The reaction of [Rh(SQ)(COD)] with an excess of triethylarsine has been studied by variable temperature EPR spectroscopy. At low temperature a new spectrum attributed to [Rh(SQ)($AsEt_3$)(COD)] is seen which is also interpreted to indicate significant unpaired electron density on the metal. Since the parent complex has the unpaired electron 99% localized on the SQ ligand, this suggests metal-to-ligand charge transfer has occurred on adduct formation and the product is formulated as a Rh(II) catecholate complex (ref. 583). NMR studies on [348] (M = R, Ir) show that rotation of the fulvalene ligand occurs and this is faster in the iridium complex. It is thought that [349] may contribute more to the description of the bonding in the latter (ref. 584).

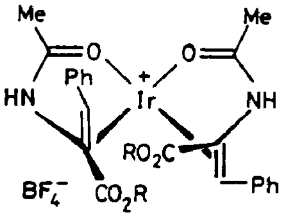


[348]



[349]

Reaction of the appropriate enamide with [$IrCl(C_2H_4)_2]_2$ forms a 2:1 mixture of [350] and [351] (R = (R)-menthyl) but if [$IrCl(C_2H_4)_2]_2$ is first treated with silver tetrafluoroborate then only [350] is obtained. This latter route also affords only [351] when R = (S)-menthyl. CHIRAPHOS rapidly replaces one enamide ligand in [350] (R = (R)-menthyl) at -70°C in dichloromethane but with [351] (R = (S)-menthyl) the reaction is slow even at -10°C. The products obtained are [352] and [353] respectively and the latter converts to the former on warming to 0°C. This indicates that [353]



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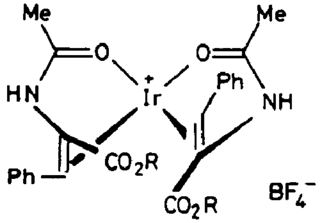
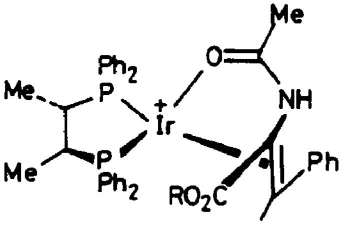


[351]

is metastable and as the rhodium analog is isostructural this observation is taken to confirm that the metastable enamide complex is the active form in rhodium-catalyzed asymmetric hydrogenations as was proposed earlier by Halpern. It was further found that mixing *rac*-CHIRAPHOS with



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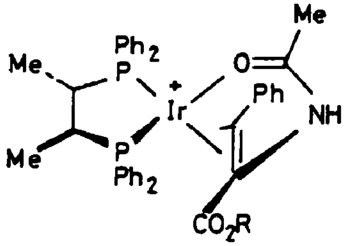
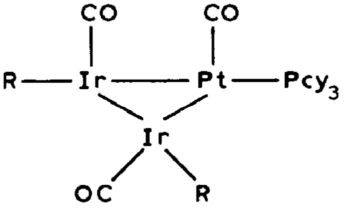


[353]

[350] at -70°C in dichloromethane, warming to -55°C for 15 min and to -20°C for 24 hours followed by addition of $[Rh(NBD)_2]BF_4$ gave a system which catalyzed the hydrogenation of methyl-(Z)-α-acetamidocinnamate with 87% selectivity to the (S)-product. A similar sequence with [351] afforded 89.5% of the (R)-product. Since the catalyst formed from $[Rh(NBD)_2]BF_4$ and (S,S)-CHIRAPHOS gives a 90% yield of the (R)-product it appears that the iridium system has effected a kinetic resolution of the diphosphine (ref. 585). Addition of indenyl potassium to $[IrCl(C_2H_4)_4]$ (prepared *in situ* from $[IrCl(cyoct)_2]_2$) forms $[(\eta^5\text{-}C_9H_7)Ir(C_2H_4)_2]$ which is converted to $[(\eta^5\text{-}C_9H_7)Ir(CO)_2]$ by carbon monoxide in hexane. Removal of excess carbon monoxide followed by addition of more $[(\eta^5\text{-}C_9H_7)Ir(C_2H_4)_2]$ and heating at reflux forms $[(\eta^5\text{-}C_9H_7)_2Ir_2(CO)_2(\mu\text{-}CO)]$. Addition of $[Pt(C_2H_4)_2(Pcy_3)]$ to a diethyl ether solution of $[(\eta^5\text{-}C_9H_7)Ir(CO)_2]$ forms [354] (R = $\eta^5\text{-}C_9H_7$) which can be protonated by tetrafluoroboric acid to give [355] (ref. 586).



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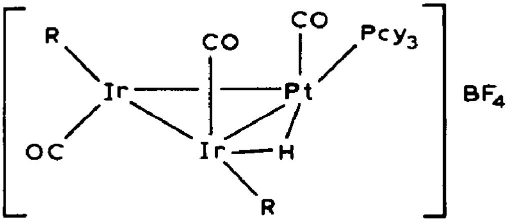
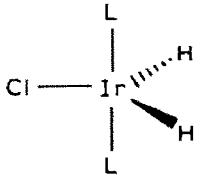


[355]

Dimethylmaleate adds to $[Ir(Me)(CO)(PPh_3)_2]$ to form a five-coordinate adduct in which the methyl and carbonyl ligands are axial in the trigonal bipyramidal structure (ref. 587). Four mols of triisopropylphosphine (L) in benzene convert $[IrCl(cyoct)_2]_2$ to $[IrClL_2]$ and when the solution is refluxed a 1:2 mixture of [356] and [357] form. Complex [357] is converted to [356] on reaction with dihydrogen and carbonylation of the original mixture forms [358] and [359]. Since isolated [357] does not convert to [356] in refluxing benzene, it is evidently not a precursor to the latter. Insight into the course of the reaction was obtained by carrying it out in deuterobenzene whereupon the products were $[IrClH_2L_2]$ and $[IrCl(D)-(C_6D_5)L_2]$. The dihydride therefore appears to arise from a reaction of $[IrClL_2]$ with the cyclooctene present in the solution (ref. 588). At room temperature, hexane solutions of $[IrCl(cyoct)_2]_2$ react with four equivalents of bis(bis(trimethylsilyl)amido)germanium to form [360] which on addition of more germanium reagent and carbon monoxide gives [361] (R = Me_3Si). This contrasts with the behavior of the analogous tin compounds towards rhodium where the product is $[RhCl(Sn(NR_2)_2)_2]_2$ (J. Chem. Soc., Chem. Commun., (1985)1592) (ref. 589).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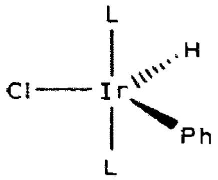
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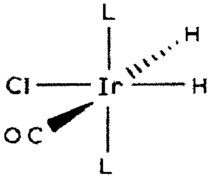
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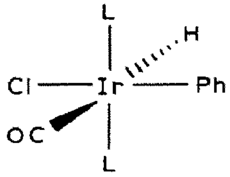
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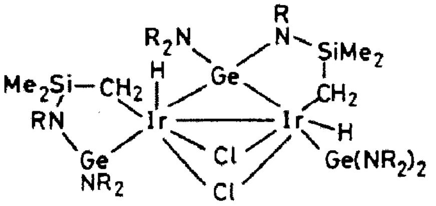
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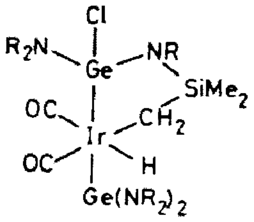
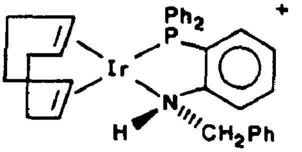

[361]

In work related to that described in ref. 567, the complexes [MCl(COD)L] (M = Rh, Ir; L = $Ph_2P(\underline{o}\text{-}C_6H_4NHR)$ (R = Et, bz)) were synthesized from $[MCl(COD)]_2$. Chloride abstraction from the iridium complexes with silver perchlorate formed the cations [362] (R = Et has same structure) and heating [362] (R = bz only) converts it to [363]. No oxidative addition of the nitrogen-hydrogen bond to the metal occurs presumably because of the presence of the electron-withdrawing COD ligand but if the ligands are added to $[IrCl(cyoct)_2]_2$, this reaction does occur (ref. 590). Ethanol solutions of $[IrCl(COD)]_2$ and cyttp form [364] (L = Cl) which reacts with thallium tetrafluoroborate in acetonitrile to yield both [364] (L = MeCN) and [365] (L = MeCN). Carbonylation of this mixture quantitatively forms [365] (L = CO) which could also be prepared directly from [364] (L = Cl), carbon monoxide and thallium tetrafluoroborate but in only 40% yield. Conformation [364] (L = Cl) appears to persist in solution on the basis of NOE experiments (ref. 591).



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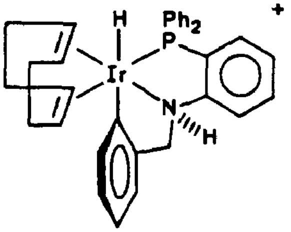

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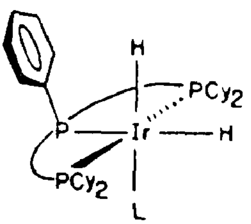

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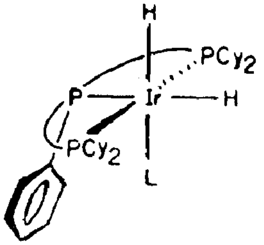
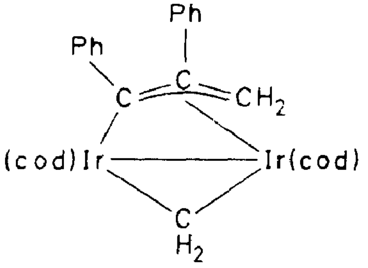


[365]

In THF solution, $[IrCl(COD)]_2$ reacts with $Li[M(CO)_4(PPh_2H)(PPh_2)]$ (M = Cr, Mo, W) yielding $[(OC)_4\overline{M(\mu\text{-}PPh_2)_2Ir}H(COD)]$ while with $Li_2[W(CO)_4(PPh_2)_2]$ the product is $Li[(OC)_4\overline{W(\mu\text{-}PPh_2)_2Ir}(COD)]$ and with $Li[Fe(CO)_3(PPh_2)_2]$, $Li[(OC)_3\overline{Fe(\mu\text{-}PPh_2)_2Ir}(COD)]$ results. Although the last is formed in high yield in solution, the isolated yield is lower due to the formation of impurities in the process. The $[(OC)_4\overline{W(\mu\text{-}PPh_2)_2Ir}(COD)]^-$ ion behaves as a nucleophile at iridium and with methyl iodide or acetic acid forms $[(OC_4\overline{W\text{-}(\mu\text{-}PPh_2)_2Ir}(R)(COD)]$ (R = Me, H respectively). These species are relatively unreactive at iridium presumably because they contain iridium(III) but under 1000 psi of carbon monoxide at 110°C the hydride complex forms

$[(OC)_4\overline{W(\mu\text{-}PPh_2)_2Ir}H(CO)_2]$. Also, $Li[(OC)_3\overline{Fe(\mu\text{-}PPh_2)_2Ir}(COD)]$ reacts with triphenylphosphine under 80 psi of syngas to form $[(OC)_3\overline{Fe(\mu\text{-}PPh_2)_2Ir}H(CO)(PPh_3)]$ (ref. 592). Reaction of $[IrCl(COD)]_2$ with methyllithium forms $[Ir_2(COD)_2(\mu\text{-}CH_2)_2]$ which adds diphenylacetylene to yield [366]. On the other hand, if methyllithium is added to a mixture of $[IrCl(COD)]_2$ and diphenylacetylene the products are [367], $[(\eta^5\text{-}Ph_6C_6H)Ir(COD)]$ and $[(\eta^5\text{-}Ph_6C_6Me)Ir(COD)]$ (ref. 593). Proton abstraction from RNHCH=NR (R = p-tolyl) with potassium tert-butoxide in toluene followed by addition of $[IrCl(COD)]_2$ forms [368] while if tert-butyl alcohol is also added, the product is [369] (ref. 594).



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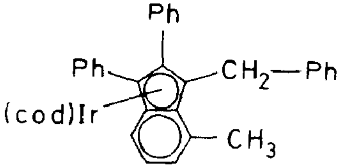

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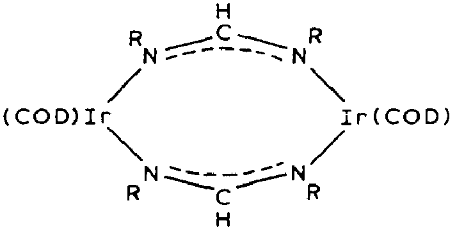

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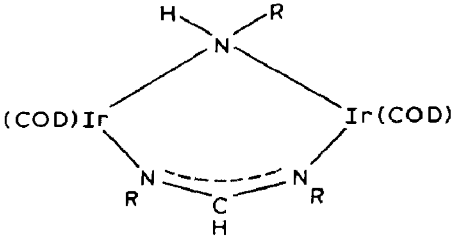
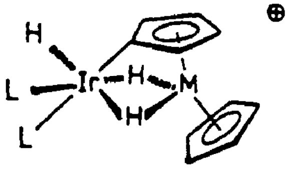


[369]

Exposure of dichloromethane solutions of the red form of $[IrCl(COD)]_2$ to air forms a product now shown to be $[Ir_2Cl_2(COD)_2(\mu\text{-}OH)_2(\mu\text{-}O)]$ rather than $[Ir_2Cl_2(COD)_2(\mu\text{-}OH)_2]$ as originally proposed. A more efficient synthesis can be achieved by bubbling dioxygen through the solution. Although the hydroxyl hydrogen atoms were not located crystallographically, their presence is indicated by the infrared spectrum. Thus the dimer contains iridium(III) rather than iridium(II) as in the original proposal (ref.

595). Iodine reacts with $[Ir(OMe)(COD)]_2$ in dichloromethane to form $[Ir_2I_2(\mu\text{-}I)_2(COD)_2]$ which on subsequent treatment with silver acetate gives a low yield of $[Ir_3(\mu\text{-}I)(\mu_3\text{-}O)_2(COD)_3]$ plus other unidentified products. The characterized complex is an unusual example of a bi-oxo-capped cluster of a Group VIII metal (ref. 596). In related work, $[Ir(OMe)(L_2)]_2$ (L_2 = COD, TFB) reacts with phosphine ligands in methanol to form $[IrH(L_2)L'_2]$ (L' = PPh_3; L'_2 = DPPE, DPPP) which are moderately active catalysts for the hydrogenation of cyclohexanone <u>via</u> hydrogen transfer from isopropanol. In ethanol, $[Ir(OEt)(COD)]_2$ reacts with triphenylphosphine with the formation of $[IrH(COD)(PPh_3)_2]$ and acetaldehyde but synthesis of the triphenylarsine analog required reaction of $[IrCl(COD)]_2$ with the ligand and sodium methoxide in methanol (ref. 597). Addition of a ligand and triethylsilane to $[Ir(OMe)(COD)]_2$ forms $[IrH_2(SiEt_3)(L)(COD)]$ (L = PPh_3, $AsPh_3$) from which the silane can be displaced by more ligand with concomitant formation of $[IrH(COD)L_2]$. The silyl iridium complexes react with ethylene to yield vinyltriethylsilane and tetraethylsilane in a 45:55 ratio when L = PPh_3 but in a 80:20 ratio when L = $AsPh_3$ (ref. 598).

Tested syntheses of $[Ir(COD)(py)(L)]PF_6$ (L = py, Pcy_3) are now available (ref. 599). Hydrogenation of $[Ir(COD)L_2]PF_6$ (L = PEt_3, PMe_2Ph, $PMePh_2$) in ethanol at 0°C followed by reaction with $[cp_2WH_2]$ forms a mixture of [370] and $[IrH_2(COD)L_2]PF_6$ possibly <u>via</u> [371] and [372] as intermediates. The tricyclohexylphosphine analog of [370] can be prepared similarly from $[IrH_2Cl(Pcy_3)_2]$ in the presence of silver tetrafluoroborate and here the second product is $[IrH_5(Pcy_3)_2]$, a species which can also be synthesized from $[IrH_2(acetone)_2(Pcy_3)_2]BF_4$ and hydrogen in the presence of ethyldiisopropylamine (ref. 600). An example of the cleavage and reformation of carbon-carbon bonds at iridium is found in the reaction of $[IrH_2(acetone)_2L_2]SbF_6$ (L = $P(\underline{p}\text{-}FC_6H_4)_3$) with substituted cyclopentanes. In neat 1,1-dimethylcyclopentane containing <u>tert</u>-butylethylene as a hydrogen acceptor the iridium complex reacts at 150°C to form [373]. Heating this complex at 150°C in 1,1-dimethylcyclopentane or as a solid at 145°C for a longer time converts it to $[(cpMe)Ir(Me)L_2]SbF_6$. Direct reaction of $[IrH_2(acetone)_2L_2]SbF_6$ with 1-methyl-1-ethylcyclopenta-2,4-diene yields [374] plus a minor amount of [375] and on heating this mixture, $[(\eta^5\text{-}C_5H_4Et)Ir(Me)L_2]SbF_6$ is



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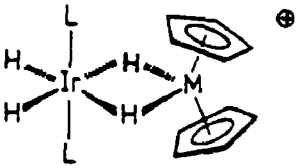

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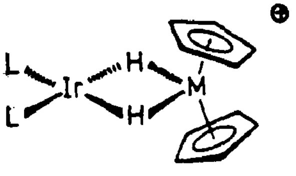

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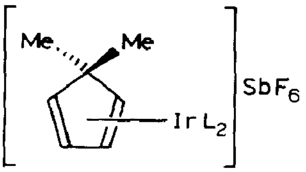

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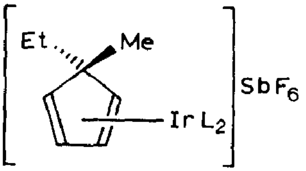

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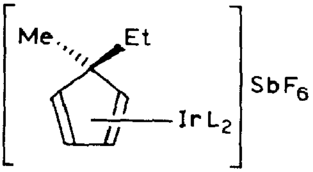
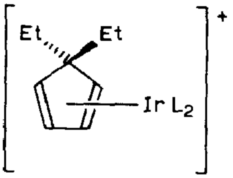


[375]

obtained indicating it is the <u>endo</u> alkyl group which transfers to the metal. Heating [376] forms [377] plus [378] which is proposed to occur as



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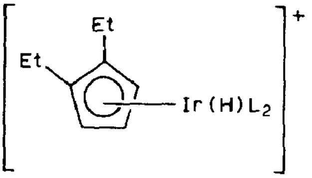

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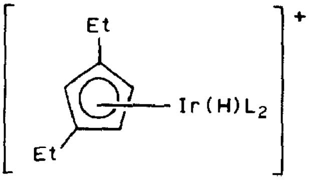
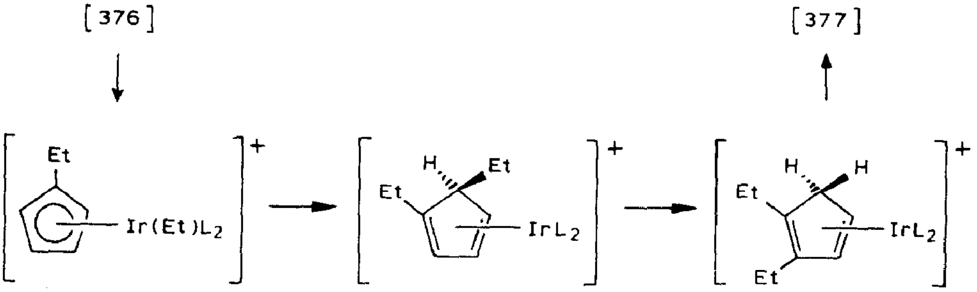


[378]

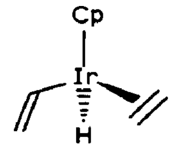
shown in Scheme LIX. The feasibility of the back-transfer of the ethyl group to the ring proposed in the second step was demonstrated by heating



Scheme LIX

[cpIr(Et)L_2]SbF_6 whereupon [(η^5-C_5H_4Et)IrHL_2]SbF_6 was formed. That no products from the β-elimination process for the ethyl group were detected indicated that no dissociation of the cyclopentadienyl group or the phosphine ligand occurred (ref. 601).

Several diketones react with $[IrCl(L_2)]_2$ (L_2 = TFB, Me_3TFB) in the presence of base to form [Ir(dike)(L_2)] (dike = 1-phenylbutan-1,3-dionate, 1,3-diphenylpropan-1,3-dionate). These add one molecule of ophen or bipy to form five coordinate complexes in which the diketonate ligands are monodentate and bonded via the central carbon atom (ref. 602). Photolysis of $[cpIr(C_2H_4)_2]$ in an argon matrix forms [379] together with a minor amount of [380]. The formation of these products is unaffected by the presence of ethylene in the matrix but now some $[cpIr(C_2H_4)]$ also appears to form. The same two products together with $[cpIr(C_2H_4)(N_2)]$ are seen in dinitrogen matrices while in a carbon monoxide matrix [379] still forms but much less [380] and $[cpIr(C_2H_4)]$ are seen and $[cpIr(CO)_2]$, $[cpIr(CO)(C_2H_4)]$ and $[cpIrH(CH{=}CH_2)(CO)]$ also appear (ref. 603). Electrochemical studies on $[Ir_2(COD)_2(\mu\text{-}pz)_2]$ show two oxidation steps in dichloromethane, the first of which is quasi-reversible and the second of which is irreversible unless water is present. Bulk electrolysis at a potential slightly more positive than the first wave mentioned above produces a two-electron oxidation and forms what is thought to be an oxidative addition product with dichloromethane. In acetonitrile only a single, two-electron oxidation step is seen and it was concluded that the details of the behavior of the complex in the cyclic voltammetric experiment are very sensitive to the presence of potential ligands in the system (ref. 604).



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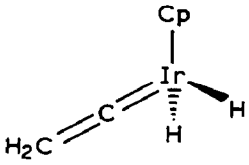
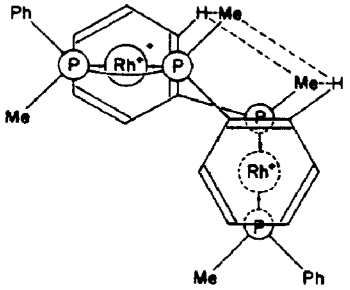


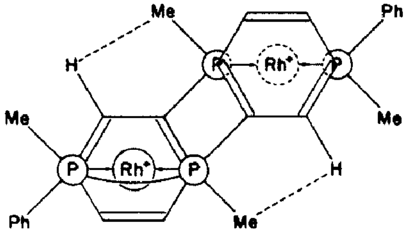
[380]

A substantial number of papers on asymmetric hydrogenation and related reactions has appeared again this year. These are largely devoted to the use of proven catalyst systems on new substrates or to the testing of complexes of new ligands on standard substrates (usually (Z)-α-acetamidocinnamic acid and its methyl ester but itaconic acid often is used). The complex $[Rh(COD)(L_2)]^+$ (L_2 = (R)-PROPHOS) catalyzes the asymmetric hydrogenation of (Z)-N-α-L-aspartyl-Δ-phenylalanine methyl ester to (L,L)-aspartame with 90% selectivity (ref. 605) but it and analogs with L_2 = (-)-NORPHOS or BPPFA were only moderately selective in the hydrogenation of prochiral olefins by hydrogen transfer from aqueous formic acid (ref. 606). The same three complexes together with analogs with L_2 = (S,S)-CHIRAPHOS or DIOP gave varying results in catalysis of the hydrogenation of crotonic acid derivatives. The best was the (-)-NORPHOS complex with (Z)-α-acetylamino-2-butenoic acid where a 91.4% enantiomeric excess was achieved (ref. 607). On the other hand, $[Rh(NBD)(L_2)]^+$ (L_2 = (S,S)-CHIRAPHOS, (R)-PROPHOS, DIOP) gave only moderate optical yields when used to catalyze the hydrogenation of prochiral ketones by hydrogen transfer from isopropanol. Treatment with base was required and a significant induction time was observed to generate the active catalyst (ref. 608). Addition of the monodentate DIOP complex [cpMn(CO)$_2$(DIOP)] to [RhCl(COD)]$_2$ (Mn:Rh = 1:1) generates a catalyst for asymmetric hydrogenation of standard substrates that gives optical yields of 75-80% (ref. 609). A DIOP analog having m-tolyl substituents on phosphorus has been synthesized and used to prepare the usual rhodium-based catalyst systems but no information appears in the abstract on their effectiveness (ref. 610). Also explored were the complexes (-)-[Rh(NBD)(L$_2$)]PF$_6$ (L$_2$ = [S-(R*,R*)]-o-bis(methylphenylphosphino)-benzene and its arsenic analog). With standard substrates hydrogenation proceeded to give 50-95% optical yields and these were generally improved if triethylamine was present. Hydrogenation of the phosphine complex in the absence of substrate formed [381] while the arsine analog formed



[381]

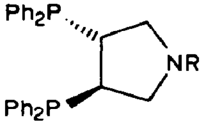
metallic rhodium under the same conditions and the meso-phosphine complex yielded [382]. Addition of methyl-(Z)-α-acetamidocinnamate (MAC) to [382]



[382]

formed (±)-[Rh(L$_2$)(MAC)]$^+$ as a mixture of diastereomers and as Halpern has previously shown for related systems, the minor diastereomer appears to yield the major chiral product on hydrogenation (ref. 611).

The ligands [383] (R = Me, bz, PhC(O), CHO, Bu^{t}OC(O), Me(OCH$_2$CH$_2$)$_n$-OCH$_2$C(O) (n = 1,3), HO$_2$C(CH$_2$)$_3$C(O), (EtO)$_3$Si(CH$_2$)$_3$NHC(O)C$_6$H$_4$C(O))(L$_2$) form [Rh(COD)(L$_2$)]$^+$ which effectively catalyze the asymmetric hydrogenation of standard substrates. The siloxy-substituted complex could be attached to a silica surface and the high selectivity was retained by the supported catalyst. When R = Me the rhodium complex could be methylated further with trimethyloxonium tetrafluoroborate to form [384] which functioned as an effective, water soluble catalyst for the asymmetric hydrogenation of sodium α-acetylaminocinnamate (refs. 612-614).



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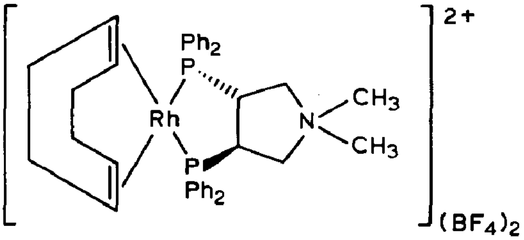
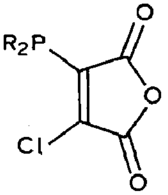


[384]

Other $[Rh(diene)(L_2)]^+$ (diene = COD, NBD; L = [385]; L_2 = [386]. R = (-)-(1R,3R,4S)-menthyl. X = O, NPh) complexes have been tested as hydrogenation catalysts.



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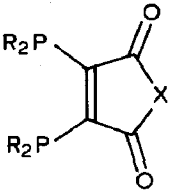
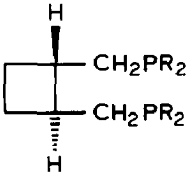


[386]

The former ligand is ineffective but the latter affords optical yields of up to 60% (ref. 615). Further ligands investigated which form analogous rhodium complexes for chiral hydrogenation catalysis are [387] and [388] (R = *m*-$NaO_3SC_6H_4$) which are effective in aqueous ethyl acetate. The latter gives better optical yields (ref. 616).



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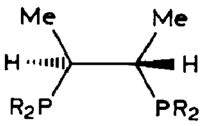
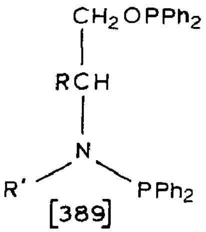


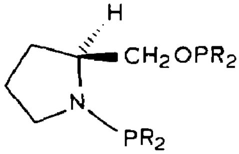
[388]

Others are the aminophosphites [389] (R = Me; R' = Me, Et. R = Pr^i, Bu^i, Bu^s, Ph, bz; R' = Me), [390] (R = Ph, cy) and [391] (R = OEt, $NHBu^n$, $O(CH_2)_2OEt$). Here, [389] gives optical yields of *ca* 85% with olefins and *ca* 50% with prochiral ketones



[389]

while [391] is better than [390]. Several of these ligands were also used to form $[Rh(L_2)(C_2H_4)_2]Cl$ which served as catalyst precursors for the



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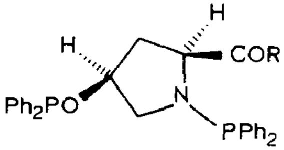
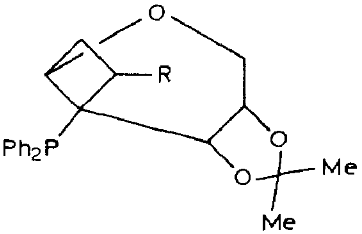


[391]

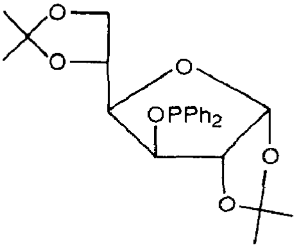
hydrosilylation of acetophenone with diphenylsilane but in most instances the optical yields were low (refs. 617-619). A final ketone hydrosilylation catalyst precursor is $[Rh(NBD)(L_2)]ClO_4$ (L_2 = (R)-o-(1-dimethylaminoethyl)phenyldi-tert-butylphosphine) and while chemical yields were reasonable no optical induction was observed (ref. 620).

The ligands [392] (R = CN, CH_2NH_2) were used in a ligand:metal ratio of 1:1 with $[RhCl(cyoct)_2]_2$ to form a catalyst precursor for asymmetric

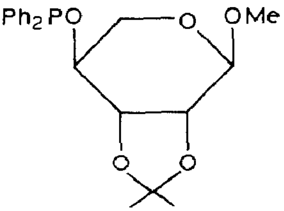


[392]

hydrogenation of standard substrates and high optical yields were obtained with R = CN (ref. 621). Other effective systems using $[Rh(COD)(L_2)]^+$ are those with L_2 = (S)- or (R)-PheNOP (ref. 622), [393], [394] and diphosphines derived from 1,2-O-isopropylidene-D-glycerol (refs. 623, 624).



[393]



[394]

The carbon-carbon double bond in monodehydro Leu-enkephalin can be hydrogenated to give a 93% yield of the (S)-product with [Rh(COD)(DIPAMP)]-BF_4 and 68% of the (R)-product with [Rh(COD)Cl(BPPM)] (ref. 625). The asymmetric transfer hydrogenation of ketones by isopropanol can be catalyzed by $[M(COD)(BDPOP)]^+$ (M = Rh, Ir) in the presence of base. Higher optical yields are achieved with the iridium complex (ref. 626). Mixtures of $[RhCl(COD)]_2$ and DIOP, (-)-NORPHOS or (-)-PPM catalyze the asymmetric hydrosilylation of prochiral oximes by diphenylsilane but the optical yields are low. At least one aryl substituent on the oxime carbon atom is necessary for effective catalysis and ketimines appear to be intermediates (ref. 627). Asymmetric transfer hydrogenation of ketones by isopropanol occurs under phase transfer conditions in the system $[RhCl(1,5\text{-}HD)]_2$/AMSO/KOH/Pr^iOH. Using acetophenone optical yields of up to 63% can be achieved at 45% conversion (ref. 628). Similar results are obtained using a catalyst prepared from [Ir(acac)(COD)], two mols of menthyldiphenylphosphine or phenyldimenthylphosphine and tetrafluoroboric acid followed by neutralization with potassium hydroxide (ref. 629).

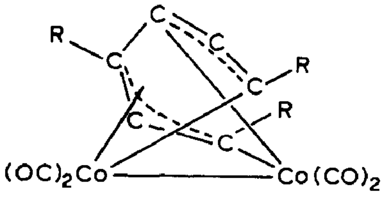
Hydrogenation of monoaryl ketones and aryl aldehydes to the corresponding hydrocarbons can be catalyzed at ambient conditions by $[RhCl(1,5\text{-}HD)]_2$ and β-cyclodextrin in THF. It is proposed that the substrate forms an inclusion complex with the cyclodextrin in which the aryl substituent is protected but the carbonyl group is exposed (ref. 630). An extension of the borate ester system for the carboxylation of benzylic bromides (see 1984 Annual Survey, J. Organometal. Chem., 305(1986)1, Scheme XLIX) shows that benzylic and other alkyl halides can be converted to carboxylic esters by formate esters and carbon monoxide in the presence of $[RhCl(1,5\text{-}HD)]_2$ and potassium iodide. Esters of aryl carboxylic acids can be formed from aryl bromides in good yield if the catalyst system also contains $[Pd(PPh_3)_4]$ (ref. 631). While $[Rh(acac)(C_2H_4)_2]$ catalyzes the formation of (2'-hydroxyethyl)-2-ethylidene-4,6-heptadienoate from BDN, ethylene oxide and carbon dioxide, palladium complexes form much better catalysts (ref. 632). The aldol reaction between aldehydes and trimethylsilyl enol ethers can be catalyzed by [Rh(COD)(DPPB)]X (X = ClO_4, PF_6) in dichloromethane or by $[Rh_4(CO)_{12}]$ in benzene (ref. 633) while $[RhCl(COD)]_2$ and phosphorus ligands (PPh_3, PBu^n_3, $P(OPr^i)_3$, $P(OEt)_3$) form a catalyst for the coupling of allenes with but-3-enoic acid. Here, the phosphine complexes give predominantly linear 3,6-dienoic acids while the phosphite complexes generate primarily branched 3,5-dienoic acids (ref. 634). Reaction of $[RhCl(COD)]_2$ with $[Ph_2P(CH_2)_nSiMe_2]_2O$ (n = 1-3) or 1,3,5-tris(2-diphenylphosphinoethyl)pentamethyl trisiloxane forms complexes presumed to contain {RhCl(COD)} moieties coordinated to each phosphorus atom that are active catalysts for the hydrosilylation of hex-1-ene by triethoxysilane. The system derived from the trisiloxane is the best and is slightly more active than [RhCl(PPh$_3$)$_3$] (ref. 635).

The complex [Rh$_2$Cl$_2$(COD)$_2$(phenazine)] forms a catalyst for the hydrogenation of olefins and aromatic nitro compounds in DMF (ref. 636) while [Rh(COD)(L)$_2$]$^+$ (L = Ph$_2$P(CH$_2$)$_n$Si(OEt)$_3$ (n = 1,3)), prepared from [Rh(acac)-(COD)], the ligand and p-toluenesulfonic acid, catalyzes olefin and diene hydrogenation either in solution or when supported on a silica surface. The heterogenized system is significantly more active (ref. 637). In aqueous methanol a mixture of [RhCL(COD)]$_2$ and excess P(p-C$_6$H$_4$SO$_3$Na)$_3$ catalyzes the isoprenylation of β-dicarbonyl compounds (ref. 638) while [MCl(COD)]$_2$ (M = Rh, Ir) alone catalyzes the Claisen rearrangement of thionobenzoates by what is proposed to be a metal-assisted, ion-pair mechanism (ref. 639). The isomerization of 4-trimethylsilylnon-1-ene to a mixture of E- and Z-4-trimethylsilylnon-2-ene is catalyzed by [RhH(PPh$_3$)$_4$], [M(NBD)(DPPB)]BF$_4$, [M(COD)(PPh$_3$)$_2$]PF$_6$ (M = Rh, Ir) and [Ir(COD)(py)(Pcy$_3$)]-PF$_6$ with the best being [Ir(COD)(PPh$_3$)$_2$]PF$_6$. This gives 97% of the E-isomer with 100% conversion at -20°C in dichloromethane (ref. 640). A catalyst prepared in situ from [RhCl(NBD)]$_2$ and triphenyl- or tri-n-butylphosphine (Rh: L = 1:3) mediates the hydroformylation of tropidine and N-substituted nortropidines. The majority of the product (86-95%) has the aldehyde function at the 3-position. Mixtures of [Rh$_4$(CO)$_{12}$] or [RhCl-(NBD)]$_2$ and tri-n-butylphosphine (Rh: L = 1:1) catalyze hydroformylation of tropidine all the way to the alcohol but with the latter complex and Rh:L = 1:2 the reaction stops at the aldehyde (ref. 641). In the presence of P(CHR(CH$_2$CH$_2$O)$_n$Me)$_3$ (R = H, Me; n = 1-3), [RhCl(COD)]$_2$ forms a WGSR catalyst in aqueous or two-phase systems (ref. 642) while [Rh(COD)(L$_2$)]PF$_6$ (L$_2$ = bipy, ophen, 2,9-dimethyl or 5,6-dimethyl or 3,4,7,8-tetramethyl derivatives of ophen) catalyze the polymerization of phenylacetylene to linear products. The first ligands provide the highest molecular weight products (ref. 643).

A variety of rhodium complexes including [Rh(acac)(C$_2$H$_4$)$_2$], [Rh(NBD)-(PPh$_3$)$_2$]BPh$_4$, [Rh(COD)(PPh$_3$)$_2$]PF$_6$, [(η^3-allyl)$_2$Rh(acac)] and [(η^3-allyl)$_2$-RhCl]$_2$ catalyze the oligomerization of BDN with carbon dioxide to 2-ethyl-2,4,9-undecatrien-4-olide. The same product can also be obtained from BDN, carbon dioxide and 2-ethylidene-6-hepten-5-olide suggesting dimerization of the BDN on rhodium occurs prior to incorporation of carbon dioxide (ref. 644). Stability constants for the complexation of olefins and alkynes with [Rh$_2$(O$_2$CMe)$_4$] and [Rh(CO)$_2$(3-(trifluoroacetyl-(1-R)-camphorate)] have been determined by complexation gas chromatography. (Z)-olefins tend to bind approximately five times more strongly to the rhodium(II) complex than do their (E)-isomers and the difference increases in the case of the rhodium (I) complex as the steric bulk adjacent to the double bond increases. The difference is attributed to a greater relief of strain on complexation in the former case (ref. 645). A large number of 1-methylcyclohexenes bearing hydroxyl, methoxy, carbonyl or carboxyl substituents remote from the double bond have been hydrogenated in the presence of $[Ir(COD)(py)(Pcy_3)]^+$ as a catalyst precursor. Hydrogen transfer from the metal to the face of the olefin containing the remote substituent occurs with much greater specificity than when palladium-on-carbon is the catalyst. This is attributed to an interaction of the remote substituent with the metal which provides a preferential orientation of the substrate on the metal. An exocyclic hydroxyl substituent provides poorer specificity than when this group is bound directly to the ring. The poorer catalyst precursor $[Ir(COD)(PPh_3)_2]^+$, in the presence of terpinen-4-ol(S), forms $[IrH_2(PPh_3)_2S_2]^+$ on hydrogenation in which it appears the terpinen-4-ol is bound only via the hydroxyl oxygen. This suggests that in the system described above the remote substituent binds first to the catalyst with the chelate effect favoring subsequent coordination of the double bond in the preferred orientation (ref. 646). Finally, $[Ir(OMe)(COD)]_2$ plus ten mols of ethyldiphenylphosphine forms a catalyst for the selective hydrogenation of the carbonyl group in benzylideneacetone (100°C, benzene, 30 atm H_2) to form 1-phenylbut-1-en-3-ol in high yield. The complexes $[IrL_4]^+$ and $[IrH_2L_4]^+$ ($L = PEtPh_2$) prepared independently are also excellent catalysts for the reaction and so the original system probably involves these or very similar species. Comparable yields of cinnamyl alcohol can be obtained from cinnamaldehyde using the first catalyst but if the L:Ir ratio is lowered to 2:1 hydrogenation of the carbon-carbon double bond occurs (ref. 647).

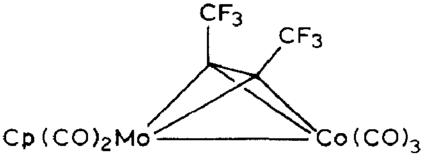
Metal Alkyne Complexes

At room temperature in heptane, $[Co_2(CO)_8]$ and $HC{\equiv}CSF_5$ form $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HC_2SF_5)]$ while at 50°C the product is $[Co_2(CO)_5(HC_2SF_5)_2]$. If the reaction is carried out at 95°C [395] ($R = SF_5$) forms from which 1,2,4-tris(pentafluorothio)benzene can be liberated on treatment with bromine.



[395]

The related complexes $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}RC_2SF_5)]$ (R = SF_5, $SiMe_3$) were also synthesized (ref. 648). Reaction of $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HFB)]$ with $[cpMo(CO)_3]^-$ or with $[cpMo(CO)_3]_2$ plus BPK forms [396]. The former route is more reliable and one carbonyl group on cobalt can be replaced by triphenylphosphine. Complex [396] exhibits two quasi-reversible, one-electron reduction processes which are thought to be addition of an electron to an orbital centered on the metal-alkyne framework followed by addition of an electron to the molybdenum (ref. 649). Coordination of a $\{Co_2(CO)_6\}$ moiety to the carbon-carbon triple bond in $[cpFe(C{\equiv}CPh)(CO)_2]$ and $[Fe(CO)_4(Bu^tP(H)C{\equiv}CPh)]$ occurs on reaction with $[Co_2(CO)_8]$. The latter adduct on refluxing in hexane forms $[FeCo_2(CO)_9(\mu_3\text{-}PBu^t)]$ plus a small amount of [397]. The last is described as the first example of a cluster-stabilized phosphaalkene (refs. 650, 651). Reaction of $Ph_2PC{\equiv}CPr^i$ with $[cpNiOs_3(CO)_9(\mu\text{-}H)_3]$ in the presence of trimethylamine N-oxide forms $[cpNiOs_3(CO)_8(Ph_2PC{\equiv}CPr^i)(\mu\text{-}H)_3]$ in which a $\{Co_2(CO)_6\}$ unit can also be bound to the alkyne (ref. 652). Ethylpropiolate inserts into the cobalt-hydrogen bond of $[(np_3)CoH]$ to yield $[(np_3)Co(C(CO_2Et)=CH_2)]$ which is oxidized to $[(np_3)Co(C(CO_2Et)=CH_2)]BPh_4$ on addition of sodium tetraphenylborate. A concerted process for the insertion is favored but has not been confirmed (ref. 653).



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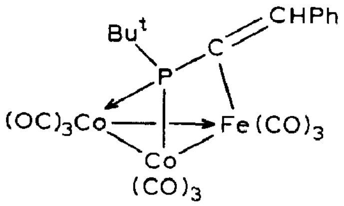
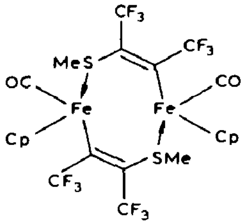


[397]

Reaction of [398] with $[Co_2(CO)_8]$ in refluxing toluene forms $[(\eta^6\text{-}C_6H_5Me)Co(\mu\text{-}\eta^2\text{-}HFB)Co(CO)_3]$ and a smaller amount of [399]. On the other hand, $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HFB)]$ and $[cp_2Fe_2(CO)_2(\mu\text{-}SMe)_2]$ in refluxing toluene yield $[cpFe(C(CF_3)=C(Me)CF_3)(CO)_2]$ (two isomers in which the methyl group is either *cis* or *trans* to iron) and small amounts of the two complexes formed in the first reaction (ref. 654). Under mild conditions diphenylacetylene and its pentafluorophenyl analog insert regiospecifically into



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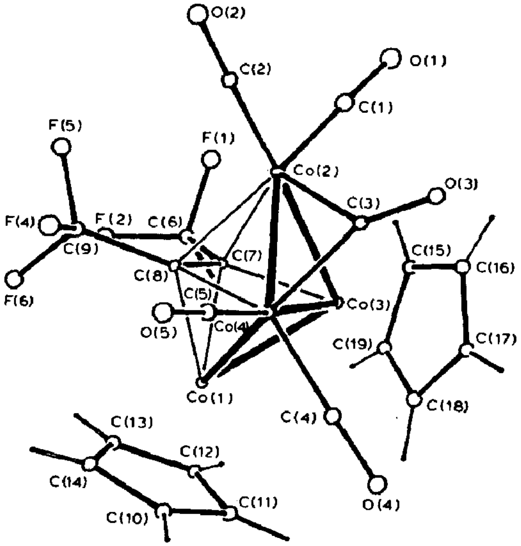
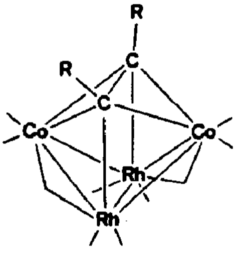


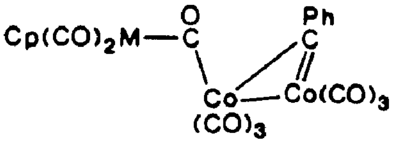
[399]

the cobalt-cobalt bond of $[Co_2Rh_2(CO)_{12}]$ to form [400] (R = Ph, C_6F_5). Reaction of [400] (R = Ph) with diphenylacetylene and carbon monoxide reversibly forms $[(OC)_3Co(\mu\text{-}\eta^2\text{-}C_2Ph_2)Rh(CO)_3]$ while with carbon monoxide



[400]

alone this complex forms again together with $[CoRh(CO)_7]$ suggesting that in the first reaction the first step is attack of carbon monoxide on [400] (ref. 655). Oxygenation of $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}PhC_2M(CO)_2cp)]$ (M = Fe, Ru) in dichloromethane/hexane forms $[cp(CO)MCo_2(CO)_6(\mu_3\text{-}CPh)]$ possibly via [401] or [402] as an intermediate. The reaction can be characterized as the oxidative decarbonylation of an acetylide and is proposed to involve attack



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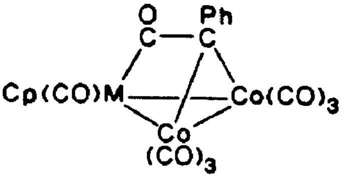
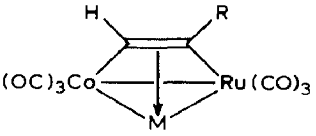


[402]

of dioxygen at the α-carbon of the acetylide (ref. 656). A reversible acetylene-to-vinylidene-to-alkylidyne transformation occurs in the successive conversions of [403] (M = cpMo(CO)$_2$; R = H, Bu^t) to [404] by refluxing in hexene and then to [405] by dihydrogen at 20 atm. Complex [405] reverts to [404] in refluxing hexane and the latter forms [403] (R = Bu^t only) on reaction with [cpMo(CO)$_3$]$^-$ in THF. Analogs of [403] (R = Me; M = cpNi. R = Bu^t; M = cpNi, cpMo(CO)$_2$, cpW(CO)$_2$) also convert to the corresponding examples of [404] in refluxing hexane. The nickel complexes form as mixtures of two isomers but the others give only one. Metal exchange reactions occur when [406] (R = Me, Ph, Bu^t) is reacted with [cpNiCO]$_2$ or [cpM(CO)$_3$]$_2$ (M = Mo, W) and [407] (R = Me, Bu^t, Ph; M = cpNi, cpMo(CO)$_2$, cpW(CO)$_2$) is obtained. As before, two isomers of the nickel complex are obtained as is the case for the others when R = Me, Ph. On the other hand when R = Bu^t a single isomer is formed with molybdenum and tungsten, a stereoselectivity which is attributed to electronic factors (refs. 657, 658). In related work, [cp$_2$Ni] reacts with [Co$_2$(CO)$_6$(μ-η^2-RC$_2$R')] to form the previously reported [cpNiCo(CO)$_3$(μ-η^2-RC$_2$R')] (R = R' = Et, Ph. R = Me; R' = Ph). These in turn react with [M(CO)$_5$] (M = Ru, Os) or [Fe$_2$(CO)$_9$]



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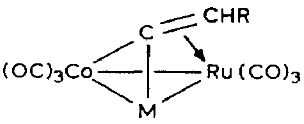

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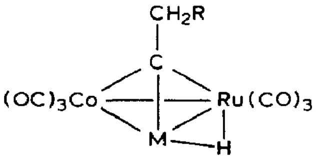

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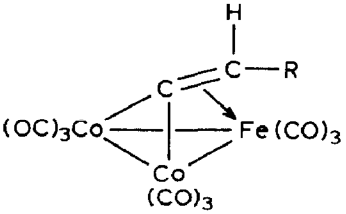

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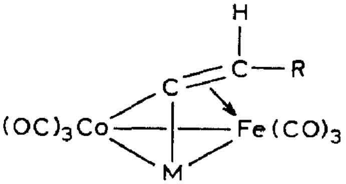
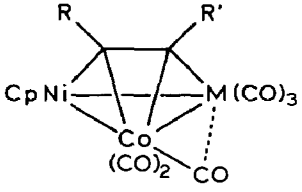
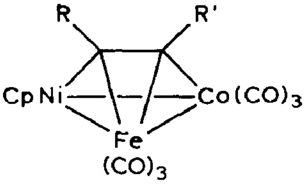


[407]

to yield [408] and [409] respectively. The observed structures are rationalized on the basis that the alkyne carbon atoms will bind the metal fragments with the highest electron acceptor ability. With the unsymmetrical

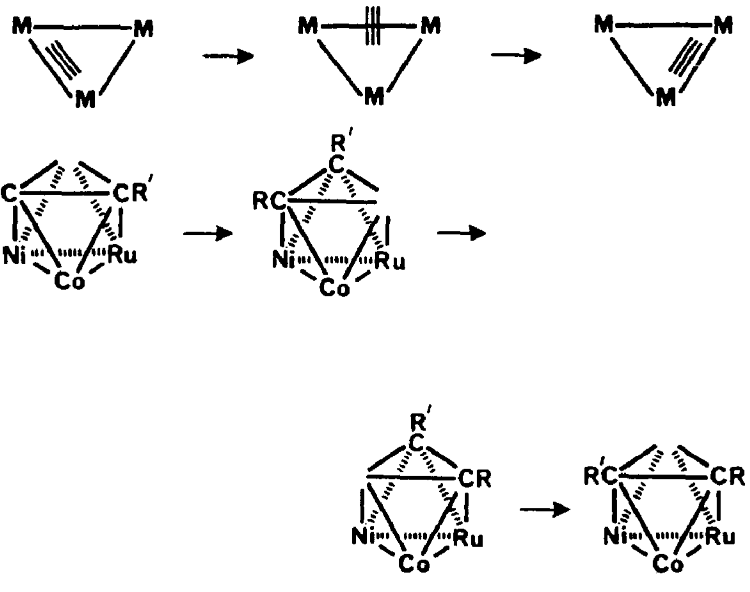


[408]



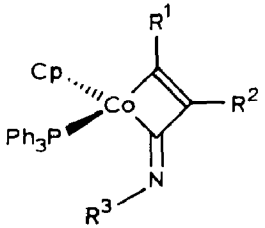
[409]

alkyne both orientations of the alkyne are seen and these isomers interconvert at elevated temperature. The symmetrical alkyne complexes also are fluxional and this is proposed to occur by one of the processes depicted in Scheme LX (ref. 659).

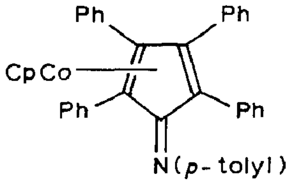


Scheme LX

The very slow addition of one equivalent of an isocyanide to benzene solutions of [cpCo(RC$_2$R')(PPh$_3$)] forms [410] (R^1 = R^2 = Ph; R^3 = Ph, p-tolyl, 2,6-Me$_2$C$_6$H$_3$. R^1 = Ph; R^2 = CO$_2$Me; R^3 = p-tolyl, 2,6-Me$_2$C$_6$H$_3$. R^3 = p-tolyl; R^1 = Ph; R^2 = CN. R^1 = H; R^2 = Ph. R^1 = Me; R^2 = CO$_2$Me). At 80°C in toluene [410] (R^1 = R^2 = Ph; R^3 = p-tolyl) forms [411] which can also be obtained by reaction with diphenylacetylene at lower temperature while at 180°C the product is a low yield of [cpCo(η^4-C$_4$Ph$_4$)]. Inhibition

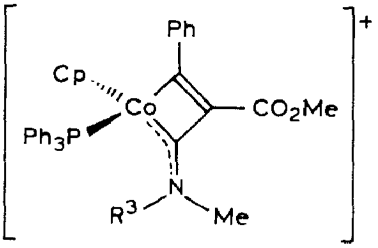


[410]

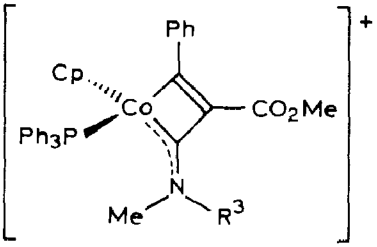


[411]

of this decomposition by triphenylphosphine suggests phosphine loss is the initial step. At 95°C in toluene isomerization of [410] (R^1 = Ph; R^2 = CO_2Me; R^3 = *p*-tolyl) to that with R^1 and R^2 interchanged occurs while with methyl iodide in benzene a mixture of [412] and [413] (R^3 = *p*-tolyl) forms.

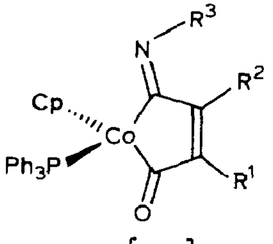


[412]

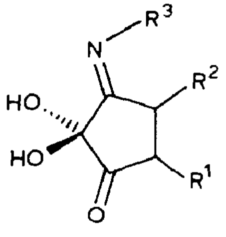


[413]

If left in solution, [412] slowly isomerizes to [413]. Carbonylation of [410] (R^1 = R^2 = Ph; R^3 = *p*-tolyl) forms a mixture of [414] and [415].

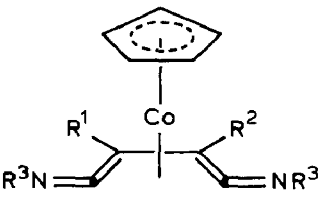


[414]

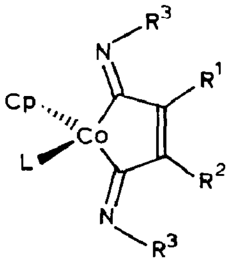


[415]

Addition of two equivalents of isocyanide to $[cpCo(R^1C_2R^2)(PPh_3)]$ in toluene at room temperature forms [416] (R^1 = R^2 = Ph; R^3 = Ph, *p*-tolyl, *o*-tolyl, Bu^t, 2,6-$Me_2C_6H_3$. R^1 = Ph; R^2 = CO_2Me, R^3 = 2,6-$Me_2C_6H_3$) which converts to [417] (R^1 = R^2 = R^3 = Ph; L = PhNC, PMe_3, CO. R^1 = R^2 = Ph; R^3



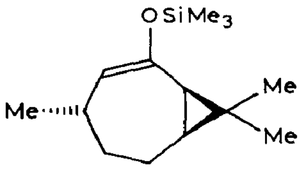
[416]



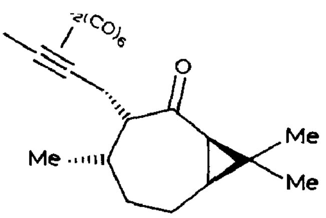
[417]

= *p*-tolyl; L = *p*-tolylNC, 2,6-$Me_2C_6H_3$,NC, CO), a species which also forms in the initial reaction in some instances, on reaction with the appropriate ligand (refs. 660, 661).

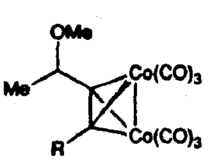
A considerable number of papers have appeared on the use of cobalt carbonyl-stabilized propargyl and other carbocations in organic synthesis. Oxidation of $[(\eta^4\text{-BDN})Co(CO)_2]_2$ with ferricinium tetrafluoroborate forms $[(\eta^4\text{-BDN})Co(CO)_2]BF_4$ which reacts with nucleophiles at -78°C to yield $[(\eta^3\text{-}C_4H_6Nu)Co(CO)_3]$ (Nu = py, H^-, Ph^-, PMe_3) in which the allylic ligand has the *anti* conformation. A double nucleophilic addition to the cation occurs on successive reaction with sodium cyanoborohydride and sodium bis(carboxymethyl)methanide whereupon the major product is (Z)-2-butenyl-dimethylmalonate (ref. 662). In another example, reaction of $[Co_2(CO)_6\text{-}(\mu\text{-}\eta^2\text{-}MeC_2CH_2)]BF_4$ with [418] forms [419] which is an intermediate in the formation of (±)-cyclocolorenone (refs. 663, 664). In instances where functionalities which are sensitive to protonic acids are present, a useful variation is to add a Lewis acid such as boron trifluoride etherate to a $\{Co_2(CO)_6\}$-stabilized propargylic ether to generate the reactive species. Thus *cis*-1-trimethylsiloxy-2-methyl styrene reacts with [420] (R = $SiMe_3$) in the presence of boron trifluoride etherate at -78°C to form [421] plus a



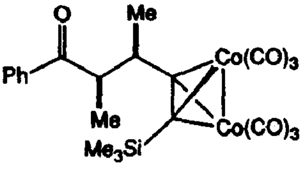
[418]



[419]

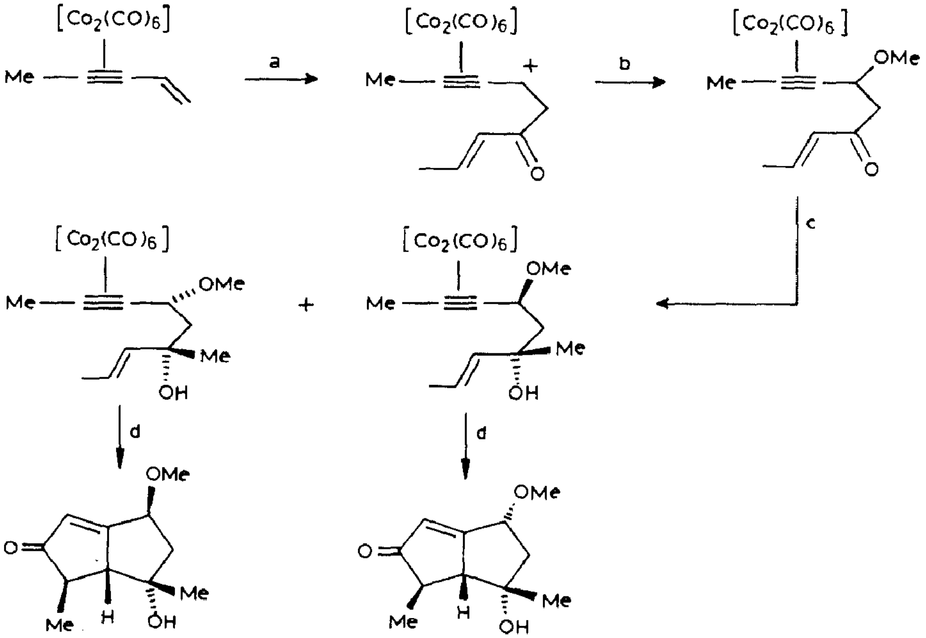


[420]



[421]

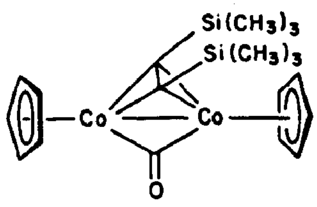
small amount of its anti diastereomer. When R = H only a slight excess of the corresponding syn product is seen suggesting that stereoselection is the result of steric interactions in the transition state (ref. 665). A particularly useful application of the type of reaction discussed above is in the formation of functionalized bicyclic molecules. Thus with nucleophiles containing a remote double bond a $\{Co_2(CO)_6\}$-complexed enyne is obtained which often can be cyclized and demetallated on heating. An example is shown in Scheme LXI. The yields of cyclized products are often significantly higher if the final step is carried out on a silica or alumina support in the absence of solvent than if done in solution (refs. 666-670). Another use of the $\{Co_2(CO)_6\}$ moiety as a protecting group is to allow selective reaction of the olefinic portion of an enyne. Thus protection of the alkyne portion of α,ω-diphenylpent-4-en-1-yne in this manner permits selective bromination of the double bond (ref. 671).



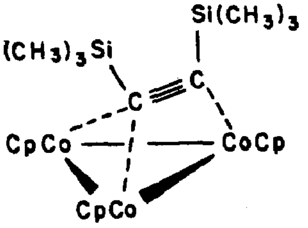
a) [trans-MeCH=CHC(O)]BF_4. b) MeOH. c) MeMgI. d) Δ, SiO_2.

Scheme LXI

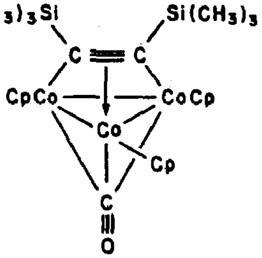
The Vollhardt group continues to publish much work on the use of $[cpCo(CO)_2]$ to mediate the coupling and cyclization reactions of compounds containing multiple bonds to carbon. The reaction of $[cpCo(CO)_2]$ with BTMSA forms $R_2C=C=C=CR_2$ (R = $SiMe_3$), $[cpCo(\eta^4-C_4(SiMe_3)_4)]$ and a variety of trinuclear, carbyne-capped products (ref. 672). Some clues to the mechanism of formation of the last products was obtained from the reaction of the more labile [cpCo(C_2H_4)$_2$] with BTMSA. In THF-d_8 at room temperature substantial conversion to [cpCo(C_2H_4)(BTMSA)] occurs as determined by proton NMR spectroscopy but on removal of solvent the product isolated was [cp$_2$-Co$_2$(μ-η^2-BTMSA)] which is proposed to contain a cobalt-cobalt double bond. This is readily carbonylated to [422] and reacts with more [cpCo(C_2H_4)$_2$] in diethyl ether at 55°C to yield [423]. Complex [423] can be carbonylated to give [424] and heating either one in *m*-xylene forms [425]. This reaction of [424] also forms [422] and a crossover experiment on the conversion of [423] to [425] indicates it proceeds intramolecularly. The analog of [425], [cp$_3$Co$_3$(μ_3-CH)$_2$] is unreactive towards carbon monoxide but with tetrafluoroboric acid etherate it forms [426] which does react with carbon monoxide at 23°C to form [427]. The latter reacts with carbon monoxide at 70°C to yield [428] while attempted chromatography on silica gel forms [429] in low yield. It is suggested that the conversion of [426] to [427] is an acid mediated alkylidyne-carbon monoxide coupling while the formation



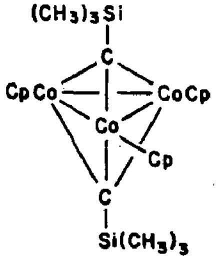
[422]



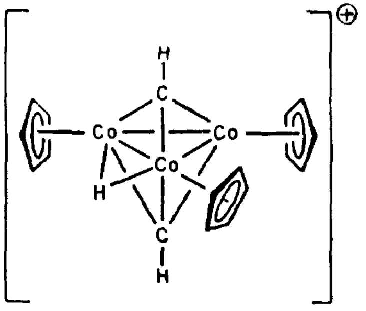
[423]



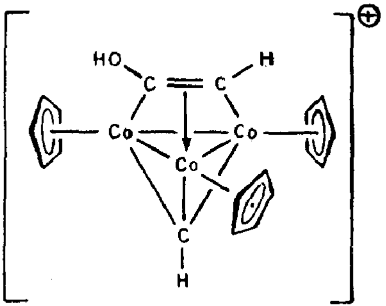
[424]



[425]

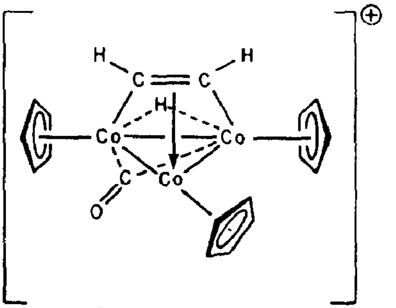


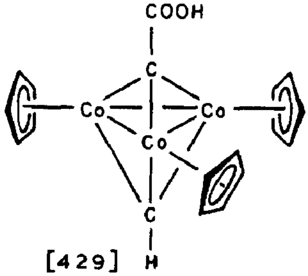
[426] $BF_4^{\ominus}$



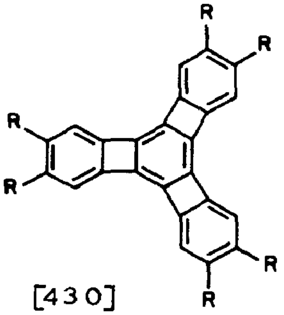
[427] $BF_4^{\ominus}$

of [428] from [427] is a decoupling of these two moieties followed by the coupling of two alkylidyne fragments (ref. 673, 674). In the area of

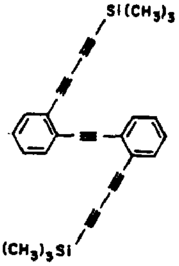

[428] BF$_4^{\ominus}$

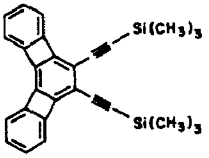

[429]

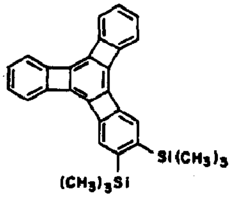
alkyne cocyclizations, hexaethynylbenzene reacts with BTMSA in the presence of [cpCo(CO)$_2$] to form [430] (R = SiMe$_3$) in which an essentially complete localization of the double bonds of the central ring is inferred from


[430]

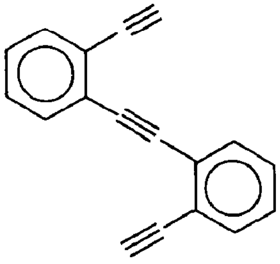
the crystal structure. Similarly, [cpCo(CO)$_2$] effects the cyclization of [431] to [432] in modest yield and the latter on reaction with potassium hydroxide in methanol and then with BTMSA and [cpCo(CO)$_2$] forms [433].


[431]

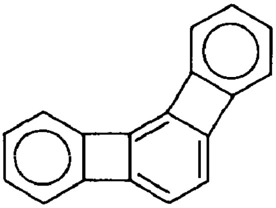

[432]


[433]

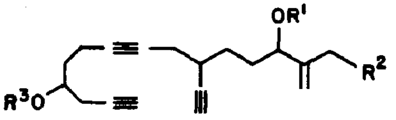
Successive reactions of [434] with [cpCo(C_2H_4)$_2$] at -30°C in THF and carbon monoxide (8 atm, 100°C) forms [435] in which significant localization of the double bonds in the central ring also occurs (refs. 675, 676). A one-step synthesis of a steroid nucleus containing an aromatized B-ring from an acyclic precursor with complete control over the stereochemistry of the C, D ring junction (100% trans) can be achieved in the reaction of [436] with [cpCo(CO)$_2$] in refluxing o-xylene under photolytic conditions whereupon [437] (R^1 = R^2 = R^3 = H. R^1 = Me; R^2 = H; R^3 = H, $MeCO_2$. R^1 = R^2 = Me; R^3 = H) is formed (ref. 677). In related work, [438] is cyclized to [439] (R^1 = β-Me; R_2 = α- or β-$OCH_2OCH_2CH_2OMe$. R^1 = α-Me; R^2 = α-OCH_2-OCH_2CH_2OMe) while the analog of [438] with a trimethylsilyl substituent on



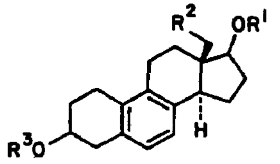
[434]



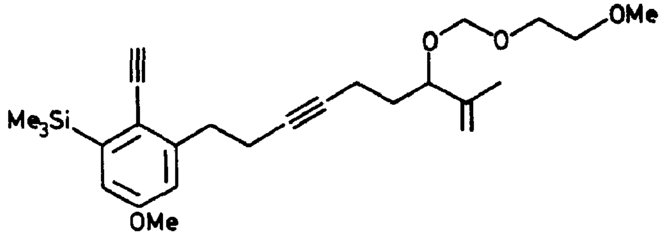
[435]



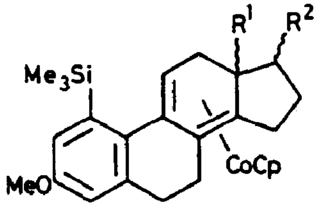
[436]



[437]

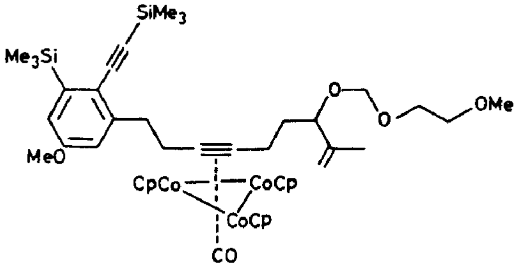


[438]



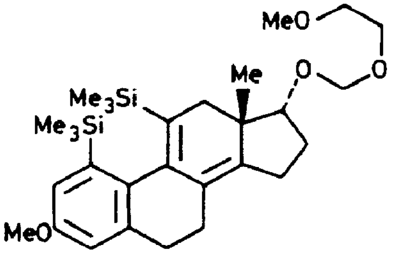
[439]

the terminal alkynyl moiety forms a low yield of [440] together with comparable amounts of [441] and [442] as the reaction is rather sluggish

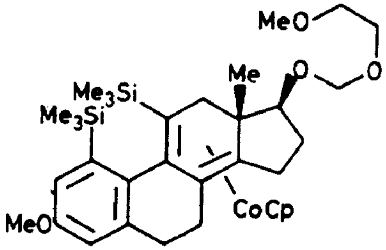


[440]

(ref. 678). The [2+2+2] cycloaddition of alkynes to the 2,3-double bonds of indole and various N-substituted pyrroles mediated by [cpCo(CO)$_2$] forms

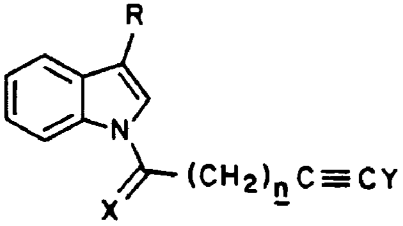


[441]

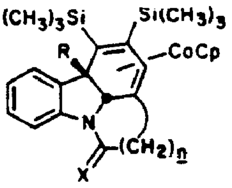


[442]

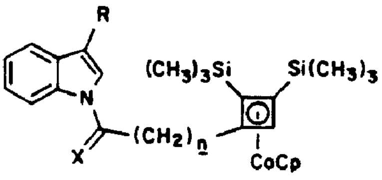
the 4a,9a-dihydro-9H-carbazole nucleus and fused dihydroindoles respectively. An example of the first is [443] (R = Y = H; X = O; n = 2) with BTMSA to give [444] and a small amount of [445] while for the latter system a



[443]

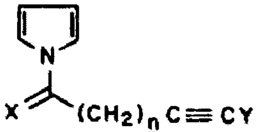


[444]

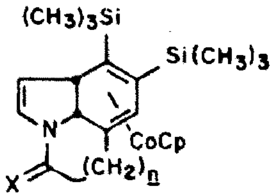


[445]

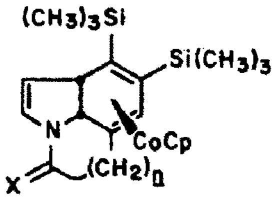
typical reaction is [446] with BTMSA to form [447] and a lesser amount of [448] (X = O; Y = H; n = 2) (refs. 679, 680). Finally, [cpCo(CO)$_2$]



[446]

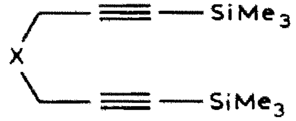


[447]

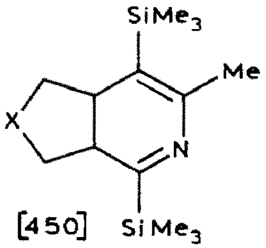


[448]

mediates the cocyclization of [449] with acetonitrile in refluxing xylene under irradiation to give [450] (X = O, CH_2) (ref. 681).

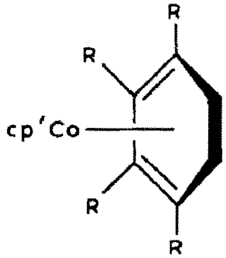


[449]



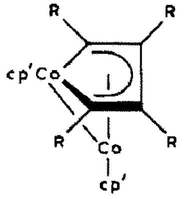
[450]

Acetylene can be cocyclized with (+)-(S)-2-(1-methylbenzyl)-6-cyanopyridine in the presence of [cpCo(COD)] to yield (+)-(S)-6-(1-methylbenzyl)-2,2'-bipyridine. This and related species prepared in the same fashion were used as ligands with $[RhCl(COD)]_2$ to form a catalyst for the asymmetric hydrogenation of acetophenone by isopropanol but low optical yields were obtained (ref. 682). In refluxing hexane, $[cp'Co(C_2H_4)_2]$ cyclotrimerizes phenyl- and diphenylacetylene to 1,3,5-triphenyl- and hexaphenylbenzene respectively. In the latter reaction $[cp'Co(\eta^4\text{-}C_4Ph_4)]$ also forms but with BTMSA only $[cp'_2Co_2(\mu\text{-}\eta^2\text{-BTMSA})]$ (see also ref. 673) was obtained while DMAD formed hexa(carboxymethyl)benzene, $[cpCo(\eta^4\text{-}C_6(CO_2Me)_6)]$ and [451] (R = CO_2Me). Reduction of $[cp'CoCl]_2$ with sodium amalgam in THF in



[451]

the presence of acetylenes formed $[cp'_2Co_2(\mu\text{-}\eta^2\text{-}C_2R_2)]$ (R = $SiMe_3$, Ph) or [452] (R = CO_2Me). With BTMSA a second product was $[cp'Co(\eta^4\text{-}C_4(SiMe_3)_4]$.

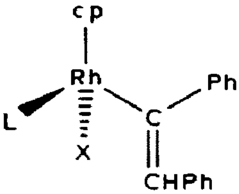


[452]

As was noted earlier for $[\mathrm{cp_2Co_2(\mu\text{-}\eta^2\text{-}BTMSA)}]$, the diphenylacetylene analog contains a cobalt-cobalt double bond and readily reacts with carbon monoxide, sulfur dioxide and tetrafluoroboric acid to yield $[\mathrm{cp'_2Co_2(\mu\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}L)}]$ (L = CO, $\mathrm{SO_2}$) and $[\mathrm{cp'_2Co_2(\mu\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}H)}]\mathrm{BF_4}$ respectively (ref. 683). Cocondensation of cobalt atoms with nitriles and acetylenes also forms substituted pyridines in good yield on warming but the reactions are less regioselective than procedures used by Vollhardt and benzenes also form (ref. 684).

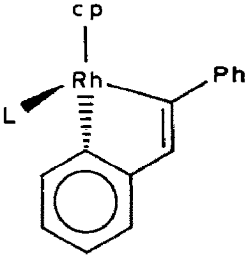
Coordination of a $\{\mathrm{Co_2(CO)_6}\}$ moiety to tha alkyne function in 17α-propynylestra-1,3,5(10)-triene-3,17β-diol occurs on reaction with $[\mathrm{Co_2(CO)_8}]$ and the complex was used to assign the 2D proton NMR spectrum of the steroid (ref. 685). The electron deformation density in $[\mathrm{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}C_2Bu^t_2)}]$ has been determined from low temperature x-ray and neutron diffraction data in conjunction with Hartree-Fock, configuration interaction calculations. The metal-metal interaction appears to occur *via* a bent metal-metal bond and the calculated π-backbonding to the alkyne ligand (*ca* 0.88 e^-) agrees well with experiment (ref. 686). Two molecular orbital calculations have also been performed on $[\mathrm{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}C_2H_2)}]$ as a model for this class of complexes. The first was used to determine the barrier to isomerization and, in contrast to Hoffmann's earlier results, by allowing the $\{\mathrm{Co(CO)_3}\}$ groups to reorient in the process there is little or no barrier to the rotation of the carbon-carbon axis from an orientation perpendicular to the metal-metal axis to one which is parallel. Nevertheless, a level-crossing still is present so this process remains symmetry-forbidden but the calculated upper limit on the activation energy for the reorientation suggests that it should be chemically accessible. In this study the analogy drawn by Hoffmann between the twist of the acetylene ligand and the forbidden tetrahedrane-to-cyclobutadiene conversion is thought not to be valid. No details on the second calculations were given in the abstract (refs. 687, 688).

Addition of acetylenes to $[\mathrm{RhCl(PPr^i_3)_2}]$, prepared *in situ* from $[\mathrm{RhCl(cyoct)_2}]_2$, forms $[\mathrm{RhCl(RC_2R')(PPr^i_3)_2}]$ (R = R' = H, Ph. R = H; R' = Ph) which is converted to $[\mathrm{cpRh(RC_2R')(PPr^i_3)}]$ by sodium cyclopentadienide. The related complex, $[\mathrm{cpRh(Ph_2C_2)(PMe_3)}]$ is obtained from $[\mathrm{RhCl(Ph_2C_2)(PMe_3)}]_2$ and sodium cyclopentadienide and reacts with methyl iodide to yield $[\mathrm{cpRhI(Me)(PMe_3)}]$. Protonation of $[\mathrm{cpRh(Ph_2C_2)(PPr^i_3)}]$ with TFA in diethyl ether forms [453] (L = $\mathrm{PPr^i_3}$; X = $\mathrm{O_2CCF_3}$) in which the trifluoroacetate ligand can be replaced by iodide or azide. Reaction with trimethylphosphine and hexafluorophosphate forms $[\mathrm{cpRh(C(Ph)\text{=}CHPh)(PMe_3)_2}]\mathrm{PF_6}$. Other reactions of [453] (L = $\mathrm{PPr^i_3}$, X = $\mathrm{O_2CCF_3}$) are with hydride reagents



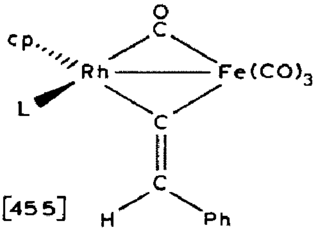
[453]

to form [$cpRh(C(Ph)=CHPh)(H)(PPr^{i}_{3})$] and then [$cpRh(\eta^{2}$-PhHC=CHPh)($PPr^{i}_{3}$)] and with methyl magnesium iodide to yield the analog with X = I. Reaction of this with more Grignard at 60°C forms the analog with X = Me which on heating eliminates methane to regenerate [$cpRh(C_2Ph_2)(PPr^{i}_{3})$]. Reaction of this last complex with tetrafluoroboric acid etherate followed by dissolution in methanol, nitromethane or acetone yields [454] (L = PPr^{i}_{3}) which

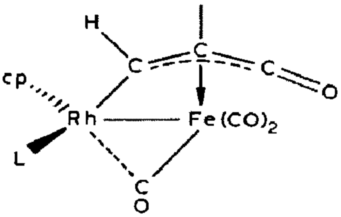


[454]

can also be obtained directly by dissolving [453] (L = PPr^{i}_{3}; X = O_2CCF_3) in the same solvents. In THF, [$cpRh(PhC_2H)(PPr^{i}_{3})$] reacts with [$Fe_2(CO)_9$] to give a mixture of [455] and [456] (L = PPr^{i}_{3}) (refs. 689, 690). Terminal alkynes react with [$Rh_2(CO)_2(\mu$-H$)_2(DPM)_2$] in benzene under hydrogen

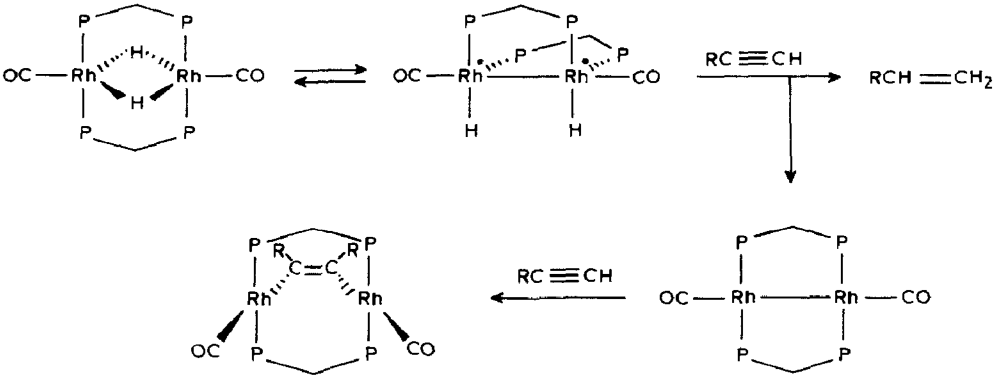


[455]



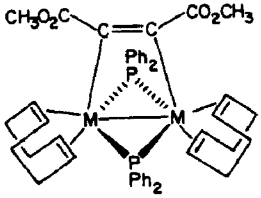
[456]

to form [$Rh_2(CO)_2(\mu$-RC=CH)(DPM$)_2$] (R = Me, OEt, Bu^{t}, CO_2Me, CH_2OH, Ph) and the corresponding terminal olefin. The rather peculiar features of the CIDNP observed in the proton NMR of the reacting solution were interpreted to indicate the existence of a metal-centered biradical and Scheme LXII was proposed (ref. 691). Complexes [457] (M = Rh, Ir) are synthesized by reaction of DMAD with [$M_2(COD)_2(\mu$-$PPh_2)_2$]. Reaction of [$RhCl(NBD)]_2$ with lithium diphenylphosphide at -78°C forms [$Rh_2(NBD)_2(\mu$-$PPh_2)_2$] which is unstable above -10°C. It appears to give species which may be analogs of [457] with but-2-yne and methylphenylacetylene but these were not studied

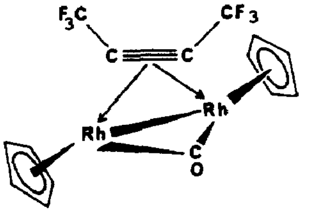


Scheme LXII

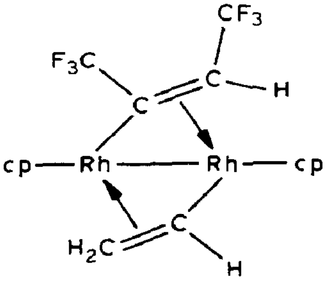
further (ref. 692). Complex [458] forms approximately equal amounts of [459] and [460] on reaction with ethylene. The reaction is slow in the dark but fast when irradiated and a trace of [cp$_3$Rh$_3$(CO)(C$_4$F$_6$)] also forms. With higher olefins analogous products are obtained as mixtures of isomers except with 3,3-dimethylbut-1-ene and styrene where steric factors appear



[457]



[458]



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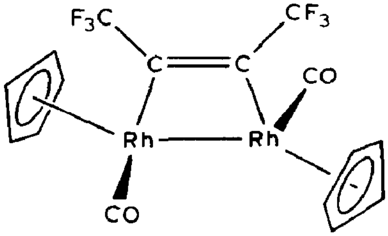
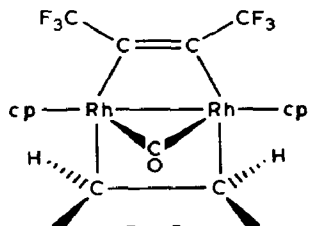
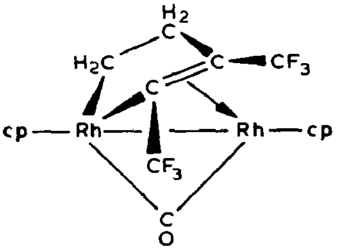


[460]

to dominate so that only the terminal carbon is σ-bonded to the metal. In the dark, [458] reacts with acrylonitrile to form [461] but under irradiation the product is thought to be [462] although the regiochemistry of the

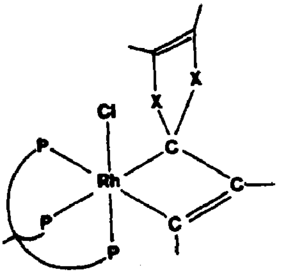


[461]

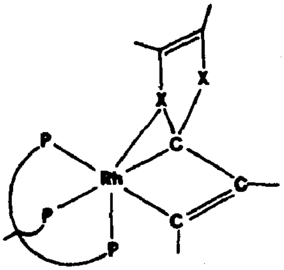


[462]

acrylonitrile-derived portion of the metallacycle is unknown. Electrochemical studies on the di-*tert*-butylacetylene analog of [458] in dichloromethane indicate the formation of a monoanion and mono- and dications. The monocation is quite stable but the other ions are less so. The behavior in acetonitrile is much more complex and the oxidized species react with the solvent to form mono- and dicationic analogs of [460] with one carbonyl ligand replaced by acetonitrile. Complex [458] itself is easier to reduce and more difficult to oxidize than the analog just described and all ionic products show a greater kinetic instability (refs. 693, 694). Full details

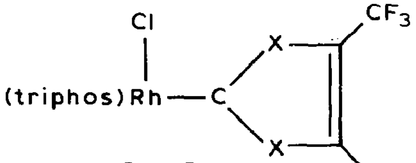


[463]



[464]

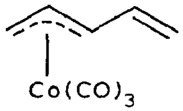
of the synthesis and properties of [463] (X = S, Se) and its reversible conversion to [464] by halide abstraction have appeared. The first complex is prepared from $[(\text{triphos})\text{RhCl}(\eta^2\text{-CX}_2)]$ and HFB and is thought to form *via* [465] which subsequently adds across the triple bond of the second acetylene molecule (ref. 695). Various rhodium-containing metallacycles catalyze the cocyclotrimerization of carboxymethyl acetylenes and organic isocyanates to form pyridones (ref. 696).



[465]

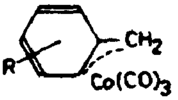
Metal π-allyl Complexes

Addition of $Na[Co(CO)_4]$ to a THF solution of 1-bromopenta-2,4-diene at -78°C forms [466] in which one carbonyl group can be replaced by triphenylphosphine. The latter isomerizes in toluene solution to the syn isomer

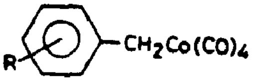


[466]

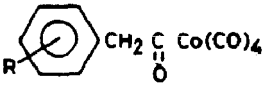
(ref. 697). Benzyl or phenylacetyl halides react with $Na[Co(CO)_4]$ in diethyl ether at room temperature to yield an equilibrium mixture of [467] - [469] (R = H, o-Me, m-Me, p-Me, p-MeO, p-Cl, 3,4-$(MeO)_2$, 2,6-Cl_2) which



[467]

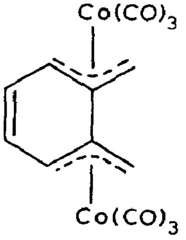


[468]



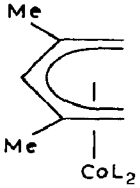
[469]

oligomerizes on standing. Related complexes form when styrenes containing most of the same substituents react with $[HCo(CO)_4]$ (ref. 698). Addition of $Na[Co(CO)_4]$ to α,α'-dibromo-o-xylene yields [470] which appears to be

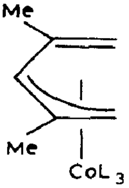


[470]

fluxional (ref. 699). The pentadienyl complex [471] (L = PEt_3) is converted by tri-n-propylphosphine to the analog with L = $PPr^n{}_3$ but with trimethylphosphine or trimethylphosphite, the product is [472] (L = PMe_3, $P(OMe)_3$). The first reaction is proposed to occur by a dissociative mechanism while the latter is thought to occur by associative attack on an η^3-pentadienyl intermediate. Complex [471] (L = PEt_3) is oxidized by

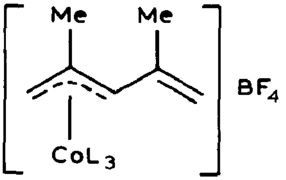


[471]



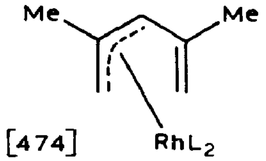
[472]

silver tetrafluoroborate or tetrafluoroboric or triflic acids to form a cation in which the bonding of the pentadienyl ligand is distorted towards that found in [472]. A one-electron inner-sphere mechanism is proposed which in the case of the acid reagents is said to imply a bimolecular reductive elimination reaction between two protonated (at the metal) forms of [471] but why this latter step occurs here (in cyclopentadienyl analogs ring protonation is the final product) is uncertain. Silver or alkyl iodides react with [471] (L = PEt_3) to replace one phosphine by iodide. In the first instance an associative attack of iodide on an η^3-pentadienyl intermediate is proposed while in the latter a cationic alkyl derivative of [471] is thought to form initially which then undergoes cobalt-carbon bond homolysis following which the iodide counterion replaces one phosphine ligand. Silver tetrafluoroborate converts [472] (L = PMe_3) to [473] and

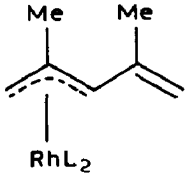


[473]

this can also be formed by addition of trimethylphosphine to the cation derived from [471]. Related rhodium complexes, [474] and [475] (L = PMe_3,

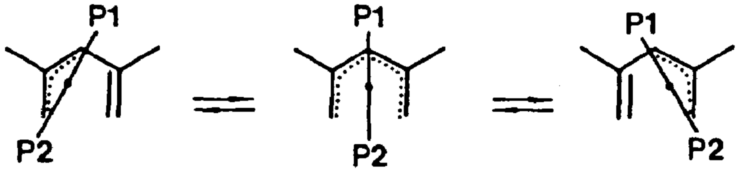


[474]



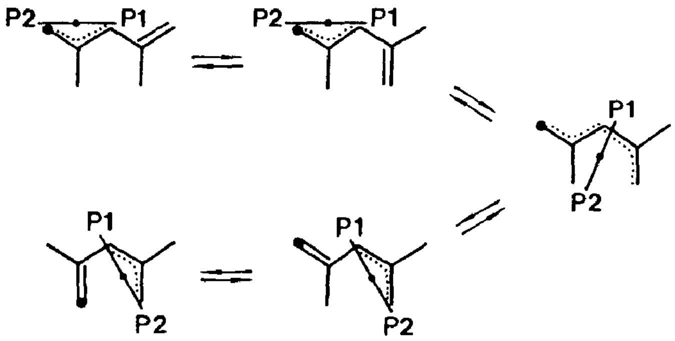
[475]

PEt_3, PPr^{i}_{3}, PBu^{i}_{3}) are synthesized from $[RhClL_2]_2$ and potassium 2,4-dimethylpentadienide with the former species being the major isomer. All are fluxional by a process proposed to be that of Scheme LXIII. At



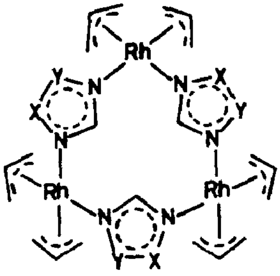
Scheme LXIII

higher temperatures an interconversion of [474] and [475] occurs as outlined in Scheme LXIV (refs. 700, 701). Addition of various nitrogen



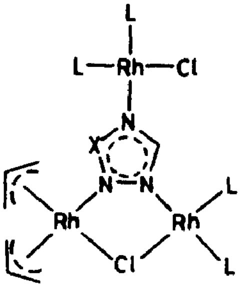
Scheme LXIV

heterocycles to $[(\eta^3\text{-}C_3H_5)_2Rh(acac)]$ forms [476] (X = Y = N, CH. X = N; Y = CH) but with $[(\eta^3\text{-}C_3H_5)_2RhCl]_2$ the initial product is $[(\eta^3\text{-}C_3H_5)RhCl(HL)]$ (L = pz, btz). The latter on deprotonation with triethylamine forms a trimer analogous to [476] but the latter gives $[(\eta^3\text{-}C_3H_5)_4Rh_2(\mu\text{-}Cl)(\mu\text{-}pz)]$



[476]

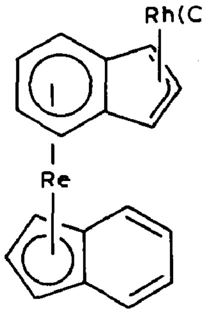
in which the bridging chloride can be replaced by hydroxide or azide. With $[RhCl(CO)_2]_2$, [476] (X = CH, N; Y = N) forms [477] (X = CH, N; L = CO)



(ref. 702).

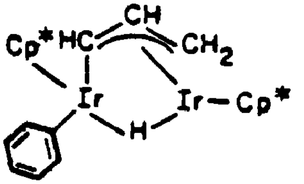
[477]

Condensation of rhenium atoms with indene forms $[(\eta^6\text{-}C_9H_8)Re(\eta^5\text{-}C_9H_7)]$ which on deprotonation with potassium hydride and reaction with $[RhCl(COD)]_2$ forms [478] (ref. 703). Diphenylmethylenecyclopropane can be coupled with but-3-enoic acid in the presence of catalytic amounts of $[RhCl(PPh_3)_3]$ to form 6,6-diphenyl-5-methyl-3-methylenehex-5-enoic acid and 7,7-diphenyl-6-methylhepta-3,6-dienoic acid. It is proposed that the

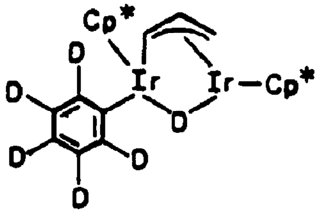


[478]

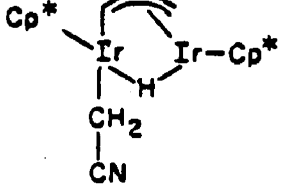
rhodium cleaves the cyclopropyl ring to form a substituted trimethylenemethane complex followed by coordination of the olefin and coupling of the organic ligands (ref. 704). On partially hydroxylated alumina [(η^3-C_3H_5)-Rh(CO)$_2$] forms isolated {Rh^I(CO)$_2$} moieties bound to oxygen atoms of the support but on silica these appear to be close enough that on treatment with dihydrogen dimerization occurs to give similarly supported {Rh$^I_2$-(CO)$_2$(μ-CO)$_2$} moieties. Similarly, supporting of [(η^3-C_3H_5)$_3$Rh] on silica forms O-bonded {Rh(η^3-C_3H_5)$_2$} moieties which on treatment with octane and then dihydrogen convert to supported {Rh$_2$H$_2$(μ-H)$_2$} moieties. It thus appears that hydrogenation promotes aggregation of rhodium species on silica. Oxygen-bonded {Rh(η^3-C_3H_5)$_2$} moieties have also been confirmed to be present when [(η^3-C_3H_5)$_3$Rh] is deposited on hydroxylated titanium dioxide (refs. 705, 706). On heating [cp'IrH(η^3-C_3H_5)] for six days at 45°C in benzene [479] is formed which converts to [480] under like conditions in deuterobenzene, a process which is reversed if [480] is heated in benzene. Heating [479] in acetonitrile or reaction with ligands forms [481] and [482] (L = (PMe$_3$, P(OMe)$_3$, CO, C_2H_4) respectively while at 100°C



[479]



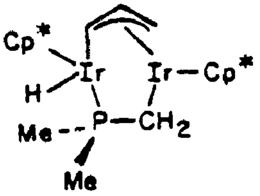
[480]



[481]

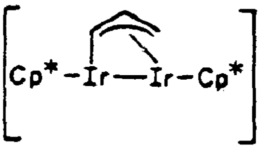
[482]

[482] (L = PMe_3) converts to [483]. With dihydrogen [479] gives [484] and the intermediate [485] is implicated in all of the above reactions (ref. 707).



[483]

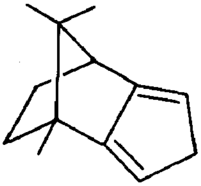
[484]



[485]

Metal Carbocyclic Complexes

Significant interest in $[(\eta^5\text{-}C_5Ph_5)M(CO)_2]$ (M = Co, Rh) has developed and several syntheses have been reported. The cobalt complex has been synthesized in low yield from pentaphenylcyclopentadiene and $[Co_2(CO)_8]$ in refluxing toluene but better routes are from bromopentaphenylcyclopentadiene and $K[Co(CO)_4]$ or $[Co_2(CO)_8]$ plus zinc in THF. The last route is the best for the rhodium analog (starting with $[RhCl(CO)_2]_2$) but it can also be obtained from $[RhCl(CO)_2]_2$ and sodium pentaphenylcyclopentadienide in hot THF. In the latter reaction $[(\eta^5\text{-}C_5Ph_5)_2Rh_2(CO)_2(\mu\text{-}CO)]$ also forms. Better yields of $[(\eta^5\text{-}C_5bz_5)M(CO)_2]$ (M = Co, Rh) are obtained with $[Co_2\text{-}(CO)_8]$ plus pentabenzylcyclopentadiene in refluxing toluene and from lithium pentabenzylcyclopentadienide and $[RhCl(CO)_2]_2$ in THF. If the first route to $[(\eta^5\text{-}C_5Ph_5)Rh(CO)_2]$ is followed in benzene the intermediate $[(\eta^5\text{-}C_5Ph_5)RhBr(CO)_2]ZnCl_3$ can be isolated. Although $[(\eta^5\text{-}C_5Ph_5)M(CO)_2]$ is inert to substitution reactions, electrochemical oxidation (one e^-) in the presence of ligands affords $[(\eta^5\text{-}C_5Ph_5)M(CO)L]$ (M = Co, Rh; L = $P(OMe)_3$, $P(OPh)_3$. M = Rh; L = PPh_3, $AsPh_3$). The last two can also be synthesized however by reaction of the ligand with $[(\eta^5\text{-}C_5Ph_5)RhBr(CO)_2]ZnCl_3$ followed by reduction with $PPN[Mn(CO)_5]$. The dicarbonyls also react with halogens to first give $[(\eta^5\text{-}C_5Ph_5)MX_2(CO)]$ and then $[(\eta^5\text{-}C_5Ph_5)MX_2]_2$ (M = Co, Rh; X = Br, I). Electrochemical reduction of $[(\eta^5\text{-}C_5Ph_5)M(CO)_2]$ (M = Co, Rh) to the radical anion is reversible for the cobalt complex but only quasi-reversible at best for the other. These radical anions are kinetically much more stable than their cyclopentadienyl analogs although their thermodynamic stability is only marginally greater. From EPR data the pentaphenylcyclopentadienyl ligand appears to remain symmetrically bonded in the radical anions and the unpaired electron is thought to occupy an orbital having significant metal $(n+1)p_y$ character (greater for rhodium) (refs. 708-711). Both [486] and [487] lose a proton on reaction with $[Co_2(CO)_8]$ and a $\{Co(CO)_2\}$ moiety becomes attached to the cyclopentadienyl ring. The latter forms only one isomer but the former forms a 3:1 mixture of endo or exo products (ref. 712). Bulk electrolysis of $[cpCo(\eta^5\text{-}C_7H_9)]^+$ in acetonitrile forms the neutral radical $[cpCo(\eta^5\text{-}C_7H_9)]$ which then dimerizes to



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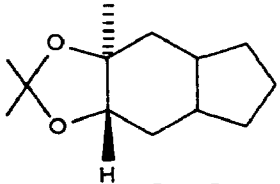
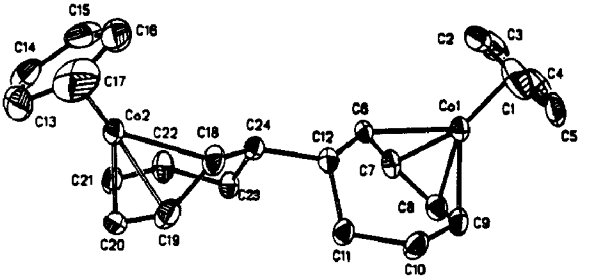


[487]

[488]. The neutral complex $[cpCo(\eta^4\text{-}C_7H_8)]$ can be reduced to the radical anion which abstracts a proton from the solvent (or supporting electrolyte)

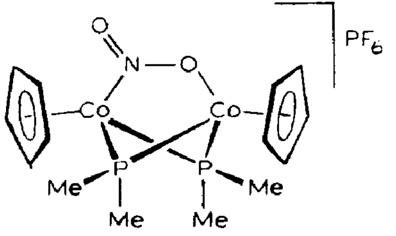


[488]

to form $[cpCo(\eta^4\text{-}C_7H_9)]$ which on further reduction is converted to $[cpCo(\eta^4\text{-}C_7H_{10})]$. This last complex shows a reversible, one-electron oxidation. The one-electron oxidation of $[cpCo(\eta^4\text{-}C_7H_8)]$ forms $[cp_2Co]^+$, possibly via $[cpCo(\eta^4\text{-}C_7H_8)]^+$ but this was not detected (ref. 713).

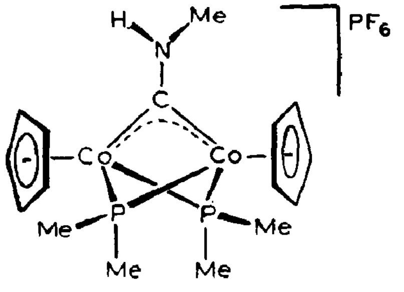
Detailed syntheses of $[cp'CoL_2]$ ($L = CO, C_2H_4$), $[cpCoI_2(CO)]$ and $[cp'_2Co_2I_2(\mu\text{-}I)_2]$ have been published (ref. 714). Treatment of cobalt(II) chloride with $Tl[C_5H_4PPh_2]$ forms $[(\eta^5\text{-}C_5H_4PPh_2)_2Co]$ which behaves as a chelating ligand towards $[Mo(CO)_4(NBD)]$ to form cis-$[(OC)_4Mo[(\eta^5\text{-}C_5H_4PPh_2)_2Co)]$ but with $[Mo(CO)_6]$, $[(\eta^5\text{-}C_5H_4PPh_2Mo(CO)_5)_2Co]$ is the product. Both the first molybdenum complex and the original cobalt complex can be oxidized to the monocations by dioxygen. Molecular orbital calculations and electrochemical studies on some of the complexes were also performed (ref. 715). FVP of $[cpCo(CO)_2]$ at 350°C forms $[cp_2Co]$ (ref. 716) while pentamethylcyclopentadienyllithium converts $[Co(acac)_2]_4$ to $[cp'Co(acac)]$ which is a good precursor to complexes containing the {cp'Co} moiety (ref. 717). Oxidative addition of cyanogen halides to $[cp'Co(CO)L]$ forms $[cp'Co(L)CN(X)]$ ($L = CO, PPh_3$; $X = Br, I$) but no reaction occurs with $[cp'Co(L)(TCNE)]$ (ref. 718). Protonation of $[cpCoL_2]$ by ammonium hexafluorophosphate occurs in toluene/ethanol to yield $[cpCo(H)L_2]PF_6$ ($L = PEt_3, PPh_3, P(OMe)_3$; L_2 = DPM, DPPE, cis-vdiphos). Both the neutral and cationic complexes of the chelating ligands were subjected to electrochemical studies. The cations undergo a chemically irreversible, one-electron reduction to liberate dihydrogen (ref. 719). Addition of pentamethylcyclopentadienyllithium to cobalt(II) halides in THF at -20°C forms $[cp'_2Co_2(\mu\text{-}X)_2]$ (X = Cl, Br, I) and the analog with X = NH_2 is obtained similarly from $[Co(NH_3)_6](BF_4)_2$. Treatment of these products with ligands or lithium dimethylamide forms $[cp'Co(X)L]$ (X = Cl, Br; L = py, PMe_2Ph. X = Cl; L = PMe_3) or $[cp'_2Co_2(\mu\text{-}X)(\mu\text{-}NMe_2)]$ (X = Cl, Br) respectively. Metathesis of $[cp'_2Co_2(\mu\text{-}Y)_2]$ with MY (= NaSMe, TlOEt, $NaNH_2$) forms $[cp'_2Co_2(\mu\text{-}Y)_2]$ while with one equivalent of lithium diphenylphosphide the product is $[cp'_2Co_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)]$. Reaction of $[cp'_2Co_2(\mu\text{-}Br)_2]$ with bipy forms a mixture of $[cp'Co(Br)(bipy)]Br$ and $[cp'Co(bipy)]$ which on treatment with moist dioxygen and hexafluorophosphate ion yields $[cp'Co(H_2O)(bipy)]PF_6$. EPR spectroscopic studies of the dimeric complexes show that some dissociation to monomeric species occurs in solution and while extremely air-sensitive they are not strong reducing agents. It is thought that their aerial oxidation may involve oxygenation rather than simple electron transfer reactions (ref. 720).

Reaction of $[cp_2Co_2(\mu\text{-}PMe_2)_2(\mu\text{-}H)]X$ with one equivalent of ligand forms $[cpCo(H)(\mu\text{-}PMe_2)_2Co(L)cp]X$ (X = PF_6; L = PMe_3, PMe_2H, $P(OMe)_3$. X = BF_4; L = CO) but the stereochemistry was not determined. In nitromethane the initial complex reacts with two equivalents of trimethylphosphite yielding *trans*-$[cp_2Co_2(P(OMe)_3)_2(\mu\text{-}PMe_2)_2](PF_6)_2$ among other products while dissolution of $[cpCo(H)(\mu\text{-}PMe_2)_2Co(PMe_2H)cp]PF_6$ in the same solvent produces $[cp_2Co_2(\mu\text{-}PMe_2)_3]PF_6$ and $[cp_2Co_2(PMe_2H)_2(\mu\text{-}PMe_2)_2](PF_6)_2$. Also in nitromethane $[cp_2Co_2(\mu\text{-}PMe_2)_2(\mu\text{-}H)]PF_6$ reacts with isocyanides to form $[cp_2Co_2(L)_2(\mu\text{-}PMe_2)_2](PF_6)_2$ (L = MeNC (*cis* and *trans* isomers), Bu^tNC (*trans* isomer), PhNC (*cis* isomer)). Additional products are *trans*-$[cp_2Co_2(CNBu^t)_2(\mu\text{-}PMe_2)]PF_6$ and [489]. The last can also be synthesized from $[cp_2Co_2(\mu\text{-}PMe_2)_2]PF_6$ and a mixture of potassium nitrite and TFA in methanol. If the isocyanide reactions are performed in methanol the products are $[cp_2Co_2(\mu\text{-}PMe_2)_2]$, $[cp_2Co_2(L)_2(\mu\text{-}PMe_2)_2](PF_6)_2$ (L = MeNC (*cis* and *trans* isomers), Bu^tNC (*trans* isomer), PhNC (*cis* isomer) and $[cpCo(H)(\mu\text{-}PMe_2)_2Co(L)cp]PF_6$ (L = MeNC,



[489]

$\mathrm{Bu^tNC}$, PhNC). Other products isolated are [490] and [491]. Reaction of [490] with methylamine in methanol forms the methyl analog of [491] (ref. 721). Reaction of $[\mathrm{AuCl(PPh_3)}]$ with $[\mathrm{cpM(PMe_3)_2}]$ (M = Co, Rh) or $[\mathrm{cp_2Co_2(\mu\text{-}PMe_2)_2}]$ in the presence of lithium hexafluorophosphate yields $[\mathrm{cpM(Au(PPh_3))(PMe_3)_2]PF_6}$ and [492] respectively while methyl magnesium iodide converts $[\mathrm{cpCo(PMe_3)_2}]$ to $[\mathrm{cpCo(MgMe)(PMe_3)_2]I}$ (ref. 722). The complex [493] (R,R = $\mathrm{CMe_2(CH_2)_3CMe_2}$) with hydrogen halides forms [494] while with $[\mathrm{ML_n(THF)}]$ ($\mathrm{ML_n}$ = $\mathrm{Cr(CO)_5}$, $\mathrm{cpMn(CO)_2}$) the product is [495]. With mercury (II) chloride the product is $[\mathrm{cpCoCl_2(PMe_3)}]$ while with $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ substitution of triphenylphosphine for trimethylphosphine in [493] is the only reaction (ref. 723). Reaction of [496] with $[\mathrm{IrCl(N_2)(PPh_3)_2}]$ forms [497] while [498] can be obtained from [496] and $[\mathrm{cpCo(\mu\text{-}CO)}]_2$, $[\mathrm{cpCoI_2(CO)}]$ plus zinc or $[\mathrm{cpCoL_2}]$ ($\mathrm{L_2}$ = COD; L = CO). For the cobalt system the first two routes are superior to the last. Also investigated was the reaction of [499] with $[\mathrm{Co(NO)_2I}]_x$ and zinc which forms [500] (ref. 724). In hot toluene, $\mathrm{As_4S_4}$ and $[\mathrm{cp'_2Co_2(\mu\text{-}CO)_2}]$ form $[\mathrm{cp'_2Co_2(CO)(As_2S_2)}]$ plus



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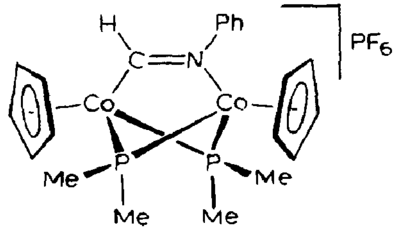

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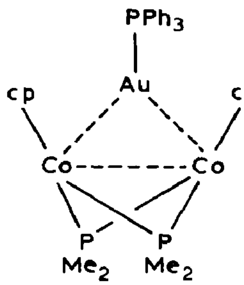

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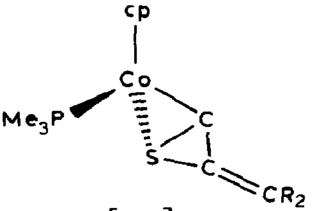

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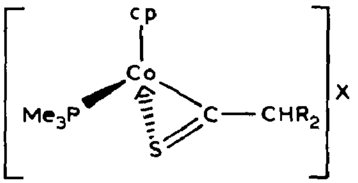

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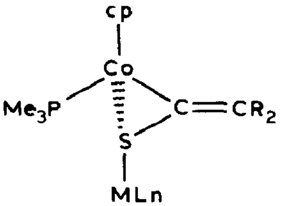

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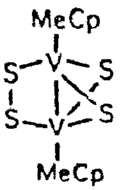

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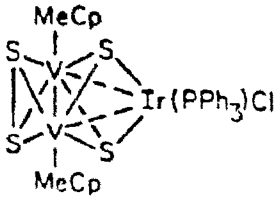

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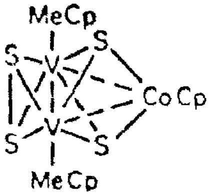
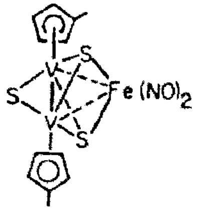


[498]

[cp'$_3$Co$_3$As$_2$S$_4$] while photolysis of [cp'Co(CO)$_2$] and As$_4$S$_4$ in THF yields [501]. Elemental selenium also reacts with [cp'$_2$Co$_2$(μ-CO)$_2$] in toluene to cleanly form [502] but with the rhodium analog, two additional products which have not been characterized were isolated. Complex [502] and its rhodium analog are also formed from elemental selenium and [cp'$_2$Co$_2$(CO)$_2$-(μ-Se)$_2$] or [cp'$_2$Rh$_2$(CO)$_2$(μ-Se)] suggesting that these products may form



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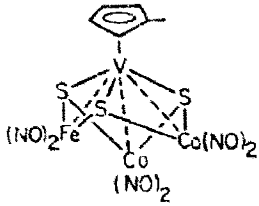

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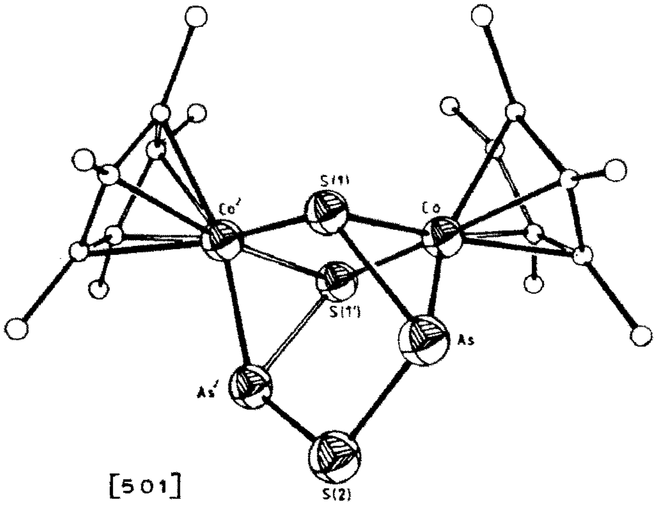

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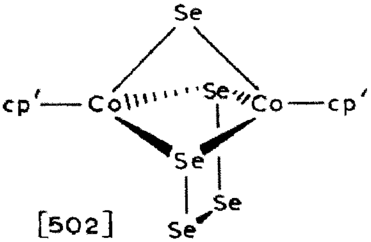
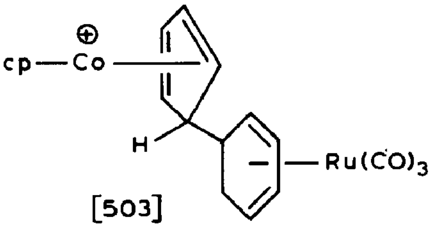


[502]

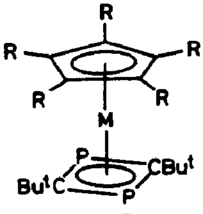
via stepwise addition of selenium to the metal-metal double bond in the original reaction. This latter route produces considerable byproducts however (refs. 725, 726).

The electrochemical rate constants for the interconversions of $[cp_2Co]^+$ and $[cp_2Co]$ in various solvents have been determined to probe the effects of dynamical properties of solvents on the kinetics of electron-transfer processes. For most solvents used, including amides and nitriles the observed rates agree well with those predicted by the solvent model which uses an overdamped solvent relaxation in a dielectric continuum. In methanol, ethanol and isopropanol, however, the rates are about fifty-fold faster than predicted. Here it is thought that a high frequency dielectric relaxation associated with the rotation of the solvent molecules may be operative (ref. 727). Cobaltocene can be quantitatively oxidized to $[cp_2Co]BF_4$ by $[cp_2Fe]BF_4$ while the same oxidant, in the presence of ligands, forms $[Co(CO)_3L_2]BF_4$ (L = PPh_3, $AsPh_3$, $SbPh_3$, SMe_2, $SeMe_2$, $TeMe_2$. L_2 = DPPE) (ref. 728). Cobaltocene also reduces $[Fe_3(CO)_9(\mu_3\text{-}PPh)_2]$ to its radical anion in acetonitrile at -40°C (ref. 729) while with $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]$ a stereospecific carbon-carbon coupling occurs to form [503] (ref. 730). Electrolysis of DMSO solution of cyclopentadiene containing alkalai metal salts at a cobalt anode forms $[cp_2Co^+]$ while the same process on acetonitrile solutions of cyclopentadiene plus diphenylacetylene containing tetraethylammonium bromide affords reasonable yields of $[cpCo(\eta^4\text{-}C_4Ph_4)]$ (refs. 731, 732).



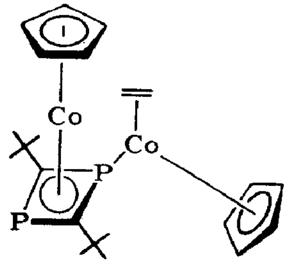
[503]

Two groups have reported the first examples of the cyclodimerization of a phosphaalkyne in the reaction of $[(\eta^5\text{-}C_5R_5)M(C_2H_4)_2]$ with $Bu^tC{\equiv}P$ to form [504] (R = H; M = Co, Rh. R = Me; M = Co, Rh, Ir). Further reaction of

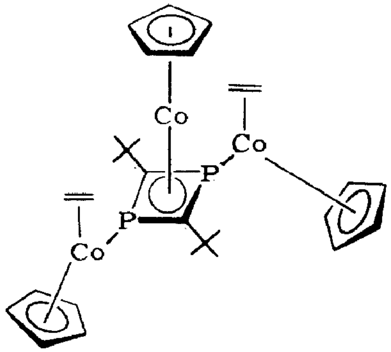


[504]

[504] (R = H; M = Co) with [cpCo(C_2H_4)$_2$] forms [505] and then [506] (refs. 733, 734). The helicene [507] on treatment with butyllithium and [$CoBr_2$·DME] followed by oxidation with iron(III) chloride forms oligomeric cobalt (III) helicene complexes with two to four helicene moieties linked through

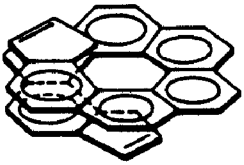


[505]



[506]

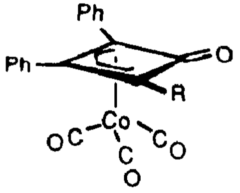
cobalt ions which are η^5-coordinated to the terminal cyclopentadienyl residues (ref. 735). The EPR spectra of [(η^5-C_5R_5)Co(η^6-$C_6R'_6$)]$^+$ (R = R' = H, Me. R = Me; R' = H. R = Me; R'_6 = Me_5H) and [(η^6-C_6Me_6)$_2$Co]$^+$ have been measured in diamagnetic host lattices and in frozen solution. The



[507]

unpaired electron resides in an e_{1g} orbital which is largely metal d_{xz} + d_{yz} in character and a dynamic Jahn-Teller effect is seen. A greater covalency in the metal-ring bonding is seen when methyl substituents are present on the rings and this is more pronounced for the five-membered ring (ref. 736). The structure of [(η^6-C_6H_6)$_3Co_3$(μ_3-CO)$_2$]BPh_4 has been determined and one metal-metal bond is longer than the other two. Analysis of the metal-metal bond distances in this and analogous 48-electron clusters with the {Co_3(μ_3-X)(μ_3-Y)} (X = CO, CS, NO; Y = O, NR, S) core reveals a correlation between the mean cobalt-cobalt distance and the covalent radius of the larger capping ligand. Since the 48-electron cluster [cp'_3Co_3(μ_3-CO)$_2$] has shorter metal-metal distance than the benzene complex it appears that the e'' HOMO of the latter is largely metal-metal antibonding in agreement with Fenske-Hall molecular orbital calculations (ref. 737).

Refluxing [$Co_4(CO)_9$(TPM)] with hexamethylbenzene in dioxane/THF forms [(η^6-C_6Me_6)$Co_4(CO)_6$(TPM)] and an analog with [2,2]paracyclophane could be similarly prepared. These complexes along with $[Co_4(CO)_{12}]$, $[(\eta^6\text{-}C_6H_5Me)\text{-}Co_4(CO)_9]$ and $[Co_4(CO)_9(TPM)]$ were studied electrochemically and show a one-electron reduction which is reversible on the cyclic voltammetric time scale except in the case of $[Co_4(CO)_{12}]$. Further reduction was observed only for $[Co_4(CO)_9(TPM)]$ and $[(\eta^6\text{-}C_6H_5Me)Co_4(CO)_9]$. Models for most of these complexes were subjected to SCF-Xα-DV molecular orbital calculations which suggest that the substituted cobalt atom binds more strongly to the rest of the cluster than does a $\{Co(CO)_3\}$ moiety. The observed redox potentials correlate well with the calculated core charges but not with the HOMO-LUMO energy gap suggesting that cluster bonding involves delocalized orbitals (ref. 738). In refluxing THF, $Na[cpM(CO)_3]$ (M = Mo, W) reacts with $[(\eta^4\text{-}C_4Me_4)Co(CO)_3]PF_6$ to form $[(\eta^4\text{-}C_4Me_4)\overline{Co(CO)(\mu\text{-}CO)_2M}cp(CO)_2]$ which can be reversibly decarbonylated to $[(\eta^4\text{-}C_4Me_4)\overline{Co(\mu\text{-}CO)_3M}cp]$. The last on reaction with DPM forms $[(\eta^4\text{-}C_4Me_4)Co(CO)(DPM)][cpM(CO)_3]$. In $[(\eta^4\text{-}C_4Me_4)\text{-}\overline{Co(\mu\text{-}CO)_3M}cp]$ the $\{cpM(CO)_3\}$ moiety is thought to be isolobal with a cyclopentadienyl ligand on the basis of the low value for ν_{CO} and the upfield shift of the proton resonances for the methyl groups (ref. 739). In refluxing 1,2-dichloroethane, $[Co_2(CO)_8]$ reacts with cyclopropenium cations to form [508] plus $[(\eta^3\text{-}C_3Ph_3R)Co(CO)_3]$ (R = Ph, Bu^t). Analogs of both with three tert-butyl substituents on the ring can also be formed from $PPN[Co(CO)_4]$ and the corresponding cyclopropenium cation. Carbon monoxide extrusion from the ring in $[(\eta^3\text{-}C_3Bu^t{}_3CO)Co(CO)_3]$ does not occur nor is ring expansion induced by addition of phosphines to $[(\eta^3\text{-}C_3Bu^t{}_3)Co(CO)_3]$. Here a carbonyl ligand is replaced on the metal. Treatment of [508] (R = H, Me, Ph) with methyllithium, phenyllithium or lithium triethylborohydride and carbon monoxide at -78°C in THF followed by warming to room temperature provides a regiospecific synthesis of 2H-pyran-2-ones but with $[(\eta^3\text{-}C_3Bu^t{}_3\text{-}CO)Co(CO)_3]$ the reaction stops at [509] presumably because of the bulk of



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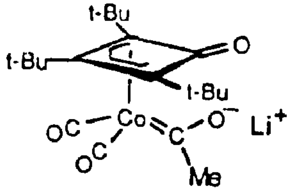
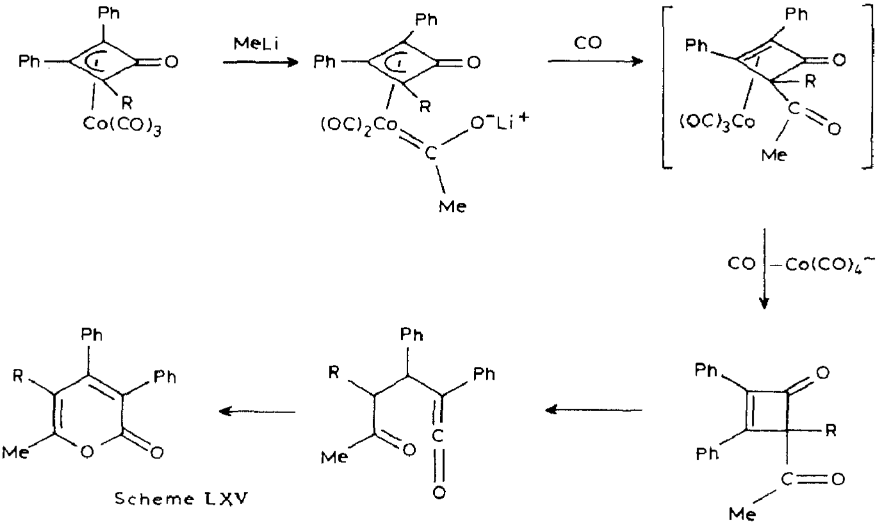
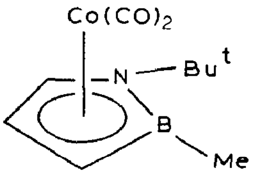


[509]

the tert-butyl substituents. In other cases, the reaction is thought to proceed as shown in Scheme LXV (refs. 740, 741).

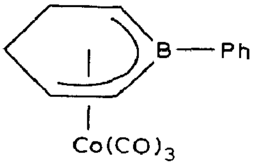


Dicobalt octacarbonyl reacts with 1-tert-butyl-2,5-dihydro-2-methyl-1H-1,2-azaborole in refluxing petroleum ether to form [510] in which the

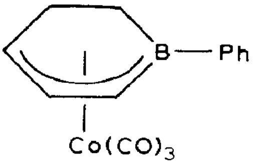


[510]

carbonyls can be replaced by COD under photolytic conditions (ref. 742). Similarly, $[Co_2(CO)_8]$ and 1-phenyl-1-boracyclohexa-2,4-diene form $[(\eta^6\text{-}PhBC_5H_5)Co(CO)_2]$ when the reaction is carried out above 60°C but at 30°C the products are [511] and [512] (ref. 743). In refluxing methanol,

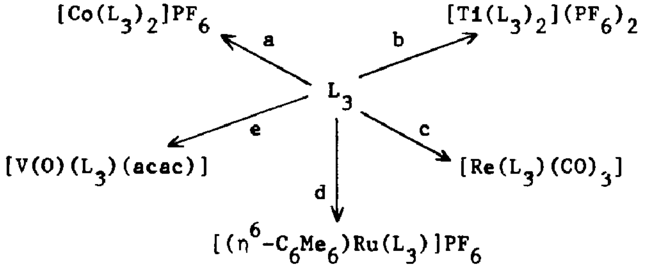


[511]



[512]

$[cpCo(DPPE)(P(O)(OMe)_2)]I$ reacts with mercury(II) iodide to form $[cpCo(DPPE)(P(O)(OMe)_2)]HgI_3$ which from the structure study was thought to be able to coordinate Lewis acids to the {P=O} moiety but this was found not to occur (ref. 744). Reaction of $[Co(acac)_3]$ with pentamethylcyclopentadienyllithium in THF at 0°C followed by addition of diethylphosphite forms $[cp'Co(\mu\text{-}P(O)(OEt)_2)_3Co(\mu\text{-}(EtO)_2(O)P)_3Cocp']$ which can be cleaved to $[cp'Co(P(O)(OEt)_2)_3]^-(L_3)$ by sodium cyanide in aerated methanol. Further reactions of the last species are shown in Scheme LXVI (ref. 745). Its

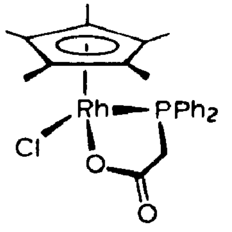


a) $[Co(acac)_3]$, HPF_6, CH_2Cl_2. b) 1. cp_2TiCl_2, H_2O; 2. PF_6^-.
c) $K_2[Re(CO)_3Br_2]$. d) $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$. e) $[V(O)(acac)_2]$.

Scheme LXVI

cyclopentadienyl analog has been used as an ionophore for lithium and sodium ions in a study of the rates of transport of these ions across artificial phospholipid vesicles. Here lithium is favored (ref. 746).

Addition of sodium diphenylphosphinoacetate to $[cp'RhCl_2]_2$ forms [513] (ref. 747] while reaction with pyridazine in acetone forms $[cp'RhCl_2(pydz)]$. Chloride abstraction from this with silver ion in the presence of

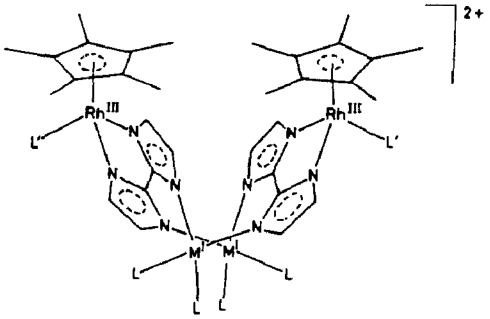


[513]

more ligand forms $[cp'RhCl(pydz)_2]X$ ($X = ClO_4$, BF_4) which can also be obtained from $[cp'RhCl(acac)]$, pyridazine and HX in aqueous acetone. Chloride abstraction from $[cp'RhCl(acac)]$ with silver ion followed by addition of pyridazine yields $[cp'Rh(pydz)(acac)]X$ ($X = ClO_4$, BF_4) while if $[cp'RhCl_2(pydz)]$ is added to $[cp'_2Rh_2Cl_4]$ following treatment with four mols of the appropriate silver salt $[cp'_2Rh_2(\mu\text{-}Cl)_2(\mu\text{-}pydz)]X_2$ ($X = ClO_4$, BF_4) forms. Addition of tetrafluoroboric acid to a mixture of $[cp'_2Rh_2(\mu\text{-}OH)_3]BF_4$ and pyridazine forms the analog $[cp'_2Rh_2(\mu\text{-}OH)_2(\mu\text{-}pydz)](BF_4)_2$

together with some [cp'$_2$Rh$_2$(μ-pydz)$_2$(μ-OH)$_2$](BF$_4$)$_3$. In the presence of a large excess of pyridazine this reaction forms [cp'Rh(pydz)$_3$](BF$_4$)$_2$ (refs. 748, 749). In acetone, a variety of pyridine derivatives form [cp'$_2$Rh$_2$L$_2$-(μ-OH)$_2$]ClO$_4$ (L = py, 2-Mepy, 3-Mepy, 4-Etpy, 4-Pr^{n}py, 4-bzpy, 2-MeOpy) when reacted with [cp'$_2$Rh$_2$(μ-OH)$_3$]ClO$_4$ in the presence of one equivalent of perchloric acid while in methanol the same reaction forms [cp'$_2$Rh$_2$(py)$_2$(μ-OMe)$_2$]ClO$_4$. Iridium analogs of both pyridine complexes were similarly prepared (ref. 750). Heating [cp'$_2$M$_2$(μ-OH)$_3$]PF$_6$ (M = Rh, Ir) in isopropanol containing potassium hexafluorophosphate for six days at 60°C forms [cp'$_4$M$_4$(μ$_3$-H)$_4$](PF$_6$)$_2$. This synthesis is more convenient than the original one which used dihydrogen (ref. 751).

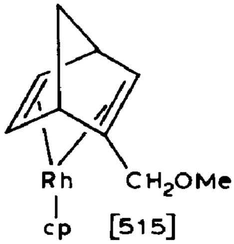
Reaction of [cp'RhCl(μ-pz)$_2$Rh(CO)$_2$] with chelating diphosphines and sodium tetraphenylborate in methanol forms [cp'Rh(μ-pz)$_2$(μ-CO)Rh(CO)(L$_2$)]-BPh$_4$ (L$_2$ = DPPP, cis-vdiphos) which loses carbon monoxide in acetone or dichloromethane solution to give [cp'Rh(μ-pz)$_2$(μ-CO)(L$_2$)]BPh$_4$. Analogs of the latter are obtained directly when the ligand used is DPM, DPPB or DPAE. The initial reaction with monodentate phosphines forms a mixture of [cp'-RhCl(μ-pz)$_2$Rh(CO)L] and [cp'Rh(μ-pz)$_2$(μ-CO)Rh(CO)L]BPh$_4$ (L = PPh$_3$, Pcy$_3$) (refs. 752, 753). Also in methanol, H$_2$biim reacts with [cp'RhCl(acac)] or [cp'Rh(acac)L']ClO$_4$ to form [cp'RhCl(Hbiim)] and [cp'Rh(Hbiim)L']ClO$_4$ (L' = py, Bu^{t}NC, PPh$_3$, P(OEt)$_3$) respectively. Addition of [Rh(acac)L$_2$] to the latter forms [514] (M = Rh; L' = py, Bu^{t}NC, PPh$_3$, P(OEt)$_3$; L$_2$ = (CO)$_2$, NBD. M = Rh; L' = Bu^{t}NC, PPh$_3$, P(OEt)$_3$; L$_2$ = TFB).



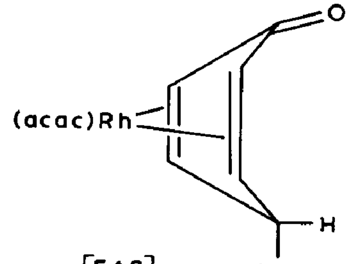
[514]

Iridium analogs with L = PPh$_3$, P(OEt)$_3$ and L$_2$ = TFB were prepared in an analogous fashion while addition of [Rh(acac)L$_2$] to [cp'RhCl(HBiim)] forms [cp'RhCl(μ-biim)RhL$_2$]$_2$ (L = CO; L$_2$ = COD) of similar structure (ref. 754). In toluene solution, addition of one equivalent of phenol to [Rh$_2$(dippe)$_2$(μ-H)$_2$] forms [Rh$_2$(dippe)$_2$(μ-H)(μ-OPh)] which is unreactive towards dihydrogen and ethylene but with carbon monoxide it gives [Rh$_2$(CO)$_2$(dippe)$_2$-(μ-CO)$_2$]. Use of an excess of phenol in the first reaction yields [(η^5-C$_6$H$_5$O)Rh(dippe)]·2C$_6$H$_5$OH in which the two phenol molecules are hydrogen-bonded to the oxygen atom of the phenolate ligand. A labelling study showed that phenol undergoes oxidative addition to $[Rh_2(dippe)_2(\mu-H)_2]$ and scrambling of hydrogen occurs before the reductive elimination of dihydrogen to yield $[Rh_2(dippe)_2(\mu-H)(\mu-OPh)]$ (ref. 755).

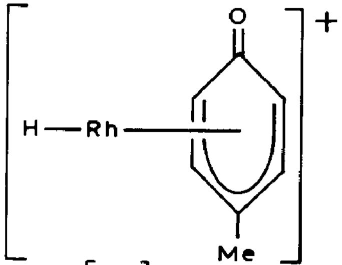
The protonation of [515] can be effected with p-fluorophenol indicating the complex is quite basic. This is attributed to an inductive effect of the {cpRh} moiety which is also proposed to explain the ready protonation of the corresponding alcohol complexes (ref. 756). The primary fragmentation processes during mass spectral analysis of [516] lead to [517] and $[(cpMe)Rh(acac)]^+$ while ion-molecule reactions of $[Rh(acac)(CO)_2]$ and p-$XC_6H_4CH_2R$ (X = Me; R = $CHCl_2$, CCl_3. X = H; R = Me) form $[(\eta^6\text{-}p\text{-}MeC_6H_4\text{-}CH{=}CY_2)Rh(acac)]^+$ (Y = H, Cl), $[(\eta^6\text{-}p\text{-}XC_6H_4CH_2R)Rh(acac)]^+$ (X = Me; R = $CHCl_2$, CCl_3) and $[(\eta^5\text{-}p\text{-}XC_6H_4CH_2)Rh(acac)]^+$ (X = Me) for the first two arenes but only the latter two ions (X = H; R = Me) for the third (refs. 757, 758). Addition of $Na[(C_7H_7)Fe(CO)_3]$ to $[RhCl(COD)]_2$ in THF affords $[(OC)_3\overline{Fe(\mu-C_7H_7)Rh}(COD)]$ which is fluxional by processes involving all the ligands. The COD ligand can be replaced by two carbonyls and this product on reaction with one equivalent of a phosphine ligand forms a mixture of [518] and [519] (PR_3 = PPh_3, PMe_3; L = CO) while with two equivalents or



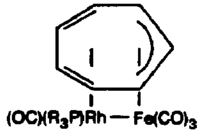
[515]



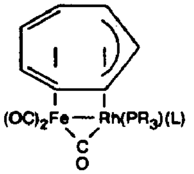
[516]



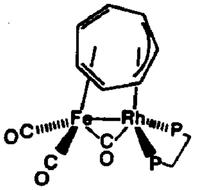
[517]



[518]

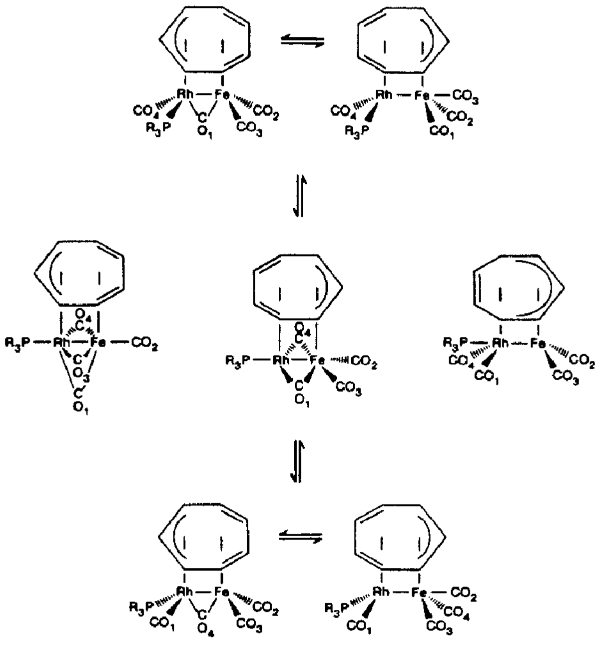


[519]

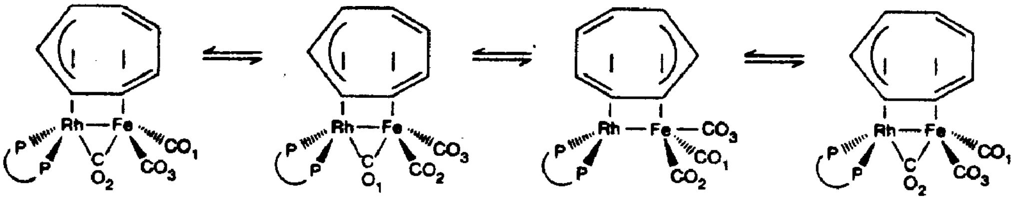


[520]

with a diphosphine the product is [519] (L = R_3P = PMe_3) or [520] ($\overset{\frown}{P\,P}$ = DPM, DPPE, dmpe) respectively. The fluxional behavior of [519] and [520] is proposed to occur as shown in Schemes LXVII and LXVIII respectively (ref. 759). Chloride abstraction from $[RhCl(DQ)]_2$ with silver perchlorate in acetone forms $[Rh(DQ)(acetone)_x]ClO_4$ from which a variety of arene complexes $[(\eta^6\text{-arene})Rh(DQ)]ClO_4$ (arene = biphenyl, diphenylmethane, naphthalene, indene, fluorene) are obtained. No tractable complex of benzophenone could be obtained here but it could with $[Rh(L_2)(acetone)_x]ClO_4$ (L_2 = COD, Me_3TFB) (ref. 760). Hydrogenation of a mixture of $[M(NBD)(PPh_3)_2]BF_6$ and thiophene in dichloromethane forms $[(\eta^4\text{-}C_4H_4S)M(PPh_3)_2]PF_6$ (M = Rh, Ir). The rhodium complex reacts with carbon monoxide to form $[Rh(CO)_2(PPh_3)_2]PF_6$ and with NBD to regenerate the starting complex while the iridium analog does not react with diolefins and only slowly reacts with carbon monoxide (ref. 761). The head-to-head and head-to-tail coupling of allene is promoted by $[Rh(DPPE)(\eta^6\text{-}C_6H_5BPh_3)]$ and under more strenuous conditions cocondensation of allene and carbon dioxide occurs (ref. 762).

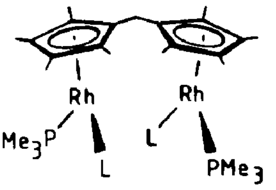


Scheme LXVII

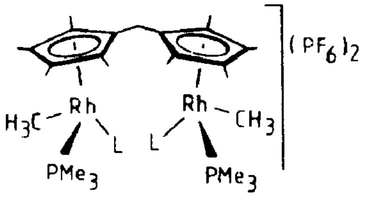


Scheme LXVIII

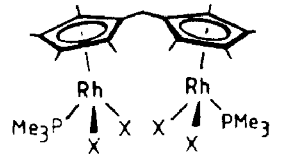
Photolysis of [cp'RhH$_2$(SiEt$_3$)$_2$] in methanol or ethanol forms [cp'RhH$_2$(SiEt$_3$)(Si(OR)$_3$)] (R = Me, Et) plus ethane. Of particular note is the alcoholysis of *only one* triethylsilyl ligand. A fifty percent conversion to [cp'RhH$_2$(SiEt$_3$)(Si(OEt)$_3$)] occurs when the original complex is photolyzed in cyclohexane containing triethylsilane and on prolonged reaction some [cp'RhH$_2$(Si(OEt)$_3$)$_2$] is also formed. This can also be obtained from [cp'Rh(C$_2$H$_4$)$_2$] and triethoxysilane. It was proposed that the original reaction proceeds *via* initial reductive elimination of triethylsilane and then possibly the formation of $[\mathrm{cp'Rh^{+}H_2(SiEt_3\bar{O}R)}]$ (ref. 763). Refluxing [cp'RhCl$_2$]$_2$ with 1,4,7,10,13,16-hexathiacyclooctadecane (L$_6$) forms *trans*-[cp'RhCl(µ-L$_6$)RhClcp']BPh$_4$ in which each metal is coordinated to two adjacent sulfur atoms on opposite sides of the ligand (ref. 764). The reaction between [RhCl(PMe$_3$)L]$_2$ and Li$_2$[Me$_4$C$_5$CH$_2$C$_5$Me$_4$] forms [521] (L = PMe$_3$, C$_2$H$_4$). When L = C$_2$H$_4$ reaction of [521] with methyl triflate yields [522] (L = C$_2$H$_4$) following metathesis with hexafluorophosphate ion. Complex [521] (L = C$_2$H$_4$) reacts with TFA and with methyl iodide in diethyl ether followed by crystallization from acetone to yield [523] (X = O$_2$CCF$_3$) and [524] respectively while [523] (X = O$_2$CCF$_3$) and phosphine ligands forms [525] (P = PMe$_3$) or [526] ($\overset{\frown}{P\,P}$ = DPM, DPPE, DPPB) after methathesis with hexafluorophosphate ion. Reaction between M$_2$[R$_4$C$_5$CH$_2$C$_5$R$_4$] (M = Tl; R = H.



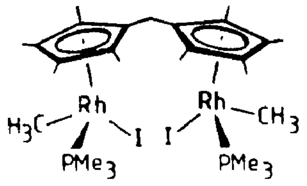
[521]



[522]



[523]



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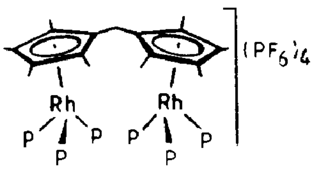
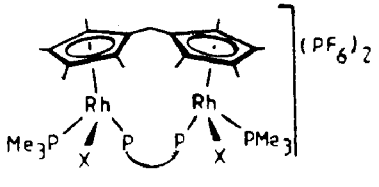
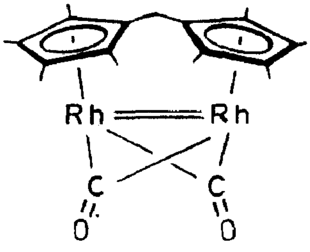


[525]

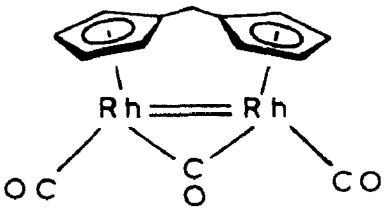


[526]

M = Li; R = Me) and $[RhCl(CO)_2]_2$ forms $[(OC)_2Rh(\eta^5\text{-}C_5R_4CH_2C_5R_4\text{-}\eta^5)Rh(CO)_2]$ with a structure analogous to [521]. This is reversibly decarbonylated on heating to yield [527] (R = Me) or [528] (R = H). The iridium complex



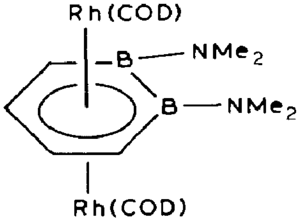
[527]



[528]

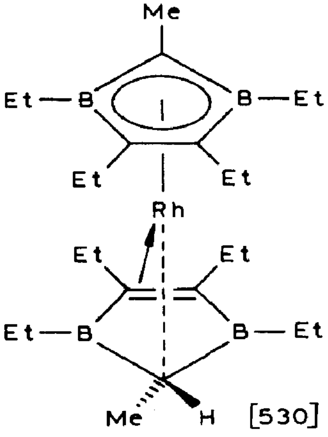
$[(OC)_2Ir(\eta^5\text{-}C_5H_4CH_2C_5H_4\text{-}\eta^5)Ir(CO)_2]$ was also synthesized in a similar fashion (refs. 765, 766).

The first example of a 1,2-diborabenzene complex is [529] which can be synthesized from $[Li(TMEDA)]_2[1,2\text{-}NMe_2\text{-}1,2\text{-}B_2C_4H_4]$ and $[RhCl(COD)]_2$ in THF

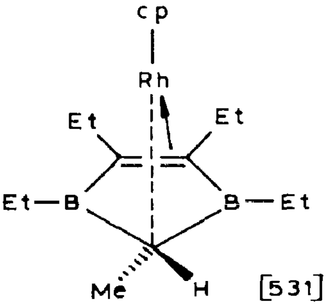


[529]

(ref. 767) while $[RhCl(C_2H_4)_2]_2$ and 1,2,3,4-tetraethyl-5-methyl-1,4-dibora-cyclopent-2-ene form $[Rh_2(Et_4B_2C_2CHMe)_2(\mu\text{-}Cl)_2]$. This can be reduced with potassium to yield [530] and reacts with sodium cyclopentadienide to form [531]. In all complexes the neutral diboracyclopentene ligand is thought



[530]



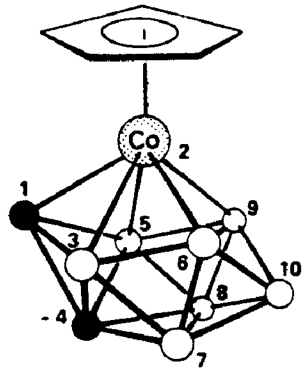
[531]

to interact with the metal through both the double bond and the saturated carbon atom (ref. 768). At room temperature, $[(\eta^6\text{-}C_6Me_6)_2Fe]$ and $[cp'M(CO)_2]$ (M = Co, Rh, Ir) form a mixture of $[cp'_2M_2(CO)_2]$ and $[(\eta^6\text{-}C_6Me_6)Fe(\mu\text{-}CO)_2Mcp']$. The latter is proposed to contain a metal-metal double bond and the iron-iridium complex reacts with diazomethane at -78°C to form a trace of $[(\eta^6\text{-}C_6Me_6)Fe(CO)(\mu\text{-}CH_2)Ir(CO)cp']$ (ref. 769).

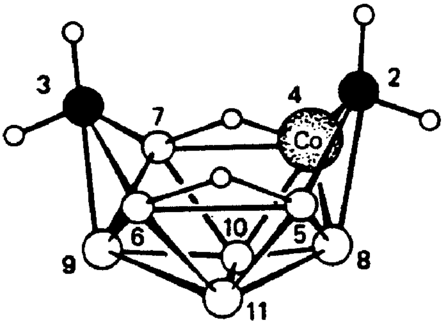
The indenyl complex, $[(\eta^5\text{-}C_9H_7)Ir(cyoct)_2]$ can be synthesized from $[IrCl(cyoct)_2]_2$ and indenyllithium. It reacts with ligands to form $[(\eta^5\text{-}C_9H_7)IrL_2]$ (L = CO, PEt_3) or $[(\eta^3\text{-}C_9H_7)IrL_3]$ (L = PMe_3, PMe_2Ph). The last is reported to be the first example of the formation of an η^3-indenyl complex from an η^5-indenyl precursor and a neutral ligand (ref. 770). Addition of $Tl[C_5H_4CF_3]$ to $[MCl(COD)]_2$ forms $[(\eta^5\text{-}C_5H_4CF_3)M(COD)]$ (M = Rh, Ir). The photoelectron spectra of the products indicate the trifluoromethylcyclopentadienyl ligand possesses a significant electron-withdrawing ability (ref. 771). Pyrazole reacts with $[cp'_2Ir_2Cl_2(\mu\text{-}Cl)_2]$ in methanolic potassium hydroxide solution to form $[cp'Ir(pz)_2(pzH)]$ which is protonated by tetrafluoroboric acid to give $[cp'Ir(pzH)_3](BF_4)_2$. The NMR spectrum (^1H) of this species shows all three pyrazole ligands to be equivalent and a dynamic hydrogen-bonding interaction between them is proposed. By contrast, protonation of $[cp'Ir(Me_2pz)_2(Me_2pzH)]$ forms $[cp'Ir(Me_2pz)(Me_2pzH)_2]BF_4$ and here only one of the dimethylpyrazole ligands hydrogen-bonds to the dimethyl pyrazolate. With pyrazoles, $[cp'_2Ir_2(\mu\text{-}OH)_3]BF_4$ in refluxing isopropanol forms $[cp'_2Ir_2(\mu\text{-}H)_2(\mu\text{-}L)]BF_4$ (L = pz, 3-Mepz, Me_2pz) which is unreactive towards carbon monoxide, *tert*-butylisocyanide or pyrazole under mild conditions (refs. 772, 773). The neutron diffraction structure and photoelectron spectrum of $[cp'IrH_2(SiEt_3)_2]$ have been obtained. In the latter, the lowest energy band is assigned to an ionization from an orbital which is primarily metal d_{z^2} in character while the next appears to arise from an orbital which is a mixture of metal $d_{x^2-y^2}$ and a π^* orbital of the pentamethylcyclopentadienyl ligand (ref. 774).

Metallaborane and -carbaborane Complexes

Formation of low yields of $[3\text{-}(\eta^5\text{-}C_9H_7)\text{-}3,1,2\text{-}CoC_2B_9H_{11}]$ occurs when $[Co(acac)_3]$ is reacted with $Tl_2[C_2B_9H_{11}]$ and then indenyllithium. This first example of an indenyl metallacarbaborane undergoes two reversible, one-electron reduction processes which are apparently metal-based. From the structure study it appears that the indenyl ring is somewhat "slipped" towards an η^3-coordination mode which is consistent with EHMO calculations (ref. 775). Cocondensation of cyclopentadiene and cobalt atoms into a mixture of cyclopentadiene and *nido*-2,6-$C_2B_7H_{11}$ forms the known compounds $[2\text{-}(cpCo)\text{-}6,9\text{-}C_2B_7H_9]$ and $[8\text{-}(cpCo)\text{-}6,7\text{-}C_2B_7H_{11}]$ plus the new species $[2\text{-}(cpCo)\text{-}1,4\text{-}C_2B_7H_9]$ ([532]) and $[4\text{-}(cpCo)\text{-}2,3\text{-}C_2B_7H_{13}]$ ([533]; terminal



[532]

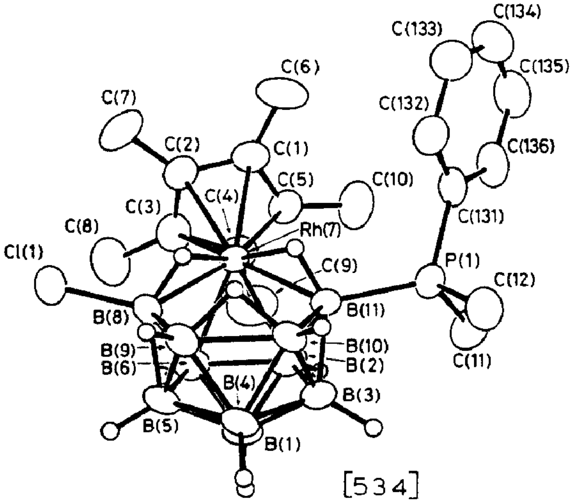


[533]

○ = B—H , ● = C—H

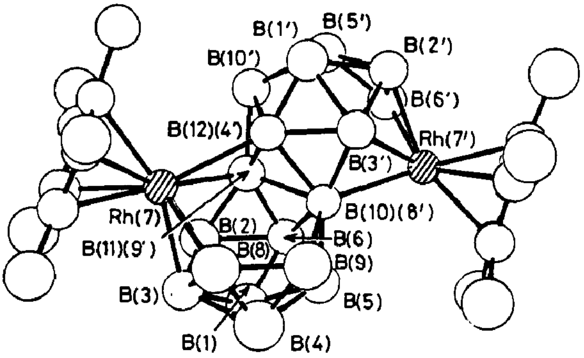
hydrogens and cyclopentadienyl group omitted). Complex [532] is the sixth isomer of this species now known and on heating at 70°C it isomerizes to [2-(cpCo)-1,6-$C_2B_7H_9$] (ref. 776).

The reaction of $[cp'RhI_2]_n$ with Tl[3,1,2-$TlC_2B_9H_{11}$] in THF forms [3,1,2-cp'$RhC_2B_9H_{11}$]. This complex, its cobalt analog and [3,6,1,2-$(cpCo)_2C_2B_8$-H_{10}] were reduced with sodium amalgam and their isomerization processes studied. The rhodium complex goes to its [2,1,7] isomer significantly more rapidly than does the cobalt complex while the dicobalt species isomerizes very slowly (ref. 777). Addition of [cp'$_2Rh_2Cl_4$] to a benzene solution of [<u>arachno</u>-$B_{10}H_{12}(PMe_2Ph)_2$] or to dichloromethane solutions of $(Et_4N)_2$[<u>anti</u>-$B_{18}H_{20}$] or [<u>arachno</u>-B_9H_{14}]$^-$ forms [534], [535] and [536] respectively. The

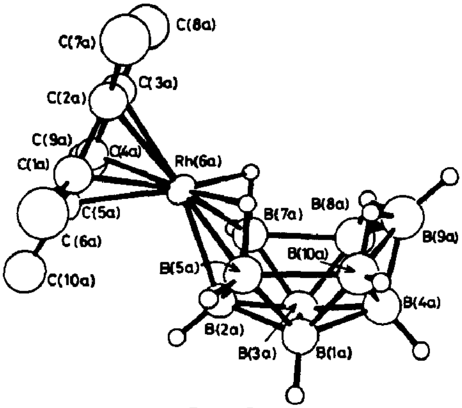


[534]

first two are obtained in modest yields while the third forms quantitatively. Complex [534] contains one B-H-B and two Rh-H-B bridging units instead of two of the former and all three bridging hydrogen atoms appear

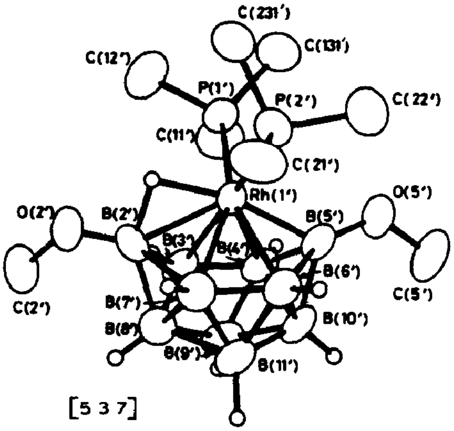


[5 3 5]



[5 3 6]

equivalent in the ^{1}H NMR spectrum (refs. 778-780). In refluxing methanol, [RhCl$_3$(PMe$_2$Ph)$_3$] reacts with (Et$_3$NH)$_2$[*closo*-B$_{10}$H$_{10}$] to form predominantly [B$_9$H$_{13}$PMe$_2$Ph] plus a low yield of [(PhMe$_2$P)$_2$Rh(H)B$_{10}$H$_8$(OMe)$_2$] [(537]) and



[5 3 7]

sometimes traces of [(PhMe$_2$P)$_2$Rh(H)B$_{10}$H$_8$Cl(OMe)] whose structure is basically the same as that for [537]. Here it appears the phosphine ligands on the starting rhodium complex are quite labile and react preferentially with the borane (ref. 781).

The 2D, ^1H-^1H COSY NMR method with simultaneous broad-band ^{11}B decoupling is proposed as an effective means of determining connectivity in polyhedral boranes and their derivatives. It is said not to be subject to the limitations of the 2D, ^{11}B-^{11}B COSY method and was applied to [*nido*-5-cp'RhB_9H_{11}] (ref. 782). The complexes [$H(PMe_3)_2IrB_8H_7Cl$] and [$H(PPh_3)$-$(Ph_2PC_6H_4)IrB_9H_8$], previously proposed by Kennedy and Greenwood to be *iso-closo*, are now thought to have two fewer skeletal electron pairs than their *closo* counterparts and are therefore proposed to be described as *hyper-closo*. This has been rebutted with the contention that the metal vertex need not contribute only three orbitals to cluster bonding and that if four are used here then no problem arises. The rebuttal is continued with the statement that to describe all structures of clusters not obeying the usual electron-counting "rules" as *hyper-closo* is not necessarily useful. Subsequently, molecular orbital calculations on $[Rh(CO)_3B_9H_9]^+$ and the corresponding anion confirm an earlier analysis by the tensor surface harmonic theory that while the anion, with n+1 skeletal electron pairs, should have a conventional deltahedral geometry, the former, with n skeletal electron pairs, should have a polar deltahedral (bicapped square antiprism) structure. These results are stated to contradict the above claim by Kennedy, *et al.* that the $\{ML_3\}$ fragment in [$H(PPh_3)(Ph_2PC_6H_4Ir)$-B_9H_8] should contribute four rather than three orbitals for cluster bonding and these authors reaffirm the *hyper-closo* characterization of the structure as most appropriate (refs. 783-785).

Addition of 1-diphenylphosphino-2-isopropenyl-*o*-carbaborane (L_2) to [$RhClL'_2$] (L' = CO; L'_2 = COD) forms [$Rh_2(L_2)_2(\mu\text{-}Cl)_2$] which is cleaved to [$RhCl(py)(L_2)$] by pyridine (ref. 786). Copolymerization of methyl methacrylate with 1-isopropenyl-(3)-1,2-dicarbaundecaborate forms a polymer which reacts with [$RhCl(PPh_3)_3$] in ethanol to form a supported analog of [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$]. This is a highly active catalyst for the hydrogenation and isomerization of olefins and dienes (ref. 787).

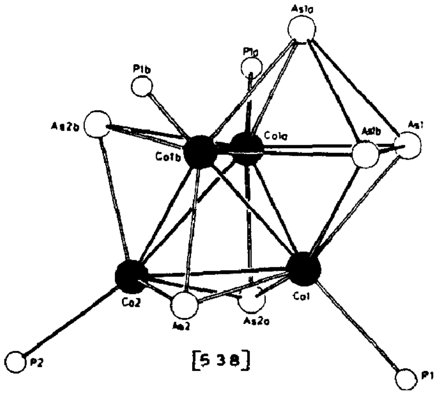
Miscellaneous Complexes

As in previous Annual Surveys this section covers those papers which do not seem to be appropriately covered elsewhere but which may be of interest to organometallic chemists. First on the list is a number of papers continuing studies of bare or ligated metal ions reacting with various organic molecules using FTMS techniques. In the Co^+-alkane (linear) system a correlation has been made between the preference of the ion for insertion into a particular carbon-carbon bond and the ionization potential of the alkyl radical so-produced. It appears that the preferred site of attack of Co^+ is on the carbon-carbon bond which will give $\{Co\text{-}alkyl\}^+$ with the highest cobalt-carbon bond energy (ref. 788). In the reactions of $\{Co(OH)\}^+$ with acyclic alkanes having three or more carbon atoms, insertion into carbon-hydrogen bonds is the predominant initial step although a fair amount of attack at carbon-carbon bonds also occurs. Following carbon-hydrogen insertion, loss of water occurs to give an activated $\{Co\text{-}alkyl\}^+$ species which generally reacts further. With cyclic alkanes, carbon-carbon bond insertion is seen with cyclopropane and cyclobutane but with cyclopentane and cyclohexane only carbon-hydrogen insertion is seen (ref. 789). Silanes react with Co^+ primarily to form dihydrogen and cobalt-silylene moieties although in some instances hydrogen abstraction occurs. Bond energy estimates were made for the cobalt-silylene bonds and also for the cobalt-carbon bonds in $\{Co\text{-}X\}^+$ (X = CH_2, CH, C). The latter used data from photoinduced rather than collision-induced dissociation of $\{CoCH_2\}^+$ (refs. 790-792). The ions $\{Co(CO)_2\}^-$, $\{Co(CO)(NO)\}^-$, $\{Co(CO)_3\}^-$ and $\{Co(CO)_2(NO)\}^-$, derived from low energy electron impact on $[Co(NO)(CO)_3]$, have been reacted with 1-nitroalkanes, 2-methyl-2-nitropropane and n-butylnitrite. In contrast to what was observed with the corresponding cations, no insertion into carbon-carbon or carbon-hydrogen bonds occurs. Instead reaction occurs by a charge-transfer mechanism with initial cleavage of carbon-nitrogen or nitrogen-oxygen bonds followed by rearrangement and/or fragmentation. Only the first two ions react with 1-chloroalkanes, straight-chain alcohols or 1,n-chloroalcohols and here the initial step is insertion into the carbon-chlorine or carbon-oxygen bond. This is followed by charge transfer to oxygen or chlorine (refs. 793, 794). Another study of the reaction of Rh^+ with alkanes reports that insertion into carbon-hydrogen bonds generally occurs and facile β-hydrogen transfer to give 1,2-dehydrogenated fragments ensues. Unlike the cobalt case β-methyl transfer is not seen except with neopentane where β-hydrogens are absent. Some carbon-carbon insertion also is seen. The observed barrier to reductive elimination of R-H or H_2 moieties from rhodium is much less than in the cobalt analogs possibly due to a high internal excitation of the primary dehydrogenation products. This also leads to the exothermic elimination of a second molecule of dihydrogen from the initial dehydrogenated product. The differences in reactivity between Rh^+ and Co^+ in these systems is attributed to differences in the sizes and shapes of the orbitals used in bonding (ref. 795).

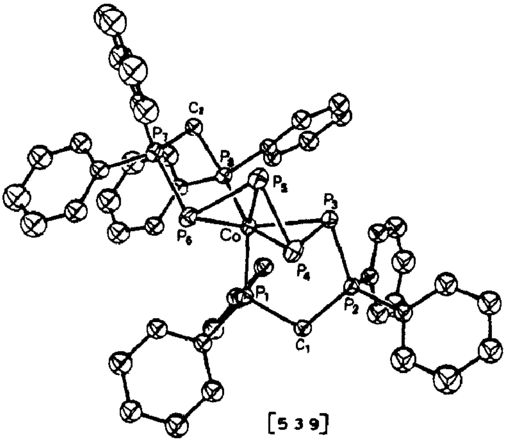
The complexes $[Co(X)(PP_3)]$ (PP_3 = $P(CH_2CH_2PPh_2)_3$; X = Cl, Br, I, CN, SCN, H) have been prepared and the bromo complex found to react with ligands in the presence of methanolic lithium hexafluoroarsenate to yield $[Co(PP_3)L]AsF_6$ (L = CO, $PPhMe_2$, PEt_3, $P(OMe)_3$, $PPh_2(OMe)$, $PMe(OPr^i)_2$, $PF_2(OMe)$). Extensive ^{31}P NMR data were obtained on the products (ref.

796). Reaction of the phenyl carboxylates RC(O)OPh (R = Me, Et, Pr^n, Ph, CF_3) with $[CoH(N_2)(PPh_3)_3]$ in toluene forms new esters RC(O)OR' with R' = Et, Pr^n, Bu^n, bz, CF_3CH_2 respectively plus $[Co(OPh)(PPh_3)]$ while $[Co(Me)(PPh_3)_3]$ forms RC(O)Me and the same cobalt complex. In the case where $[CoH(N_2)(PPh_3)_3]$ was reacted with CF_3CO_2Et the intermediate $[(Ph_3P)_3Co(OCH(CF_3)(OEt)]$ was isolated suggesting that the cobalt-hydrogen bond adds across the carbon-oxygen double bond of the initial ester. Transfer of the phenoxy group to cobalt and elimination of aldehyde follow with the aldehyde then dimerizing to give the final product (ref. 797). A mixture of $[Co_2(N_2)(PPh_3)_6]$ and another phosphine (P:Co = 2:1) forms a catalyst for the cyclization of 4-pentenal to cyclopentanone. The best addend is DPPE which gives a relatively long-lived catalyst (ref. 798). The species $[CoH(Cl)(PPh_3)_2]$, proposed to be prepared <u>in situ</u> from cobalt(II) chloride, the phosphine and sodium borohydride mediates the conversion of terminal alkynes to <u>trans-trans</u>-1,3-dienes (ref. 799).

Bis(trimethylsilyl)phenylarsine reacts with $[CoCl_2(PPh_3)_2]$ in THF to form [538] (phenyl groups omitted) (ref. 800) while in refluxing <u>n</u>-butanol/THF $[Co(H_2O)_6](BF_4)_6$ plus two mols of DPM and 1.5 mols of white phosphorus yields [539] which is a monocation and which on photolysis in the presence



[538]

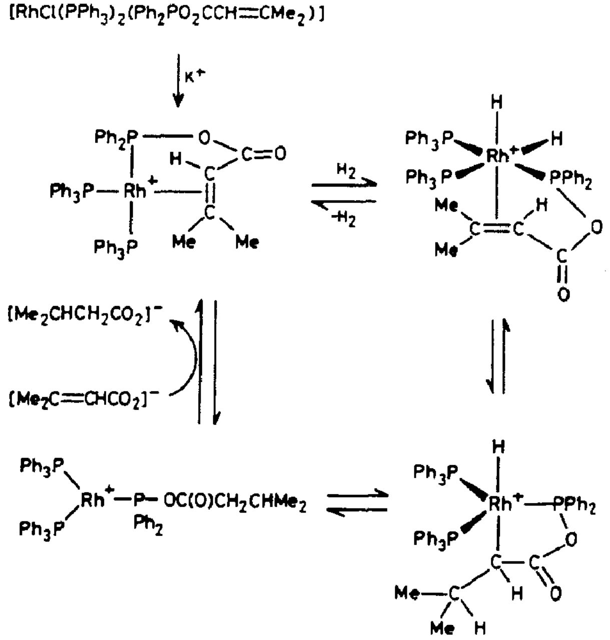


[539]

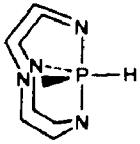
of $[M(CO)_6]$ (M = Cr, W) forms a derivative with an $\{M(CO)_5\}$ moiety attached to P_5. Neither cobalt(II) chloride in the above reaction nor $[Co(DPPE)_2]^+$ reacted with white phosphorus indicating the need for coordinative unsaturation at the metal. In [539] the metal is considered to be formally Co(-1) while the $\{P_4\}$ moiety is formally dipositive and functions as an eight-electron donor (ref. 801). The reaction of cobalt(II) with phosphites (L) to give $[CoL_5]^+$ plus $[CoL_6]^{3+}$ has been studied. A minimum basicity of the ligand is required for the reaction to proceed and subtle steric effects are also apparent. It is suggested that the ligand shape is important in addition to its overall bulk (ref. 802). Thermal reaction of $[CoCl(PMe_3)_3]$ with dmpm in THF forms $[CoCl_2(dmpm)(PMe_3)]$ plus the paramagnetic dimer $[Co_2(PMe_3)_2(\mu\text{-dmpm})_2(\mu\text{-}PMe_2)]$. The latter can also be formed from a mixture of $[CoCl_2(PMe_3)_3]$ and dmpm on reduction with magnesium or potassium or from $[Co(PMe_3)_4]$ and 1.5 equivalents of dmpm but not when this latter mixture is treated with lithium dimethylphosphide. These results suggest the dimer forms by a metal centered process and the bridging dimethylphosphide group is thought to arise from homolysis of a phosphorus-carbon bond of trimethylphosphine at the metal (ref. 803). Ethylcyanoformate reacts with $[Co(H)(np_3)]$ to form $[Co(CN)(np_3)]$ and ethyl formate. An initial coordination of the cyanoformate via the π-bonds of the cyano group is proposed to occur (ref. 804). The electrochemical reduction of $[CoCl_2(PPh_3)_2]$ in propylene carbonate forms a catalyst for the highly selective dimerization of ethylene to but-1-ene (ref. 805) while photolysis of solutions of $[Co(H)(PPh(OEt)_2)_4]$ containing allylic compounds effects their isomerization to the corresponding 1-propenyl derivatives. The same complex can be electrochemically oxidized to a cobalt(II) species which catalyzes double bond migration in 3-phenylpropene but further oxidation to cobalt(III) lowers the activity significantly (refs. 805a, 806).

Heating a mixture of $[Co(H_2O)_6](BF_4)_2$, triphos and arsenic selenide or telluride in ethanol/THF forms $[(triphos)Co(\eta^3\text{-}As_2E)]BF_4$ (E = Se, Te) while $[Co(H_2O)_6](ClO_4)_2$ and triphos when reduced with sodium borohydride in the same solvent in the presence of elemental tellurium forms $[(triphos)Co(\mu\text{-}\eta^2\text{-}Te_2)Co(triphos)]$. The former complex (E = Se) reacts with $[Rh(COD)(THF)_x]BF_4$ and triphos at room temperature to form $[(triphos)Co(\mu\text{-}\eta^3\text{-}As_2Se)Rh(triphos)](BPh_4)_2$ after metathesis. This reacts with more $[Rh(COD)(THF)_x]^+$ and ligand to form $[(triphos)Rh(\mu\text{-}\eta^3As_2Se)Rh(triphos)](BPh_4)_2$ which is also the product when the original reaction is carried out at reflux in the presence of tetraphenylborate ion (refs. 807-809). In related work, $[(triphos)M(\eta^3\text{-}P_3)]$ (M = Co, Rh, Ir) is methylated by methyl triflate or trimethyloxonium tetrafluoroborate yielding air-sensitive $[(triphos)M(\eta^3\text{-}P_3Me)]^+$. The methylated phosphorus atom forms shorter bonds to the metal and to the other phosphorus atoms than do the others (ref. 810). The reaction of $[RhH_3(triphos)]$ with $[Zn(OAr)_2(THF)_2]$ (Ar = 2,4,6-$Bu^t{}_3C_6H_2$) forms $[(triphos)Rh(\mu\text{-}H)_3Zn(OAr)_2]$ which is thought to also contain a metal-metal bond. The same complex with $[Zn(N(SiMe_3)_2)_2]$ yields $[(triphos)Rh(\mu\text{-}H)_2Zn(N(SiMe_3)_2)]$ which is thought to form via initial formation of a species similar to the product of the first reaction followed by a binuclear reductive elimination of bis(trimethylsilyl)amine (ref. 811).

The ester $Ph_2POC(O)CH{=}CMe_2$(L) functions as a simple ligand and with $[RhCl(PPh_3)_3]$ forms $[RhCl(PPh_3)_2L]$ which catalyzes the hydrogenation of substituted acrylic acids in acetone containing potassium hydroxide. In benzene the olefinic moiety can be hydrogenated presumably because the chelate effect promotes interaction of the olefinic substituent with the metal (note that $[RhCl(PPh_3)_3]$ itself is not active for hydrogenation of 3-methylbut-2-enoic acid). Scheme LXIX is proposed for the catalysis by $[RhCl(PPh_3)_2L]$ (ref. 812). The phosphorane [540] forms the very air-sensitive complex [541] when reacted with $[RhCl(PPh_3)_3]$ at low temperature and



Scheme LXIX



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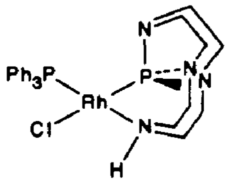
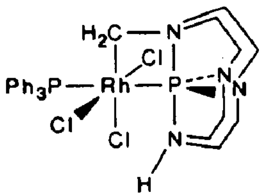


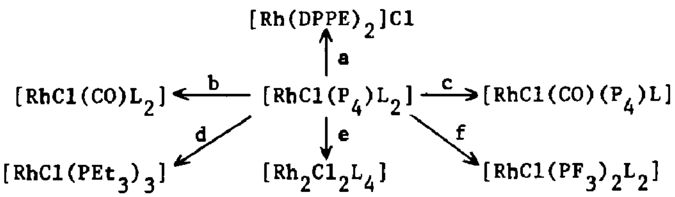
[541]

on dissolution in dichloromethane is converted to [542] by a process which is effectively a three-fragment oxidative addition (ref. 813). Full



[542]

details of the synthesis and chemistry of $[MX(P_4)L_2]$ (M = Rh; X = Cl; L = PPh_3, p-tolyl$_3$P, m-tolyl$_3$P, $AsPh_3$. M = Rh; X = Br, I; L = PPh_3. M = Ir; X = Cl; L = PPh_3) have appeared. The complexes are prepared in dichloromethane at -78°C and most involve η^2-coordination of the P_4 ligand although in the triphenylarsine complex η^3-coordination may occur. Some chemistry of these complexes is shown in Scheme LXX. EHMO and SCF-Xα-SW calculations

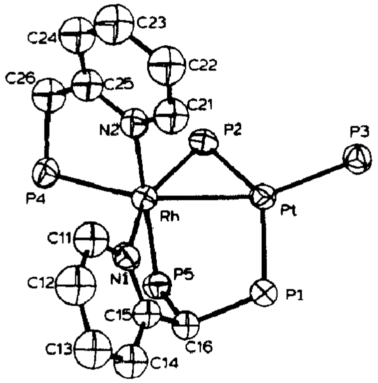


a) DPPE (L = PPh_3). b) CO, -78°C (L = PPh_3). c) CO, -78°C (L = $AsPh_3$). d) PEt_3 (L = PPh_3). e) $[RhClL_3]$ (L = PPh_3). f) PF_3 (L = PPh_3).

Scheme LXX

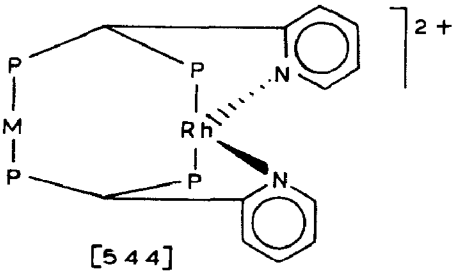
on $[RhCl(P_4)(PH_3)_2]$ as a model for the triphenylphosphine complex support the proposed analogy between the η^2-P_4 moiety and an η^2-olefin or $-S_2$ ligand with the π-backbonding described as a three-orbital, four-electron interaction. From the latter calculations the most important covalent interaction is an in-plane π-overlap of a rhodium $4d_{xy}$ orbital with a π^* orbital on the P_2 edge bonded to the metal although an important σ-component also is present. Most of the bands observed in the electronic spectrum are assigned to metal-to-ligand charge-transfer absorptions (ref. 814). The tetrathiosquarate complex $[Rh_2(PPh_3)_4(\mu\text{-}C_4S_4)]$ is synthesized from $[RhCl(PPh_3)_3]$ and potassium tetrathiosquarate in THF (ref. 815).

Cyclic voltammetric studies on $[Rh(P(OPr^i)_3)_4]^+$ have been interpreted as involving a two-electron reduction to $[Rh(P(OPr^i)_3)_4]^-$ but on reoxidation two, one-electron processes occur with $[Rh(P(OPr^i)_3)_4]$ being formed as an intermediate. This last species is thought to be the source of the blue color observed when one equivalent of electrons have been passed in a controlled-potential reduction of $[Rh(P(OPr^i)_3)_4]^+$ but it is proposed to form <u>via</u> conproportionation of $[Rh(P(OPr^i)_3)_4]^-$ with $[Rh(P(OPr^i)_3)_4]^+$ rather than by a direct, one-electron reduction. It is stable in solution at -20° but decomposes at room temperature possibly by metallation of a ligand methyl group (ref. 816). Addition of $[Pt(C_2H_4)(PPh_3)_2]$ to a dichloromethane solution of $[Rh(NP_2)_2]BF_4$ forms $[RhPt(\mu\text{-}NP_2)(\mu\text{-}PPh_2)(Ph_2PCH_2\text{-}C_5H_4N)(PPh_3)](BF_4)_2$ whose cation is shown as [543] (phenyl groups omitted).



[543]

With $[M(NO_3)(PPh_3)_2]$ (M = Ag, Au), $[Rh(NP_2)_2]BF_4$ forms [544] (M = Ag, Au) which when M = Au reacts with carbon monoxide and hydrogen halides to form [545] and [546] (X = Cl, Br) respectively (ref. 817). The structure of $[RhH_2(L_2)(PPh_3)_2]PF_6$ (L_2 = PhN=CHCH=NPh) has been determined and it has the



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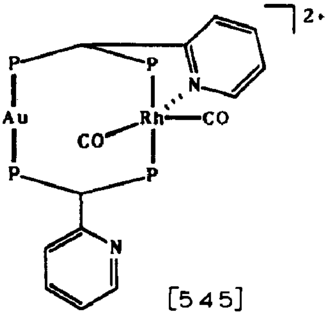
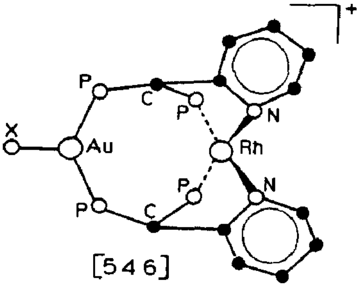
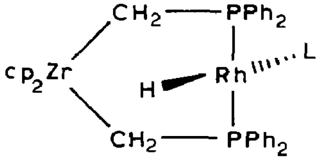


[545]



[546]

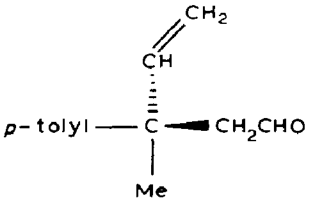
phosphine ligands trans to one another. Dihydrogen is eliminated on reaction with carbon monoxide, and DMAD to yield $[Rh(CO)(L_2)(PPh_3)_2]^+$ and $[Rh(DMAD)(L_2)(PPh_3)_2]^+$ respectively. This also occurs with methyl iodide but the product is thought to contain a weakly-coordinated methyl iodide molecule rather than being an oxidative adduct (ref. 818). The kinetics of oxidative addition of iodine to $[Rh(tfac)(P(OPh)_3)_2]$ to form the trans-diiodo product are interpreted in terms of a two-stage process. The first step is considered to be a cis-oxidative addition of iodine with isomerization to the trans product occurring subsequently (ref. 819). Cocondensation of rhodium atoms with toluene forms a red-brown solution on melting which is stable to -50°C. Addition of phosphorus ligands to this yields $[Rh(H)L_4]$ (L = $P(OMe)_3$, ½DPPE) suggesting that the red-brown material contains a rhodium-hydrogen bond. The full nature of the complex has not been determined but it appears to be trinuclear (ref. 820). Complex [547] (L = PPh_3) can be prepared from $[RhH(PPh_3)_4]$ and $[cp_2Zr(CH_2PPh_2)_2]$ and is an active catalyst for hydroformylation of hex-1-ene. The selectivity decreases with time but can be improved, along with the activity, if two mols of triphenylphosphine are added (ref. 821).



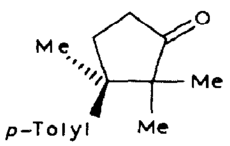
[547]

Triethylamine reacts with mer-$[RhCl_3(DMSO)_3]$ in acetone to form mer-trans-$[RhCl_3(DMSO)(MeCH{=}NEt_2)]$ by dehydrogenation of one alkyl group on the amine. Isomerization to the mer-cis isomer occurs on standing (ref. 822). Addition of three mols of silver perchlorate to mer-$[MCl_3(PMe_2Ph)_3]$ (M = Rh, Ir) yields mer-trans-$[MCl_2(OH_2)(PMe_2Ph)_3]ClO_4$ which is fluxional by a process proposed to involve dissociation and recoordination of water and rearrangements of the resulting square pyramidal intermediate (ref. 823). The cluster $[Rh_{55}(PPh_3)_{12}Cl_6]$, for which a complete elemental analysis and molecular weight are available, is proposed to be the product of reduction of $[RhCl(PPh_3)_3]$ with diborane in THF. The related cluster $[Rh_{55}(PBu^t_3)_{12}Cl_{20}]$ in dichloromethane solution degrades to Rh_{13} clusters, among other species, at a platinum electrode. If water is also present, electrophoresis is observed with the cluster migrating to the cathode. Aggregation of the Rh_{13} clusters occurs to form species proposed to be $[(Rh_{13})_{13}]_n$ (refs. 824, 825). The electronic and EPR spectra of $[Rh(SQ)L_2]$ (SQ = semiquinones; L = CO, PPh_3, $AsPh_3$, $P(OPh)_3$; L_2 = COD) and the EPR spectra of the products of the reactions of some of these with dihydrogen, tributyltin hydride and diethylgermane have been measured. The unpaired electron in the former complexes is localized primarily on the semiquinone ligand but the metal-to-ligand charge-transfer band frequencies are quite dependent on the nature of L and the substituents on the semiquinone (refs. 826, 827).

Hydrogenation of $[Rh(acac)(P(OPh)_3)_2]$ in the presence of excess phosphite forms $[RhH(P(OPh)_3)_4]$ which catalyzes olefin isomerization. Treatment with carbon monoxide forms $[RhH(CO)(P(OPh)_3)_3]$, also obtained directly from the acetylacetonate complex plus phosphite under syngas, which is an olefin hydroformylation catalyst (ref. 828). Other catalyst systems are those based on $[RhCl(L_3)]$ (L_3 = bis(2-diphenylphosphinoethyl)amine) and its iridium analog for olefin hydrogenation (kinetic and activation parameters determined) (refs. 829, 830), $[RhCl(PPh_3)_3]$ alone for the regioselective reduction of cinnamyl acetate to trans-β-methyl styrene by 1,3-dimethyl-2-phenylbenzimidazoline (ref. 831) and $[RhCl(PPh_3)_3]$ in combination with $Li_4SiM_{12}O_{40}$ (M = Mo, W) for the selective hydrogenation of phenylacetylene to β-methyl styrene (ref. 832). Other systems based on $[RhCl(PPh_3)_3]$ include those using triethylenediamine which catalyze the formation of methyl and ethyl formates from the corresponding alcohols, dihydrogen and carbon dioxide (ref. 833), one which catalyzes the hydrogenation of imines in alcoholic solvents under mild conditions (ref. 834) and one which catalyzes the addition of 1,3-dienes to 3-alkenoic acids to form 3,6-dienoic acids. In this last system $[RhH(PPh_3)_4]$, $[Rh(O_2CMe)(PPh_3)_3]$ and $[Rh(COD)(PPh_3)_2]PF_6$ were also active but not as effective as $[RhCl(PPh_3)_3]$. The high regioselectivity observed is attributed to the formation of metallacyclic intermediates (ref. 835). Further uses of $[RhCl(PPh_3)_3]$ are to mediate the cyclization of [548] to [549] (ref. 836) and to catalyze the hydrosilylation of α,β-unsaturated esters (ref. 837) and quinones (ref. 838).



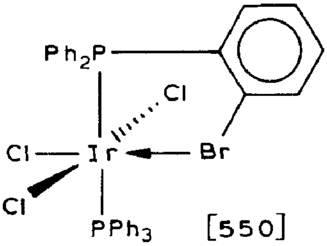
[548]



[549]

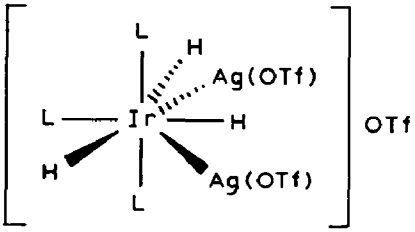
The cleavage of carbon-carbon double bonds by dioxygen to form aldehydes is catalyzed by $[RhCl(PPh_3)_3]$ and related complexes (ref. 839) while the catalytic activity of $[RhCl(PPh_3)_3]$ analogs supported on polymers via pendant diphenylphosphino groups is said to be quite dependent on the preparative conditions. In particular binding of rhodium by two such groups appears necessary for best results (ref. 840). The complexes $[RhClL_2]$ ($L = (EtO)_3Si(CH_2)_nP(menthyl)_2$ ($n = 1, 3, 5$)) prepared *in situ* from $[RhCl(C_2H_4)_2]$ have been examined in solution and on silica surfaces for asymmetric hydrogenation catalysis. The latter were more stable and selective than the homogeneous counterparts but some leaching did occur (ref. 841). A mechanistic study of ketone hydrogenation by hydrogen transfer from an alcohol in the presence of $[RhH(PPh_3)_4]$ postulates ligand dissociation and subsequent π-coordination of the keto group to the metal (ref. 842) while $[RhH(CO)(PPh_3)_3]$ catalyzes the isomerization of α-trimethylsilylketones to the corresponding enol ethers (ref. 843) and $[RhH(PPh_3)_4]$ mediates the oxidation of 2-alkyl-1,4- or -1,5-diols to β-alkyl-γ-lactones or γ-alkyl-δ-lactones respectively in the presence of 4-phenylbut-3-en-2-one as a hydrogen acceptor (ref. 844). The last complex also catalyzes the oxidation and isomerization of *cis*- and *trans*-4-*tert*-butylcyclohexanol (ref. 845).

$[IrH_2(PPh_3)_2(acetone)_2]BF_4$, which together with related complexes is active for the stoichiometric or catalytic dehydrogenation of cycloalkanes to cycloalkenes and arenes (ref. 846), reacts with bipy to form $[IrH_2(bipy)(PPh_3)_2]BF_4$ which on treatment with $[Au(NO_3)(PPh_3)]$ and more tetrafluoroborate ion yields $[(Ph_3P)_2(bipy)\overline{Ir(\mu\text{-}H)_2Au}(PPh_3)](BF_4)_2$. The hydride location is proposed from NMR data and unlike $[IrH_2(NO_3)(PPh_3)_2Au(PPh_3)]BF_4$ no further gold moieties can be added. Reaction of $[IrH(CO)(PPh_3)_3]$ with $[Au(NO_3)(PPh_3)]$ and potassium hexafluorophosphate forms *mer*-$[IrH(CO)(AuPPh_3)(PPh_3)_3]BF_4$ while $[IrAu_2(H)(NO_3)(PPh_3)_4]BF_4$ reacts with triphenylphosphine to form $[Au(PPh_3)_2]^+$ and $[IrH(AuPPh_3)(PPh_3)_3]^{2+}$. The latter has a square pyramidal structure with an apical $\{AuPPh_3\}$ ligand (ref. 847). Water oxidatively adds to $[IrL_4]PF_6$ ($L = PMe_3$) yielding *cis*-$[IrH(OH)L_4]PF_6$ which is thermally stable to 100°C. In D_2O the latter forms *cis*-$[IrH(OD)L_4]PF_6$ which also does not undergo reductive elimination and reverts to the hydroxide complex on exposure to air. The hydroxide complex in methanol yields *cis*-$[IrH(OMe)L_4]PF_6$ which is also obtained together with *cis*-$[IrH_2L_4]PF_6$ from $[IrL_4]PF_6$ and methanol. The methoxide complex is stable to 70°C but reacts immediately with tetranitromethane to reductively eliminate methanol. The results of the reaction of $[IrL_4]PF_6$ with methanol suggest it proceeds *via* oxidative addition of methanol to $[IrL_3]^+$ to form $[IrH(OMe)L_3]^+$ which then undergoes either β-elimination or addition of a fourth phosphine ligand. $[IrL_4]PF_6$ also adds hydrogen sulfide to yield *cis*-$[IrH(SH)L_4]PF_6$ which is unreactive towards alcohols unlike its hydroxy analog (ref. 848). Halide abstraction from *mer*-$[IrCl_3L_3]$ ($L = PMe_2Ph$) by silver perchlorate in aqueous methanol under carbon monoxide forms *mer-trans*-$[IrCl_2(CO)L_3]ClO_4$ which in dichloromethane solution is converted to *mer-trans*-$[\mathrm{IrCl_2(CO_2H)L_3}]$ by aqueous potassium hydroxide. The last reverts to the carbonyl complex on treatment with acetic or trifluoroacetic acids and with lithium bis(trimethylsilyl)amide forms a 3:1 mixture of *mer-trans*- and *mer-cis*-$[\mathrm{IrHCl_2L_3}]$. With thallium formate in methanol $[\mathrm{IrCl_3L_3}]$ forms *mer-trans*-$[\mathrm{IrCl_2(OC(O)H)L_3}]$ which is unaffected by refluxing in THF (ref. 849). Hydrated iridium(III) chloride and *o*-bromophenyldiphenylphosphine(L) in refluxing ethanol form $[\mathrm{IrCl_3L_2}]$ which reacts with triphenylphosphine yielding [550] (ref. 850).



[550]

Under 60 atm of carbon dioxide $[\mathrm{IrH(PMe_3)_4}]$ reacts with dicyanomethane in hot THF to yield $[\mathrm{IrH_2(PMe_3)_4}][\mathrm{O_2CCH(CN)_2}]$ which involves the formation of a carbon-carbon bond between carbon dioxide and an activated alkane. The same reaction with $[\mathrm{M(L_2)_2}]\mathrm{Cl}$ forms $[\mathrm{MHCl(L_2)_2}][\mathrm{O_2CCH(CN)_2}]$ ($\mathrm{M = Rh;\ L_2 = dmpe.\ M = Ir;\ L_2 = depe}$) (ref. 851). Oxidative addition of tetrafluoroboric or perfluorobutane sulfonic acids to $[\mathrm{Ir(N_2)Cl(PPh_3)_2}]$ at -25°C forms *trans*-$[\mathrm{IrH(X)Cl(N_2)(PPh_3)_2}]$ ($\mathrm{X = FBF_3,\ OSO_2C_4F_9}$) in which two good leaving groups are present. The products catalyze the isomerization of phenyl- or 1,2-diphenyloxirane to the corresponding acetaldehyde derivatives and react with ligands at low temperature to form *trans*-$[\mathrm{IrH(L)Cl(N_2)(PPh_3)_2}]\mathrm{BF_4}$ ($\mathrm{L = H_2O}$, MeOH, acetone, THF, MeCN, CO, $\mathrm{C_2H_4}$) or *trans*-$[\mathrm{IrHCl(PPh_3)_3}]\mathrm{X}$ (ref. 852). Addition of thionitrosodimethylamine to *mer*-$[\mathrm{IrHCl_2(PPh_3)_3}]$ in toluene/diethyl ether yields *trans*-$[\mathrm{IrCl_2H(S{=}NNMe_2)(PPh_3)_2}]$ while with $[\mathrm{IrHCl(MeCN)_2(PPh_3)_2}]^+$ the product is *cis*-$[\mathrm{IrHCl(S{=}NNMe_2)_2(PPh_3)_2}]^+$ (ref. 853). In refluxing ethanol/hydrochloric acid, $\mathrm{(NH_4)_2[IrCl_6]}$ reacts with excess triisopropylphosphine yielding *trans*-$[\mathrm{IrH_2Cl_2(PPr^i{}_3)_2}]$ which is the first example of a paramagnetic iridium(IV) hydride. At room temperature in solution this species appears to undergo a reductive elimination of dihydrogen to form the diamagnetic iridium(III) complex $[\mathrm{IrHCl_2(PPr^i{}_3)_2}]$, a process which can be reversed on cooling. For this reason it is proposed that the dihydrogen formed remains somehow associated with the product complex leading to a characterization of the equilibrium as a temperature-dependent ligand-to-metal $\rightleftarrows$ metal-to-ligand charge transfer process (refs. 854, 855). Treatment of *mer*-$[\mathrm{IrH_3(PPh_3)_3}]$ with two equivalents of silver triflate in acetone forms [551] ($\mathrm{L = PPh_3}$).



[551]

The hydride ligands were not located in the structure determination but the positions indicated were suggested by NMR data (ref. 856).

List of Abbreviations

acac = acetylacetonate
AMSO = N-acetyl-(S)-methionine-(R,S)-sulfoxide
BDN = buta-1,3-diene
BDPOP = 2,4-bis(diphenylphosphinyloxy)pentane
biim = 2,2'-biimidazolate
bipy = 2,2'-bipyridine
BPK = benzophenone ketyl
BPPFA = (R)-{1-[(S)-2,1'-bis(diphenylphosphino)ferrocenyl]ethyl}dimethylamine
BPPM = (2S,4S)-N-*tert*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine
br = 1,3-diisocyanopropane
BTD = 2,1,3-benzothiadiazole
BTMSA = bis(trimethylsilyl)acetylene
btz = benzotriazolate
btzH = benzotriazole
bz = benzyl
CAMP = methylcyclohexyl-*o*-anisylphosphine
(S,S)-CHIRAPHOS = (S,S)-2,3-bis(diphenylphosphino)butane
CIDNP = Chemically Induced Dynamic Nuclear Polarization
4-CNpy = 4-cyanopyridine
COD = cycloocta-1,5-diene
COT = cyclooctatetraene

cp = cyclopentadienyl
cp' = pentamethylcyclopentadienyl
cpMe = methylcyclopentadienyl
CTAB = cetyltrimethylammonium bromide
cy = cyclohexyl
cydiop = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(dicyclohexylphosphino)butane
cyoct = cyclooctene
cyttp = bis(3-dicyclohexylphosphinopropyl)phenylphosphine
DAB = 1,4-diphenyl-1,4-diazabuta-1,3-diene
DABCO = 1,4-diazabicyclo[2.2.2]octane
dacoda = 1,5-diazacyclooctane-N,N'-diacetate
dahd = 3,4-diacetyl-2,4-hexadien-2,5-diolate
DAM = bis(diphenylarsino)methane
DAP = 2,6-diallylpyridine
DAPM = diphenylarsinodiphenylphosphinomethane
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene
DEAD = diethylacetylene dicarboxylate
DIOP = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DIPAMP = (R,R)-1,2-bis(*o*-anisylphenylphosphino)ethane
dimen = 1,8-diisocyanomethane
dippb = 1,4-bis(diisopropylphosphino)butane
dippe = 1,2-bis(diisopropylphosphino)ethane
dippp = 1,3-bis(diisopropylphosphino)propane
dipy = bis(pyridin-2-yl)amide
DMA = N,N-dimethylacetamide
DMAD = dimethylacetylene dicarboxylate
DME = 1,2-dimethoxyethane
dmgH = dimethylglyoximate
dmmm = bis(dimethylphosphinomethyl)methylphosphine
dmpm = bis(dimethylphosphino)methane
DMSO = dimethylsulfoxide
DNMR = Dynamic Nuclear Magnetic Resonance
(DO)(DOH)pn = diacetylmonoxime diacetylmonoximato propane-1,3-diyldiimino
DPM = bis(diphenylphosphino)methane
dpma = bis(diphenylphosphinomethyl)phenylarsine
dpmp = bis(diphenylphosphinomethyl)phenylphosphine
DPPB = 1,4-bis(diphenylphosphino)butane
DPPE = 1,2-bis(diphenylphosphino)ethane

DPPP = 1,3-bis(diphenylphosphino)propane
DQ = duroquinone
EHMO = Extended Hückel Molecular Orbital
ENDOR = Electron Nuclear Double Resonance
EPR = Electron Paramagnetic Resonance
EXAFS = Extended X-ray Absorption Fine Structure
FTIR = Fourier Transform Infrared
FTMS = Fourier Transform Mass Spectrometry
FVP = Flash Vacuum Pyrolysis
H_2biim = 2,2'-biimidazole
1,5-HD = hexa-1,5-diene
H_2dahd = 3,4-diacetyl-2,4-hexadien-2,5-diol
Hdipy = bis(pyridin-2-yl)amine
HFB = hexafluorobut-2-yne
Him = imidazole
HMPA = hexamethylphosphoramide
Httz = tetrazole
Htz = 1,2,4-triazole
im = imidazolate
MAS = Magic Angle Spinning
3-Mepy = 3-Methylpyridine
4-Mepy = 4-Methylpyridine
Me_2Onapy = 5,7-dimethyl-1,8-naphthyridin-2-one
Me_2pz = 3,5-dimethylpyrazolate
Me_2pzH = 3,5-dimethylpyrazole
Me_3TFB = trimethyltetrafluorobenzobarrelene
NBD = bicyclo[2.2.1]heptadiene
NH_2bpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole
NMP = N-methylpyrrolidine
NOE = Nuclear Overhauser Enhancement
(-)NORPHOS = (2R,3R)-(-)-2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene
Np = neopentyl
NP_2 = 2-[bis(diphenylphosphino)methyl]pyridine
np_3 = tris(2-(diphenylphosphino)ethyl)amine
OEP = octaethylporphyrin
OFCOT = octafluorocyclooctatetraene
Onapy = 1,8-naphthyridin-2-one
ophen = 1,10-phenanthroline
oq = 8-oxoquinolinate
OTf = trifluoromethanesulfonate ("triflate")

PAMP = methylphenyl-*o*-anisylphosphine

PES = photoelectron spectroscopy

(S)-PheNOP = 2-(S)-3-phenyl-2-N-methyl-2-N-phenyl-diphenylamino-1-diphenylphosphinoxypropane

PPD = (E,E)-1-phenyl-1,2-propanedione dioximate

(-)PPM = (2S,4S)-4-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidine

PPN = bis(triphenylphosphine)iminium cation

(R)-PROPHOS = (R)-1,2-bis(diphenylphosphino)propane

py = pyridine

pydz = pyridazine

py-SH = pyridine-2-thiol

pz = pyrazolate

pzH = pyrazole

salen = N,N'-ethylenebis(salicylaldiminato)

SQ = *o*-semiquinone

syngas = synthesis gas (H_2/CO)

tcbiim = 4,4',5,5'-tetracyano-2,2'-biimidazolate

TDA = tris(dioxa-3,6-heptyl)amine

TEMPO = 2,2,6,6,-tetramethylpiperidinyloxy

TFA = trifluoroacetic acid

tfac = trifluoroacetylacetonate

TFB = tetrafluorobenzobarrelene

TFTMAA = 1,1,1-trifluoro-5,5,5-trimethylpentandionate

tht = tetrahydrothiophene

TMB = 2,5-dimethyl-2,5-diisocyanohexane

TMEDA = N,N,N',N'-tetramethylethylenediamine

TPD = Temperature Programmed Decomposition

TPM = tris(diphenylphosphino)methane

TPP = tetraphenylporphyrin

triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane

TTP = tetra-*p*-tolylporphyrin

ttz = tetrazolate

tz = 1,2,4-triazolate

vdiphos = 1,2-bis(diphenylphosphino)ethylene

vy = vinyl

WGSR = Water-Gas-Shift Reaction

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