COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1984*

JOEL T. MAGUE
Department of Chemistry, Tulane University, New Orleans, Louisiana 70118 (U.S.A.)

CONTENTS

Introduction

The volume of work reported in this area continues to be large although a considerable portion extends earlier studies rather than breaking new ground. As in past years, those papers appearing in less-available journals are covered in abstract form only (so-indicated in the list of references) and reports dealing solely with the results of crystal structure determination are omitted. A list of abbreviations used appears at the end of the text.

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A monograph on the organometallic chemistry of rhodium and iridium appeared late in 1983. Although it is a welcome reference, it is rather dated as its coverage, with the exception of a brief supplement, does not extend much beyond 1979 (ref. 1). A chapter covering rhodium nitrosyl complexes can be found in a supplement volume of the Gmelin series covering rhodium (ref. 2). Also appearing this year is another major reference work on organometallic compounds of the cobalt group (ref. 3). Approximately forty reviews dealing at least in part with this area have been published including ones covering alkyl cobalt tetracarbonyls and derivatives (ref. 4), the photochemistry of transition metal alkyl complexes (ref. 5), σ-bonded complexes of the cobalt group (ref. 6) and μ-(α,ω)-alkanediyl complexes (ref. 7). Portions of a review on cyclometallated compounds incorporating a heterocyclic donor atom in the metallated ligand concern those of the cobalt group (ref. 8) while cis-alkyl and -acyl rhodium and iridium hydrides (ref. 9), the reactivity of metal-carbon multiple bonds (ref. 10) and the oxidative addition of carbon-hydrogen bonds to rhodium and iridium complexes (ref. 11) have also been covered. Three other reviews are concerned with model systems for vitamin B_{12} and factors which affect the strength of the axial cobalt-carbon bond in these complexes (refs. 12-14).

Reactions relevant to cobalt-catalyzed hydroformylation which involve cobalt carbonyl radicals have been reviewed (ref. 15) as have the substitution reactions of cobalt carbonyls (ref. 16), complexes containing carbonyl groups coordinated through both carbon and oxygen (ref. 17), the synthesis of polyhedral clusters (ref. 18) and clusters containing main group hetero atoms (ref. 19). Cobalt group complexes are among those described in reviews of carbonyl insertion reactions of square planar complexes (ref. 20), redistribution reactions of organotransition metal complexes (ref. 21) and the chelate effect in the formation of square planar complexes of bidentate phosphorus and arsenic ligands (ref. 22).

Reviews of catalysis by compounds of the cobalt group include those on the hydrogenation of carbonyl compounds using supported compounds of the group VIII metals (ref. 23), hydrogenation and hydroformylation with $[HCo(CO)_4]$ (ref. 24), the oxidative addition and hydrogen transfer reactions of polyethers coordinated to organorhodium complexes (ref. 25) and the rhodium-catalyzed hydrogenation of $\{C=O\}$ and $\{C=N\}$ functionalities (ref. 26). Also available is a report on the use of the polyhydral skeletal electron pair method for describing the bonding in and electronic structures of metal cluster complexes (ref. 27).

Examples of cobalt, rhodium and iridium complexes are treated in an account of electron-transfer reactions of mononuclear organotransition metal compounds (ref. 28) while two more reviews cover asymmetric hydrogenation of prochiral olefins catalyzed by chiral rhodium complexes (ref. 29) and the rhodium-catalyzed hydroformylation of fatty acid esters (ref. 30). The cobalt group also appears in a review of the reactions of alkynes with metal atoms (ref. 31) while the use of $[cpCo(CO)_2]$ to mediate the cyclization and cocyclization of alkynes for the synthesis of natural product precursors has been extensively reviewed (ref. 32).

Complexes containing ligands bound <u>via</u> an η^3-allyl moiety as well as through another site have been covered (ref. 33) as have cobalt sandwich compounds (ref. 34) and reactions involving nucleophilic addition to coordinated cyclic hydrocarbons (ref. 35). Also available are reviews on the Arbusov-like dealkylation reactions of phosphite complexes (ref. 36) and the chemical properties of copolymers of $[cpCo(CO)_2]$ with ethylene and acetylene (ref. 37).

Two further reviews cover metallaboranes (refs. 38, 39) while the final two deal with iridium hydride complexes of bridging and chelating di(tertiary)phosphines (ref. 40) and matrix isolation studies of organometallic intermediates (ref. 41).

<u>Dissertations</u>

The catalysis of olefin hydrogenation by $[RCo(CO)_2(P(OMe)_3)_2]$ (R = Me, MeC(O)) (ref. 42) and the synthesis of [cp'Rh(R)(X)L] (R = alkyl, aryl; X = H, halogen; L = tertiary phosphine) (ref. 43) have been described. Other dissertations cover the acid cleavage of the cobalt-carbon bond in $[RCo(dmgH)_2py]$ (R = alkyl) (ref. 44) and the reaction of $[IrX(CO)(DPPE)_2]^{2+}$ (X = Cl, Br) with nucleophiles to generate formyl and hydroxycarbene complexes (ref. 45).

Derivatives of $[Co_2(CO)_8]$ have been used as homogeneous catalysts for methanol homologation and the asymmetric hydrogenation of unsaturated compounds (ref. 46). Other dissertations report on the fluxional behavior of $[Pr^iCHCCo_3(CO)_9]^+$ (ref. 47), the hydrogenolysis of methylcyclopropane over supported catalysts derived from mixed rhodium-cobalt cluster carbonyls (ref. 48) and the use of $[Cl_nM(Co(CO)_4)_{4-n}]$ (M = Ge, Sn; n = 1-3) supported on alumina to catalyze the hydrogenation of carbon monoxide (ref. 49).

Mixed metal systems studied include $[cp'Rh(\mu-PMe_2)_2Mo(CO)_4]$ (ref. 50), $\{[(\eta^5-C_5H_4Me)Fe(CO)_2PPh_2]M\}PF_6$ (M = Rh, Ir) (ref. 51) and $[\overline{Fe(CO)_4(\mu-AsMe_2)}$-$Co(CO)_3]$ together with rhodium and iridium derivatives of $[(\eta^5-C_5H_4P(\underline{p}$-tolyl$)_2)Mo(CO)_3]^-$ (ref. 52). The synthesis of $[M(CO)L(\mu-pz)]_2$ (M = Rh, Ir; L = phosphine, phosphite, arsine) is the subject of another dissertation (ref. 53) while others report on the synthesis and properties of polynuclear complexes of rhodium and iridium containing bridging ligands such as PNP (ref. 54), dpmp (ref. 55) and DPM (ref. 56). The reactions of $[RhCl(CO)_2]_2$

with substituted cyclopropanes have been described (ref. 57) as has the use of $[RhCl(PPh_3)_3]$ and $[RhCl(CO)(PPh_3)_2]$ for the catalytic decarbonylation of aldehydes and acid chlorides (ref. 58) and the binding of $[Rh(CO)(PPh_3)_2]^+$ to nucleosides and purine and pyrimidine bases (ref. 59).

Other dissertations describe iridium complexes of cyttp (ref. 60), of phosphine-substituted acetylacetone for the synthesis of mixed metal compounds (ref. 61), of $Bu^t{}_2PCH_2C_6H_3CH_2PBu^t{}_2$ (ref. 62) of PPh_2(*o*-XC_6H_4) (X = CHO, CO_2H, CH_2OH, OH) and their intramolecular oxidative addition products (ref. 63) and reactions of low-valent iridium complexes with osmium tetroxide and peroxycarboxylic acids (ref. 64).

The chemistry of $[cpCo(NO)]_2$ has been reported (ref. 65) as has the synthesis and rearrangements of [cpCo(diene)] complexes (ref. 66) and the synthesis of homoleptic cobalt alkene complexes by the metal-atom-vapor technique (ref. 67). Studies of rhodium olefin complexes include those on the reactions with electrophiles (ref. 68), on the synthesis of $\{[(NBD)Rh]_3P_3O_9\}$, $\{[(NBD)Rh]_5(Nb_2W_9O_{19})_2\}^{3-}$ and $[(cp'Rh)_2Nb_2W_4O_{19}]$ (ref. 69), the use of dibenzo[a,e]cyclooctatetraene in a test to discriminate between homogeneous and heterogeneous catalysis in systems using rhodium and iridium complexes (ref. 70) and the valence isomerization of quadricyclane and related compounds catalyzed by $[RhCl(NBD)]_2$ (ref. 71). Two iridium systems reported include the synthesis of iridium hydride and olefin hydride complexes (ref. 72) and oxidative addition reactions of [Ir(COD)(ophen)]Cl together with reactions of $[MH(CO)(PPh_3)_3]$ (M = Rh, Ir) with dihydrogen, ethylene and phenylacetylene (ref. 73).

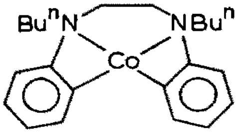
The photoelectron spectra of $[Co_2(CO)_6(alkyne)]$ complexes is the subject of another dissertation (ref. 74) while two more report on the use of $[cpCo(CO)_2]$ to mediate the cyclization of diynes (ref. 75) and the formation of nitrogen-containing heterocycles by the cocylization of alkynes and nitriles (ref. 76). The chemistry of the bis(alkylidyne) complexes $[RCCo_3cp_3CR]$ has also been described (ref. 77).

Three final dissertations report the reactions of $[Co_2(CO)_8]$ with cyclopropenyl cations to generate η^3-cyclopropenyl and η^3-oxocyclobutenyl complexes (ref. 78), the chemistry of the three isomers of $[(PPh_3)_2RhC_2B_9H_{11}]^-$ (ref. 79) and the photoinduced modification of the selectivity of $[RhCl(PPh_3)_3]$ in its catalysis of olefin hydrogenation (ref. 80).

Metal-carbon σ-bonded Complexes

Carbonylation of a mixture of anhydrous cobalt(II) chloride, *tert*-butyllithium and triphenylphosphine in diethyl ether provides a moderate yield of $[Co(Bu^t)(PPh_3)(CO)_3]$ which on redissolution undergoes β-elimination to form $[CoH(PPh_3)(CO)_3]$ (ref. 81). The reaction of $[CoBr_2(THF)_2]$ and N,N'-di-*n*-butyl-N,N'-bis(*o*-lithiophenyl)ethylenediamine affords [1] (ref. 82) while

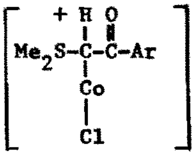
$[\mathrm{CoCl_2(THF)_{1.5}}]$ and 3-dimethylaminopropyllithium form the air- and moisture-



[1]

sensitive salt $\mathrm{Li_2[Co(CH_2CH_2CH_2NMe_2)_4]}$ (ref. 83). Aryl Grignard reagents react with $[\mathrm{CoCl_2L_2}]$ to form the square planar complexes $[\mathrm{CoR_2L_2}]$ (L = $\mathrm{PEtPh_2}$, $\mathrm{PEt_2Ph}$, $\mathrm{PEt_3}$; R = 2,3,4,6-$\mathrm{Cl_4C_6H}$, 2,3,5,6-$\mathrm{Cl_4C_6H}$, 2,3,6-$\mathrm{Cl_3C_6H_2}$, 2,6-$\mathrm{Cl_2C_6H_3}$). Those with R = 2,3,5,6-$\mathrm{Cl_4C_6H}$ and 2,6-$\mathrm{Cl_2C_6H_3}$ reacted with DPPE to form $[\mathrm{CoR_2(DPPE)}]$ (ref. 84). The di-Grignard reagent $\mathrm{BrMg(CH_2)_4MgBr}$, on reaction with $[\mathrm{cpCoI_2(PPh_3)}]$ and $[\mathrm{cp'IrCl_2(PPh_3)}]$ gave the metallacycles $[\mathrm{cp\overline{CoCH_2(CH_2)_2CH_2}(PPh_3)}]$ and $[\mathrm{cp'\overline{IrCH_2(CH_2)_2CH_2}(PPh_3)}]$. The rhodium analog of the latter was prepared from $[\mathrm{cp'RhCl_2(PPh_3)}]$ and 1,4-dilithiobutane (ref. 85).

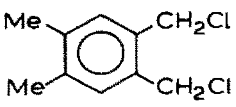
The sulfur ylides $[\mathrm{Me_2\overset{+}{S}-\overset{-}{C}H-C(O)Ar}]$ (Ar = Ph, *p*-tolyl) react with anhydrous cobalt(II) chloride to form [2] (ref. 86). Three reactions of



$$\left[\begin{array}{c}\mathrm{Me_2\overset{+}{S}-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-Ar}\\ \quad | \\ \quad\mathrm{Co}\\ \quad | \\ \quad\mathrm{Cl}\end{array}\right]\mathrm{Cl}$$

[2]

$[\mathrm{Co(CO)_4}]^-$ are those with [3] to form [4] (ref. 87), with phthalimidoacetyl



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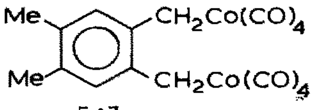
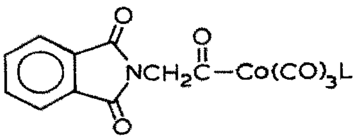
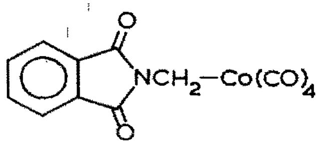


[4]

chloride in the presence of triphenylphosphine and with N-chloromethylphthalimide to give [5] (L = $\mathrm{PPh_3}$) and [6] respectively. Addition of

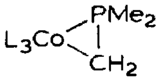


[5]



[6]

triphenylphosphine or carbon monoxide to [6] converts it to [5] (L = PPh_3 or CO respectively) while [5] (L = PPh_3) is reduced by hydrazine to $[Co(CO)_3(PPh_3)]_2$ (ref. 88). Related acyls, $[RR'CHC(O)Co(CO)_4]$ (R = R' = Me; R = Et, R' = H) can be formed in essentially quantitative yields by the addition of $[HCo(CO)_4]$ to the appropriate ketene at low temperature. This contrasts with earlier reports in which the yields were very low. The complexes appear stable for a day at room temperature in a carbon monoxide atmosphere (ref. 89). Dimethylphosphinomethyllithium reacts with $[CoCl(PMe_3)_3]$, $[Co(Cl)(CO)(PMe_3)_3]$ and $[Co(Br)Me_2(PMe_3)_3]$ to give [7] - [9] respectively (L = PMe_3). In analogous reactions, $Li[CH(PMe_2)_2]$ and $[CoCl(PMe_3)_3]$ or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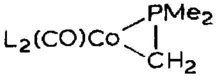
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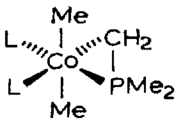
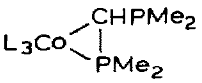
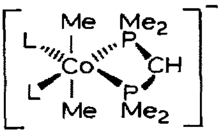

[9]

$[Co(Br)Me_2(PMe_3)_3]$ form [10] and [11] respectively (L = PMe_3). Complex [11] subsequently rearranges to [12] (ref. 90). Oxidative addition of dihalomethanes and halogens to $[cpCo(CO)(PMe_3)]$ at low temperature yields $[cpCo(PMe_3)(CH_2X)X]$ and $[cpCo(PMe_3)(CO)X]X$ (X = Br, I) respectively. Treatment


[10]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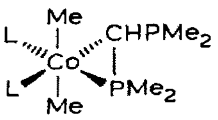
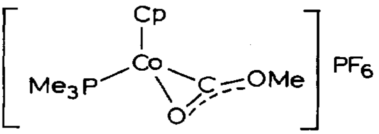
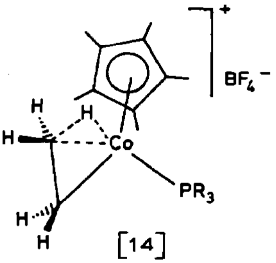

[12]

of the former with NaEH forms $[\mathrm{Cp}\overline{\mathrm{CoCH_2E}}(\mathrm{PMe_3})]$ (E = S, Se) which is converted to $[\mathrm{cp}\overline{\mathrm{CoCH_2E}}\mathrm{Me}(\mathrm{PMe_3})]\mathrm{PF_6}$ by successive reactions with methyl iodide and hexafluorophosphate ion. This last complex (E = S) reacts further with sodium iodide and trifluoroacetic acid to give $[cpCoI(SMe)(PMe_3)]PF_6$. Potassium methoxide attacks the carbonyl group in $[cpCo(PMe_3)(CO)X]X$ giving first $[cpCo(C(O)OMe)(PMe_3)X]$ and then with a second equivalent of the base, $[\mathrm{cp}\overline{\mathrm{CoOC}}(\mathrm{OMe})_2(\mathrm{PMe_3})]$. This complex reacts with alkyl halides followed by metathesis with hexafluorophosphate ion to yield [13] which on treatment with sodium iodide forms $[cpCo(C(O)OMe)I(PMe_3)]$ (ref. 91).



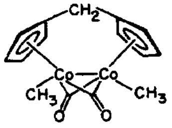
[13]

Protonation of [cp'Co(C_2H_4)L] (L = PMe_3, PPh_3, P(p-tolyl)$_3$) with tetrafluoroboric acid etherate yields [14] which contains an agostic hydrogen in the resulting ethyl group. This finding contrasts with that obtained in the same reaction with [cpRh(C_2H_4)PMe_3] where the product appears to be [cpRhH(C_2H_4)PMe_3] (ref. 92). A full report is now available on the synthesis, thermal decomposition and carbonylation of [$cp_2Co_2(CO)_2R_2$]. These are formed together with [$cp_2Co_2(\mu\text{-}CO)_2$] on reaction of Na[$cp_2Co_2(\mu\text{-}CO)_2$] with RX (R = Me; X = CF_3SO_3, I. R = Et, CF_3CH_2; X = I) at low temperature. On warming to room temperature, [$cp_2Co_2(CO)_2Me_2$] first forms [$cpCo(CO)_2$] and [$cpCo(CO)Me_2$] with the latter complex decomposing to give acetone plus cobalt clusters including [$cp_2Co_2(CO)_3$], [$cp_3Co_3(CO)_3$] and [$cp_4Co_4(CO)_2$]. The ethyl derivative thermally decomposes to give pentan-3-one, ethane, ethylene and several cobalt clusters but no ketone was formed from the trifluoroethyl complex. Carbonylation of [$cp_2Co_2(CO)_2Me_2$] at low temperature yields a mixture of [$cpCo(CO)_2$], [$cpCo(CO)Me_2$], [$cp_2Co_2(CO)_2$(Me)(C(O)Me)] and [$cp_2Co_2(CO)_2(C(O)Me)_2$]. The same reaction with [$cp_2Co_2(CO)_2Et_2$] gives only [$cpCo(CO)_2$] and [$cp_2Co_2(CO)_2(C(O)Et)_2$] while [$cp_2Co_2(CO)_2(CH_2CF_3)_2$] yields [$cpCo(CO)_2$] and [$cpCo(CO)(CH_2CF_3)_2$]. Thermolysis of [$cp_2Co_2(CO)_2(C(O)R)_2$] in a carbon monoxide atmosphere gives a quantitative yield of the corresponding ketones and [$cpCo(CO)_2$] at a rate which is much faster than was found for the parent dialkyl complexes. Crossover experiments on the reactions leading to ketone production show that extensive scrambling of the alkyl groups occurs before [$cpCo(CO)R_2$] forms suggesting that cleavage of [$cp_2Co_2(CO)_2R_2$] to form [cpCo(CO)R] is the initial step.

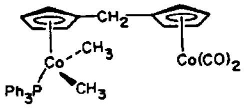


[14]

Intermolecular alkyl transfer then ensues to yield $[cpCo(CO)R_2]$ which subsequently decomposes to form the ketone. While this scheme adequately explains the data from the crossover experiments, the observation that [15] reacts with triphenylphosphine to give [16] suggests that some of the $[CpCo(CO)R_2]$ formed in the thermolysis of $[cp_2Co_2(CO)_2R_2]$ may occur by intramolecular alkyl transfer (ref. 93). Extended-Hückel molecular orbital calculations have been performed to explore the course of dinuclear reductive elimination reactions. Although these used manganese complexes as models, the results are suggested to be applicable to reactions such as those depicted in Scheme I (ref. 94).

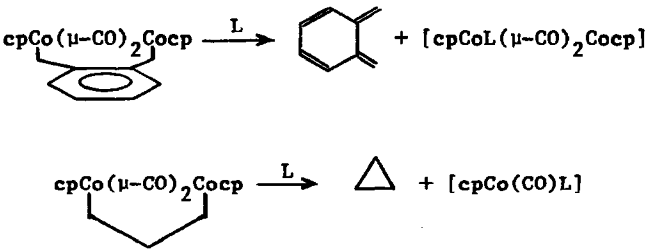


[15]



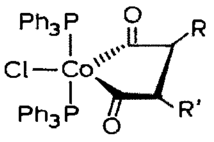
[16]

$$[cp'CoMe_2L] + [cp'CoH_2L] \longrightarrow CH_4$$

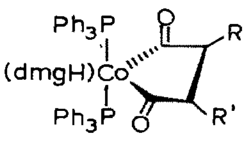


Scheme I

Ring-opening of aziridine occurs on reaction with $[CoH(CO)_3L]$ (L = CO, PPh_3) and the product isolated is formulated as $[\overline{CoNH_2CH_2CH_2C}(O)(CO)_2L]$ (ref. 95). The synthesis of tetrasubstituted p-benzoquinones from cyclobutene-3,4-diones is mediated by $[CoCl(PPh_3)_3]$. The initial product is the maleoyl complex [17] (R = R' = Me. R = Me; R' = OMe. R,R' = $(CH_2)_n$ (n = 4, 5)) which on subsequent reaction with an acetylene in the presence of silver tetrafluoroborate forms the desired product. Alternatively [17] may be converted to [18] by reaction with dimethylglyoxime and then reacted with the desired acetylene (ref. 96).



[17]



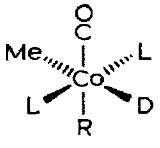
[18]

Interest in acylcobalt tetracarbonyls and their derivatives continues to be high. Successive treatment of $[MeC(O)Co(CO)_3(P(OMe)_3)]$ with sodium ethoxide and methyl iodide in THF effects its decarbonylation to $[MeCo(CO)_3(P(OMe)_3)]$ while reaction of $K[Co(CO)_4]$ and methyl iodide in toluene in the presence of $(MeO)_2PCH_2CH_2P(OMe)_2(L_2)$ affords $[MeC(O)Co(CO)_2(L_2)]$. These and related complexes have been studied as catalysts for olefin hydrogenation and isomerization. The incorporation of deuterium into the isomeric octenes formed during the reacton of oct-1-ene with deuterium in the presence of $[MeCo(CO)_2L_2]$ (L = phosphine or phosphite) suggested the establishment of the equilibria of Scheme II (ol = olefin; R = alkyl) with the equilibration

$$\begin{tikzcd}
{[MeCo(CO)_2L_2] + ol} \arrow[r, shift left] & {[MeC(O)Co(CO)(ol)L_2]} \arrow[l, shift left] \arrow[d, shift right] \\
{[MeC(O)CoD_2(ol)L_2]} \arrow[r, shift left] \arrow[d, shift left] & {[MeCo(CO)(ol)L_2] + CO} \arrow[l, shift left, "D_2"'] \arrow[u, shift right] \\
{[MeCo(CO)(R)(D)L_2]} \arrow[u, shift left] &
\end{tikzcd}$$

Scheme II

occurring more readily than $[MeCo(CO)(R)(D)L_2]$ eliminates octane. Moreover the preponderance of octane over methane by a factor of 10^6 suggested that the structure of this last species is [19]. The complexes $[MeC(O)Co(CO)_2(L_2)]$ and $[MeCo(CO)_3L]$ were also studied as catalysts. The former behaved



[19]

similarly to [$MeCo(CO)_2L_2$] although it was less active and plagued by decomposition. The latter also was less active but produced proportionately more methane suggesting that the alkyl hydride species produced by addition of hydrogen may have a structure different from [19]. In all cases, both radical and bimolecular pathways could be excluded (ref. 97). By contrast, in the stoichiometric reaction of [$RC(O)Co(CO)_4$] with [$HCo(CO)_4$] (R = *n*-hexyl) to produce *n*-heptanal and [$Co_2(CO)_8$] the kinetics were consistent with the radical process of Scheme III in which the second step was proposed

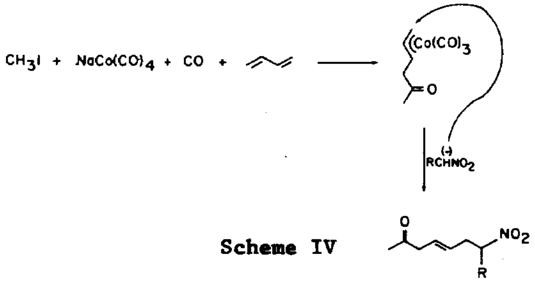
$$[RC(O)Co(CO)_4] \rightleftarrows [RC(O)\cdot,\cdot Co(CO)_4]$$

$$[RC(O)\cdot,\cdot Co(CO)_4] + [HCo(CO)_4] \rightarrow RCHO + [\cdot Co(CO)_4]$$

$$2[\cdot Co(CO)_4] \rightarrow [CO_2(CO)_8]$$

Scheme III

to be rate-determining (ref. 98). In a synthetic application, [$MeC(O)Co(CO)_3$], produced *in situ* from $Na[Co(CO)_4]$ and methyl iodide under carbon monoxide, mediates the reaction of 1,3-dienes with alkyl nitronates to give nitro enones as depicted in Scheme IV. In this example a 25% yield of the product was realized while the same reaction with cyclohexa-1,3-diene afforded a 74% yield (ref. 99).

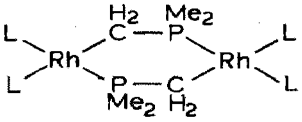


Scheme IV

Reaction of trimethylsilyl azide with *mer*-[$CoMe_3(PMe_3)_3$] yields *mer*-[$CoMe_2(N_3)(PMe_3)_3$] which on carbonylation gives [$Co(CO)(N_3)(PMe_3)_2$] among other products. By contrast, the same reaction with *p*-tolylazide forms [$CoMe_2(MeN{\cdots}N{\cdots}N(p\text{-tolyl}))(PMe_3)_2$]. With *fac*-[$MMe_3L_3$] (M = Rh; L = PMe_3. M = Ir; L = PMe_2Ph), trimethylsilylazide produced *fac*-[$MMe_2(N_3)L_3$] (ref. 100). An alkyl group transfer from *cis*-[$CoR_2(bipy)_2]ClO_4$ (R = Me, Et) to *p*-benzoquinone occurs in acetonitrile in the presence of magnesium perchlorate as a catalyst. The starting complexes appear to initially form a charge-transfer complex with the quinone (ref. 101). EXAFS studies on solutions of Co(II)

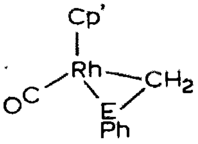
2-ethylhexanoate and trimethylaluminum provide evidence for the presence of disordered metal clusters as well as species with cobalt-carbon bonds (ref. 102).

Addition of lithium bis(trimethylsilyl)amide to toluene solutions of $[Rh(PMe_3)_4]O_2CMe$ affords [20] (L = PMe_3) which can be hydrogenated to



[20]

fac-$[RhH_3(PMe_3)_3]$. Here the amide appears to function as a strong base rather than as a ligand (ref. 103). Reaction of $[cp'Rh(CO)I(CH_2I)]$ with Li[EHPh] (E = P, As) yields [21] which is characterized as containing a phosphine- or arsinemethylene moiety stabilized by coordination to the metal. The arsenic complex on dissolution in pentane undergoes partial conversion to [22] (ref. 104). The related complexes [23] (E = S, Se; L = PMe_3) displace THF from $[ML_n(THF)]$ to form [24] (E = S; ML_n = $Cr(CO)_5$. E = Se; ML_n = $Cr(CO)_5$, $W(CO)_5$, $cpMn(CO)_2$). Reaction of $[cp'Rh(CO)I(CH_2I)]$ with NaSeH forms an analog of [23] (L = CO) from which the corresponding analogs of [24] can be prepared in like fashion (ref. 105). Cleavage of the dimers $[cp'RhX_2]_2$ by phosphines yields $[cp'RhX_2L]$ (X = Cl, Br, I; L = PMe_3, PPh_3, P(*p*-tolyl)$_3$) which can be converted to $[cp'Rh(R)X(L)]$ (X = Cl, Br, I; R = cyclopentyl, Pr^n, CH_2Bu^t, Ph, *o*-tolyl, *m*-tolyl, *p*-tolyl, 2,5-$Me_2C_6H_3$,



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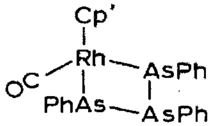

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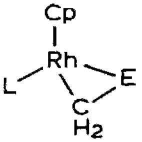

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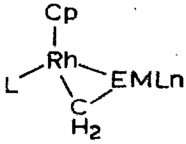
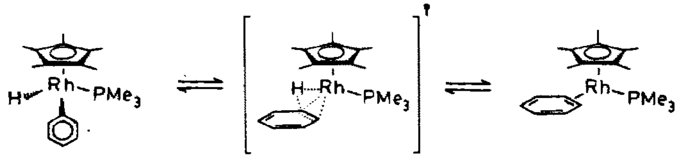


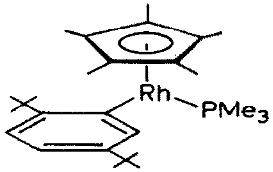
[24]

3,5-$Me_2C_6H_3$, 3,4-$Me_2C_6H_3$, *p*-$R'C_6H_4$ (R' = CF_3, F, OMe, NMe_2), vy, bz, C(Me)=CH_2, cyclopent-1-enyl) by the appropriate organolithium or Grignard reagents. The aryl complexes show evidence for hindered rotation about the rhodium-carbon bond and when L = PPh_3 or P(*p*-tolyl)$_3$ hindered rotation about the rhodium-phosphorus bond is also seen. The structure of [cp'Rh(Ph)Br(PMe_3)] was determined and as there was no evidence for a π-component in the rhodium-carbon bond, the hindered rotation must result from steric interactions. In a second paper two routes from [cp'Rh(Ar)X(PMe_3)] (X = Cl, Br, I) to [cp'Rh(Ar)H(PMe_3)] are reported. When Ar = Ph, *p*-tolyl, *m*-tolyl, 3,5-$Me_2C_6H_3$, 3,4-$Me_2C_6H_3$, *p*-$F_3CC_6H_4$, *m*-$F_3CC_6H_4$, *p*-anisyl, *m*-anisyl, *o*-anisyl this is accomplished with Na[$H_2Al(OCH_2CH_2OMe)_2$] while when Ar = 2,5-$Me_2C_6H_3$ successive reaction with silver hexafluorophosphate and Li[$HBBu^s_3$] was employed. The latter route was also used to obtain the cyclopent-1-enyl analog. In solution the aryl hydride complexes isomerize *via* a [1,2] shift involving an η^2-arene intermediate as depicted in Scheme V. The plausibility of this process has been established by the isolation of [25] from the reduction of



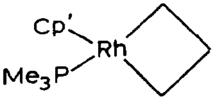
Scheme V

[cp'Rh(PMe_3)Cl_2] with Na[$H_2Al(OCH_2CH_2OMe)_2$] to give [cp'Rh(PMe_3)H_2] followed by irradiation at low temperature in perdeuteromethylcyclohexane solution



[25]

and addition of *p*-$Bu^t{}_2C_6H_4$. Irradiation of [cp'Rh(PMe_3)H_2] in liquid propane afforded [cp'Rh(PMe_3)H(Pr^n)] *via* oxidative addition of a carbon-hydrogen bond to the {cp'Rh(PMe_3)} moiety (refs. 106, 107). Other workers have also investigated this latter reaction and found the photochemically-generated {cp'Rh(PMe_3)} to react analogously with ethane and cyclopropane at -60°C to give [cp'Rh(PMe_3)H(R)] (R = Et, *cyclo*-C_3H_5). Reductive elimination of alkane occurs on warming to -10°C but if bromoform is added to the alkyl hydride complexes at -60°C the considerably more stable complexes [cp'Rh(PMe_3)Br(R)] are formed. While the reactivity of {cp'Rh(PMe_3)} towards insertion into carbon-hydrogen bonds is comparable to that of its iridium analog, it is more discriminating in that only primary carbon-hydrogen bonds are attacked while the iridium species is almost equally as reactive towards secondary carbon-hydrogen bonds. In addition to the photochemical route just described, [cp'Rh(PMe$_3$)H(cyclo-C$_3$H$_5$)] can also be formed from [cp'Rh(PMe$_3$)H(Pr^n)] and cyclopropane at -10°C. In the presence of cyclopropane at 0-10°C an intramolecular rearrangement to [26] competes with the reductive elimination of cyclopropane. Complex [26] can also be prepared by reaction of [cp'Rh(PMe$_3$)I(cyclo-C$_3$H$_5$)] with silver tetrafluoroborate to first give [cp'Rh(PMe$_3$)(η^3-C$_3$H$_5$)]BF$_4$ followed by reaction with hydride reagents. In this latter step, a novel addition of hydride to the central carbon of the allyl group appears to occur (refs. 108, 109). In related work, [cp'Ir(PMe$_3$)H$_2$] on irradiation in pentane forms a mixture of pentyl hydride complexes [cp'Ir(H)(R)(PMe$_3$)] (R = n-C$_5$H$_{11}$, CHEt$_2$, CH(Me)Pr^n). Heating this mixture in pentane at 110°C in a sealed tube converts the secondary pentyl hydride complexes to [cp'Ir(H)(n-C$_5$H$_{11}$)PMe$_3$] while under the same conditions in cyclohexane as the solvent the amount of [cp'Ir(H)(n-C$_5$H$_{11}$)(PMe$_3$)] remains unchanged but the other two isomers are converted to [cp'Ir(H)(cyclo-C$_6$H$_{11}$)(PMe$_3$)]. Further heating to 140°C established the equilibrium of Scheme VI with an equilibrium constant of 10.8. From this it was



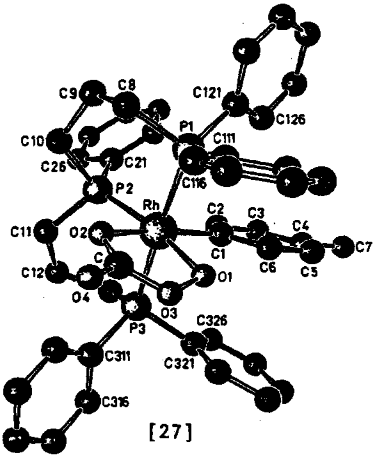
[26]

$$[\text{cp'Ir(H)(cyclo-C}_6\text{H}_{11})(\text{PMe}_3)] + n\text{-C}_5\text{H}_{12} \rightleftarrows [\text{cp'Ir(H)(}n\text{-C}_5\text{H}_{11})(\text{PMe}_3)] + \text{cyclo-C}_6\text{H}_{12}$$

Scheme VI

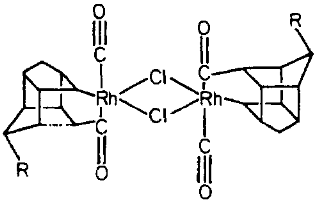
determined that the iridium-carbon bond strength in the n-pentyl complex is approximately 5.5 kcal/mol stronger than that in the cyclohexyl complex. Thus a primary alkyl group binds more strongly than a secondary alkyl group which explains why the secondary pentyl complexes are converted to the n-pentyl complex. In all these processes it is presumed that reductive elimination of alkane from the alkyl hydride complexes occurs to form {cp'Ir(PMe_3)} to which oxidative addition of a new carbon-hydrogen bond can occur. It was further found that heating [cp'Ir(H)(cyclo-C_6H_{11})(PMe_3)] in cyclooctane at 140°C under 20 atm pressure of methane gave [cp'Ir(H)(Me)-(PMe_3)] again demonstrating the greater strength of primary carbon-iridium bonds. This last complex can also be prepared by treatment of [cp'Ir(Me)-Cl(PMe_3)] with lithium borohydride (ref. 109a).

Heating [Rh(DPPE)(η-$C_6H_5BPh_3$)] with various phosphines or amines (L) in THF yielded [Rh(Ph)(DPPE)L] via cleavage of the π-bonded phenyl group from the tetraphenylborate moiety. The same reaction using formaldehyde in place of the Lewis base ligand gave a mixture of several compounds but again it appeared that a phenyl group had been transferred to the metal (ref. 110). A phenyl group transfer also occurs in the reaction of [Rh(dbm)$(CO)_2$] with excess triphenylstibine which gives [Rh$(Ph)_2$(dbm)$(SbPh_3)_2$] (ref. 111). The complex [Rh(mesityl)(CO)$(PPh_3)_2$] gives a mixture of [Rh(mesityl)$(P(OMe)_3)_3$] and [Rh(mesityl)$(P(OMe)_3)_2$(PPh_3)] on reaction with the phosphite under mild conditions. The related complexes [M(R)(CO)$(PPh_3)_2$] (R = CH_2SiMe_3, p-tolyl; M = Rh, Ir) and [Ir(CH_2SiMe_3)(bdpp)] undergo reaction with carbon dioxide under 30-60 atm pressure but a mixture of products results. However with [Rh(p-tolyl)(bdpp)] the peroxycarbonate complex [27] is obtained. Since the use of rigorously purified carbon dioxide in this reaction yields only an unstable adduct and no formation of [27] is noted until oxygen is introduced, it is thought that in the original reaction traces of oxygen were present (refs. 112, 113).



[27]

Isomerization of 1,3-dihomocubane to dicyclopentadiene occurs on reaction with [RhCl(NBD)$]_2$ presumably via initial oxidative addition of a strained carbon-carbon bond to the metal. With [RhCl$(CO)_2]_2$ a metal-containing product proposed to be [28] (R = H) was formed which on heating, or more efficiently on reaction with triphenylphosphine, formed the ketone [29]. An analog of [28] with R = OH was prepared similarly from the parent carbinol but when the substituent is carboxymethyl no stable complex was formed. Instead the products were [29] (R = C(O)OMe) and [30] - [32]. With [33], $[RhCl(CO)_2]_2$ formed [28] and [29] (R = =O) plus [34]. The rate constants for these reactions were found to correlate well with the calculated strain energies of the parent homocubanes (ref. 114). In related work, $[RhCl(CO)_2]_2$ reacts with pentacyclo$[5.3.1.0^{2,6}.0^{3,5}.0^{5,9}]$undecane to yield [35] which on further reaction with triphenylphosphine at room temperature formed [36] rather than the expected ketone [37]. Refluxing a chloroform solution of



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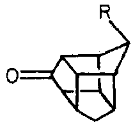

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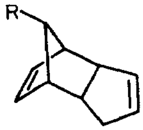

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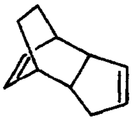

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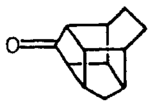
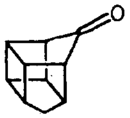


[32]



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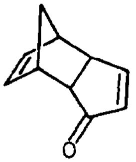

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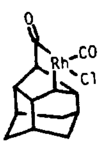

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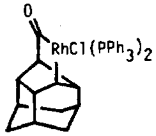
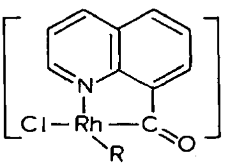


[36]

[37]

[36] or of [35] plus triphenylphosphine gave back the starting hydrocarbon (ref. 115). A variety of 8-acylquinolines react with $[RhCl(C_2H_4)_2]_2$ to form [38] which can be solubilized as their pyridine adducts [39] (L = py; R = bz, Et, Me, CD_2Ph, $C\equiv CPh$). Reductive elimination from [39] is promoted by



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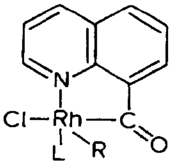
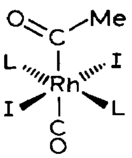
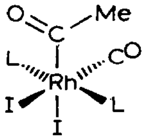


[39]

addition of carbon monoxide or trimethylphosphine (ref. 116). Oxidative addition of methyl iodide to $[Rh(PPh_3)_3](HC(SO_2CF_3)_2)$ (see also reference 756) yields the square pyramidal complex $[RhMeI_2(PPh_3)_2]$ which reacts further with sulfur dioxide to form $[Rh(S(O)_2Me)I_2(PPh_3)_2]$ and with various Lewis base ligands to give $[Rh(Me)(L)I_2(PPh_3)_2]$ (L = py, $CNBu^t$) or $[Rh(Me)I_2L_3]$ (L = PMe_3, $P(OMe)_3$). Addition of carbon monoxide to $[Rh(Me)I_2(PPh_3)_2]$ occurs reversibly to initially give $[Rh(C(O)Me)I_2(PPh_3)_2]$ and on prolonged treatment [40] and [41] (L = PPh_3). Complexes [40] and [41] interconvert

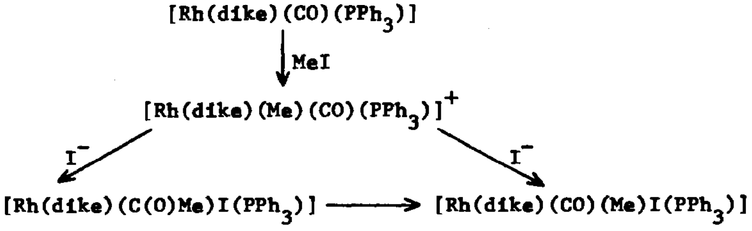


[40]



[41]

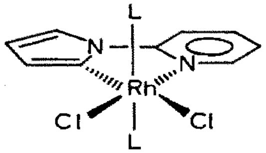
via the five-coordinate acyl precursor but apparently do not do so directly. Reductive elimination of methyl iodide can also occur from the five-coordinate acyl (ref. 117). Two kinetic studies have been made on the oxidative addition of methyl iodide to square planar rhodium(I) complexes. The first proposed mechanism of Scheme VII (dike = acac, tfac, hfac) (ref.



Scheme VII

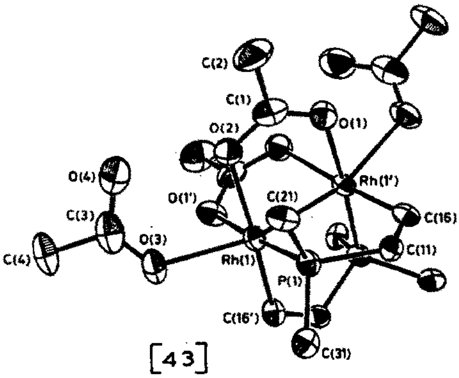
118). The second used $Bu^n_4N[Rh(CO)_2I_2]$ and found that solvent effects were modest, that the presence of excess halide ion produces a moderate enhancement which was interpreted as a salt effect and that added Lewis bases produced a substantial rate enhancement. Since neither $[Rh(CO)_2(L)I]$ (L = Lewis base) nor $[Rh(CO)_2I_2]^-$ by itself reacted as fast as did the latter in the presence of both L and excess I^- it was proposed that either $[Rh(CO)_2(L)I_2]^-$ or $[Rh(CO)_2I_3]^{2-}$ is the most reactive species towards methyl iodide (ref. 119).

The rate of oxidative addition of propanoyl chloride to $[RhCl(PPh_3)_3]$ is accelerated up to ten-fold by the addition of small amounts of linear polyethers. The results were attributed to a through-space interaction of the ether oxygens with the rhodium thereby increasing the electron density on the metal (ref. 120). Refluxing xylene solutions of $[Rh_2Cl_6(PBu^n_3)_4]$ and 2-(pyrrolyl)pyridine causes the formation of the o-metallated complex [42]



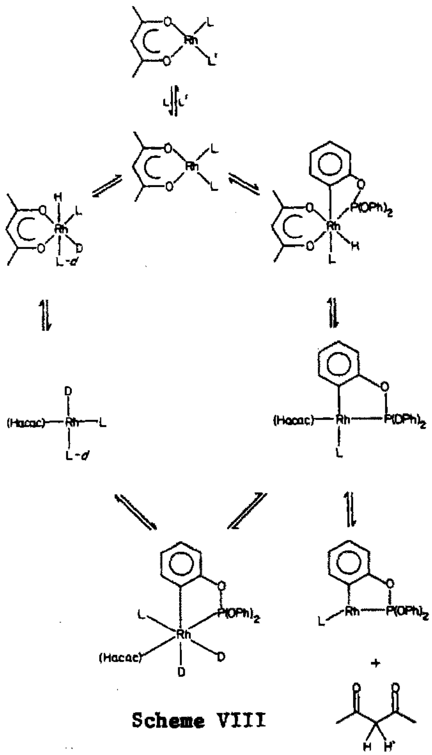
[42]

(L = PBu^n_3) (ref. 121). Similarly, refluxing a solution of $[Rh_2(O_2CMe)_4(MeOH)_2]$ and triphenylphosphine in glacial acetic acid forms the o-metallated triphenylphosphine complex [43] (outer portions of the phenyl rings omitted for clarity) (ref. 122). The oxidative addition of deuterium to $[Rh(acac)(P(OPh)_3)_2]$ at 75°C has been monitored by NMR. Deuterium incorporation into the o-positions of the phenyl rings of the phosphite ligands and



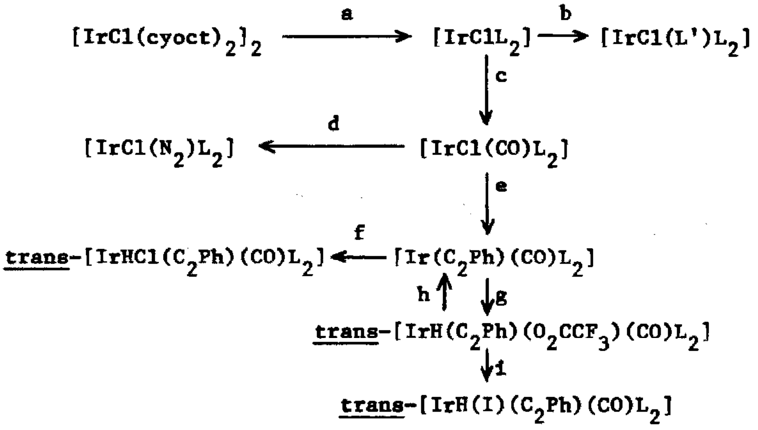
[43]

into the γ-position of the acetylacetonate ligand was observed to occur at the same rate. At 60°C however the deuteration of the phenyl rings occurs much more rapidly. When run in the presence of excess phosphite or acetylacetone, deuterium incorporation occurred into both free and bound ligands implying ligand exchange occurs and does so at a rate which is faster than for deuterium incorporation. Using deuterated phosphite ligands in the original complex allows deuterium incorporation into the acetylacetonate ligand in the absence of added hydrogen or deuterium. The results are explained by the mechanism of Scheme VIII (refs. 123, 124).



Scheme VIII

The synthesis of a number of acetylide and related complexes of iridium is outlined in Scheme IX (L = PPr^i_3) (ref. 125). Replacement of the triphenylphosphine ligands in $[Ir(R)(CO)(PPh_3)_2]$ by tridentate phosphines occurs readily to give $[Ir(R)(CO)(L_3)]$ (R = CH_2SiMe_3; L_3 = bdpp, $MeP(CH_2CH_2CH_2PPh_2)_2$, $PhP(CH_2CH_2PPh_2)_2$. R = CH_2Bu^t; L_3 = bdpp. R = *p*-tolyl; L_3 = $PhP(CH_2CH_2PPh_2)_2$). With the analogous rhodium complex (R = CH_2Bu^t, *p*-tolyl) however the carbonyl group is also replaced on reaction with bdpp. Oxidative addition of carboxylic acids to $[Ir(R)(CO)(PPh_3)_2]$ yields *trans*-$[IrH(O_2CR')(R)(CO)(PPh_3)_2]$ when R = Ph, *p*-tolyl and R' = Me or when R = *p*-tolyl, 2,4-$Me_2C_6H_3$ and R' = Et but when R = CH_2Bu^t or CH_2SiMe_3 subsequent

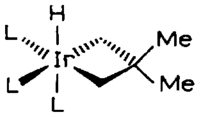


a) L in pentane. b) L' (= py, MeCN). c) CO in pentane. d) $PhC(O)N_3$.
e) LiC≡CPh. f) HCl in benzene. g) TFA. h) Nacp. i) NaI.

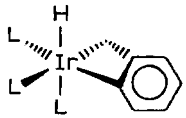
Scheme IX

reductive elimination of RH and further oxidative addition of the acid occurs to yield $[IrH(O_2CR')_2(CO)(PPh_3)_2]$ (R' = Me, Et, Pr^i). This last set of complexes can be reconverted to $[Ir(O_2CR')(CO)(PPh_3)_2]$ by heating in toluene. The rhodium analogs $[Rh(O_2CR')(CO)(PPh_3)_2]$ (R' = Me, Bu^t, p-tolyl) form directly on reaction of $[Rh(R)(CO)(PPh_3)_2]$ (R = CH_2SiMe_3, p-tolyl) with the appropriate carboxylic acid. This difference in behavior between rhodium and iridium is also seen in the reactions of [M(R)(bdpp)] (M = Rh; R = CH_2Bu^t, p-tolyl. M = Ir; R = CH_2Bu^t, CH_2SiMe_3) with carboxylic acids where the products are $[Rh(O_2CR')(bdpp)]$ (R' = Me, p-tolyl) and $[IrH(O_2CR')_2(bdpp)]$ (R' = Me, Et) (refs. 126, 127).

Hydrated rhodium(III) and iridium(III) chlorides metallate 2-phenylpyridine and benzo(h)quinoline in refluxing glycerol or 2-methoxyethanol to form $[M_2(C\text{-}N)_4(\mu\text{-}Cl)_2]$ (M = Rh, Ir; C-N = metallated ligand) as a racemate. The electronic absorption and emission spectra were measured. For the rhodium complexes the emission appeared to involve an intraligand π-π^* process while for iridium it appeared to be a metal-ligand charge transfer process (ref. 128). Neopentyllithium reacts with cis-$[IrH(CH_2CN)(PMe_3)_4]$ to give [44] (L = PMe_3) while [45] (L = PMe_3) is formed when benzylmagnesium bromide is used (ref. 129). Bromomethyl methyl ether adds to $[IrH(PMe_3)_4]$ to give $[Ir(CH_2OMe)H(PMe_3)_4]Br$ which is deprotonated to $[Ir(CH_2OMe)(PMe_3)_4]$ by potassium tert-butoxide. This in turn undergoes ligand displacement on refluxing with di(p-tolyl)acetylene in deuterobenzene to form [46] (Ar = p-tolyl).

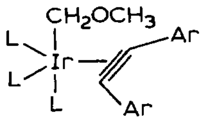


[44]

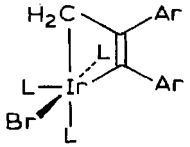


[45]

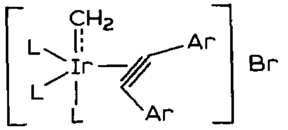
Treatment of [46] with bromotrimethylsilane converts it to [47] possibly via [48] as an intermediate. In dichloromethane solution [47] slowly isomerizes



[46]

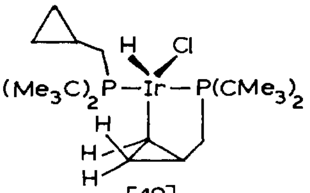


[47]

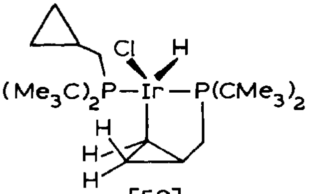


[48]

to the mer isomer. This work is part of a study of the possible involvement of transition metal methylene species in carbon-carbon bond formation as has been suggested in one mechanistic proposal for the Fischer-Tropsch process (ref. 130). Reaction of $[IrCl(cyoct)_2]_2$ with di-tert-butylcyclopropylmethylphosphine yields a mixture of [49] and [50]. These react with hydrogen to

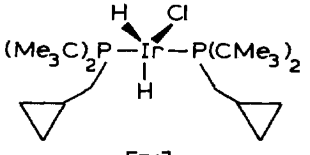


[49]

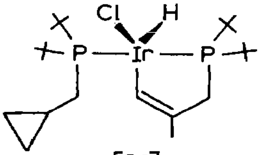


[50]

form [51] and with dichloromethane to give [52]. Carbonylation of [52]

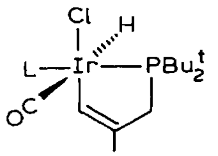


[51]

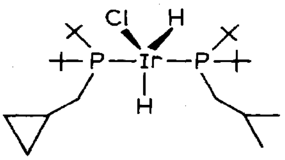


[52]

yields [53] (L = $Bu^t{}_2PCH_2$-◁) while with hydrogen [54] is formed (ref. 131). A kinetic study of the reductive elimination of the carbaborane 7-Ph-1,

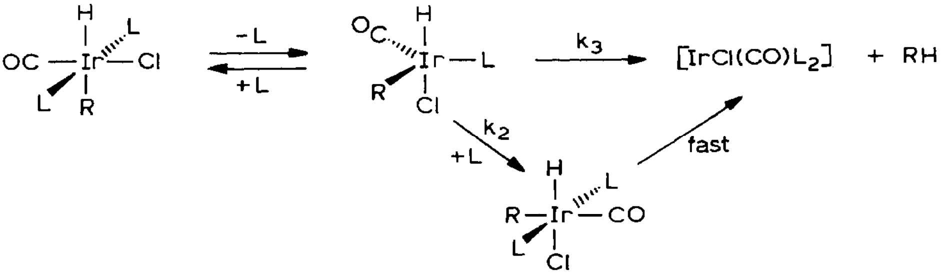


[53]



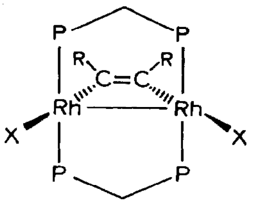
[54]

$7\text{-}C_2B_{10}H_{11}$ from trans-$[Ir(H)(R)Cl(CO)(PPh_3)_2]$ (R = $7\text{-}Ph\text{-}1,7\text{-}C_2B_{10}H_{10}$) was reported to indicate the mechanism of Scheme X (L = PPh_3). Support for the postulated phosphine dissociation was provided by the observation that $[Ir(H)(R)Cl(CO)(PPh_3)_2]$ reacted with carbon monoxide to yield $[Ir(H)(R)Cl(CO)_2(PPh_3)]$ (ref. 132). Further studies have been reported on $[(2,2'\text{-bipyridinyl-}C^3,N')bis(2,2'\text{-bipyridine})Ir](BF_4)_2\cdot H_2O$. The proton and ^{13}C NMR spectra were analyzed in detail and the ^{13}C resonance for the metallated carbon atom in the unique ligand identified. All proton resonances associated with this ligand were also assigned (ref. 133).

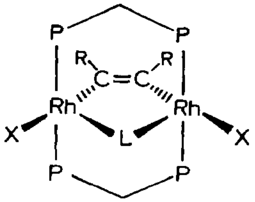


Scheme X

A significant area of continuing research is concerned with binuclear complexes bridged by DPM or by methylene ligands. In the first group, complexes of the type [55] (X = Cl; R = CO_2Me) are prepared from $[RhCl(COD)]_2$, DPM and DMAD. That with X = Cl and R = CF_3 has been reported previously (1982 Annual Survey, refs. 120, 121) and can be converted to the iodo analog by metathesis with potassium iodide in methanol/dichloromethane. Reversible insertion into the metal-metal bond occurs on reaction with carbon monoxide or sulfur dioxide to give [56] (X = Cl; L = CO, SO_2; R = CF_3, CO_2Me. X = I; L = CO, SO_2; R = CF_3). Complex [55] (X = Cl; R = CF_3) adds one equivalent of methyl isocyanide to give a mixture of two isomers of

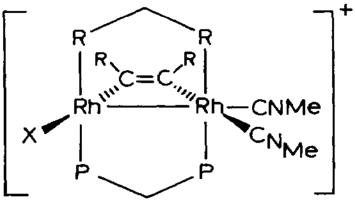


[55]

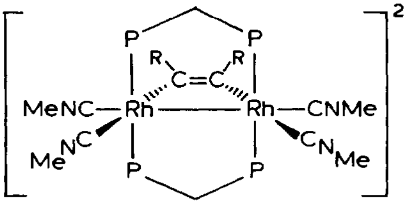


[56]

the mono-adduct while when X = Cl and R = CO_2Me a single species forms. Addition of a second equivalent of the isocyanide forms the cationic species [57] (X = Cl; R = CF_3, CO_2Me) which is converted to [58] by excess isocyanide

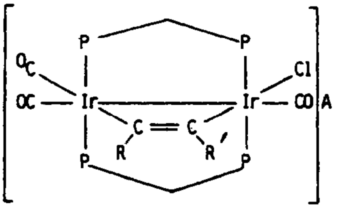


[57]

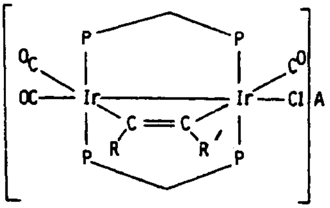


[58]

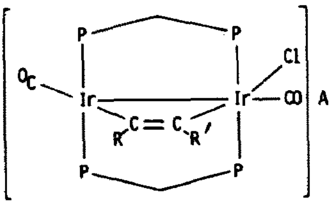
(ref. 134). A new, high-yield synthesis of $[Ir_2(CO)_3Cl(\mu\text{-}CO)(DPM)_2]A$ (A = BPh_4, ClO_4, PF_6) has been reported. All three salts react with electronegatively-substituted acetylenes to form the mixture of isomers [59a,b] (R = R' = CO_2Me). Isomer [59b] slowly converts to [59a] on standing in dichloromethane solution and more readily on refluxing in THF under carbon monoxide. With methyl propiolate only [59a] (R = H, R' = CO_2Me; A = BPh_4) forms. On refluxing [59a,b] (R = R' = CO_2Me; A = ClO_4, PF_6) in THF under a nitrogen purge one carbonyl ligand is lost to form [60] which undergoes chloride exchange between the two metals presumably <u>via</u> a chloride-bridged intermediate. Complex [60] readily adds ligands to give [61] (L = CO, $P(OMe)_3$, MeCN). By contrast, [59a,b] (R = R' = CO_2Me; A = BPh_4) on refluxing in THF under a nitrogen purge gives a mixture of [62] and [63]. Complex [63] (R = R' = CO_2Me; A = ClO_4) can also be prepared from [60] (R = R' = CO_2Me; A = ClO_4) and one equivalent of sodium tetraphenylborate suggesting that it is



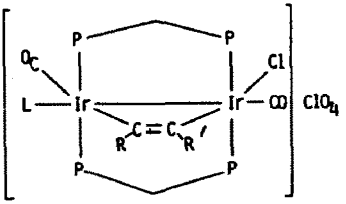
[59a]



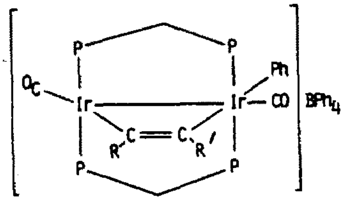
[59b]



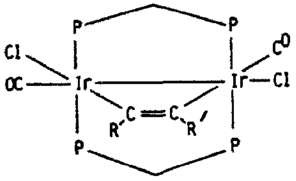
[60]



[61]

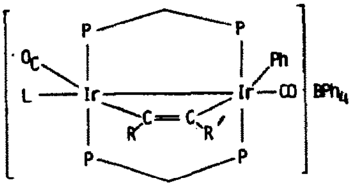


[62]

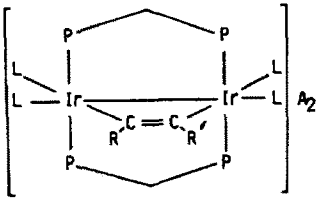


[63]

the cationic dicarbonyl complex which attacks the tetraphenylborate ion in the first reaction. Unlike [60], [63] is not fluxional in solution but it does add ligands to give [64] (R = R' = CO_2Me; A = BPh_4; L = CO, CNBu^t). Also [59a,b] reacts with excess tert-butylisocyanide to form [65] (L =

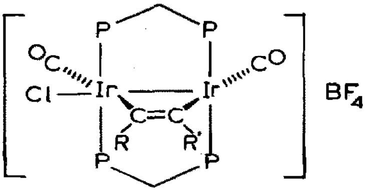


[64]



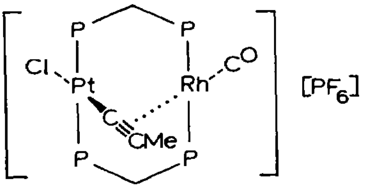
[65]

CNBu^t; R = R' = CO_2Me; A = BPh_4) (ref. 135). Complex [63] (R = R' = CO_2Me, CF_3, H) also forms when $[IrCl(CO)(DPM)]_2$ is treated with the appropriate acetylene and can be converted to [60] (R = R' = CF_3, CO_2Me; A = BF_4) on reaction with silver tetrafluoroborate. Addition of carbon monoxide forms [59a] (R = R' = CO_2Me, CF_3; A = BF_4). Addition of acetylenes to $[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BF_4$ forms [66] (R = R' = CF_3, CO_2Me) which slowly isomerizes to



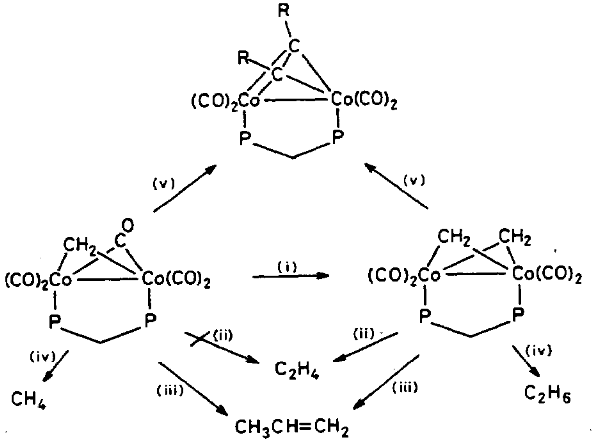
[66]

[60] (R = R' = CF_3, CO_2Me; A = BF_4) in solution and reacts with carbon monoxide to give [59a] (R = R' = CF_3, CO_2Me; A = BF_4) (ref. 136). The complex [PtCl(C≡CMe)(μ-DPM)$_2$Rh(CO)]PF_6 has been found from an x-ray crystal structure study to contain an interaction of the acetylide moiety with the rhodium as depicted in [67] (ref. 137).



[67]

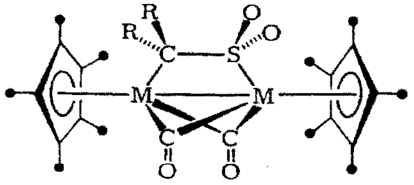
Some chemistry of the methylene-bridged complex [$Co_2(CO)_4$(μ-CO)(μ-CH_2)(μ-DPM)] is outlined in Scheme XI. The observation that [$Co_2(CO)_4$(μ-CH_2)$_2$(μ-DPM)] forms only ethylene on pyrolysis while [$Co_2(CO)_4$(μ-CH_2)(μ-CO)(μ-DPM)] does not was taken as evidence for the intramolecular coupling of



(i) CH_2N_2. (ii) Δ, 80°-90°C. (iii) C_2H_4. (iv) H_2 at 80°-90°C.
(v) RC≡CR (R = CF_3, Ph).

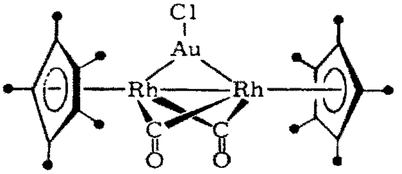
Scheme XI

the methylene groups and was considered to provide support for the proposal that the Fischer-Tropsch hydrocarbon synthesis involves coupling of surface methylene groups. The products observed in the reactions with hydrogen suggested that hydrogen initially undergoes oxidative addition followed by reductive elimination of alkane (ref. 138). Further examples of alkylidene-bridged complexes, [cp'$_2M_2(CO)_2$(μ-CH(CHO))] (M = Co, Rh) and [cp'$_2Co_2$(μ-CO)$_2$(μ-CHMe)] have been synthesized from [cp'$_2M_2$(μ-CO)$_2$] and the appropriate diazoalkane. In this type of complex there appears to be no correlation between the metal-metal distance found in those whose structures have been determined and the formal metal-metal bond order determined from the 18-electron rule (refs. 139, 140). A simplified method for the preparation of the complexes $[cp'_2Rh_2(CO)_2(\mu\text{-}CRR')]$ (R = R' = $(CH_2)_8Me$, *cyclo*-C_3H_5. R = *cyclo*-C_3H_5; R' = Me. R, R' = $(CH_2)_n$ (n = 3, 4, 7, 11), $CH_2CH(Me)(CH_2)_8$-$CH(Me)CH_2$, $CH_2CH{=}CH(CH_2)_4$) and $[cp'_2Co(\mu\text{-}CO)_2(\mu\text{-}CRR')]$ (R = R' = $(CH_2)_8Me$. R, R' = $CH_2CH{=}CH(CH_2)_4$, $(CH_2)_n$ (n = 3, 4, 7)) involves reaction of $[cp'_2M_2$-$(\mu\text{-}CO)_2]$ with the appropriate hydrazone, $RR'C{=}NNH_2$, in THF in the presence of manganese dioxide thereby eliminating the necessity of preparing diazoalkanes (ref. 141). Sulfur dioxide reacts with binuclear rhodium and cobalt complexes in a variety of ways. With $[cp'_2M_2(\mu\text{-}CO)_2]$ and $[cp'_2Co_2(\mu\text{-}CO)$-$(\mu\text{-}CH_2)]$ it simply adds to the metal-metal bond to give $[cp'_2M_2(CO)_2(\mu\text{-}SO_2)]$ (M = Co, Rh) and $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}SO_2)]$. However with $[cp'_2Rh_2(\mu\text{-}CO)$-$(\mu\text{-}CPh_2)]$ rearrangement occurs to yield the carbene complex $[cp'Rh(CO)$-$(\mu\text{-}SO_2)Rh({=}CPh_2)(cp')]$ while with $[cp'_2M_2(CO)_2(\mu\text{-}CR_2)]$ (M = Rh, Co; R = H. M = Rh; R = Ph) the product is [68]. Other reactions of $[cp'_2Rh_2(\mu\text{-}CO)_2]$

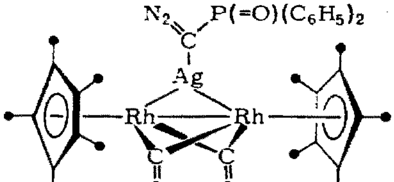


[68]

are those with elemental selenium to give $[cp'_2Rh_2(CO)_2(\mu\text{-}Se)]$, with [AuCl-(CO)] to form [69], with diazodiphenylphosphinylmethylsilver to yield [70] and with α-diazoketones. In the last system the initial product is the

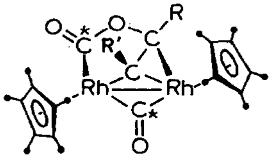


[69]



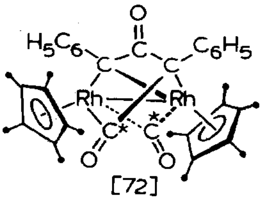
[70]

expected methylene-bridged species $[cp'_2Rh_2(CO)_2(\mu\text{-}CR(C(O)R'))]$ (R = R' = CO_2Et; R = Me, R' = C(O)Me; R = Et, R' = C(O)Et) but when R = R' = Me, Ph, *p*-anisyl or R = Me and R' = Ph a further reaction ensues to form [71] *via* nucleophilic attack of the keto group on a carbonyl ligand. With 1,3-dioxo-2-diazoindane $[cp'_2Rh_2(\mu\text{-}CO)_2]$ gives the simple methylene-bridged dimer,

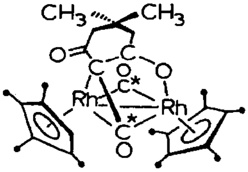


[71]

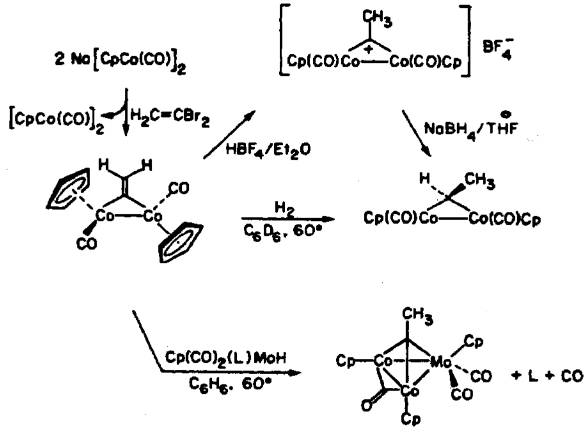
but with $PhC(=N_2)C(O)C(=N_2)Ph)$ the initially-formed $[cp'_2Rh_2(CO)_2$-$(\mu$-$C(Ph)C(O)C(=N_2)Ph)]$ reacts further to give [72]. In the same reaction, diazodimedone forms [73] (refs. 142, 143). The electron impact induced decomposition of $[cp'_2M_2(CO)_2(\mu$-$CRR')]$ (M = Co, Rh; R = R' = H. R = H; R' = CF_3. M = Rh; R = R' = D, Me, CO_2Me. R = H; R' = Me, Et, CO_2Et. R = COMe; R' = CO_2Bu^n. R, R' = $(CH_2)_5$), $[cp'_2Co_2(\mu$-$CO)(\mu$-$CPh_2)]$ and $[cp'_2Co_2(\mu$-$CO)_2$-$(\mu$-$CRR')]$ (R = CO_2Et; R' = H, CO_2Et. R, R' = $(CH_2)_5$) has been studied. A general feature is the loss of the alkylidene fragment as H_2CRR' with the necessary hydrogen being abstracted from the cp' rings. Also, the alkane elimination was preceded by loss of a carbonyl ligand (ref. 144). In related work, the radical anion $[cpCo(\mu$-$CO)_2]^{\dot{-}}$ as its sodium salt reacts with 1,1-dibromoethylene to form $[cp_2Co_2(CO)_2(\mu$-$C{=}CH_2)]$ whose chemistry is outlined in Scheme XII (L = CO, PPh_3) (ref. 145).



[72]

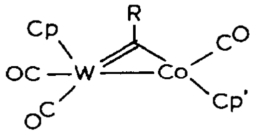


[73]

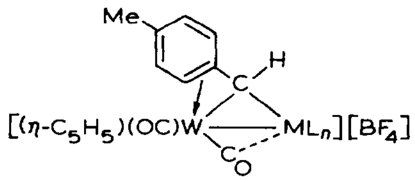


Scheme XII

Protonation of [74] (R = *p*-tolyl) with tetrafluoroboric acid yields [75]

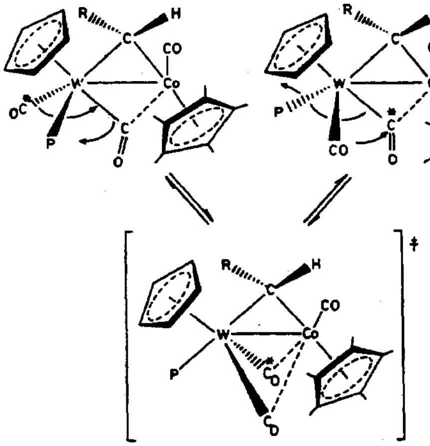


[74]



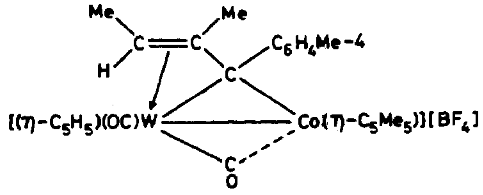
[75]

(ML_n = cp'Co(CO)) which adds a phosphine ligand at tungsten to give a species which is fluxional as depicted in Scheme XIII. Complex [75] reacts

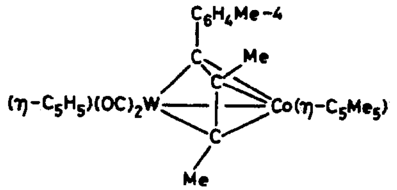


Scheme XIII

with but-2-yne and with lithium tri-*sec*-butylborohydride to give [76] and [74] respectively. Complex [76] can also be formed by protonation of [77]

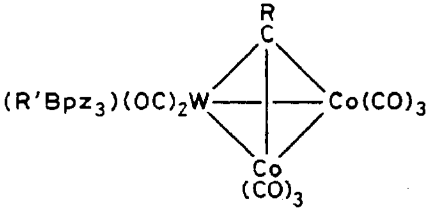


[76]

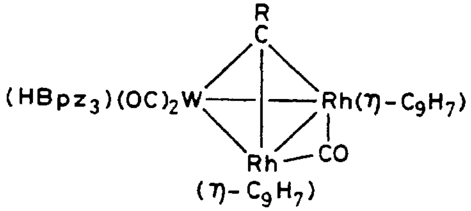


[77]

with tetrafluoroboric acid (refs. 146, 147). Reaction of [$(R'Bpz_3)W(\equiv CR)(CO)_2$] with [$Co_2(CO)_8$] or with [$(\eta^5-C_9H_7)Rh(CO)_2$] yields [78] (R = *p*-tolyl; R' = H, pz. R = Me; R' = H) and [79] (R = *p*-tolyl; R' = H) respectively (ref. 148). The complex [cp'Cu(THF)] can be prepared at low temperature from copper(I) chloride and pentamethylcyclopentadienyllithium and displays

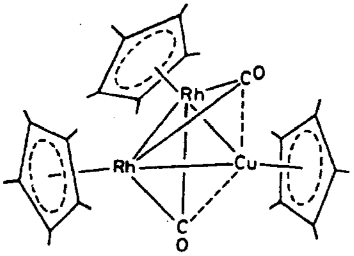


[78]



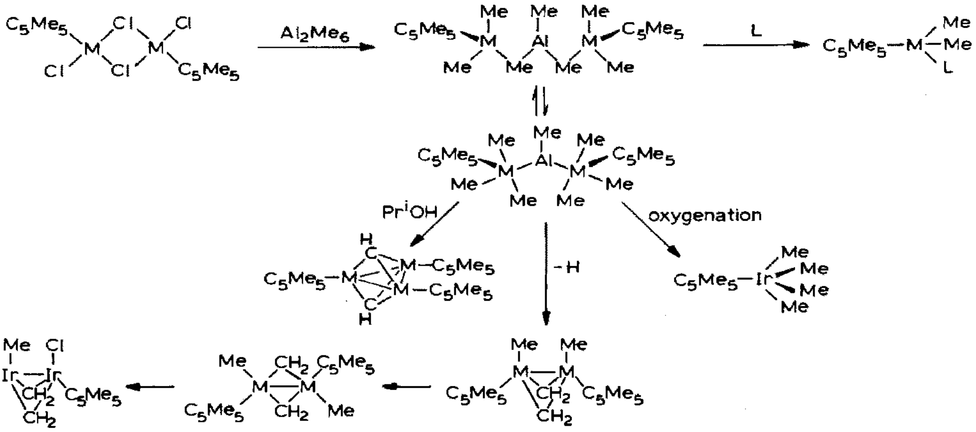
[79]

a "carbene-like" reactivity towards metal-metal and metal-carbon multiple bonds. Thus on reaction with $[cp'_2Rh_2(\mu\text{-}CO)_2]$, for example, the product is [80] (ref. 149).



[80]

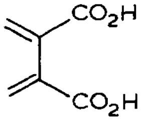
Protonation of a *cis*-, *trans*-mixture of $[cp'_2Rh_2Me_2(\mu\text{-}CH_2)_2]$ with hydrogen chloride in pentane forms $[cp'_2Rh_2Cl_2(\mu\text{-}CH_2)_2]$ which reacts further with Grignard reagents to give $[cp'_2Rh_2R_2(\mu\text{-}CH_2)_2]$ (R = Et, Pr^n, Bu^n) as a mixture of *cis* and *trans* isomers and with halide and pseudohalide ions to give *trans*-$[cp'_2Rh_2X_2(\mu\text{-}CH_2)_2]$ (X = Br, I, N_3, SCN, CN, NCO). Donor ligands displace chloride from $[cp'_2Rh_2Cl_2(\mu\text{-}CH_2)_2]$ in a stepwise fashion in the presence of hexafluorophosphate to give *cis*- plus *trans*-$[cp'_2Rh_2Cl(L)(\mu\text{-}CH_2)_2]PF_6$ and then *trans*-$[cp'_2Rh_2(L)_2(\mu\text{-}CH_2)_2](PF_6)_2$ (L = MeCN, CO, H_2O). The bis(acetonitrile) complex can also be formed directly from $[cp'_2Rh_2Me_2(\mu\text{-}CH_2)_2]$ by protonation in acetonitrile solution and on treatment with carbon monoxide can be reversibly converted to $[cp'_2Rh_2(CO)(MeCN)(\mu\text{-}CH_2)_2]^{2+}$ and $[cp'_2Rh_2(CO)_2(\mu\text{-}CH_2)_2]^{2+}$. This last species on reaction with sodium carbonate in methanol forms $[cp'_2Rh_2(CO_2Me)_2(\mu\text{-}CH_2)_2]$. In the presence of hexafluorophosphate ion $[cp'_2Rh_2Cl_2(\mu\text{-}CH_2)_2]$ reacts with carboxylic acids to form $[cp'_2Rh_2(\mu\text{-}O_2CR)_2(\mu\text{-}CH_2)_2]PF_6$ (R = Me, CF_3) and with neutral bidentate ligands to give $[cp'_2Rh_2(\mu\text{-}L_2)(\mu\text{-}CH_2)_2](PF_6)_2$ (L_2 = DPM, pyridazine). If the protonation of $[cp'_2Rh_2Me_2(\mu\text{-}CH_2)_2]$ is performed with one equivalent of *p*-toluenesulfonic acid in donor solvents the product is $[cp'_2Rh_2Me(L)(\mu\text{-}CH_2)_2]^+$ (L = MeCN, Bu^tCN, PhCN, py, α-picoline, CO). The same reaction with $[cp'_2Rh_2R_2(\mu\text{-}CH_2)_2]$ (R = Et, Pr^n, Bu^n) in acetonitrile produces analogous species (L = MeCN). All of these undergo a *cis* → *trans* isomerization in solution which is proposed to proceed *via* a $\{Rh(\mu\text{-}R)(\mu\text{-}CH_2)_2Rh\}$ intermediate formed following dissociation of the ligand L (refs. 150, 151). A more extensive report of the reaction of $[cp'_2M_2Cl_4]$ (M = Rh, Ir) with hexamethyldialuminum has appeared and the major results are presented in Scheme XIV (L = PPh_3, C_2H_4) (ref. 152).



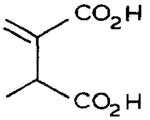
Scheme XIV

A substantial number of studies continue to be reported on vitamin B_{12}, its derivatives and model compounds. One problem still unresolved is a full understanding of the mechanism(s) of biological reactions promoted by B_{12} such as in the diol dehydratase and methylmalonyl-CoA mutase systems. Two studies of the thermolysis of adenosylcobalamin have resulted in determinations of the cobalt-carbon bond dissociation energy. Although the derived values differ significantly (26±2 *vs* 32 kcal/mol) both groups conclude that these values are too high to be consistent with the rates observed for the biological reactions promoted by B_{12}. It thus appears that the required coenzyme must induce a weakening of the cobalt-carbon bond by 10-15 kcal/mol, probably by causing a deformation of the corrin ring which exerts steric pressure on the 5'-deoxyadenosyl moiety. The reason for the discrepancy between the two bond dissociation energy values is not apparent although the studies used rather different conditions (refs. 153, 154). Another series of papers reports on the dealkylation of methyl- and ethylcobalamin and the corresponding aquocobinamides by various metal ions such as $[PtX_4]^{2-}$ (X =

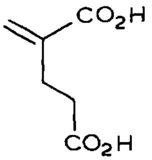
Cl, CN, SCN) $[FeCl_n]^{3-n}$ and $[HgCl_n]^{2-n}$. In all instances the initial step appears to be a rapid association of the metal complex with the corrin ring which is followed by a rate-determining electron transfer to the added metal. The alkyl radical which results can then react with sources of hydrogen (predominantly solvent) or, in the third system, be trapped by the mercury(I) species generated in the first step (refs. 155-157). The zinc reduction of aquocobalamin in glacial acetic acid is proposed to generate a five-coordinate Co(III) corrinoid species with an axial hydride ligand since subsequent introduction of ethylene forms ethylcobalamin. Similarly, zinc reduction of cyanoaquocobinamide followed by reaction with propylene gives isopropylcobinamide (ref. 158). Reaction of vitamin $B_{12}s$ with bromomethylitaconic acid gives the expected alkylated cobalt corrinoid complex. Photolysis of this species in a pH 7 buffer provides a 60% yield of [81] plus lesser amounts of [82] and [83]. The first results from a β-elimination process while the others arise from cobalt-carbon bond homolysis and



[81]



[82]



[83]

heterolysis respectively. The same products are seen when the alkylated species is decomposed by cyanide ion but here [83] predominates suggesting the major pathway is now displacement of the alkyl carbanion by the cyanide (ref. 159). In B_{12} derivatives containing the $\{CoCH_2X\}$ moiety (X = OH, NH_2) the 1,2-shift of the X function is considered to occur by a three-step process via radical intermediates although interaction of the cobalt with an α-hydrogen may also be involved (ref. 160). The same group has also investigated the mechanism of B_{12}-catalyzed activation and cleavage of carbon-hydrogen bonds and concluded that the original cobalt-carbon bond exhibits a carbenoid character (ref. 161). In a final paper on alkylcobalamins it was found that in the base-off form the ^{31}P chemical shifts of the phosphodiester moiety in the nucleotide portion were essentially the same while in the base-on form this parameter was not constant and the values observed could be correlated with the apparent free energy of coordination of the base (5,6-dimethylbenzimidazole). This was attributed to the existence of different conformations of the phosphodiester moiety across the series as a result of differing cobalt-nitrogen (of the 5,6-dimethylbenzimidazole) bond lengths (ref. 162).

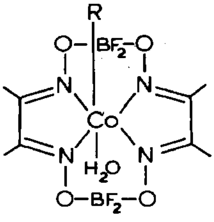
Cobaloximes and related complexes continue to attract attention although a greater precentage of the work reported this year appears to focus on their chemistry as an independent area rather than as a model for vitamin B_{12} chemistry. Reaction of $[Co(dmgH)_2]^-$ with 4-chloro-4,4-dialkylbut-3-ynes in the presence of pyridine forms $[(R_2C(C\equiv CMe))Co(dmgH)_2py]$ (R = Me; R_2 = $(CH_2)_5$) whereas the same reaction with the analogous prop-1-ynes yields the allenyl derivatives $[(RR'C=C=CH)Co(dmgH)_2py]$ (R = R' = H, Me. R = H; R' = Me). The results are considered to indicate that steric effects are important in determining the course of the reaction. The allenyl complex (R = R' = H) yields only allene when treated with sodium borohydride in ethanol but from the other two some of the acetylene, $HC\equiv CCHRR'$ (R = H, Me; R' = Me), is seen in addition to the appropriate allene. The same treatment of the first set of complexes, $[(R_2C(C\equiv CMe))Co(dmgH)_2py]$ (R = H, Me), also gives a mixture of allenes and acetylenes ($R_2C=C=CHMe$ and $MeC\equiv CCR_2H$). The results are all consistent with a mechanism involving an initial one-electron reduction of the cobalt complex followed by homolysis of the cobalt-carbon bond (refs. 163, 164). The reaction of $[Co(dmgH)_2py]$ with (-)-methyl-β-chloro-β-(2-methylnaphthyl)acrylate gives the corresponding organocobalt complex with complete retention of configuration about the carbon-carbon double bond suggesting displacement of chloride by the cobalt anion in a concerted process (ref. 165). Photolysis of $[(allyl)Co(dmgH)_2py]$ and related species in the presence of arylsulfonyl chlorides promotes a regiospecific radical chain reaction to form sulfones (ref. 166). In related work, photolysis of pent-4-enylcobaloximes in the presence of trichloromethanesulfonyl chloride forms 2-(β,β,β-trichloroethyl)sulfolanes also by a radical process. The observation that secondary alkylcobaloximes catalyze the photochemical reactions of olefins with trichloromethanesulfonyl chloride to also form β,β,β-trichloroethylsulfolanes was taken to indicate the formation of 3,3,3-trichloropropyl radicals which capture sulfur dioxide (ref. 167). While cobalt-carbon bond cleavage is the primary process in the reaction of chlorine or bromine with $[RCo(dmgH)_2py]$ (R = 2-furyl- or 2-thienylmethyl), when R = 3-furyl- or 3-thienylmethyl halogenation of the heterocyclic ring occurs more rapidly (ref. 168). The hydroxide-induced decomposition of $[RCo(dmgH)_2py]$ (R = 2-alkoxyalkyl) gives a mixture of the corresponding olefin and alcohol but the tetrahydrofurfuryl complex forms pent-4-en-1-ol (ref. 169). Treatment of $[ClCo(dmgH)L]$ (L = 4-cyanopyridine) with ethyl iodide, sodium borohydride and sodium hydroxide in aqueous methanol not only alkylates the cobalt but also converts the 4-cyanopyridine ligand into a methyl-4-pyridine-carboximidate moiety. An interconversion of the E- and Z-isomers of the imidate ligand was observed (ref. 170).

In the substitution of thiourea for water in [RCo(dmgH)$_2$(H$_2$O)] (R = Et, bz, CF$_3$CH$_2$, CH$_2$X (X = Cl, Br, I)) the activation enthalpy was found to be dependent on both steric and electronic effects associated with the alkyl group (ref. 171). The structure of *trans*-[(adamantyl)Co(dmgH)$_2$(1-methylimidazole)] which was prepared by the standard method shows it to possess the longest cobalt-carbon bond yet found (2.154(5) Å) in this type of complex (ref. 172). The Raman spectra of [(X$_3$C)Co(dmgH)$_2$(4-*tert*-butylpyridine)] (X = H, D) have been analyzed and all bands including ν_{Co-C} have been assigned (ref. 173). Cyclic voltammetric studies have been performed on [RCo(dmgH)$_2$(H$_2$O)] (R = alkyl, bz) and the observed $E_{\frac{1}{2}}$ values were found to correlate with the cobalt-carbon distance (ref. 174). Further ^{19}F NMR studies have been reported on [RCo(dmgH)$_2$(H$_2$O)] (R = *p*- or *m*-FC$_6$H$_4$) and analogs containing the ligands dpgh, salen, saloph and BAE in place of dmgH to assess the extent of inductive and resonance interactions of the aryl group with the metal. In all instances this group is characterized as a σ-donor. The results also indicate that the π-donor ability of the aryl group decreases as its σ-donor capacity increases but the variation is rather small (ref. 175). Exposure of [((R)-1-(methoxycarbonyl)ethyl)-Co(dmgH)$_2$py]·MeOH to x-rays causes a change in the unit cell dimensions without a loss of crystallinity. The solvent methanol is lost from the crystal and the methylcarbonylethyl group undergoes a rotation about the cobalt-carbon bond. Further exposure leads to complete racemization of the complex but without any loss of crystallinity (ref. 176).

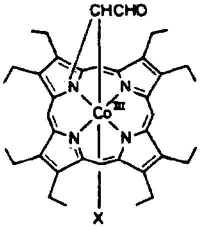
The electrochemical oxidation of [MeCo(salen)] in non-aqueous media is characterized as an ECE process involving reversible, one-electron steps (ref. 177). Photolysis of this complex and analogs in viscous media such as glycerol and polyvinylalcohol films generates [Co^{II}(salen)] which is stabilized against further reaction by the medium (refs. 178, 179). Reaction of [RCo(7-Me-salen)en] (R = Me, Et) with weak acids (LH$^+$ (L = py, γ-picoline, PhNH$_2$, NH$_2$OH, H$_2$O)) in methanol causes conversion to [RCo(7-Me-salen)L$_2$] (ref. 180). Reduction of [Co(saloph)] with sodium borohydride in aqueous methanol followed by addition of alkyl halides and Lewis bases yields [RCo(saloph)L] (R = CH$_2$CN; L = 3,5-lutidine, 1-methylimidazole. R = CH$_2$CF$_3$, bz, *neo*-C$_5$H$_{11}$, Me, Et, Pr^i, Bu^i, *n*-C$_3$H$_6$CN, cy, CH$_2$C(Me)(CO$_2$Et)$_2$; L = py, 4-*tert*-butylpyridine, 4-dimethylaminopyridine). NMR studies of the mechanism of exchange of L in [(NCCH$_2$)Co(saloph)(2,6-lutidine)] indicates it occurs by a D process. The rate is ten orders of magnitude faster than in the analogous dmgH complex and this is suggested to result from a *cis*-effect of the saloph ligand which is partly a ground state effect and partly the result of a greater stability of the five-coordinate intermediate when saloph is the ligand. This is supported by the isolation of [(*neo*-C$_5$H$_{11}$)Co-

(saloph)] when the original synthesis is carried out in the absence of L (ref. 181).

The rates of the reversible alkyl group transfer from [84] to Cr(II) (R = Me, Et, bz, CHO_2Me) have been measured and an S_N2 mechanism involving cobalt-carbon bond homolysis is proposed (ref. 182). Photolysis of [RCo-(BAE)] (R = Me, Pr^n, Bu^n, Bu^s) also causes homolysis of the cobalt-carbon bond (ref. 183). In cyclic voltammetric studies on <u>cis</u>-$[Me_2Co(bipy)_2]ClO_4$ and <u>trans</u>-$[Me_2Co(TIM)]ClO_4$ a reductive cleavage of one cobalt-carbon bond occurs in an irreversible electron-transfer process (ref. 184). The related species $[CoMe_2(TIM)]$ is demethylated by lead(II) ion in aqueous solution to give $[PbMe_4]$ but no reaction is observed with methylcobalamin (ref. 185). Complex [85] (X = Cl, O_2CMe, ClO_4) can be formed from [Co(OEP)X] and diazoacetaldehyde or from [Co(OEP)] and the diazo compound in the presence of oxygen and the anion. It is thermally unstable and on electrochemical reduction the organic group is completely transferred to the porphyrin ring. At this point, the cobalt ion can be replaced by zinc(II) (ref. 186). Aryl olefins can be converted to benzylic alcohols by borohydride in the presence of [Co(TPP)] as a catalyst. Intermediate alkyl cobalt species are proposed to be formed (ref. 187).



[84]

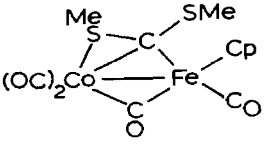


[85]

Substitution of water in $[MeRh(dmgH)_2(H_2O)]$ by other ligands (e.g. N_3^-, SCN^-, I^-, py, thiourea) occurs approximately one hundred times more rapidly than in the cobalt analog. An I_d process is proposed and bond-making in the rate-determining step is thought to be more important here than with the cobalt complex (ref. 188). Toluene and related arenes react with $[Rh(OEP)]_2$ to give [RhH(OEP)] plus $[Rh(CH_2Ar)(OEP)]$ (Ar = Ph, *m*-tolyl, xylyl). Under more strenuous conditions, the hydride complex is reconverted to $[Rh(OEP)]_2$ with loss of hydrogen thereby permitting complete conversion of the starting complex to the alkylated product. A reversible cleavage of $[Rh(OEP)]_2$ to [•Rh(OEP)] is proposed as the initial step (ref. 189).

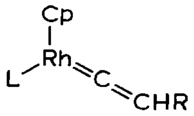
Metal Carbene Complexes

Addition of $Na[Co(CO)_4]$ to $[cpFe(=C(SMe)_2)(CO)(MeCN)]PF_6$ affords [86].

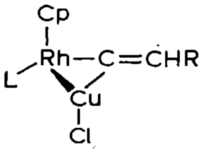


[86]

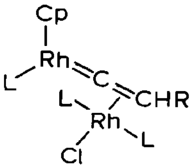
Molecular orbital calculations indicate that there is significant σ-bonding between cobalt and the carbon and one sulfur atom of the dithiocarbene ligand as well as π-backbonding from the cobalt to this ligand (ref.190). The ketenylidene complex [87] adds copper(I) chloride to give [88] (L = PPr^i_3; R = H) and $[RhClL_2]$ to form [89] (L = PPr^i_3; R = H, Ph). Complex



[87]

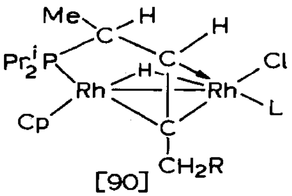


[88]

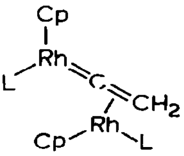


[89]

[89] rearranges to [90] and when R = H can be converted to [91] on reaction

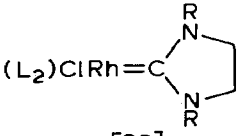


[90]



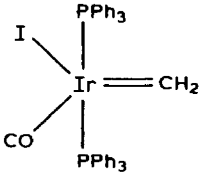
[91]

with sodium cyclopentadienide (ref. 191). Complexes [92] (L_2 = COD; R = Me, Ph. L = phosphine; R = Me, bz) catalyze the hydrosilylation of acetophenone and methyl ethyl ketone by triethyl- and diphenylsilane to give silyl ethers. The same systems catalytically hydrosilylate alkynes to form vinyl silanes in which stereospecific *trans* addition occurs (ref. 192).

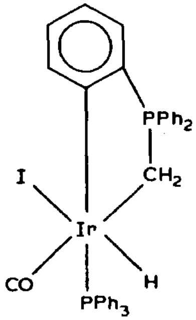


[92]

The carbene complex [93] is formed from $[IrI(CO)(PPh_3)_2]$ and diazomethane at -50°C and on warming to room temperature reacts further to give [94].

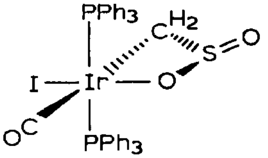


[93]



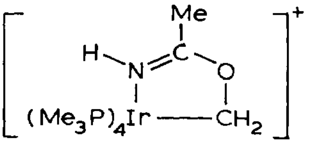
[94]

Addition of sulfur dioxide to [93] yields [95] which converts to $[IrCl_2I(CO)(PPh_3)_2]$ on reaction with hydrogen chloride (refs. 193, 194). Protonation



[95]

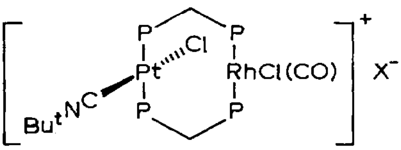
of *cis*-$[IrH(CHO)(PMe_3)_4]PF_6$ with tetrafluoroboric acid etherate yields what appears to be the hydroxycarbene complex *cis*-$[(PMe_3)_4Ir(=CH(OH))H]^{2+}$ although it has not yet been fully characterized. Migration of the hydride ligand to the carbene occurs on addition of acetonitrile to give $[(PMe_3)_4Ir(CH_2OH)(MeCN)]^+$ which reacts with base (e.g. py, PMe_3) to form [96] (ref. 195).



[96]

Metal Isocyanide Complexes

Further results of the substitution reactions of $[\mathrm{Co(CNR)_5}]^+$ (R = Ph, *o*-tolyl, *p*-$\mathrm{ClC_6H_4}$, 2,6-$\mathrm{Et_2C_6H_3}$) with phosphines have been reported. Monosubstitution occurs in all cases with $\mathrm{P(NEt_2)_3}$ and with $\mathrm{P(CH_2CH_2CN)_3}$ when R = *p*-$\mathrm{ClC_6H_4}$ and 2,6-$\mathrm{Et_2C_6H_3}$. Di-substitution occurs with P(*n*-$\mathrm{C_6H_{13}})_3$ except when R = 2,6-$\mathrm{Et_2C_6H_3}$ and with $\mathrm{P(CH_2CH_2CN)_3}$ when R = Ph, *o*-tolyl (ref. 196). Addition of $\mathrm{Li(TCNQ^-)}$ to $[\mathrm{Rh(CNR)_4}]\mathrm{Cl}$ (R = 2,6-$\mathrm{Me_2C_6H_3}$) forms $[\mathrm{Rh(CNR)_4}][\mathrm{TCNQ}^{\overset{\bullet}{-}}]$. The structure of the product consists of stacks of alternating pairs of cations and anions (ref. 197). Reduction of a mixture of $[\mathrm{RhCl(COD)}]_2$ and bulky isocyanides with sodium amalgam forms $[\mathrm{Rh_2(CNR)_6(\mu\text{-}C{=}NR)_2}]$ (R = 2,6-$\mathrm{Me_2C_6H_3}$, 2,4,6-$\mathrm{Me_3C_6H_2}$, 2,6-$\mathrm{Me_2}$-4-$\mathrm{BrC_6H_2}$) in which a rapid bridge-terminal exchange of isocyanide ligands occurs (ref. 198). Transmetalation occurs when $[\mathrm{RhCl(CO)_2}]_2$ reacts with $[\mathrm{MCl(CNR)(\mu\text{-}DPM)_2AgCl}]^+$ and the product is [97] (M = Pt; R = $\mathrm{Bu^t}$; X = $[\mathrm{Rh(CO)_2Cl_2}]$, $\mathrm{BPh_4}$). The analog with M = Pd;



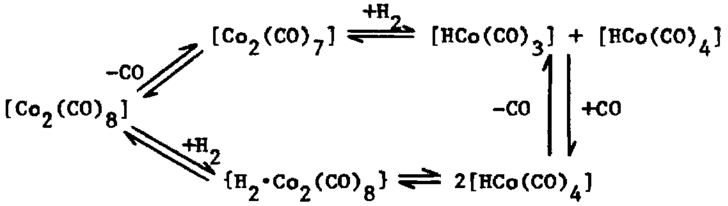
[97]

R = *p*-tolyl; X = Cl was characterized in solution but not isolated (ref. 199). Reaction of $[\mathrm{Rh_2(O_2CMe)_4}]$ with an excess of *tert*-butylisocyanide gives $[\mathrm{Rh_2(O_2CMe)_4(CNBu^t)_2}]$ in which the isocyanide ligands occupy axial positions. With the trifluoroacetate analog the product obtained analyzed as $[\mathrm{Rh_2(O_2CCF_3)_4(CNBu^t)_4}]$ but appeared from NMR studies to be either a mixture of species or at least a mixture of isomers of $[\mathrm{Rh_2(\mu\text{-}O_2CCF_3)_2(O_2CCF_3)_2(CNBu^t)_4}]$ (ref. 200). Pulse radiolysis of $[\mathrm{Rh_2br_4}]^{2+}$ in acetonitrile/*tert*-butyl alcohol forms $[\mathrm{Rh_2br_4}]^+$. The rate of addition of a solvated electron to the dimer was measured. The electronic absorption spectrum of the product was interpreted to indicate that the added electron was delocalized over both metals in a *p*-σ-type metal-metal bonding orbital rather than localized on one metal (ref. 201).

Metal Carbonyl Complexes and Related Compounds

a) Homonuclear Carbonyl Compounds

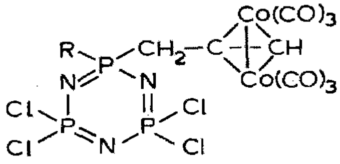
Two additional syntheses of [$Co_2(CO)_8$] have been reported. The first uses a cobalt powder prepared from anhydrous cobalt(II) chloride and lithium naphthalenide in glyme and provides an 80% yield when treated with carbon monoxide at 95 atm and 100°C (ref. 202). The second uses Co_3O_4 or cobalt(II) carbonate which is heated with syngas at 150°-160°C in n-butanol for a short time (ref. 203). In dry THF solution [$Co_2(CO)_8$] remains unchanged under carbon monoxide in contrast to earlier reports of its disproportionation although in the absence of carbon monoxide a slow conversion to [$Co_4(CO)_{12}$] occurs. Evidently in the earlier work traces of moisture must have been present since on addition of water to the above solution disproportionation is observed with the cobalt(II) ion produced forming complexes and ion pairs with the water, the THF and the [$Co(CO)_4$]$^-$ ion. Addition of carbon monoxide to the wet solution regenerates [$Co_2(CO)_8$] demonstrating the reversibility of the disproportionation (ref. 204). An equilibrium state containing 67% [$HCo(CO)_4$] is reached when [$Co_2(CO)_8$] is placed in a syngas atmosphere at 95 atm and 80°C. Addition of oct-1-ene to this system produces a new steady-state system containing [$HCo(CO)_4$], [$Co_2(CO)_8$] and [(n-C_8H_{17}-C(O))$Co(CO)_4$] in the ratio 1:7:2. Aldehyde production is observed to begin once this steady state is attained and as the olefin is consumed, the proportion of the acyl complex decreases and eventually the original equilibrium mixture of [$HCo(CO)_4$] and [$Co_2(CO)_8$] is reestablished. It thus appears that formation of aldehyde occurs preferentially from the reaction of the acyl complex with hydrogen rather than with [$HCo(CO)_4$]. The equilibration of [$Co_2(CO)_8$] and [$HCo(CO)_4$] is proposed to occur as shown in Scheme XV. The lower path is proposed to be necessary since the rate of formation of [$HCo(CO)_4$] is not strongly inhibited by increasing the pressure of carbon monoxide. No evidence was found for radicals (refs. 205, 206). Alkanes exhibit a lower degree of fragmentation under γ-irradiation when they contain dissolved [$Co_2(CO)_8$]. Under these conditions, the cobalt-containing products include [$Co_4(CO)_{12}$] and [$RCCo_3(CO)_9$] (R = alkyl). Under the same



Scheme XV

conditions in benzene, $[HCCo_3(CO)_9]$, $[Co_2(CO)_6(C_6H_8)]$ and $[Co_3(CO)_9(C_6H_7)]$ form. The results suggest that $\{Co_2(CO)_6\}$ and its derivatives are efficient radical scavengers (ref. 207). The kinetics of the oxidation of $[Co_2(CO)_8]$ to cobalt(II) benzoate by benzoyl peroxide have been measured (ref. 208).

Further aspects of the chemistry of $[Co_2(CO)_8]$ include its reaction with acetylenic phosphazines to form [98] and [99] (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^t, allyl) (ref. 209), with the phosphaalkyne $Bu^tC{\equiv}P$ to give [100] (ref. 210) and with $[cpFe(CO)L(SiH_3)]$ (L = CNMe, $CNBu^t$) to yield [101] (ref. 211).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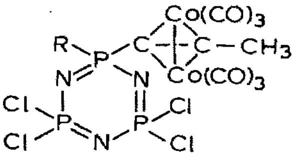
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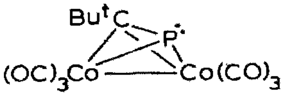
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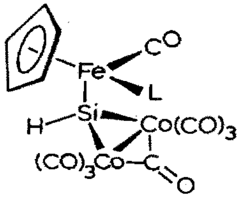
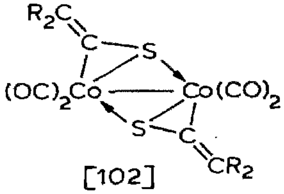
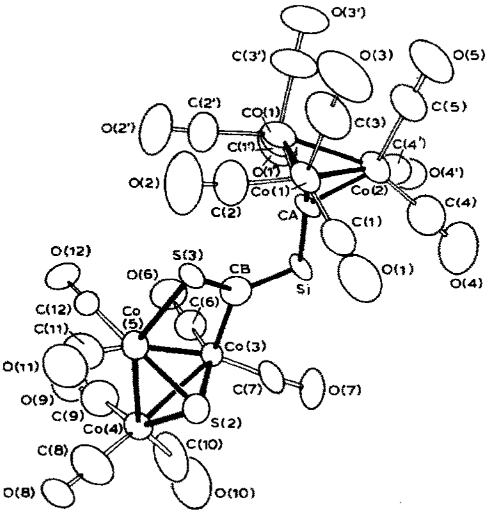

[101]

Complexes [98] and [99] catalyze the cyclotrimerization of diphenylacetylene and the cocyclotrimerization of this acetylene with the alkynyl phosphazines, while [100] reacts with $[W(CO)_5(THF)]$ to add a $\{W(CO)_5\}$ moiety to the phosphorus. Thioketenes readily react with $[Co_2(CO)_8]$ to form [102] (R = Bu^t;


[102]

R_2 = $CMe_2(CH_2)_3CMe_2$). Related complexes containing cyclopentadienyl ligand in place of the carbonyls and without a metal-metal bond can be got from the thioketenes and [cpCo(CO)$_2$] in refluxing hexane and in this case, [cpCo(CO)-(η^2-S-C=CR$_2$)] (R_2 = $CMe_2(CH_2)_3CMe_2$) also forms. This last complex undergoes replacement of carbon monoxide by phosphine ligands and these products in turn can be methylated at sulfur by methyl iodide (ref. 212). Two more of the large number of products obtained from reaction of carbon disulfide have been structurally characterized ([103] and [104]). The former has previously been incorrectly formulated as [$Co_4(CO)_{10}(CS_2)$] (refs. 213, 214).



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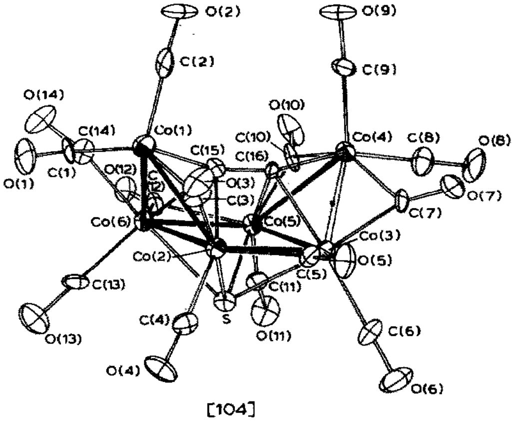
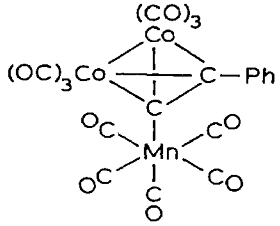


[104]

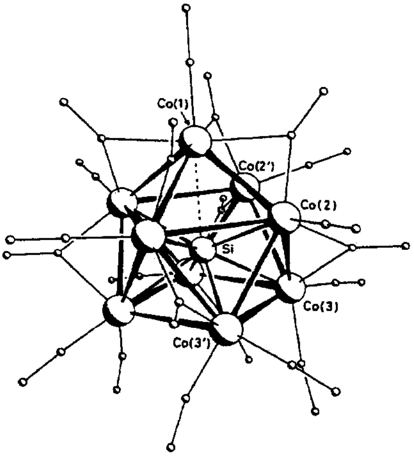
Other reactions of [$Co_2(CO)_8$] are those with [(PhC≡C)Mn(CO)$_4$L] (L = Pcy$_3$) to form [105] (ref. 215) and with E_2Ph_4 to give [$Co_2(\mu$-EPh$_2)_2(CO)_6$] (E = P, As, Sb) or [Co(EPh)(CO)$_4$] (E = Bi) which are converted to [Co(EPh$_2$)(CO)$_3$-PPh$_3$] (E = As, Sb, Bi) on reaction with triphenylphosphine (ref. 216). With cyclooctasulfur they give a mixture of four complexes, the last of which has now been identified as $[Co_6(\mu_3\text{-}S)_8(CO)_6]$ (ref. 217). Whereas dithiocarboxylate esters generally react with $[Co_2(CO)_8]$ to give $[RCCo_3(CO)_9]$ with the alkylidyne moiety arising from the original acid function, the reaction of $[Co_2(CO)_8]$ with $[cpFe(CO_2)(C(S)SMe)]$ yields $[MeSCCo_3(CO)_9]$ instead (ref. 218). The reaction of $[Co_2(CO)_8]$ with bis(diisopropylamino)phosphine eventually gives a low yield of $[Co_3(CO)_9(\mu_3\text{-}PNPr^i{}_2)]$ although a variety of other species are evident at earlier stages (ref. 219).



[105]

Electrolysis of a mixture of $[Co(acac)_2]_4$, tri-n-butylphosphine and tetra-n-butylammonium tetrafluoroborate in methanol under carbon monoxide at an aluminum anode at 60°C yields $[Co_2(CO)_6(PBu^n{}_3)_2]$. At room temperature $[Co(CO)_3(PBu^n{}_3)_2][Co(CO)_4]$ is also formed. In the absence of phosphine and under a syngas atmosphere the major product is $[HCo(CO)_4]$. Use of a cobalt anode obviates the need for $[Co(acac)_2]_4$ and the product is $[HCo(CO)_3(PBu^n{}_3)]$. These systems were used to prepare *in situ* catalysts for cyclohexene hydroformylation (ref. 220). Electrochemical reduction of $[Co_2(CO)_6L_2]$ ($L = PPhMe_2$, $P(OPh)_3$) at temperatures below -15°C forms $[Co(CO)_3L]^-$ which reacts with more $[Co_2(CO)_6L_2]$ to form $[Co(CO)_4]^-$ and $[Co_2(CO)_5L_3]$. The cross reaction of $[Co(CO)_3(PPhMe_2)]^-$ with $[Co_2(CO)_6(P(OPh)_3)_2]$ forms $[Co(CO)_3(P(OPh)_3)]^-$ and $[Co_2(CO)_6(PPhMe_2)_2]$ (ref. 221). Photolysis of $[Co(CO)_3L][Co(CO)_4]$ ($L = PBu^n{}_3$) in methanol yields a 7:3 mixture of $[Co_2(CO)_6L_2]$ and $[Co_2(CO)_7L]$ while in the presence of one equivalent of ligand the products are $[Co_2(CO)_6L_2]$ and $[Co(CO)_2L_3][Co(CO)_4]$ (4:1). With a large excess of ligand only $[Co(CO)_2L_3][Co(CO)_4]$ is seen. Photolysis of $[Co(CO)_3L_2](O_2CMe)$ in methanol causes replacement of one carbonyl ligand by the acetate anion which in turn can be replaced by phosphines to give $[Co(CO)_2L_3](O_2CMe)$. This last species is the product if the photolysis is performed in the presence of excess phosphine ligand. Under hydrogen pressure the acetate salt yields an approximately equimolar mixture of $[HCo(CO)_3L]$ and $[HCo(CO)_2L_2]$. This reaction is inhibited by carbon monoxide and in this instance favors $[HCo(CO)_3L]$ while in the presence of excess phosphine ligand the products are $[HCo(CO)_2L_2]$ and $[Co(CO)_2L_3]^+$ (ref. 222). Addition of $[V(CO)_6]$ to solutions of $[Co(CO)_4]^-$ in toluene oxidizes the cobalt species to $[Co_2(CO)_8]$. A similar redox reaction occurs with $[cp_2Co]$ to give $[cp_2Co][V(CO)_6]$ and an outer sphere mechanism is proposed for both (ref. 223). No significant reaction is observed to occur between oxygen and $[Co(CO)_4]^-$ in the gas phase, a result which is attributed to the closed-shell configuration of the cobalt (ref. 224).

In refluxing dichloromethane $[\mu_4\text{-}Si(Co_2(CO)_7)_2]$ reacts with an excess of $Et_4N[Co(CO)_4]$ to give a low yield of crystals containing cocrystallized $(Et_4N)_2[Co_9(\mu_8\text{-}Si)(CO)_{21}]$ ([106]) and $Et_4N[Co(CO)_4]$. The overall geometry of the cluster is similar to that of $[Rh_9P(CO)_{21}]^{2-}$ but inasmuch as [106] has one fewer electrons it is paramagnetic. The analogous germanium complex does not give a germanium-encapsulated cluster presumably because the cavity is not large enough (ref. 225). The photolysis of $[R_3SiCo(CO)_4]$ in the presence of R'_3SiH yields $[R'_3SiCo(CO)_4]$ and R_3SiH. The mechanism was elucidated by a matrix isolation study, the results of which are outlined in Scheme XVI (ref. 226).

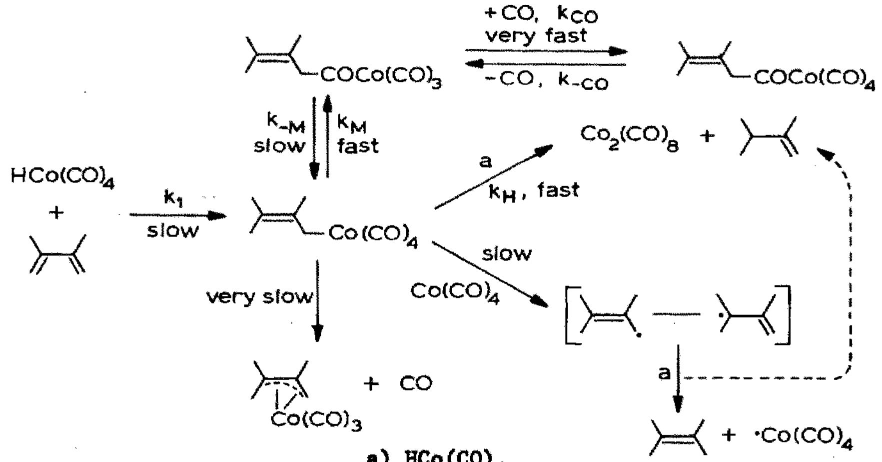


[106]

$$\begin{tikzcd} \lbrack Et_3SiCo(CO)_4\rbrack \arrow[r, shift left, "h\nu"] & \lbrack Et_3SiCo(CO)_3\rbrack + CO \arrow[l, shift left, "\Delta"] \arrow[d, "HSiPh_3"] \\ \lbrack Ph_3SiCo(CO)_4\rbrack & \underline{fac}\text{-}\lbrack Co(H)(SiEt_3)(SiPh_3)(CO)_3\rbrack \arrow[l, "\Delta", "-HSiEt_3"'] \end{tikzcd}$$

Scheme XVI

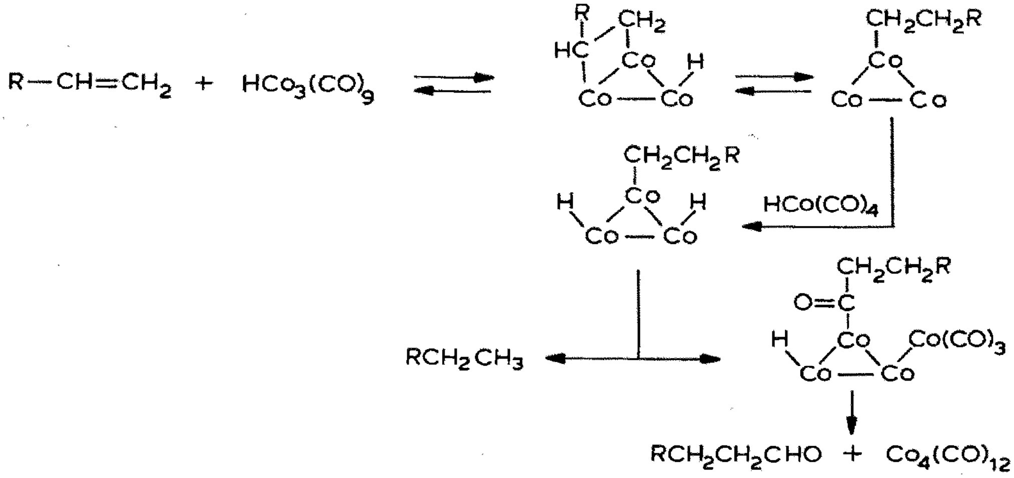
The reaction of $[HCo(CO)_4]$ with conjugated diolefins, in particular cis-2,3-dimethylbuta-1,3-diene, and carbon monoxide has been studied in detail. When the [$HCo(CO)_4$]/diene ratio, is large little uptake of carbon monoxide is observed and hydrogenation of the diene to monoene is the primary process. When the ratio is small, significantly more carbon monoxide uptake occurs and acyl- and alkylcobalt tetracarbonyls are the major products. The results are interpreted in Scheme XVII (ref. 227). A stoichiometric hydroformylation of tert-butylethylene by a mixture of



a) $HCo(CO)_4$

Scheme XVII

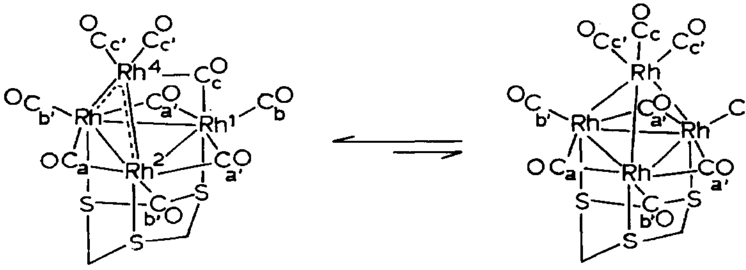
[$HCo(CO)_4$] and [$HCo_3(CO)_9$] occurs at 15°C to give 3-tert-butylpropanol and [$Co_4(CO)_{12}$]. When [$DCo(CO)_4$] is used, the deuterium is incorporated into the aldehyde function suggesting the process of Scheme XVIII (ref. 228).



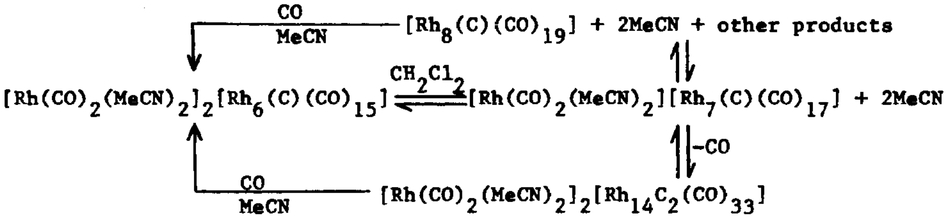
Scheme XVIII

While carbon monoxide substitution into $[Co_4(CO)_9(TPM)]$ appears to occur <u>via</u> a D mechanism, the more rapid substitution of $[Co_4(CO)_{12}]$ by phosphorus ligands to give $[Co_4(CO)_{11}L]$ (L = PPh_3, $P(OMe)_3$) is considered to proceed <u>via</u> an interchange or an associative process. In the latter study no cluster fragmentation was observed and it was thought that the addition of the phosphine prior to or in concert with loss of carbon monoxide is facilitated by a momentary cleavage of a metal-metal bond (refs. 229, 230).

A kinetic study of the reaction of $[Rh_4(CO)_{12}]$ with carbon tetrachloride suggested that the products, $[RhCl(CO)_2]_2$ and $[Rh_6(CO)_{16}]$, form independently (ref. 231). Reaction of $[Rh_4(CO)_{12}]$ with 1,3,5-trithiacyclohexane yields $[Rh_4(CO)_5(\mu\text{-}CO)_4(\overline{SCH_2SCH_2SCH_2})]$ whose structure is shown on the left of Scheme XIX. The molecule is fluxional and the process responsible is proposed to be that of Scheme XIX (ref. 232). Oxidation of $[Rh_7(CO)_{16}]^{3-}$ as well as redox condensations of other rhodium cluster carbonyls form $[Rh_{11}(CO)_{11}(\mu\text{-}CO)_{12}]^{3-}$ which appears to be an important intermediate in pyrolytic syntheses of larger clusters (ref. 233). Combination of $K_2[Rh_6(C)(CO)_{15}]$ and $[Rh(CO)_2(MeCN)_2]BF_4$ in acetonitrile containing aqueous sulfuric acid in a carbon monoxide atmosphere followed by solvent removal, extraction with dichloromethane and metathesis with $(PPN)_2SO_4$ yields $(PPN)_2[Rh_{14}C_2(CO)_{12}(\mu\text{-}CO)_{21}]$. Since the same combination of rhodium complexes in water alone simply gives $[Rh(CO)_2(MeCN)_2]_2[Rh_6(C)(CO)_{15}]$ it was concluded that the condensation reaction occurred in the dichloromethane solution. Critical to the success of this reaction is the proportion of acetonitrile in the solvent mixture since if it is too low, $[Rh_8(C)(CO)_{19}]$ forms instead. The system is thought to be described by Scheme XX (ref. 234). The cluster anion $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ which has been formed previously as a byproduct in the synthesis of $[Rh_{10}(S)(CO)_{22}]^{2-}$ can be prepared in better yield from $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ and potassium thiocyanate in refluxing THF or with K_2S_x (x = 1-8) at room temperature. Other routes to it are the reactions of $[Rh_6(CO)_{15}]^{2-}$ with sulfur, of $[Rh_5(CO)_{15}]^-$ with sulfur and carbon monoxide and of $[RhCl(CO)_2]_2$ or $[RhCl_2(CO)_2]^-$ with sulfide ion. The



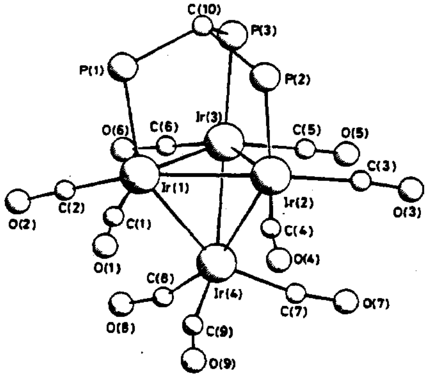
(Scheme XIX)



Scheme XX

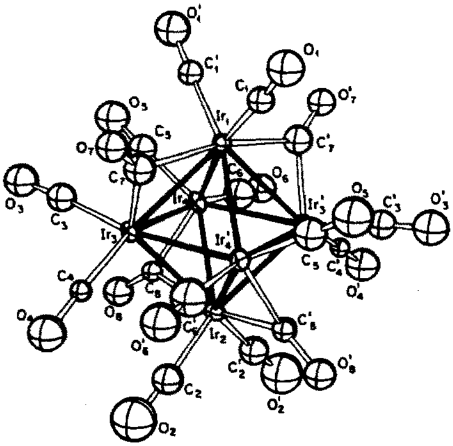
selenium analog could also be synthesized from $[Rh_4(CO)_{12}]$ and potassium selenocyanate (ref. 235).

Depending on the amount of ligand used, bidentate phosphines react with $[Ir_4(CO)_{12}]$ or $[Ir_4(CO)_{11}Br]^-$ to form $[(Ir_4(CO)_{11})_2(\mu\text{-}L_2)]$, $[Ir_4(CO)_{10}(L_2)]$ or $[Ir_4(CO)_8(L_2)_2]$ (L_2 = DPM, DPPE, DPPP, dmpe, vdiphos). Displacement of bromide ion from $[Ir_4(CO)_{11}Br]^-$ by trifluorophosphine yields $[Ir_4(CO)_{11}(PF_3)]$ which is stable only in the solid state. On reaction with water or alcohols it is converted into $[Ir_4(CO)_{11}(PF_2OR)]$ (R = H, Me, Et, Pr^n, Bu^n) (ref. 236). The proposal based on ^{31}P NMR data, that the ligand in $[Ir_4(CO)_9(TPM)]$ is coordinated to single iridium atom (P. E. Garrou, Chem. Revs., 81(1981)229) has been shown to be incorrect by a determination of the structure of the complex ([107]). An unusual feature is the absence of bridging carbonyl ligands which is in contrast to what is usually observed in substituted derivatives of $[Ir_4(CO)_{12}]$, in particular $[Ir_4(CO)_9((Et_2P)_3SiMe)]$. This study provides another example of the limitations of the method of using ^{31}P NMR chemical shifts to determine the mode of coordination of bidentate phosphine ligands (ref. 237). The anion $[HIr_4(CO)_{11}]^-$ is not deprotonated in pyridine or methanol solution containing an eight-fold excess of potassium hydroxide. Partial deprotonation occurs in isopropylamine and complete conversion to $[Ir_4(CO)_{11}]^{2-}$ can be accomplished with



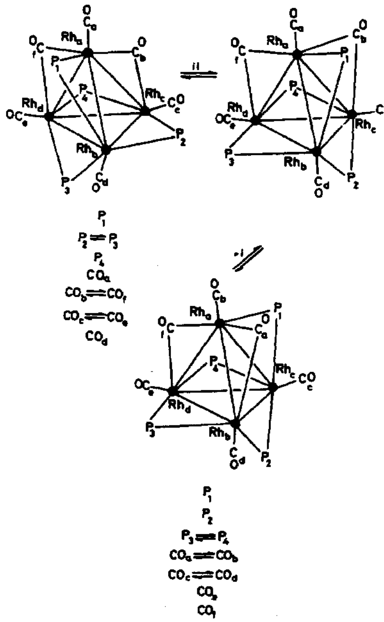
[107]

potassium tert-butoxide in DMSO. The dianion can be reconverted to $[HIr_4(CO)_{11}]^-$ by acetic or p-toluenesulfonic acids and reacts with hydrogen to give $[H_2Ir_4(CO)_{10}]^{2-}$ (ref. 238). Protonation of $(Me_4N)_2[Ir_6(CO)_{15}]$ with trifluoroacetic acid in dichloromethane yields $[HIr_6(CO)_{15}]^-$ which was isolated as its tetramethylammonium salt together with some starting material and a new black isomer of $[Ir_4(CO)_{12}]$ ([108]) by slow crystallization. Also reported is the structure of the red isomer which is isostructural with its rhodium analog (ref. 239).



[108]

First in the area of spectroscopic and theoretical studies are two reports of the inelastic neutron scattering spectra of $[HCCo_3(CO)_9]$ and $Cs[HCo_6(CO)_{15}]$ in which ν_{C-H} and ν_{Co-H} respectively were observed. This is the first observation of the former vibration and the first instance in which ν_{M-H} has been assigned in a cluster in which the hydride occupies an octahedral hole (refs. 240, 241). Proton NMR spectra of the siloxane oligomers $[OSi(Me)Co(CO)_4]_n$ ($n = 4,5$) and related species containing both iron and cobalt moieties indicate that four isomers are present in the tetramer but only two in the pentamer (refs. 242, 242a). Variable temperature ^{13}C and two-dimensional ^{31}P NMR spectra have been obtained for $[Rh_4(CO)_4(\mu\text{-}CO)_2(\mu\text{-}PPh_2)_4]$ which provide evidence for the presence of two dynamic processes involving exchange of the phosphido groups. These are depicted in Scheme XXI which also gives an indication of which ligands exchange and which do not (ref. 243). The ^{13}C NMR spectrum of solid $[Co_2(CO)_8]$ has been observed over a temperature range by the magic-angle-spinning technique and confirms an earlier proposal that the molecule is fluxional in the solid state. At temperatures below -41°C separate signals for the terminal and bridging carbonyls are seen and at higher temperatures these coalesce as a bridge-terminal exchange process sets in (ref. 244).



i) Low temperature process. ii) High temperature process.

Scheme XXI

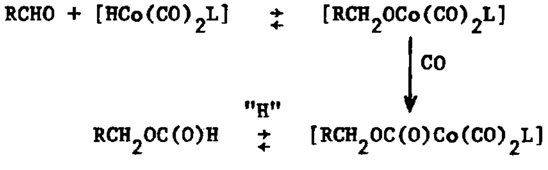
Two theoretical studies of $[HCo(CO)_4]$ using the SCF-Xα-SW method have appeared. The calculated charge on the hydride is -0.27 which is close to that determined by NMR studies and is much closer to the experimental value than are values from previous calculations. The HOMO is determined to be predominately cobalt 3d in character while the LUMO contains a mixture of cobalt 3d and Co-CO plus Co-H σ^* character. Thus the lowest energy band seen in the photoelectron spectrum is a combination of ligand field and metal-to-ligand charge transfer processes rather than wholly the latter as previously assigned. This new assignment is more consistent with the primary photoprocess observed in matrix studies which involves loss of either carbon monoxide or hydrogen (refs. 245, 246). Quite different results have been obtained using a self-consistent, modified extended Hückel method in that the HOMO is predicted to be predominantly ligand in character. Nevertheless the results are said to be consistent with the photoelectron spectra and measurements of the cobalt-carbon and cobalt-hydrogen bond energies (ref. 247). Other calculations on $[Co(CO)_{4-n}L_n]^-$ (L = $P(OH)_3$, PH_3) as models for phosphite and phosphine complexes using the Fenske-Hall method indicate that the HOMO-LUMO gap decreases with increasing values of n and for a given value of n is less when L = $P(OH)_3$ than when L = PH_3. Experimentally the proton acidity of $[HCo(CO)_{4-n}L_n]$ (L = phosphine or phosphite) decreases with increasing n suggesting that this acidity is related to the π-acceptor characteristics of the other ligands in the conjugate base.

Taken together, the results suggest that the greater is the HOMO-LUMO gap in the conjugate base, the more stable is the base and therefore the more acidic should be the conjugate acid (ref. 248). A series of metal carbonyls including $[Co_2(CO)_8]$ have been examined theoretically and it was concluded that the π-backbonding component of the metal-carbon bond is the major portion of the bonding interaction (ref. 249).

The electronic structure of $[Ir_4(CO)_{12}]$ has been explored by SCF-Xα-SW calculations (ref. 250) and by XPS and UPS when supported on iridium films, pyrolytic graphite and amorphous carbon (ref. 251). A topological electron-counting theory has been proposed as an alternative to the skeletal electron-pair method for obtaining the electron count for large polyhedral clusters. Applications to polyhedra having 4-15 and 17 vertices are also discussed (refs. 252, 253).

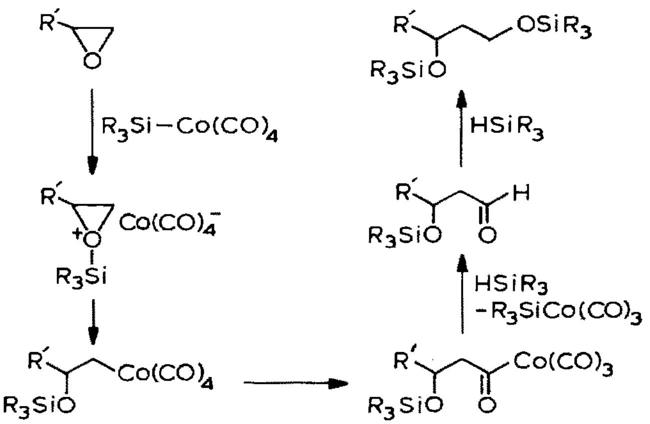
Again this year there is a substantial number of papers reporting the use of carbonyl complexes and their derivatives as catalysts or catalyst precursors for a variety of primarily organic applications. In the main these do not dwell on the nature of the active species or on the mechanism of the process. Terpenes are hydrogenated using catalysts derived from $[Co_2(CO)_6L_2]$ and $[HCo(CO)_2L_2]$ ($L = PBu^n{}_3$) (ref. 254) while related species prepared <u>in situ</u> from $[Co_2(CO)_8]$ and several di(tertiaryphosphines) catalyze the hydroformylation of ethylene, propylene, acrylonitrile and methylacrylate. The best ligand is DPPE followed by $Ph_2PC{\equiv}CPPh_2$, vdiphos and DPPP in that order. Addition of DPPB or DPM gives species less active than $[Co_2(CO)_8]$ itself. The $[Co_2(CO)_8]$/DPPE system with propylene also yields isobutyl alcohol, <u>n</u>-butyric acid, <u>i</u>-butyric acid and propyl butyrate as side products with the yield of C_4 alcohols increasing with increasing temperature. Addition of water to this last system caused the production of significant quantities of C_7 ketones at the expense of C_4 aldehydes (refs. 255-257). With the addition of monodentate phosphines such as triphenyl-, tributyl- or trimethylphosphine and pentaphenylphosphole $[Co_2(CO)_8]$ forms catalysts for the hydroformylation of dicyclopentadiene. Cracking, hydrogenation and aldol condensation products were also found. The yield of hydroformylation products was not improved by the presence of the phosphine but the catalyst stability was (ref. 258). Another group studying the $[Co_2(CO)_8]$/DPPE system found it was an effective catalyst when a CO/H_2O feed was used in place of syngas presumably because it also catalyzes the WGSR. A virtually quantitative yield of dimethyl-4-oxopimelate was obtained from methyl acrylate under these conditions while acrylonitrile formed propionitrile and 2-cyanopropanal as the major products. The system also catalyzed the aminomethylation of propylene by piperidine and morpholine (refs. 259-261). The high pressure (4000 psi) hydroformylation of hex-1-ene catalyzed by mixtures of

$[Co_2(CO)_8]$ and monodentate phosphines has been studied. As the phosphine/Co increases to 4:1 and the cone angle of the ligand decreases, an increase in the proportion of heptyl formate in the product is seen. This is explained by the equilibria of Scheme XXII with the second step favored by high carbon monoxide pressure and sterically undemanding ligands. The $[Co_2(CO)_8]$ was also reacted with diphenylphosphinophenoxypoly(aryloxy)phosphazines and polystyrene functionalized with diphenylphosphino groups to form supported catalysts. The activity of these systems decreased with time and in the latter system some benzene was seen. In homogeneous systems when the ligand was triphenyl-, tribenzyl- or tri(p-tolyl)phosphine, benzene or toluene was also found suggesting that under reaction conditions some cleavage of phosphorus-carbon bonds occurred. This was also observed in $[Rh_4(CO)_{12}]$/triphenylphosphine hydroformylation systems and occurred to a greater extent than with cobalt. Under the same conditions, however, no phosphorus-carbon bond cleavage occurred when tri-n-butylphosphine was used (refs. 262-264). An *in situ* infrared study of the hydroformylation system prepared from cobalt naphthenate and tri-n-butylphosphine (L) under syngas showed that in the absence of olefin, with pressures less than 10 kg/cm² and with a phosphine/cobalt ratio of 3:1 $[Co_2(CO)_6L_2]$, $[HCo(CO)_3L]$ and $[HCo(CO)_2L_2]$ were present. At pressures of 20 kg/cm² and with phosphine/cobalt ratios less than 2:1 $[Co_2(CO)_7L]$ and $[HCo(CO)_4]$ were also identified. In the presence of olefin under hydroformylation conditions only the first three species were present in detectable quantities (ref. 265). The supported species $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PR)]$ (R = polymer supported dibenzo-18-crown-6) is reported to be a better olefin hydroformylation catalyst than its homogeneous counterpart (R = Ph) (ref. 266).



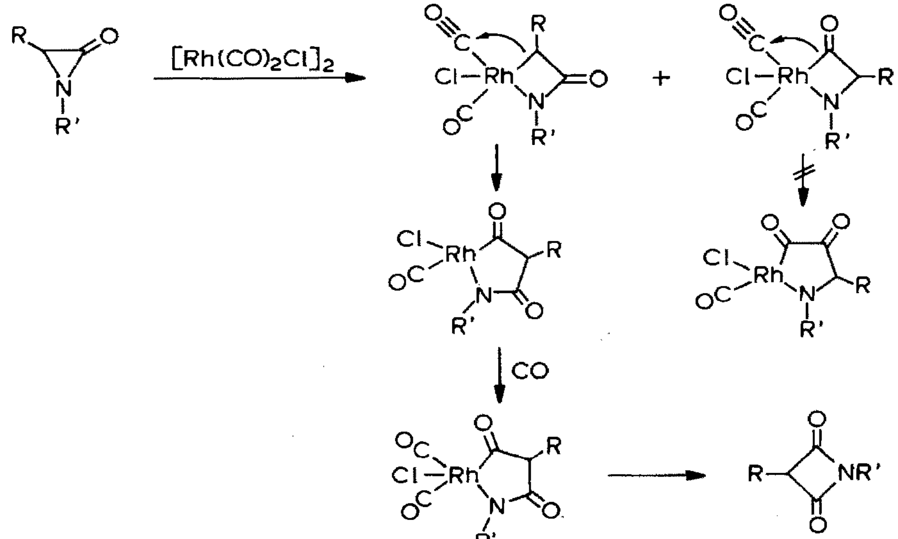
Scheme XXII

The reductive formylation of iodobenzene to benzaldehyde is catalyzed by $[Co(CO)_3PPh_3]_2$ but the yield is quite low (ref. 267). Examples of the use of $[Co_2(CO)_8]$ as catalyst precursors are in the conversion of alkyl bromides to α-keto carboxylic acids having two additional carbon atoms in the presence of tert-butanol and lithium hydroxide (ref. 268), the polymerization of allene by a living chain mechanism (ref. 269) and the addition of perfluoropropyl iodide to ethynyltrimethylsilane to give $C_3F_7CH{=}CISiMe_3$. It also catalyzes the addition of perfluoropropyl iodide to vinyltrimethylsilane (ref. 270). Another example is in the regio- and stereoselective ring-opening of oxiranes in the presence of trialkylsilanes which is proposed to occur as shown in Scheme XXIII and provides 1,3-bis(siloxy) species which



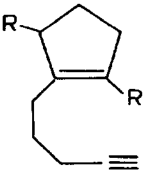
Scheme XXIII

can be hydrolyzed to 1,3-diols (ref. 271). It as well as $[Co_4(CO)_{12}]$ and $[RhCl(CO)_2]_2$ also promotes the conversion of aziridinones to azetidin-2,4-diones as depicted in Scheme XXIV for the rhodium system (R = R' = Bu^t,

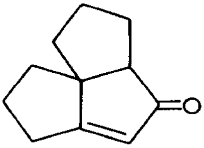


Scheme XXIV

1-adamantyl. R = Bu^t; R' = 1-adamantyl. R = 1-adamantyl; R' = Bu^t) (ref. 272). Finally, $[Co_2(CO)_8]$ mediates the cyclization of [109] (R = H) to give



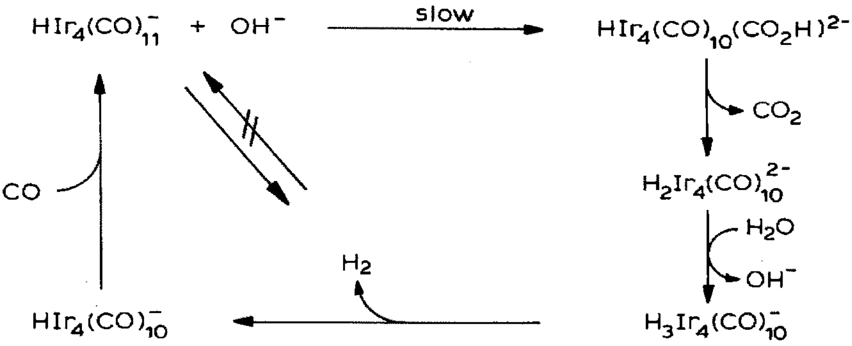
[109]



[110]

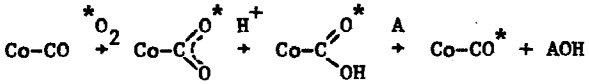
the angularly fused triquinane skeleton [110] but when R = Me no cyclization occurs (ref. 273).

Mercaptans can be catalytically desulfurized to hydrocarbons using the phase transfer system $[Co_2(CO)_8]/NaOH/H_2O/C_6H_6/Bu^n{}_4NHSO_4$ (ref. 274). Although most attempts to incorporate carbon monoxide α to the keto group in cyclobutanone failed, in the presence of $[Co_2(CO)_8]$, methyldiethylsilane and triphenylphosphine at 175°C and a 50 atm pressure of carbon monoxide 1,2-bis(methyldiethylsiloxy)cyclopentene was formed. The initial step is presumed to be the transfer of the silyl group from $[MeEt_2SiCo(CO)_4]$ to the oxygen of the cyclobutanone (ref. 275). In what must have been a very tedious study, the $[HCo(CO)_4]$-catalyzed hydroformylation of all forty two (!) octene isomers has been investigated. Extensive isomerization of the initial olefin can occur but at a relatively slow rate. The distribution of aldehyde isomers varies but little with the extent of conversion and hydroformylation appears to be inhibited at and near tertiary carbon atoms (ref. 276). In the presence of o-phenanthrolines, particularly the 3,4,5,6,7,8-hexamethyl derivative, $[Rh_6(CO)_{16}]$ forms a catalyst for the reduction of nitrobenzene to aniline under water-gas-shift conditions. The active species is proposed to be a mononuclear complex containing one phenanthroline ligand (ref. 277). A 77% yield of C_2 hydrocarbons, largely ethane, is formed from the hydrogenation of carbon monoxide catalyzed by a mixture of $[Rh_4(CO)_{12}]$ and dibromoaluminum hydride (ref. 278). On the other hand using $[Ir_4(CO)_{12}]$ and amines in pentane gives primarily methanol. Use of phosphines rather than amines decreases the rate of hydrogenation but increases the selectivity to methanol while halide promoters increase the selectivity to C_2 products such as ethylene glycol (ref. 279). The system $[Ir_4(CO)_{12}]/2\text{-methoxyethanol}/H_2O/K_2CO_3$ is a catalyst for the WGSR. Soon after initiation the activity of the catalyst drops to a significantly lower value which is proposed to be due to the irreversible formation of $[Ir_8(CO)_{20}]^{2-}$. Scheme XXV shows the proposed catalytic cycle which is entered by the formation of $[HIr_4(CO)_{11}]^-$. This is generated by attack of hydroxide on $[Ir_4(CO)_{12}]$ and subsequent loss of carbon dioxide (ref. 280).



Scheme XXV

Also continuing to receive considerable attention is the nature of the species resulting when carbonyl complexes are deposited on solid supports and the use of these as catalysts. When $[Co_2(CO)_8]$ is deposited on silica or in the cages of X- and Y-type zeolites it is converted to $[Co_4(CO)_{12}]$ in an irreversible process that is inhibited by carbon monoxide. A weak interaction of the cluster with the surface via hydrogen bonding between bridging carbonyls and surface hydroxyl groups is proposed. On silica/alumina the same behavior is noted but in addition new and more reactive species form which are thought to be sub carbonyls. Similar species are also seen together with $[Co(CO)_4]^-$ when $[Co_4(CO)_{12}]$ in the zeolites is heated. On alumina $[Co_2(CO)_8]$ converts to $[Co_4(CO)_{12}]$ and then to several other species including $[Co(CO)_4]^-$ which can be carbonylated to regenerate the parent carbonyls. Oxidation of the silica/alumina and zeolite systems generates substantial quantities of carbon monoxide but very little carbon dioxide or carbonate suggesting that the primary oxidation process is of the cobalt to cobalt(II) which now has little affinity for carbon monoxide. Interestingly when the oxidation is performed with $^{18}O-^{18}O$, substantial amounts of $C^{18}O$ are released. This is proposed to occur as shown in Scheme XXVI (A = acid site on surface) (refs. 281, 282). Other workers report that



Scheme XXVI

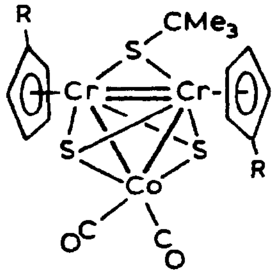
$[Co_2(CO)_8]$ on silica or alumina forms $[Co_4(CO)_{12}]$ having both tetrahedral and C_{3v} symmetries as well as cobalt(II) species and cobalt oxides (ref. 283) while on titanium dioxide, dehydroxylated alumina or Y-type zeolites clusters formulated as $[Co_6(CO)_{16}(L_s)_n]$ (L_s = surface oxide or hydroxyl site) are said to form. These occur on the alumina only at low loadings and on the zeolite $[Co(CO)_4]^-$ and $[Co_6(CO)_{15}]^{2-}$ are also proposed to form (ref. 284). These clusters may well be the sub carbonyls referred to in the first study but there is no indication that the two groups were aware of each other's work.

In studies of Fischer-Tropsch catalysts $[Co_2(CO)_8]$ was deposited on alumina, thermally decarbonylated and briefly contacted with syngas. The clusters $[Co_4(CO)_x]$ ($x = 2$-6) and $[Co_4(CO)_yC]$ ($y = 0, 1, 2, 4, 11$) were identified on the surface. The presence of the latter series was taken as evidence for the surface methylene polymerization mechanism (ref. 285). In a variant of Fischer-Tropsch system, $[Co_4(CO)_{12}]$ was reacted with phosphine-modified silica surfaces and contacted with syngas in the presence and absence of methanol. The results suggest that acetate formation may arise from methoxide attack on a coordinated carbonyl ligand (ref. 286). Other related studies have been reported on catalysts prepared from $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$ deposited on silica, alone or modified with surface aminopropyl groups, and on alumina alone or impregnated with potassium for carbon monoxide hydrogenation (refs. 287, 288) and for carbon monoxide oxidation or ethylene hydrogenation (ref. 289). Pyrolysis of $[Co_2(CO)_8]$ supported on silica, alumina, titanium dioxide or magnesium oxide catalyzed the hydrogenation of ethylene to ethane by a carbon monoxide-water mixture however when supported on carbon the major product was pentan-3-one. The cobalt was considered to remain zerovalent (ref. 290). In contrast, when $[Rh_4(CO)_{12}]$ is pyrolyzed on alumina it is proposed to form divalent species with metal-metal bonds (ref. 291).

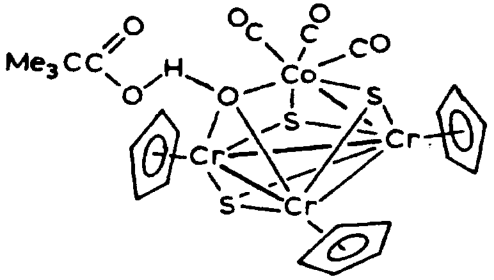
An XPS study of $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PR)_2]$ (R = polystyrene-divinylbenzene copolymer) shows the binding energies to be greater than in the unsupported analog (R = Ph). The complex is a very selective catalyst for hex-1-ene hydroformylation (ref. 292). Raman and photoacoustic spectra of $[Co_2(CO)_6(PPh_3)_2]$ supported on alumina suggest that a carbonyl ligand is hydrogen-bonded to a surface hydroxyl group and that an interaction also occurs between one of these groups and a phenyl ring of the phosphine ligand. Partial decarbonylation occurs on heating and the hydrogen-bonding interaction disappears. At 170°C a tetracobalt cluster forms (ref. 293). Polymeric ferrocenylenephenylphosphines containing coordinated cobalt carbonyl moieties are active as hydroformylation catalysts (ref. 294). Three final papers report on $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ supported on silica and alumina. On the latter the tetrarhodium complex converts to the hexarhodium species and above 353 K decomposition occurs. As the residence time increases oxidative fragmentation occurs to give $\{Rh^I(CO)_2\}$ moieties and ultimately metal crystallites. The exchange of ^{14}CO with the surface species occurs much more rapidly with the fragments than with the intact clusters suggesting an associative process with the former and a dissociative one with the latter. Treatment with methyl iodide and syngas generates small amounts of ethyl iodide (refs. 295-297).

b) Heteronuclear Metal-Metal Bonded Compounds

The antiferromagnetic cluster [111] and its methylcyclopentadienyl analog are synthesized from $[R_2Cr_2(\mu\text{-}SBu^t)_2(\mu\text{-}S)]$ (R = cp, $\eta^5\text{-}C_5H_4Me$) and $[Co_2(CO)_8]$. The same reaction in the presence of pivalic acid in refluxing benzene gives [112] which is also antiferromagnetic. Complex [111] reacts with pivalic acid in refluxing toluene to give [113] (refs. 298, 299).

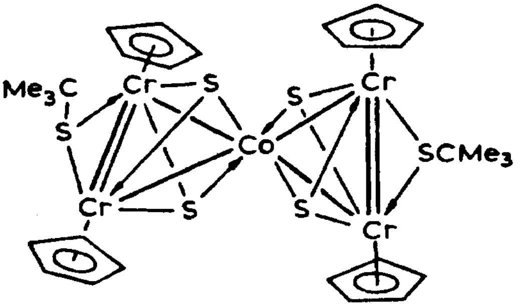


[111]



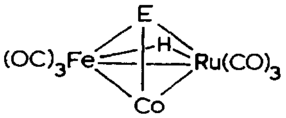
[112]

Photolysis of $[cpFe(CO)(\mu\text{-}CO)_2Co(CO)_3]$ in an argon matrix causes loss of one or more carbonyl groups depending on the duration of irradiation. In a mixed argon/carbon monoxide matrix heterolytic cleavage of the metal-metal bond occurs giving $[cpFe(CO)_3]^+$ and $[Co(CO)_4]^-$ while in an argon/nitrogen matrix $[cpFeCo(CO)_3(N_2)(\mu\text{-}CO)_2]$ is seen. The position of the dinitrogen ligand in this molecule was not established (ref. 300).

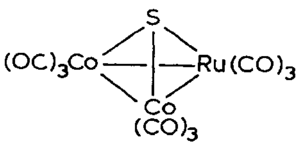


[113]

A sizeable number of papers have appeared on the the synthesis of metal clusters containing several different metal atoms. The complexes [114] (E = PMe, S) are formed from $[(OC)_4Ru(\mu\text{-}PHMe)Co(CO)_3]$ and $[Fe(CO)_4(PMeHCl)]$ or from [115] and $Na_2[Fe(CO)_4]$ followed by protonation with hydrogen chloride

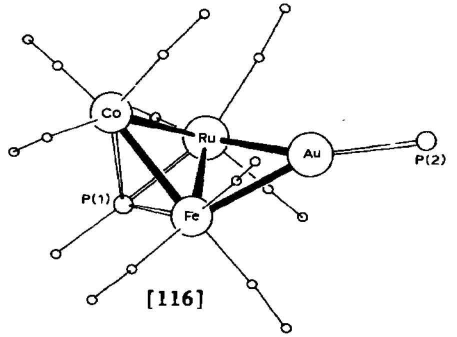


[114]



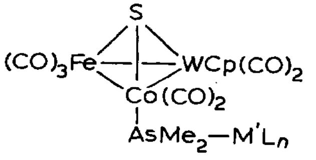
[115]

respectively. Complex [114] reacts successively with potassium hydride and $[AuCl(PPh_3)]$ to form [116] (ref. 301). Addition of $Na_2[Fe(CO)_4]$ to $[Co_3(CO)_9(\mu_3\text{-}E)]$ (E = S, Se, PR (R = Bu^t, Ph, NEt_2, OBu^n, SEt)) yields $[FeCo_2(CO)_9(\mu_3\text{-}E)]$ which reacts further with $Na[cpM(CO)_3]$ in the presence of

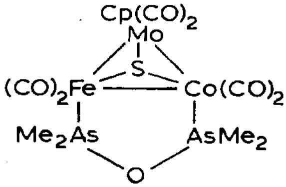


[116]

catalytic amounts of sodium benzophenone ketyl to form $[cpMFeCo(CO)_8(\mu_3\text{-}E)]$ (E = S, Se, $PNEt_2$; M = Mo, W) and with excess $Na_2[Fe(CO)_4]$ followed by acidification to give $[HFe_2Co(CO)_9(\mu_3\text{-}E)]$ in which the hydride ligand bridges the two iron atoms. Dissolution of the hydride complex in ethanol and addition of PPN forms $PPN[Fe_2Co(CO)_9(\mu_3\text{-}E)]$ (ref. 302). From $[cpMFeCo(CO)_8(\mu_3\text{-}S)]$ and $[Me_2AsM'L_n]$ in refluxing benzene is obtained [117] (M = Cr, Mo, W; $M'L_n$ = $cpCr(CO)_3$. M = Cr; $M'L_n$ = $cpMo(CO)_3$, $cpW(CO)_3$. M = Mo; $M'L_n$ = $cpFe(CO)_2$, $Mn(CO)_5$) while at room temperature with dimethylaminodimethylarsine (M = Mo) the ultimate product is [118]. Presumably the initial

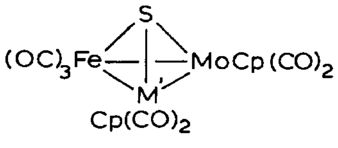


[117]



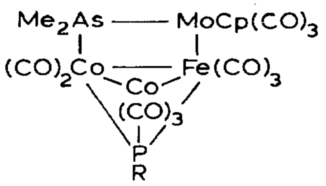
[118]

substitution product hydrolyzes. Complexes [117] (M = Mo; $M'L_n$; = $cpMo(CO)_3$, $cpW(CO)_3$) in refluxing toluene convert to [119] (M' = Mo, W). Analogs of

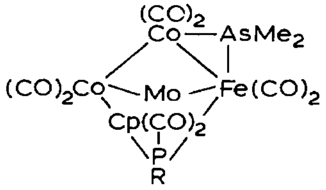


[119]

[119] with ruthenium in place of the iron could be prepared similarly (ref. 303). In related work [FeCo$_2$(CO)$_9$(μ_3-PR)] (R = Me, Ph) forms [120] on reaction with [Me$_2$AsMocp(CO)$_3$] in toluene at room temperature and at reflux temperature this converts to [121]. Carbonylation of [121] (R = Me) gives back [FeCo$_2$(CO)$_9$(μ-PMe)] plus [Me$_2$AsMocp(CO)$_3$] while the phenyl analog gives [cpMoFeCo(CO)$_8$(μ_3-PPh)] instead. The analog of [121] with R = Bu^t however is carbonylated first to a mixture of [Me$_2$AsCo(CO)$_3$]$_x$ and [122] (M = Mo) with the latter further reacting to form [cpMoFeCo(CO)$_8$(μ_3-PBu^t)]. The tungsten counterpart reacts analogously. Also, complexes [123] are reversibly carbonylated to [124] (M = Mo, W; M' = Fe, Ru) (ref. 304). Chemical oxidation of [Co$_3$(CO)$_9$(μ_3-E)] (E = S, PPh) gives the monocation which is only stable in solution. The related complexes [FeCo$_2$(CO)$_9$(μ_3-E)] (E = S,



[120]



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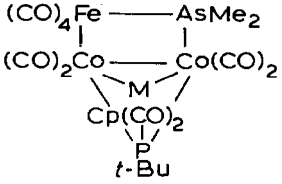

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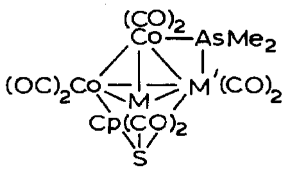
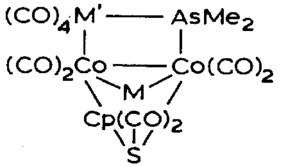
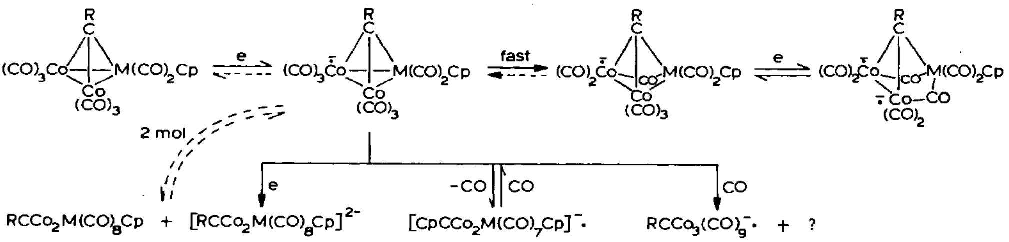


[123]



[124]

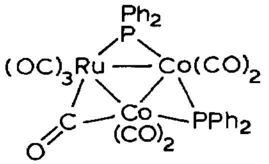
PPh) can be reduced with [cp$_2$Co] or sodium naphthalenide to give C[FeCo$_2$(CO)$_9$(μ_3-E)] (C = cp$_2$Co$^+$, PPN) which are stable in the solid state. Iodine reacts with [Co$_3$(CO)$_9$(μ_3-PR)] (R = Ph, NEt$_2$, OBu^n) to form [Co$_4$(CO)$_8$(μ-CO)$_2$(μ_4-PR)$_2$] (ref. 305). The electrochemical reduction of the capped triangular clusters [MM'M"(μ_3-E)] (E = PPh, PMe, CPh, CMe, S, Se; M' = M" = Co(CO)$_3$; M = Co(CO)$_3$, Fe(CO)$_3$, Ru(CO)$_3$. M" = Co(CO)$_3$; M = Fe(CO)$_3$, Ru(CO)$_3$; M' = cpMo(CO)$_3$. E = GePh, GeMe; M = M' = M" = Co(CO)$_3$. M = M' = Co(CO)$_3$; M" = cpMo(CO)$_3$. E = CPh; CMe; M = M' = Co(CO)$_3$; M" = cpCr(CO)$_3$, cpMo(CO)$_3$, cpW(CO)$_3$. E = PBu^t, PNEt$_2$; M = M' = Co(CO)$_3$; M" = Fe(CO)$_3$) has been studied. All are reduced to the radical anion but as the number of different metal atoms in the cluster increases, the ease of subsequent chemical processes also increases. The most complex behavior is noted with the complexes [cpMCo$_2$(CO)$_8$(μ_3-CR)] (R = Me, Ph; M = Cr, Mo, W) and a possible interpretation of the observed results is given in Scheme XXVII (refs. 306, 307).



Scheme XXVII

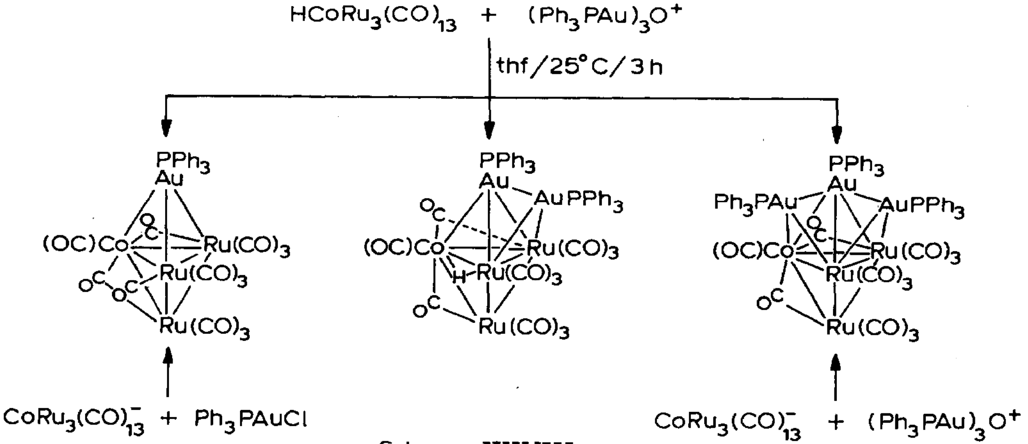
A facile replacement of an {Fe(CO)$_3$} moiety in the ketenylidene cluster [Fe$_3$(CO)$_9$(μ_3-CCO)]$^{2-}$ occurs on reaction with [Co$_2$(CO)$_8$] to give the analogous [Fe$_2$Co(CO)$_9$(μ_3-CCO)]$^-$ in which the CCO vector is also tilted towards the plane of the metal atoms. Protonation of the new cluster forms [Fe$_2$Co(CO)$_9$(μ-CO)(μ_3-CH)] (ref. 308).

A set of heterometallic pentanuclear clusters can be readily formed from K[MCo$_3$(CO)$_{12}$] and [LM'Cl] and are formulated as [MCo$_3$(CO)$_{12}$M'L] (M = Fe, Ru; M' = Cu, Ag; L = 1-phenyl-3,4-dimethylphosphole. M = Fe, Ru; M' = Cu; L = MeCN). However when Na[RuCo$_3$(CO)$_{12}$] reacts with [RhCl(CO)$_2$]$_2$ or [cpMo(CO)$_3$Cl] the products are [RhCo$_3$(CO)$_{12}$] plus [Ru$_3$(CO)$_{12}$] and [cpMo(CO)$_3$]$_2$, [cpMoCo$_3$(CO)$_{14}$] and [HRuCo$_3$(CO)$_{12}$] respectively (ref. 309). At room temperature [(η^6-*p*-cymene)RuCl$_2$(PPh$_2$X)] (X = H, Cl) forms [(OC)$_4$Ru(μ-PPh$_2$)Co(CO)$_3$] and [(η^6-*p*-cymene)(CO)Ru(μ-PPh$_2$)Co(CO)$_3$] plus traces of [Ru(CO)$_3$(μ-PPh$_2$)]$_2$ and [Ru$_2$Co(CO)$_{10}$(μ-PPh$_2$)]. When performed in refluxing THF the same set of complexes plus [125] formed (ref. 310). Reduction of [(OC)$_4$Ru(μ-PPh$_2$)Co(CO)$_3$] with sodium borohydride in THF followed by treatment with methanolic



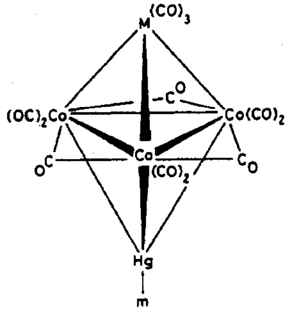
[125]

tetraethylammonium chloride forms $Et_4N[(OC)_3H\overline{Ru(\mu\text{-}PPh_2)Co}(CO)_3]$. This site selective substitution of carbon monoxide by hydride is attributed to a significantly greater affinity of ruthenium for hydride ligands and this preference is suggested as the reason for the observed efficacy of mixed ruthenium-cobalt systems as hydrogenation catalysts (ref. 311). Heating a solution of $[Co_2(CO)_8]$ and $[Ru_3(CO)_{12}]$ in an atmosphere of syngas containing ethanethiol forms $[RuCo_2(CO)_9(\mu_3\text{-}S)]$ which reacts further with $[cpM(CO)_3]_2$ to give $[cpMRuCo(CO)_8(\mu_3\text{-}S)]$ (M = Mo, W) and with dimethylphenylphosphine (L) to give initially two isomers of $[RuCo_2(CO)_8L(\mu_3\text{-}S)]$ and, on further substitution, $[RuCo_2(CO)_7L_2(\mu_3\text{-}S)]$ and $[RuCo_2(CO)_6L_3(\mu_3\text{-}S)]$ (ref. 312). The addition of $\{Au(PPh_3)^+\}$ fragments to ruthenium-cobalt clusters is shown in Scheme XXVIII. Although the addition probably does not occur in a stepwise



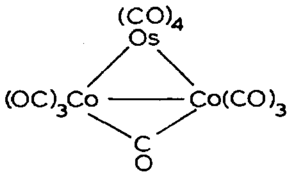
Scheme XXVIII

fashion, the first fragment appears to add to the least hindered $CoRu_2$ face with subsequent additions occurring at the most open sites which remain, subject to the constraint of also forming the largest amount of Au-Au interaction. Thus, although the $\{Au(PPh_3)\}$ moiety has been considered to be a hydride equivalent in clusters, when more than one is present the positioning is no longer useful as an indicator of the position of a hydride ligand in the corresponding hydride cluster (ref. 313). One equivalent of mercury (II) bromide reacts with $Na[RuCo_3(CO)_{12}]$ to give [126] (M = Ru) as a 4:1



[126]

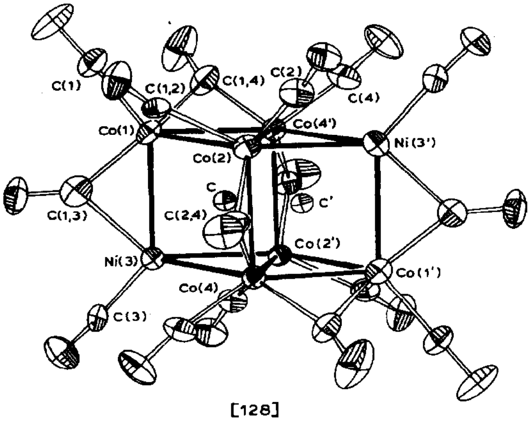
mixture of the complexes with m = Br and m = $Co(CO)_4$. The former is converted to the latter reaction with $Na[Co(CO)_4]$. An iron analog (M = Fe; m = HgBr) can be prepared similarly and both the bromide complexes undergo metathesis with $Na[cpMo(CO)_3]$ to give [126] (M = Fe, Ru; m = $cpMo(CO)_3$) (ref. 314). The major product of the room temperature reaction of $[H_2Os(CO)_4]$ with $[Co_2(CO)_8]$ is [127] which fragments under 100 atm of carbon



[127]

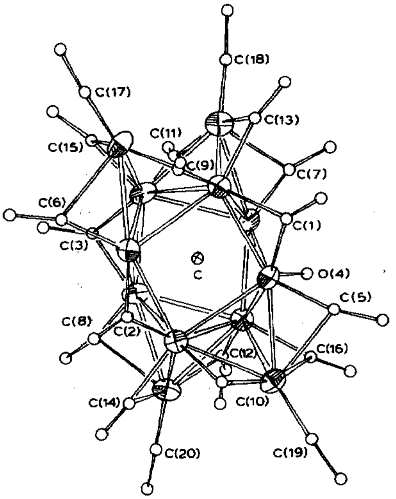
monoxide to give $[Co_2(CO)_8]$ and $[Os(CO)_5]$. Minor products of the initial reaction are $[H_2Co_2Os_2(CO)_{12}]$ and $[HOsCo(CO)_8]$ (ref. 315).

The slow addition of $[ClCCo_3(CO)_9]$ to a two-fold excess of $[Ni_6(CO)_{16}]^{2-}$ in THF forms a mixture of clusters including $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ ([128]) and

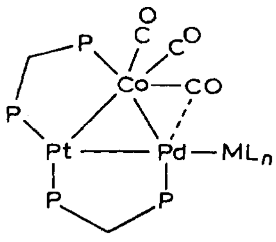


[128]

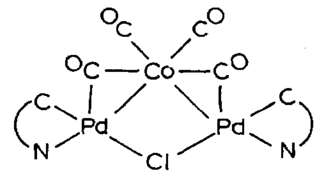
$[Co_3Ni_9C(CO)_{20}]^{3-}$ ([129]). In [128] the carbon-carbon distance is 1.494(11) Å but a delocalized interaction supported by the metal atoms is proposed in preference to a localized carbon-carbon bond. The structural study of [129] indicated a random distribution of nickel and cobalt atoms in the approximately square antiprismatic core but the four peripheral atoms are thought to all be nickel. It fragments when treated with syngas in acetonitrile to give $[Ni(CO)_4]$, $[Co(CO)_4]^-$, methane, ethylene and ethane. The C_2 hydrocarbons comprise 80% of the organic products but it was not proven that they arise from the carbide in the cluster. Complex [128] could also be formed from [129] and $[ClCCo_3(CO)_9]$ (refs. 316, 317). At 0°C $[PtPdCl_2(\mu\text{-DPM})_2]$ reacts with two equivalents of $Na[Co(CO)_4]$ to form [130] ($ML_n = Co(CO)_4$). The $\{Co(CO)_4\}$ moiety can be replaced by iodide ion and this latter species on reaction with $Na[ML_n]$ ($ML_n = Co(CO)_4$, $Fe(CO)_3NO$, $Mn(CO)_5$) gives other examples of [130] (ref. 318). One bridging chloride ligand in the metallated complex $[Pd_2(\overset{\frown}{NC})_2(\mu\text{-}Cl)_2]$ ($\overset{\frown}{NC}$ = o-dimethylaminomethylphenyl, o-dimethylaminobenzyl, 8-quinolinylmethyl) can be replaced by $[Co(CO)_4]^-$ to give [131]



[129]

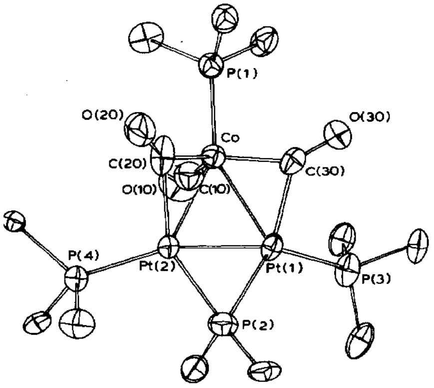


[130]



[131]

(ref. 319). Thermolysis of $[Co_2Pt_2(CO)_8(PPh_3)_2]$ under nitrogen forms [132] (only the α-carbons of phenyl rings are shown) which is considered to



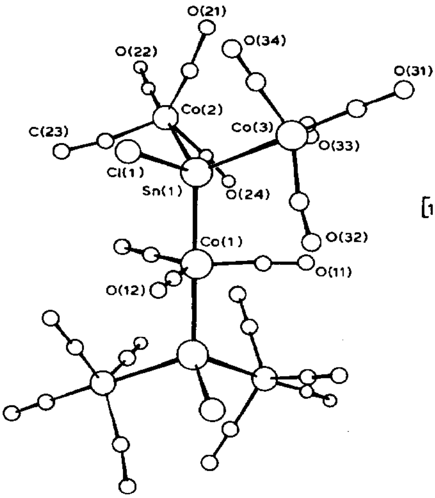
[132]

contain a dimeric Pt(I) moiety bridged by diphenylphosphido and $[Co(CO)_3(PPh_3)]^-$ units. The complex undergoes an irreversible one-electron oxidation and a reversible one-electron reduction. The reduced complex subsequently decomposes to $[Co(CO)_3(PPh_3)]^-$ and other unidentified products (ref. 320).

Reaction of $Na[Co(CO)_4]$ and copper(I) chloride in THF acidified with hydrochloric acid forms $[Cu(Co(CO)_4)]_4$ which contains an eight-membered ring of alternating metal atoms (ref. 321). Several lanthanide metals react with $Hg[Co(CO)_4]_2$ in THF at room temperature to form $Ln(THF)_n[Co(CO)_4]_2$ (Ln = Sm, Eu; n = 4. Ln = Yb; n = 3) which can also be prepared from the appropriate diiodides and $Tl[Co(CO)_4]$ at -70°C (refs. 322, 323). Other cobalt-lanthanide complexes, $[cp_2M(\mu\text{-}CO)Co(CO)_3]$ (M = Sm, Yb, Ho), are formed from the corresponding trichlorides on reaction with $Na[Co(CO)_4]$ followed by sodium cyclopentadienide (ref. 324).

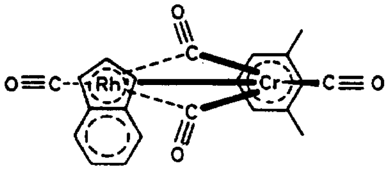
Indium(I) halides react with $[Co_2(CO)_8]$ in dichloromethane-pyridine mixtures to yield $[InXpy_2(Co(CO)_4)_2]$ (X = Cl, Br, I) which are presumably octahedral indium(III) complexes although no determination of the stereochemistry appears to have been made (ref. 325).

The expected $[(HBpz_3)SnCo_3(CO)_9]$ was not formed when potassium tris-(pyrazolato)borate was added to a THF solution of $ClSn[Co(CO)_4]_3$. Instead the product is $[Co(HBpz_3)_2][Sn_2Co_5Cl_2(CO)_{19}]$ in which the anion has the structure [133] (ref. 326). Electrochemical studies on $[Ph_3ECo(CO)_3L]$ (E = Si, Ge, Sn; L = CO, PPh_3, $P(OPh)_3$) reveal the presence of an irreversible, one-electron reduction to form $\{Ph_3E\cdot\}$ and $[Co(CO)_3L]^-$. In $[ClSn(Co(CO)_4)_n(cpFe(CO)_2)_{3-n}]$ (n = 1-3) the ease of reduction decreases as the number of tin-cobalt bonds decreases. Also the tin-cobalt bond is cleaved in preference to the tin-chloride bond (ref. 327). The hydride complexes $[HFeCo_3(CO)_{12}]$ and $[HCo(CO)_4]$ have been used as hydride sources for the reduction of dinitrogen in cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W). Only with the tungsten was any significant quantity of hydrazine and ammonia formed (ref. 328).



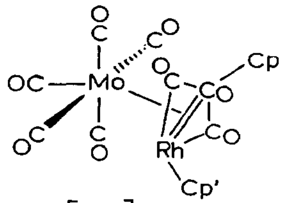
[133]

Complex [134] has been studied by variable-temperature NMR spectroscopy and the indenyl ring shown to undergo a hindered rotation. This unusually high rotational barrier is thought to be due to an asymmetric coordination of this ligand to the rhodium (ref. 329). The air-sensitive complex



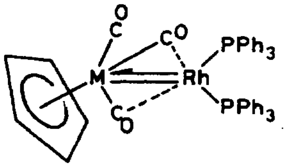
[134]

$[(OC)_4(PMe_3)Cr(\mu\text{-}PBu^t{}_2)Rh(CO)(PMe_3)]$ which contains one semibridging carbonyl ligand can be synthesized from $Li[Cr(CO)(PBu^t{}_2)]$ and $[RhCl(PMe_3)_3]$ at -100°C. It can also be formed by reaction of either $[(OC)_5Cr(\mu\text{-}PBu^t{}_2)Rh(COD)]$ or $[(OC)_5Cr(\mu\text{-}PBu^t{}_2)Rh(CO)_2]$ with trimethylphosphine. The first of these two complexes is prepared from $Li[Cr(CO)_5(PBu^t_2)]$ and $[RhCl(COD)]_2$ and is converted to the second under 3 atm pressure of carbon monoxide. With $[CoCl(PMe_3)_3]$, $Li[Cr(CO)_5(PBu^t_2)]$ forms $[(OC)_3(PMe_3)\overline{Cr(\mu\text{-}CO)(\mu\text{-}PBu^t_2)Co}(CO)(PMe_3)]$ while $Li[Fe(CO)(PBu^t_2)]$ gives $[(OC)_3(PMe_3)\overline{Fe(\mu\text{-}PBu^t_2)Co}(CO)_2(PMe_3)]$. Unexpectedly the reaction of $Li[Mo(CO)_5(PBu^t_2)]$ with $[CoCl(PMe_3)_3]$ did not give a bimetallic product (refs. 330, 331). The THF ligand in $[Mo(CO)_5(THF)]$ is replaced by $[cp'_2RhCo(\mu\text{-}CO)_2]$ to form [135] in which the

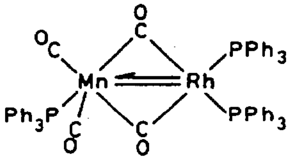


[135]

formal rhodium-cobalt double bond is considered to be an inorganic olefin analog. Variable-temperature NMR studies show that the $\{Mo(CO)_5\}$ moiety undergoes hindered rotation about an axis through the center of the cobalt-rhodium vector. Extended Hückel molecular orbital calculations on the dirhodium analog support this bonding model but the rotational barrier appears to be largely steric in origin rather than electronic (ref. 332).

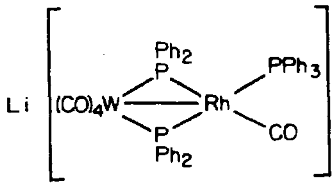


[136]

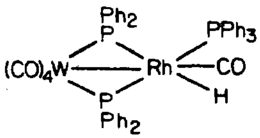


[137]

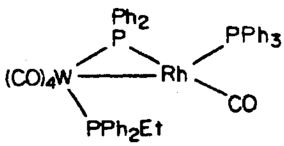
Complexes [136] (M = Mo, W) and [137] are formed from $[RhCl(PPh_3)_3]$ and $Na[cpM(CO)_3]$ and $Na[Mn(CO)_5]$ respectively. The metal-metal bond can be cleaved photochemically (ref. 333). Interaction of $Li_2[W(CO)_4(PPh_2)_2]$ with $[RhCl(CO)(PPh_3)_2]$ yields [138] which on protonation forms [139]. Complex [139] in turn reacts with ethylene to give [140]. With $[IrCl(CO)(PPh_3)_2]$, $Li_2[W(CO)_4(PPh_2)_2]$ forms the iridium analog of [138] which can be methylated



[138]

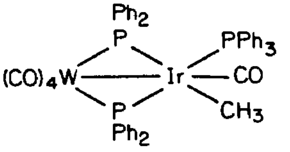


[139]

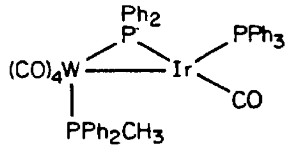


[140]

by methyl triflate to give [141]. Heating [141] in toluene causes the methyl group to transfer to a bridging phosphide ligand forming [142]. This



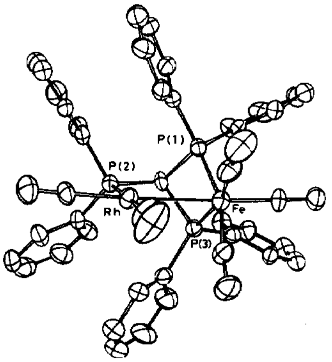
[141]



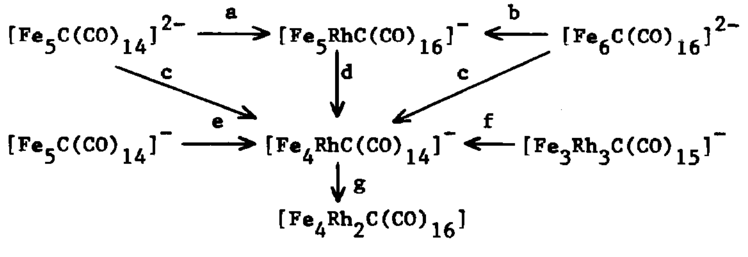
[142]

last observation suggests that the conversion of [139] to [140] by ethylene involves initial formation of an unstable rhodium ethyl complex followed by transfer of the ethyl group to a bridging phosphide ligand (ref. 334).

The uncoordinated phosphorus atom in [Fe(CO)$_3$(TPM)] renders it capable of acting as a ligand and on reaction with [RhCl(CO)$_2$]$_2$ [143] is formed (ref. 335). The synthesis and interconversion of rhodium-iron carbide clusters in diglyme is outlined in Scheme XXIX. Also, the reaction of hydrated rhodium



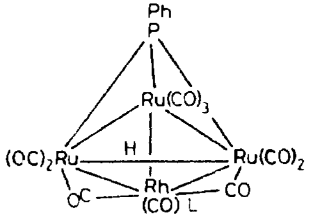
[143]



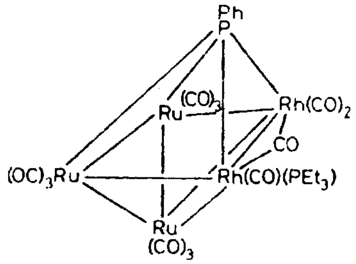
a) $RhCl_3 \cdot 3H_2O$ or [RhCl(CO)$_2$]$_2$, 25°C. b) $RhCl_3 \cdot 3H_2O$, 45°C.
c) $RhCl_3 \cdot 3H_2O$, 90°C. d) 90°C. e) $RhCl_3 \cdot 3H_2O$, 100°C.
f) $RhCl_3 \cdot 3H_2O$. g) [RhCl(CO)$_2$]$_2$

Scheme XXIX

(III) chloride with $[Fe(CO)_5]$ or $Na_2[Fe(CO)_4]$ in diglyme at 60°C or with $[Fe(CO)_5]$ and sodium amalgam in diglyme at 110°C yields $[Rh_5Fe(CO)_{16}]^-$. The structure of this complex appears to be the same as that of $[Rh_6(CO)_{16}]$ with the iron atom disordered over all six vertices of the octahedral core. The structure of $[Fe_5RhC(CO)_{16}]^-$ is similar except that four of the carbonyl ligands are semi-bridging on octahedral edges rather than face-bridging and the rhodium atom is disordered only between the two axial sites. The carbide lies at the center of the octahedron of metal atoms (refs. 336-338). The major product of the reaction of $PPN[Ru_3H(CO)_9(\mu_3\text{-}PPh)]$ with $[Rh(CO)_3L_2]^+$

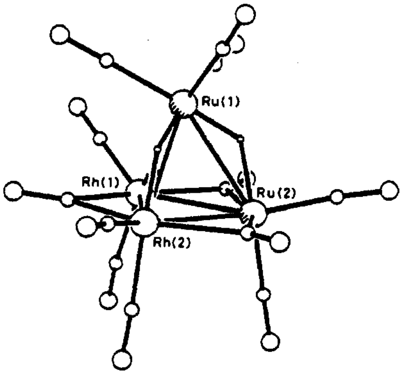


[144]



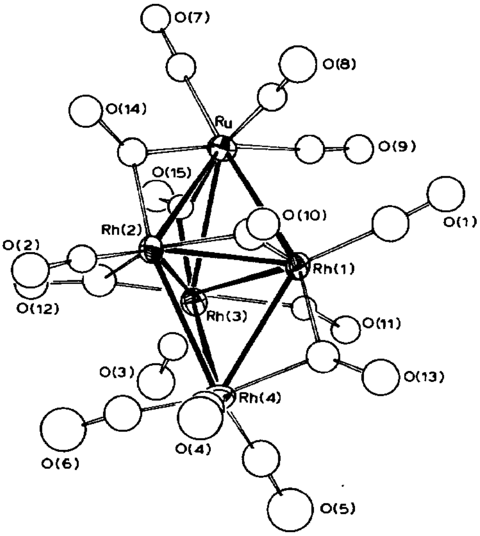
[145]

(L = PEt_3, PPh_3) is [144] while minor ones identified are [145] and $[H_2Ru_3(CO)_8L(\mu_3\text{-}PPh)]$. With $[Ir(COD)(PEt_3)_2]^+$ this last species (L = PEt_3) is the major product together with smaller amounts of the iridium analog of [144] (L = PEt_3) (ref. 339). Among several products obtained from the reaction of $Na[Rh(CO)_4]$ and $[Ru_3(CO)_{12}]$ followed by acidification with phosphoric acid is $[Rh_2Ru_2(\mu\text{-}H)_2(\mu\text{-}CO)_3(CO)_9]$ ([146]) (ref. 340) while from $[Ru_3(CO)_{12}]$ and

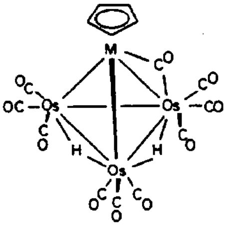


[146]

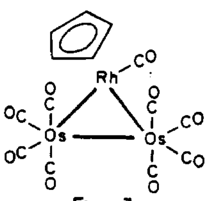
$[Rh_4(CO)_{12}]$ in methanolic sodium hydroxide under carbon monoxide was obtained $(PPN)_2[RuRh_4(CO)_{15}]$ ([147]) (ref. 341). The major products of the prolonged reaction of $[cpRh(CO)_2]$ with $[H_2Os_3(CO)_{10}]$ are [148] (M = Rh) and [149] which appear to form concurrently (ref. 342).



[147]

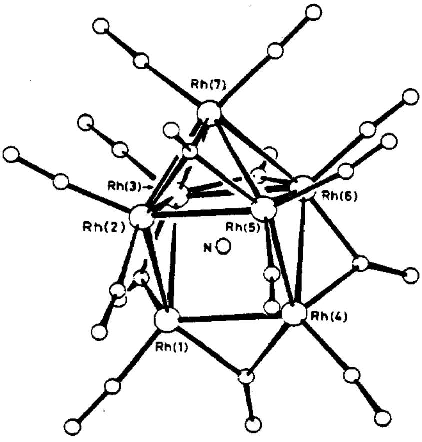


[148]



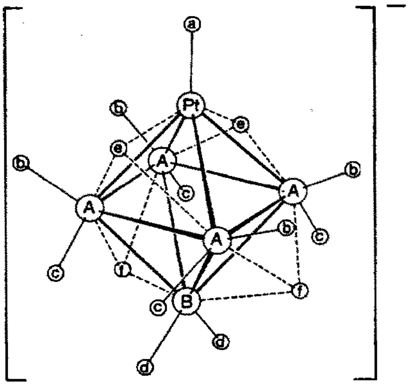
[149]

In refluxing THF, $Ph_4P[Rh_6N(CO)_{15}]$ reacts with $Ph_4P[M(CO)_4]$ (M = Co, Rh, Ir) to form $Ph_4P[Rh_6M(N)(CO)_{15}]^{2-}$ whose structure (M = Rh) is shown as [150]. The cobalt and iridium analogs have the same structure but in the former the cobalt atom is equally disordered over the sites labelled as Rh(2) and Rh(5) in [150] while in the latter the iridium atom is disordered over the sites labelled Rh(7) and Rh(2) in a 9:1 ratio (ref. 343). Reaction of sodium hexachloroplatinate(IV) with five equivalents of hydrated rhodium (III) chloride and carbon monoxide in a mixture of methanol and sodium carbonate forms $Na[PtRh_5(CO)_{15}]$ ([151]) A = B = Rh, while with four equivalents

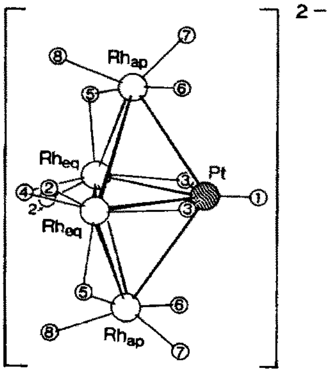


[150]

of rhodium in methanolic sodium hydroxide the product is $Na_2[PtRh_4(CO)_{14}]$ ([152]) which is stable only under carbon monoxide. Complex [151] is also formed from $[Pt_{12}(CO)_{24}]^{2-}$ and five equivalents of $[Rh_{12}(CO)_{30}]^{2-}$ in THF under carbon monoxide. Additional chemistry of these clusters is shown in Scheme XXX. The structure of $[PtRh_4(CO)_{12}]^{2-}$ is shown as [153]. Complex



[151]

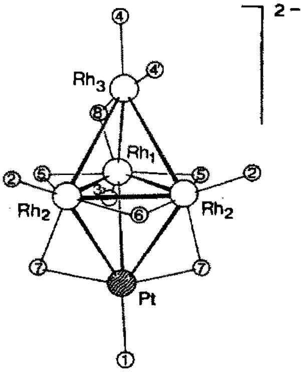


[152]

$$\begin{tikzcd}
{[PtRh_5(CO)_{15}]^-} \arrow[r, shift left, "a"] & {[Rh_5(CO)_{15}]^- + [Pt_3(CO)_6]_n^{2-}} \arrow[l, shift left, "b"] \\
{[PtRh_4(CO)_{14}]^{2-}} \arrow[u, "{d,e}"] \arrow[r, shift left, "b"] & {[PtRh_4(CO)_{12}]^{2-}} \arrow[l, shift left, "c"]
\end{tikzcd}$$

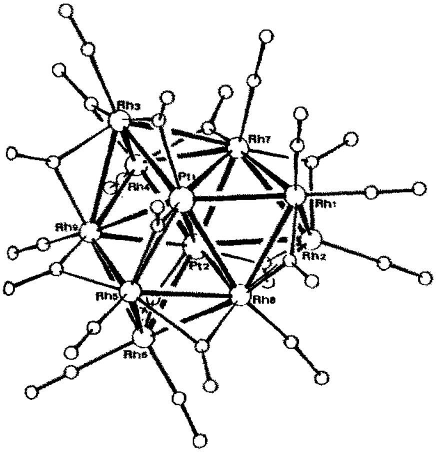
a) CO, > 1 atm. b) N_2 flush or vacuum. c) CO, 1 atm. d) $[Rh(CO)_2(MeCN)_2]^+$, CO, MeCN. e) $[Rh_6(CO)_{16}]$, CO, THF($[Rh_5(CO)_{15}]^-$ is also formed).

Scheme XXX



[153]

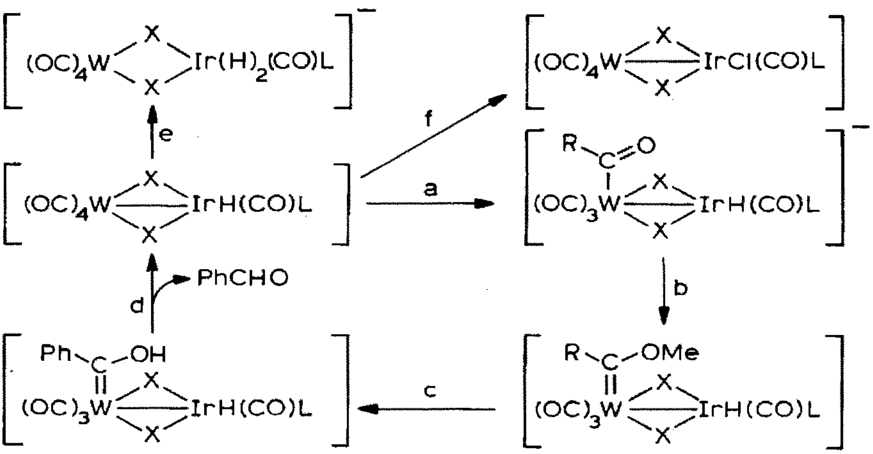
[151] is static at -90°C but at -50°C an exchange process involving the carbonyls labelled b, c and e occurs. At -75°C [152] undergoes a bridge-terminal exchange process of the carbonyls CO(5)-CO(8) while at 25°C all carbonyls except CO(1), CO(3) and CO(4) exchange. Complex [153] is static at -90°C but fluxional at higher temperatures although the details of the process remain unclear. Further work in the prolonged pyrolysis of [151] in refluxing methanol has led to the identification of a small amount of $[Pt_2Rh_9(CO)_{22}]^{3-}$ ([154]) among the products which also include $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ and $[PtRh_{12}(CO)_{24}]^{4-}$. Complex [154] is proposed as an immediate



[154]

precursor to $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ (refs. 344, 345).

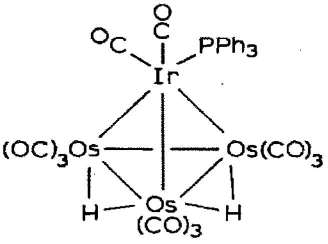
Protonation of the iridium analog of [138] forms $[(OC)_4\overline{W(\mu\text{-}PPh_2)_2Ir}(H)(CO)(PPh_3)]$ which can also be formed from $Li[W(CO)_4(PPh_2H)(PPh_2)]$ and $[IrCl(CO)(PPh_3)_2]$. In a similar reaction $[IrCl(CO)(PPh_3)_2]$ and $Li[M(CO)_5(PPh_2)]$ give $[(PPh_3)(CO)_4\overline{M(\mu\text{-}PPh_2)Ir}(CO)_2(PPh_3)]$ (M = Mo, W). The tungsten complex reacts reversibly with hydrogen and carbon monoxide to give $[(PPh_3)(CO)_4W(\mu\text{-}PPh_2)IrH_2(CO)_2(PPh_3)]$ and $[(PPh_3)(CO)_4W(\mu\text{-}PPh_2)Ir(CO)_3(PPh_3)]$ (two isomers) respectively with cleavage of the metal-metal bond. Other chemistry of $[(OC)_4\overline{W(\mu\text{-}PPh_2)_2Ir}H(CO)(PPh_3)]$ is outlined in Scheme XXXI (X = PPh_2; L = PPh_3) (ref. 346). Reaction of $[IrH(CO)_2(PPh_3)_2]$ with $[H_2Os_3(CO)_{10}]$ in refluxing dichloromethane yields [155] (ref. 347) while $[cp'Ir(CO)_2]$ with $[Pt(C_2H_4)_3]$ at 0°C in diethyl ether forms [156] in which the carbonyl ligands exchange sites (ref. 348). Although $[Pt_2Ir_2(\mu\text{-}CO)_3(CO)_4(PPh_3)_3]$ ([157] (L = PPh_3)) is formed from $[Pt_{12}(CO)_{24}]^{2-}$ and $[IrCl(CO)(PPh_3)_2]$ in acetonitrile/chloroform on purging with nitrogen, neither the rhodium analog nor $[Ir(CO)(NO)(PPh_3)_3]$, $[IrCl(CO)(NO)(PPh_3)_2]^+$, $[IrCl(COD)]_2$ or $[Ir(DPPE)_2]^+$ gave mixed-metal clusters. Complex [157] is unreactive towards methanolic potassium hydroxide and hydrogen at low pressure but under high pressure a



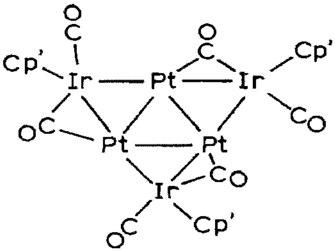
a) 2LiR (R = Me, Ph), 25°C, THF. b) $[Me_3O]BF_4$, THF.
c) TFA, acetone, -40°C. d) Warm to 0°C. e) $[MeC(O)]SbCl_6$
f) $LiBHBu^s_3$, THF.

Scheme XXXI

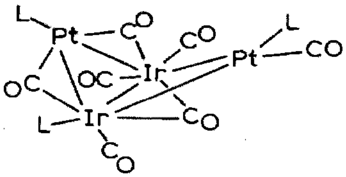
new and as yet uncharacterized complex is formed. It shows low catalytic activity for the disproportionation of cyclohexene to cyclohexane and benzene but is somewhat better for olefin hydrogenation (ref. 349).



[155]



[156]



[157]

EXAFS studies have been made on [$Rh_4(CO)_{12}$], [$RhCo_3(CO)_{12}$] and [$Rh_2Co_2(CO)_{12}$] together with [$Rh_2Co_2(CO)_{12}$] supported on alumina. The last appears to maintain its integrity on the surface but is thought to have a structure somewhat distorted from that of the free cluster due to interactions of some of the carbonyl ligands with the surface. Heating the supported cluster removes the carbonyl ligands and cleaves the rhodium-rhodium bond but leaves the rhodium-cobalt bonds intact. Both this cluster and [$RhCo_3(CO)_{12}$] on alumina retain the integrity of the tetrametallic core when reduced with hydrogen but when mixtures of rhodium(III) and cobalt(II) chlorides are deposited on alumina and reduced with hydrogen, metal particles of significantly larger size form and segregation of the cobalt from the rhodium occurs (ref. 350). Extended Hückel molecular orbital calculations on [$(\eta^6-C_6H_6)Cr(CO)(\mu-CO)_2Rh(CO)cp'$] and on [$cpCo(\mu-CO)_2Rh(PH_3)cp$] as model for the known dimethylphenylphosphine complex suggest that the bonding between the two parts of the molecules occurs primarily through the two semibridging carbonyl groups rather than <u>via</u> a dative chromium- or cobalt-rhodium bond (ref. 351).

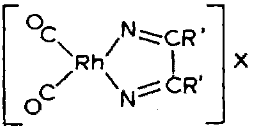
The alkylidyne complex [$cpNiCo_2(CO)_6(\mu_3-CMe)$] and related complexes serve as catalyst precursors for pent-1-ene hydroformylation. An approximately 9:1 ratio of aldehyde over alcohol is produced but a substantial portion of the aldehyde is the branched-chain isomer (ref. 352). Mixtures of [$Co_2(CO)_8$] with [$Ru_3(CO)_{12}$] or [$Fe_3(CO)_{12}$] and also [$FeCo_3(CO)_{12}$]$^-$ alone form catalysts for cyclohexene hydroformylation which are much better than [$Co_2(CO)_8$] alone. The enhanced activity is thought to possibly be due to formation of a ruthenium or iron hydride which readily reacts with an intermediate cobalt acyl complex (ref. 353). In related work, mixtures of [$Co_2(CO)_8$] and [$Ru_3(CO)_{12}$] in molten tetra-<u>n</u>-butylphosphonium bromide catalyze the conversion of syngas to C_1-C_3 alcohols and their acetate esters. Infrared spectroscopic studies on the system indicated the major species present were [$HRu_3(CO)_{11}$]$^-$, [$Ru(CO)_3Br_3$]$^-$ and [$Co(CO)_4$]$^-$; no significant quantities of heterobimetallic complexes were detected. At high cobalt/ruthenium ratios a 68% selectivity to acetic acid is achieved. Although methanol forms at approximately the same rate in the absence of cobalt, the yield is improved when it is present suggesting that the species identified spectroscopically may not be the key active species in the mixed-metal system (refs. 354, 355). The tetrametallic clusters [$Co_{4-n}Rh_n(CO)_{12}$] ($n = 0, 2, 4$) in the presence of up to nine equivalents of a phosphine or a phosphite (L) and [$Rh_4(CO)_{12-n}L_n$] ($n = 1$-4) catalyze the hydroformylation of cyclohexene, pent-1-ene and styrene. In the Co_2Rh_2 and Rh_4 clusters the maximum activity is noted when five to six equivalents of the ligand are present and while the quantity of ligand used has little effect on the regioselectivity, its nature does. No evidence for cluster fragmentation was observed with phosphite ligands but this does occur in the presence of aryl phosphines (see also refs. 263, 264). These same two clusters were also studied with the same substrates in the presence of phenyl- and diphenylphosphine in an attempt to generate phosphido-bridged clusters in situ. The former ligand produced an inactive system but with one or two equivalents of diphenylphosphine plus two to four equivalents of a tertiary phosphine or phosphite an effective catalyst formed. Larger quantities of diphenylphosphine caused a decrease in activity and the preformed clusters $[Rh_3(CO)_5(\mu\text{-}PPh_2)_3]$ and $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ were inactive (refs. 356, 357).

On interaction of $[Rh_nCo_{4-n}(CO)_{12}]$ (n = 0-2, 4) and $[Ir_nCo_{4-n}(CO)_{12}]$ (n = 0, 2, 4) with Dowex and Amberlite resins or with silica, fragmentation and redistribution of metal atoms generally occurs. With the bimetallic clusters a segregation of the metals is seen; for example with $[Rh_2Co_2(CO)_{12}]$, $[Co(CO)_4]^-$ and $[RhCl_2(CO)_2]^-$ are seen with the latter apparently arising from residual chloride in the resin. Also supported in this manner were $[Rh_5Pt(CO)_{15}]^-$ and $[Rh_{12}(CO)_{30}]^{2-}$. It is not clear whether or not fragmentation occurred but no decarbonylation was seen when the supported clusters were treated with hydrogen. The former is relatively stable thermally but the latter decarbonylates on heating. Little catalytic activity was noted (refs. 358, 359). The cluster $[H_2Rh(acac)Os_3(CO)_{10}]$ on alumina is a catalyst for carbon monoxide hydrogenation with a behavior very similar to rhodium metal on alumina which may suggest decomposition of the cluster on the support (ref. 360). Finally, $[Rh_nCo_{4-n}(CO)_{12}]$ (n = 0-2, 4) have been supported on alumina, silica and zirconium dioxide, thermally decomposed and used as Fischer-Tropsch catalysts. On alumina all clusters give catalysts producing C_1-C_5 hydrocarbons with a selectivity to methane of greater than 70% while on zirconium dioxide all the rhodium-containing clusters produced ethanol as well as other oxygenates. In general rhodium appeared superior to cobalt in the extent of conversion and the support had a strong effect on selectivity when rhodium was present but not with the all-cobalt system (ref. 361).

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

The chloride ligand in $(Bu^n{}_4N)_3[Co(CN)_5Cl]$ is replaced by carbon monoxide to give $(Bu^n{}_4N)_2[Co(CN)_5(CO)]$ which on photolysis in aqueous perchloric acid forms $(Bu^n{}_4N)_2[Co(CN)_5(H_2O)]$ (ref. 362).

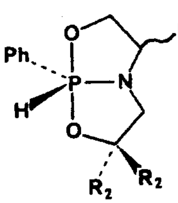
A significant number of papers report on reactions of $[RhCl(CO)_2]_2$ and its derivatives although rather few novel results have been found. With diphenylphosphinoacetic acid or 2-thienyldiphenylphosphine (L) in benzene under a nitrogen purge further examples of trans-$[RhCl(CO)L_2]$ form. The insolubility of the complex of the first ligand in non-coordinating solvents is attributed to intermolecular hydrogen bonding between the carboxylic acid groups. This complex undergoes standard oxidative addition reactions but coordination of the carboxyl group also appears to occur and inseparable mixtures of products result. With [Rh(acac)(CO)$_2$] the former ligand gives cis-[$\overline{\text{Rh}(\text{Ph}_2\text{PCH}_2\text{C(O)O}}$)(CO)L]. The 2-thienyldiphenylphosphine complex reversibly adds one carbonyl ligand (refs. 363, 364). Addition of two equivalents of tri-tert-butylphosphine (L) to [RhCl(CO)$_2$]$_2$ forms [RhCl(CO)L]$_2$ which reacts further with trimethylsilylthioethers to give [Rh(CO)L(μ-Cl)(μ-SR)Rh-(CO)L] (R = Pr^i, Bu^n, Bu^t, Ph, p-tolyl, p-XC$_6$H$_4$ (X = F, Cl), (EtO)$_3$Si(CH$_2$)$_2$, (MeO)$_3$Si(CH$_2$)$_3$) the last two of which permit anchoring the complex to a silica surface. Triphenylphosphine analogs were also prepared and many of the complexes were active as catalysts for the isomerization of oct-1-en-3-ol to octan-3-one, of 4-allylanisole to cis- and trans-1-propenylanisole and of the hydrogenation of α,β-unsaturated ketones by formic acid (ref. 365). Other ligands forming [RhCl(CO)L$_2$] complexes from [RhCl(CO)$_2$]$_2$ are 9H-telluroxanthine and 10-ethyl-3,7-dimethylphenotellurazine. The products undergo oxidative addition reactions with iodine. The same ligands replace the cyclooctene ligand in [Rh(oq)(cyoct)(CO)] to give [Rh(oq)(CO)L]. In both sets of complexes L can be replaced by triphenyl- and tri-n-butylphosphine (ref. 366). The bidentate ligands 2-methylthioethyldiphenylphosphine, its arsenic analog and 2-phenylthiomethylpyridine (L$_2$) forms cis-[RhCl(CO)(L$_2$)] from [RhCl(CO)$_2$]$_2$ but with [RhCl$_2$(CO)$_2$]$^-$ the product is [RhCl$_2$(CO)(L$_2$)]$_2$. It is somewhat surprising that these ligands would form rhodium(II) complexes in this reaction but no information is available from the abstract to indicate how this formulation was established. No isolable products could be obtained from the reaction of these ligands with [IrCl$_2$(CO)$_2$]$^-$ (ref. 367). Other products from [RhCl(CO)$_2$]$_2$ are [RhCl(CO)(L)(L')] (L = 3-aminocoumarin; L' = CO, PPh$_3$) which are catalyst precursors for olefin hydrogenation (ref. 368), [RhCl(CO)$_2$(PhNO)] which decomposes at 70°C under carbon monoxide to form primarily aniline and carbon dioxide, possibly via a nitrene intermediate, (ref. 369) and the diazadiene complexes [158] (R = cy, Ph, p-tolyl, p-HOC$_6$H$_4$; R' = H, Me. R = p-anisyl; R' = H. X = [RhCl$_2$(CO)$_2$]).



[158]

In complexes [158] some intermolecular metal-metal interaction is evident and most decompose in solution (ref. 370). The ammonium salts $LH[RhCl_2(CO)_2]$ are formed when $[RhCl(CO)_2]_2$ reacts with amines (L = py, γ-picoline, benzotriazole) in the presence of hydrochloric acid while when L = ophen and 4,4'-bipyridine, $LH_2[RhCl_2(CO)_2]_2$ is obtained. The benzotriazolium and $[ophenH_2]^{2+}$ salts eliminate hydrogen chloride to form $[RhCl(L)(CO)_2]$ and $[(RhCl(CO)_2)_2(\mu\text{-ophen})]$ respectively (ref. 371).

With one equivalent of the cyclic phosphazine $(FPNBu^t)_2(L)$, $[RhCl(CO)_2]_2$ forms [(cis-$RhCl(CO)_2)_2(\mu\text{-L})]$ which is converted to trans-$[RhCl(CO)(L)_2]$, a complex which can be prepared directly from $[RhCl(CO)_2]_2$ and three equivalents of the ligand. Further reaction of this last complex with the ligand gives a species proposed to be a polymer with $\{Rh_2(CO)_2(\mu\text{-Cl})_2\}$ moieties bridged by the ligand (ref. 372). Two equivalents of the aminophosphorane [159] (R_1 = Me, Et; R_2 = H, Me) react with $[RhCl(CO)_2]_2$ to give the diastereoisomeric mixture [160a, b] in which the tautomeric form of the ligand is present. The optical isomers were separated (R_1 = Me; R_2 = H) and used as catalysts for the asymmetric hydrogenation of (Z)-α-acetamidocinnamic acid. The activity and optical yields were both low. An analog of [160] is formed similarly from [161] but if only one mol of ligand is used, [162] is formed which is photosensitive in solution. A second equivalent of ligand converts [162] to the monomer (refs. 373, 374). The cyclic phosphite [163] (R = Me, Et, Bu^s, l-menthol) forms [164] (L = CO, C_2H_4) on reaction with $[RhCl(CO)_2]_2$ and $[RhCl(C_2H_4)_2]_2$ respectively. Both products react with carbon monoxide



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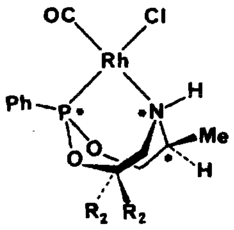
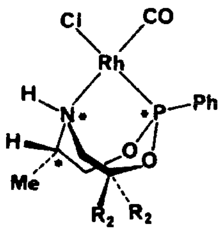
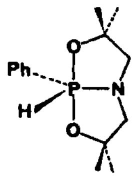


[160a]



[160b]



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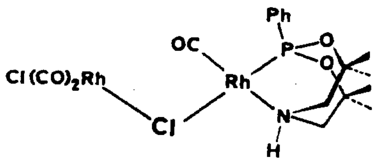

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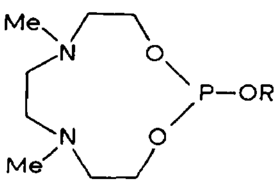
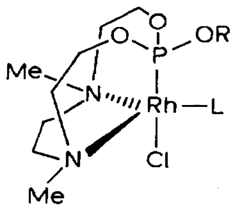
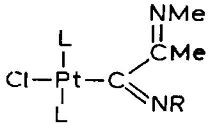


[163]



[164]

to form a purple species whose structure was not established but as a carbonyl absorption was found at 1720 cm^{-1} it was felt that it is binuclear (ref. 375). Sodium tris(pyrazolyl)methylgallate and sodium bis(pyrazolyl)dimethylgallate react with $[RhCl(CO)_2]_2$ to give $[(MeGapz_3)Rh(\mu\text{-}CO)_3Rh(pz_3GaMe)]$ and $[(Me_2Gapz_2)Rh(CO)_2]$ respectively. The first on heating in benzene is converted to $[Rh(CO)_2(\mu\text{-}pz)]_2$ while in the presence of triphenylphosphine the product is $[Rh(CO)(PPh_3)(\mu\text{-}pz)]_2$. No cleavage of the pyrazolylgallate ligand occurs when $[(Me_2Gapz_2)Rh(CO)_2]$ reacts with the phosphine and the product is $[(Me_2Gapz_2)Rh(CO)(PPh_3)]$. Partial cleavage does occur when the bis(pyrazolyl)dimethylgallate ion reacts with $[RhCl(COD)]_2$ and $[(Me_2Gapz_2)Rh(COD)]$ plus $[Rh(COD)(\mu\text{-}pz)]_2$ form but with $[RhCl(PPh_3)_3]$ the product is $[(Me_2Gapz_2)Rh(PPh_3)_2]$. These complexes are fluxional *via* an inversion of the chelate ring. Attempts to obtain the analogous bis(3,5-dimethylpyrazolyl)dimethylgallate complexes led only to dimethylpyrazolyl-bridged dimers so cleavage of the pyrazolylgallate ligand evidently occurred (refs. 376, 377). The ligand N,N-bis(2-pyridylethyl)aniline and analogs with the phenyl ring substituted at the *para* position by chlorine, fluorine and methyl groups (L) initially coordinate in a bidentate fashion on reaction with $[RhCl(CO)_2]_2$ in the presence of sodium tetraphenylborate to form $[Rh(CO)_2(L)]BPh_4$ which undergoes a reversible conversion to $[Rh(CO)(L)]BPh_4$ presumably by displacement of a carbonyl ligand by the initially uncoordinated pyridyl group (ref. 378). The platinum complex [165] (L = PPh_3; R = *p*-anisyl) also reacts with stoichiometric quantities of $[RhCl(CO)_2]_2$ or with $[RhCl(COD)]_2$ and sodium perchlorate to give [166] (L_2 = $(CO)_2$, COD; X = ClO_4).



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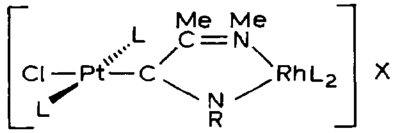
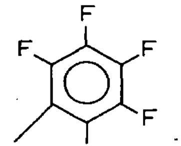


[166]

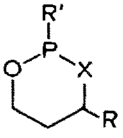
With an excess of the rhodium reagent, analogs with X = $[RhCl_2L_2]^-$ are obtained (refs. 379, 380). Several phosphorus ligands replace one carbonyl ligand in $[Rh(oq)(CO)_2]$ to form $[Rh(oq)(CO)(L)]$ (L = PPh_3, $PPh_2(2\text{-}Br\text{-}3,4,5,6\text{-}F_4C_6)$, $P(OPh)_3$, $P(OMe)_3$). The second product in refluxing toluene converts to [167] and a species formulated as $[Rh_2Br(oq)L_2]$ but which may also contain a metallated phosphine ligand (ref. 381).



[167]

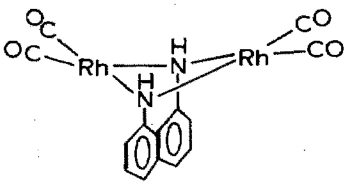
Reaction of $[RhCl(CO)(PPh_3)_2]$ with carbon disulfide and triphenylphosphine in methanol forms $[Rh(CO)(PPh_3)_2(S_2CPPh_3)]^+$. Similarly with $[RhCl(P(OPh)_3)_2]_2$ and various phosphines (L' = $P(\underline{p}\text{-}XC_6H_4)_3$ (X = H, Me, OMe)) the products are $[Rh(P(OPh)_3)_2(L')(S_2CL')]^+$. By contrast, $[Ir(COD)L'_2]^+$ simply forms $[Ir(COD)(CS_2)L'_2]^+$ which is converted to $[Ir(CO)_3L'_2]^+$ on reaction with carbon monoxide (ref. 382). Standard methods have been used to prepare $[Rh(CO)L_n(PPh_3)_{3-n}]ClO_4$ (n = 1, 2; L = tht, SMe_2, SEt_2), $[M_2(CO)_2(PPh_3)_2(\mu\text{-}L)_2](ClO_4)_2$ (L = dth, $MeS(CH_2)_3SMe$, 2,2,7,7-tetramethyl-3,6-dithiaoctane; M = Rh, Ir) and $[Ir(COD)(CO)_n(PPh_3)_{3-n}]$ (n = 1, 2) (ref. 383). The interaction of $\{Rh(CO)(PPh_3)_2\}^+$ moieties with the base pairs between cytidine and 6- or 8-mercaptoguanosine has been studied by NMR. Both cytidine and mercaptoguanosine complexes were detected (ref. 384). A variety of β-diketonate anions and related species react with $[RhCl(CO)(PPh_3)_2]$ to form five-coordinate complexes $[Rh(CO)(L_2)(PPh_3)_2]$ (L_2 = acac, bzac, oq, salicylaldehyde(-H), benzophenone(-H)) (ref. 385). Under 1750 psi of carbon dioxide in hot toluene $[Rh(BH_4)(CO)(Pcy_3)_2]$ is converted to the formate complex $[Rh(O_2CH)(CO)(Pcy_3)_2]$, a transformation which can also be effected using formic acid in dichloromethane (ref. 386). A mixture of $[RhH_2ClL_2]$ and $[RhCl(CO)L_2]$ (L = PBu^t_3) is converted by diborane in ethanol to a pyrophoric solid proposed to be $[Rh_{55}Cl_{20}L_{12}]$ with a cuboctahedral arrangement of metal atoms. The solid takes up six equivalents of carbon monoxide (ref. 387). The labile perchlorate ligand in $[Rh(OClO_3)(CO)(PPh_3)_2]$ is replaced by unsaturated aldehydes in benzene to form $[Rh(RCH{=}CHCHO)(CO)(PPh_3)_2]ClO_4$ (R = H, Me) in which coordination through oxygen rather than the olefinic bond is proposed. The aldehyde can be replaced in turn by acrylonitrile, propionitrile, acetone and triphenylphosphine (ref. 388). Photolysis of $[(Rh(CO)_2)_2TPP]$ forms $[Rh^{II}(TPP)]$ which then dimerizes.

Presumably the remaining rhodium is converted to the metal. It was concluded that neither the lowest singlet excited state nor the ground state triplet of the starting material is involved in the process but rather that homolytic cleavage of a rhodium-nitrogen bond occurs in the active excited state (ref. 389). Addition of 2,3,4,5-tetrabromo-*o*-benzoquinone (L) to [RhX(CO)(PPh$_3$)$_2$] (X = Cl, I) gives a mixture of *cis*- and *trans*-[RhCl(CO)-(PPh$_3$)$_2$(L)] or [RhI(CO)(PPh$_3$)$_2$(L)] plus [RhI(CO)(PPh$_3$)(L)] respectively. The *cis*- isomer of the chloride complex converts to the *trans*- isomer in acetone solution, probably *via* dissociation of a phosphine ligand (ref. 390). Two reactions of [Rh(acac)(CO)$_2$] are those with [168] (L. X = O; R = H, Me; R' = Et$_2$N, morpholino. R = H; R' = Me$_2$N, piperidino. X = NPr^i; R



[168]

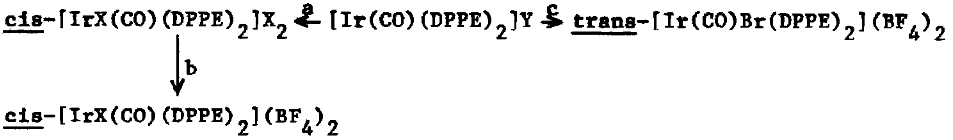
= H; R' = Me$_2$N, Et$_2$N, EtO, H$_2$N(CH$_2$)$_3$O) to give [Rh(acac)(CO)(L)] (refs. 391, 392) and with 1,8-diaminonaphthalene to form [169]. Complex [169] reacts with triphenylphosphine to replace one carbonyl group on each metal and the



[169]

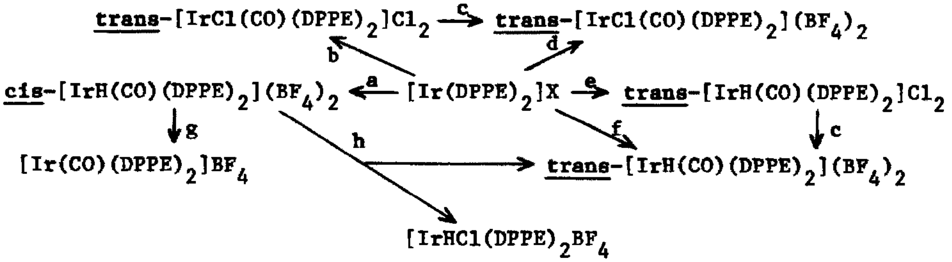
phosphine complex oxidatively adds iodine with formation of a metal-metal bond (ref. 393). A mixture of [RhCl(CO)$_2$]$_2$, [Rh(acac)L$_2$] (L = η^3-C$_3$H$_5$; L$_2$ = TFB) and 1,2,4-triazole (tz) forms [Rh$_3$(μ_3-tz)(μ_2-Cl)ClL$_2$(CO)$_4$] in which a weak metal-metal interaction occurs (ref. 394). Reaction of [RhH(CO)-(PPh$_3$)$_3$] with Cs[NSO$_2$] in refluxing acetonitrile forms *trans*-[Rh(NSO)(CO)-(PPh$_3$)$_2$] and triphenyphosphine oxide. The structure of the complex has been determined (ref. 395).

Some chemistry of [Ir(CO)(DPPE)$_2$]$^+$ and [Ir(DPPE)$_2$]$^+$ is shown in Schemes XXXII and XXXIII. The *cis*-isomers are formed by kinetic control. Cyclic voltammetric studies on [Ir(CO)(DPPE)$_2$]$^+$ show that the two-electron oxidation is irreversible. When chloride ion is present *cis*- and *trans*-[IrCl(CO)-(DPPE)$_2$]$^{2+}$ are formed upon oxidation (ref. 396). The analogous complex [Ir(CO)(vdiphos)$_2$]BPh$_4$ reacts with tetrasulfurtetranitride in hot THF to form $[\overline{\mathrm{IrSNSN}}(\mathrm{vdiphos})]_2$. The structure was determined but a disorder in IrS_2N_2 ring made it impossible to describe the details of the bonding in this portion of the molecule (ref. 397).



a) X_2 (X = Cl, Br), CO, CH_2Cl_2 (Y = Cl). b) NH_4BF_4.
c) CO, $NOBF_4$, MeCN (Y = Br).

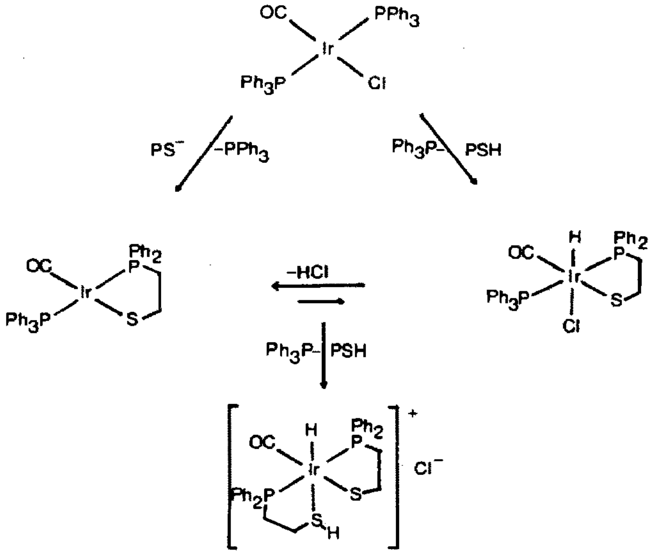
Scheme XXXII



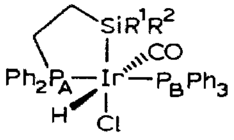
a) CO, $HBF_4 \cdot Et_2O$, CH_2CL_2 ($X = BF_4$). b) 1. CO, CH_2Cl_2. 2. NOCl (X = Cl).
c) BF_4^-. d) $[cp_2Fe]BF_4$, CO, CH_2Cl_2 (X = Cl). e) CO, HCl, CH_2Cl_2 (X = Cl).
f) 1. $HBF_4 \cdot Et_2O$, CH_2Cl_2. 2. CO ($X = BF_4$). g) py, Et_3N or OH^-.
h) Cl^-.

Scheme XXXIII

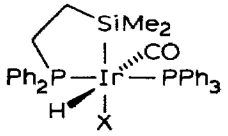
Vaska's complex, $[IrCl(CO)(PPh_3)_2]$, is the starting point for quite a number of syntheses of iridium(I) and -(III) complexes. With 2,11-bis-(diphenylphosphinomethyl)benzo[c]anthracene (L_2) it forms $[IrCl(CO)(L_2)]$ in which the ligand spans trans-positions in the coordination sphere. Oxidation with copper(II) chloride forms mer-$[IrCl_3(CO)(L_2)]$ which decomposes in solution at 50°C. The same complex results on addition of a stoichiometric quantity of chlorine in carbon tetrachloride. Also formed is a second species which reacts further to form $[IrH(CO)Cl_2(L_2)]$. However when $[IrCl(CO)(L_2)]$ is oxidized with hexachloroiridate(IV) in acetonitrile only decomposition occurred (ref. 398). Reaction of $[IrCl(CO)(PPh_3)_2]$ with pyrazole and potassium hydroxide in benzene/methanol or with potassium pyrazolate in benzene forms *trans*-$[Ir(pz)(CO)(PPh_3)_2]$. Analogs with 3,5-dimethyl-,3,5-bis(trifluoromethyl)- and 3,5-dimethyl-4-nitropyrazolate were prepared similarly. The 3,5-dimethylpyrazolate complex is protonated by tetrafluoroboric acid to form the corresponding cationic complex of the neutral pyrazole ligand. The pyrazolate complexes add hydrogen to form *cis*-dihydride complexes and react with hydrogen chloride to give $[IrHCl_2(CO)(PPh_3)_2]$. The substituted pyrazolate complexes are monomeric in solution but in their mass spectra evidence is seen for dimers which are formed *via* loss of a phosphine ligand from the monomers (refs. 399, 400). The ligand 2-diphenylphosphinoethanethiol (PSH) and its anion (PS^-) react with $[IrCl(CO)(PPh_3)_2]$ as shown in Scheme XXXIV (ref. 401). Oxidative addition of a silicon-hydrogen bond in a series of 2-diphenylphosphinoethylsilanes occurs on reaction with $[IrCl(CO)(PPh_3)_2]$ to form [170] ($R^1 = R^2 =$ Me, Ph. $R^1 =$ Me; $R^2 =$ Ph, H. $R^1 =$ Ph; $R^2 =$ H) which is obtained as a mixture of diastereoisomers when $R^1 \neq R^2$. Complex [170] ($R^1 = R^2 =$ Me) reacts with sodium halides in acetone to form [171] (X = Br, I), with lithium aluminum hydride to give [172] (X = H), and with more ligand in the presence of triethylamine



Scheme XXXIV

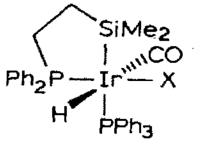


[170]

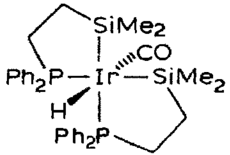


[171]

to yield [173]. Complex [172] is also formed from 2-diphenylphosphinoethyldimethylsilane and $[Ir(H)(CO)(PPh_3)_3]$ and with an excess of the ligand



[172]



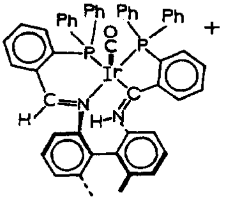
[173]

converts to [173]. An interesting feature of the conversion of [170] (R^1 = R^2 = Me) to [172] is the change in stereochemistry. An attempt to methylate [170] (R^1 = R^2 = Me) with methylmagnesium iodide formed [171] (X = I) instead but the desired complex was thought to form when methylmagnesium chloride was used. Reaction of [170] (R^1 = R^2 = Me) with lithium aluminum deuteride formed a mixture of [172] (X = D) and the isomer having the opposite arrangement of hydride and deuteride ligands. The single isomer ([172] (X = D)) is the initial product of the oxidative addition of 2-diphenylphosphinoethyldimethylsilane to $[IrD(CO)(PPh_3)_3]$ but on standing in solution the same isomeric mixture forms. The observation that [172] shows no exchange with deuterium gas was considered to indicate that the isomerization occurs intramolecularly (refs. 402, 403). Other reactions of $[IrCl(CO)(PPh_3)_2]$ are those with $Me_3SiCH_2C(=CH_2)CH_2CH_2Cl$ in refluxing toluene to form the trimethylenemethane complex $[(\eta^4\text{-}C(CH_2)_3)IrCl(CO)(PPh_3)]$ (or the cation $[(\eta^4\text{-}C(CH_2)_3)Ir(CO)(PPh_3)_2]PF_6$ if carried out in toluene/acetonitrile in the presence of potassium hexafluorophosphate) (ref. 404) and with diarylditellurides to form *trans*-$[Ir(TeR)_2Cl(CO)(PPh_3)_2]$ (R= Ph, *p*-tolyl, *p*-$R'C_6H_4$ (R = Cl, OEt)). The observation of an ESR signal during the course of the reaction and the detection of intermediates suggested it proceeds as indicated in Scheme XXXV (L = PPh_3) (ref. 405). Fluorination of

$$\begin{tikzcd}
{[IrCl(CO)L_2] + R_2Te_2} \arrow[r, leftrightharpoons] & {[IrCl(CO)L_2,Te_2R_2]} \arrow[d, shift left, "k_2"] \\
{[Ir(TeR)_2Cl(CO)L_2]} & {[\cdot IrCl(TeR)(CO)L_2] + RTe\cdot} \arrow[u, shift left, "k_{-2}"] \arrow[l, "k_3"']
\end{tikzcd}$$

Scheme XXXV

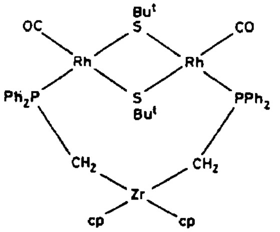
mer-$[IrCl_2(PF_2)(PEt_3)_2(CO)]$ with xenon difluoride gives *mer*-$[IrCl_2(PF_4)(CO)(PEt_3)_2]$ (ref. 406). The macrocyclic ligand 2,2'-bis{*o*-(diphenylphosphino)benzylidene]amino}-6,6'-dimethylbiphenyl (PPNN) has been prepared and from $[RhCl(COD)]_2$ and $[IrCl(N_2)(PPh_3)_2]$ the complexes [*d*,*l*-M(PPNN)]BPh_4 (M = Rh, Ir) were synthesized. The rhodium complex was unreactive towards hydrogen and reacted only incompletely with carbon monoxide. The iridium complex did form cis-[IrH_2(PPNN)]BPh_4 but it has yet to display any significant catalytic activity. With carbon monoxide several complexes were formed including [174] in which the metal has shifted its coordination from one of the



[174]

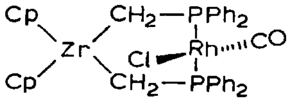
nitrogen atoms to the adjacent methine carbon with a corresponding 1,2-hydrogen shift (ref. 407).

A substantial number of papers has appeared dealing with the chemistry of ligand-stabilized bi- and trimetallic complexes particularly those of the A-frame type. With [$Rh_2(CO)_4(\mu\text{-}SBu^t)_2$], [$cp_2Zr(CH_2PPh_2)_2$] forms [175] which



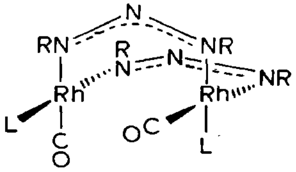
[175]

is a better catalyst than [$RhH(CO)(PPh_3)_3$] for the hydroformylation of hex-1-ene and displays no induction period. The selectivity to straight-chain aldehyde is low however. An analog with 1,5-bis(diphenylphosphino)-pentane was synthesized similarly and while it gives a more selective catalyst for n-heptanal production, it displays a long induction period. It is proposed that the zirconium atom functions as an electron reservoir to facilitate the oxidation state changes which occur in the catalytic cycle but this remains to be definitely established (ref. 408). The same ligand with [$RhCl(CO)_2$]$_2$ in a mixture of pentane, toluene and THF forms [176] (ref.



[176]

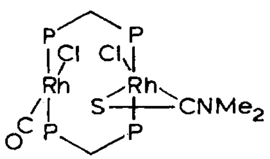
409). One arm of TPM is free in cis-[Mo(CO)$_4$(TPM)] and the complex can function as a ligand on reaction with [RhCl(COD)]$_2$ and carbon monoxide to form trans-[RhCl(CO)(cis-[Mo(CO)$_4$(TPM)])$_2$]. The complex displays an interesting virtually-coupled ^{31}P NMR spectrum in which all molybdenum-bound phosphorus atoms appear equally coupled to the other two. The TPM ligand also bridges an edge of the metal triangle in [RCCo$_3$(CO)$_7$(TPM)] (R = H, Cl) which is formed from [RCCo$_3$(CO)$_9$] at room temperature. On heating this complex or on performing the original reaction at elevated temperature the ligand caps the face of the complex giving [RCCo$_3$(CO)$_6$(TPM)] (ref. 410). The triazenido complex [177] (R = p-tolyl; L = CO) is oxidized in three,



[177]

reversible one-electron steps. The analog with R = p-tolyl and L = PPh$_3$ is oxidized by p-fluorophenyldiazonium hexafluorophosphate to [Rh$_2$(CO)$_2$(PPh$_3$)$_2$(μ-RN$_3$R)$_2$]PF$_6$. The similar complex [Rh$_2$(CO)$_3$(PPh$_3$)(μ-PhNC(Me)NPh)$_2$] shows one reversible and one irreversible one-electron oxidation step. The first can also be accomplished by reaction with ferricinium salts to give [Rh$_2$(CO)$_3$(PPh$_3$)(μ-PhNC(Me)NPh)$_2$]$^+$ in which one carbonyl group can be replaced by Lewis base ligands. These species on reduction with sodium borohydride yield [Rh$_2$(CO)$_2$(PPh$_3$)(L)(μ-PhNC(Me)NPh)$_2$] (L = PPh$_3$, AsPh$_3$, P(OPh)$_3$) (ref. 411).

Although no reaction occurs between the A-frame complex [Rh$_2$(CO)$_2$(μ-OH•Cl)(DPM)$_2$] and carbon monoxide under 1 atm pressure, at 30 psi it converts to [RhCl(CO)(DPM)]$_2$. It also reacts with sulfur dioxide to form [Rh$_2$(CO)$_2$(μ-SO$_2$)(μ-Cl)(DPM)$_2$]HSO$_4$. The related complexes [Rh$_2$(CO)$_2$(μ-X)(DPM)$_2$]ClO$_4$ (X = NCS, N$_3$) react with carbon monoxide to give [Rh$_2$(CO)$_2$(μ-CN)(μ-CO)(DPM)$_2$]ClO$_4$ and [Rh$_2$(CO)$_2$(μ-NCO)(DPM)$_2$]ClO$_4$ respectively. The former complex shows fluxional behavior which is thought to be the result of an asymmetric coordination of the cyanide ligand (possibly approaching a μ-η^1,η^2 bonding mode) (ref. 412). Among the reactions of [Rh$_2$Cl$_2$(μ-CO)(DPM)$_2$] is that with dimethylthiocarbamoyl chloride to form [178] which reversibly loses chloride in solution to give [179]. The cation [179] is also obtained as its tetrafluoroborate salt when the original reaction is run in the presence of sodium tetrafluoroborate. It can be decarbonylated by trimethylamine oxide to [180] and reacts with sodium borohydride to form



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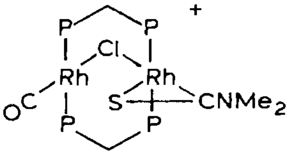
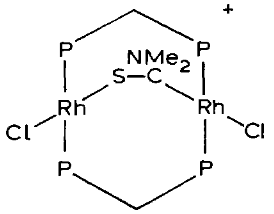


[179]

[181] (solv = MeCN, THF) (ref. 413). Another reaction is with acyl isothiocyanates in which an interconverting mixture of [182] and [183] (R = OEt, Ph) forms. These add carbon monoxide and methyl isocyanide to give [184] (R = OEt) and [185] (R = OEt, Ph) contaminated with some $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]Cl$. When R = OEt, they also react with isothiocyanates to give [186] (R = OEt_2CX (X = NCO_2Et, NMe, NPh, NC(O)Ph, S)). These reactions are thought



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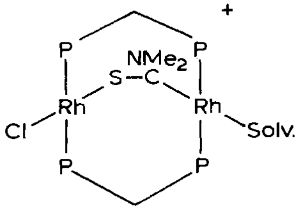

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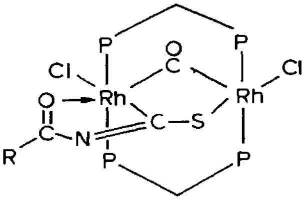

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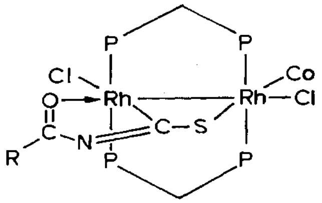

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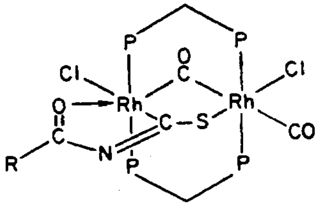

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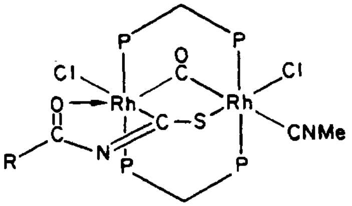

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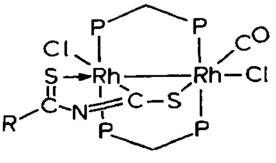
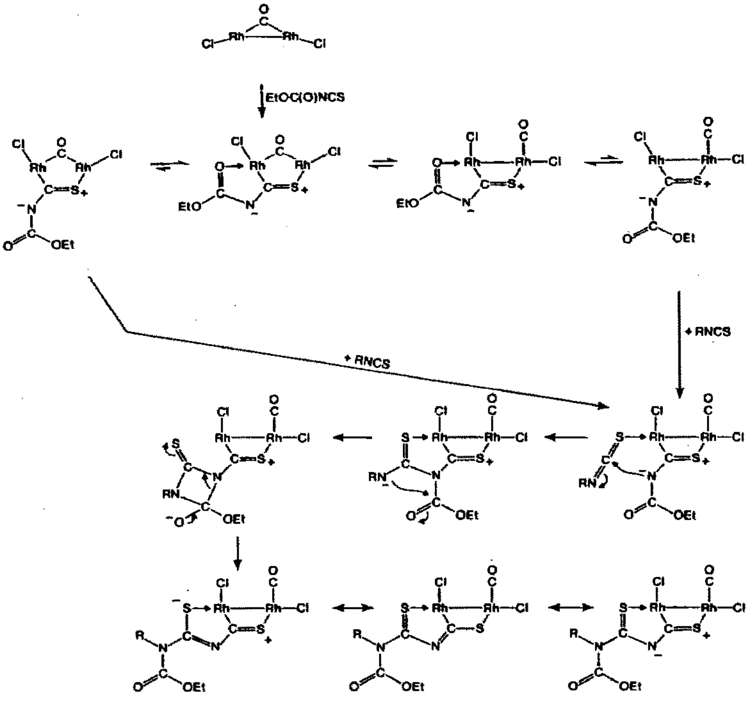


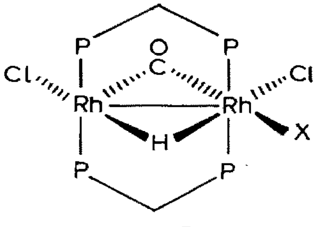
[186]

to occur as depicted in Scheme XXXVI (DPM ligands omitted for clarity).



Scheme XXXVI

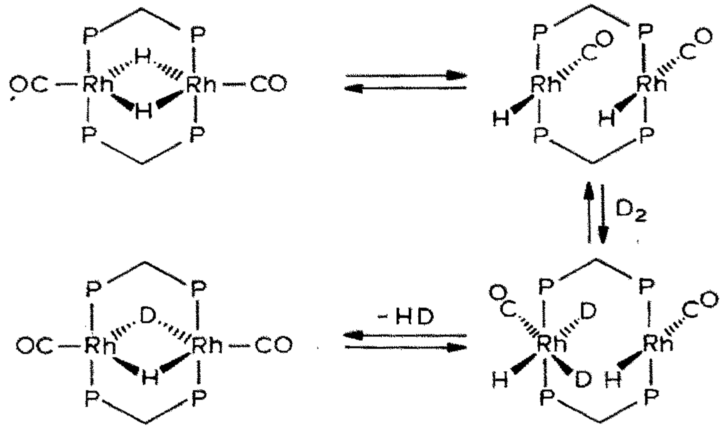
Direct reaction of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ with methyl or phenyl isothiocyanate gives the face-to-face dimers $[Rh_2Cl_2(CO)(RNC)(DPM)_2]$ (R = Me, Ph) and large amounts of other unidentified products (ref. 414). Finally, protonation of the metal-metal bond in $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ gives [187] (X = Cl, BF_4, p-$MeC_6H_4SO_2$) which are fluxional in solution. With the latter two, the



[187]

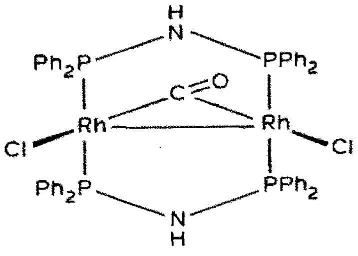
ligand X is thought to dissociate and recoordinate to the other metal while in the first complex loss of hydrogen chloride and readdition to the other metal is thought to be occurring (ref. 415). The complex obtained from the sodium borohydride reduction of $[RhCl(CO)(DPM)]_2$ in ethanol and originally formulated as $[Rh(CO)(DPM)]_2$ has now been shown to be $[Rh_2(CO)_2(\mu\text{-}H)_2(DPM)_2]$. It is stable in the presence of hydrogen but otherwise decomposes to

$[Rh_2(CO)_3(DPM)_2]$ and other unidentified species, possibly through initial formation of $[Rh(CO)(DPM)]_2$ by reductive elimination of hydrogen. In the presence of deuterium, H/D exchange occurs as proposed in Scheme XXXVII and on reaction with tetrafluoroboric acid or hydrogen halides the products are hydrogen plus $[Rh_2(CO)_2(\mu\text{-}H)(DPM)_2]BF_4$ and $[RhX(CO)(DPM)]_2$ (X = Cl, Br) respectively. In the latter reaction (X = Br), $[Rh_2Br_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2]Br$ also forms while with methyl iodide under hydrogen the products are methane and $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}I)(DPM)_2]$ (ref. 416).



Scheme XXXVII

Addition of bis(diphenylphosphino)amine (L_2) to $[RhCl(CO)_2]_2$ initially forms $[Rh(CO)(L_2)_2]Cl$ which on heating in methanol forms a mixture of $[Rh(L_2)_2]Cl$ and [188]. The latter reacts with carbon monoxide to form [189] which subsequently loses a carbonyl group forming [190]. Complex [189] associates in the solid state *via* hydrogen bonds between the N-H group of the ligand, the chloride counterion and solvent methanol molecules (ref. 417). Complex [191] (R = OPh) is converted by sodium amalgam under hydrogen



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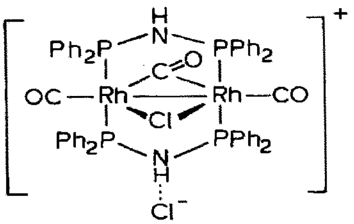

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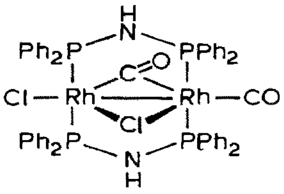
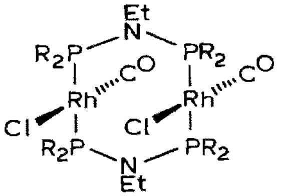


[190]

to [192], by mercury alone to [193] and is reduced by sodium naphthalenide under hydrogen to a mixture of [194] and [195]. Heating [194] in THF with



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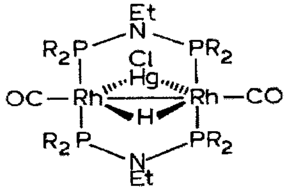

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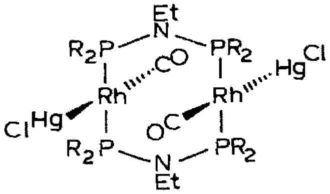
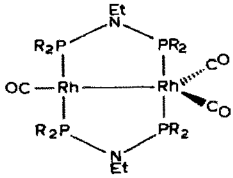


[193]

trimethylamine oxide converts it to [195] which adds carbon monoxide to regenerate [194] (ref. 418). A low yield of [196] is obtained from Ph_4As-$[Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]$ and DPM. Better yields and fewer byproducts result



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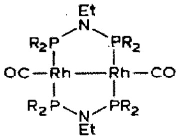

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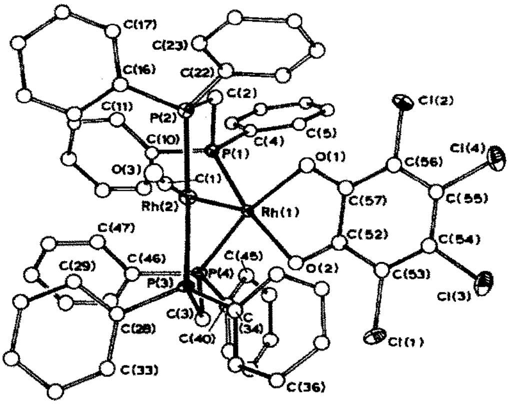
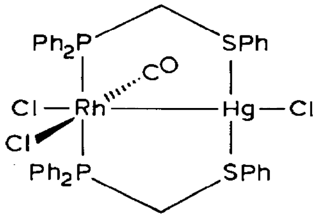


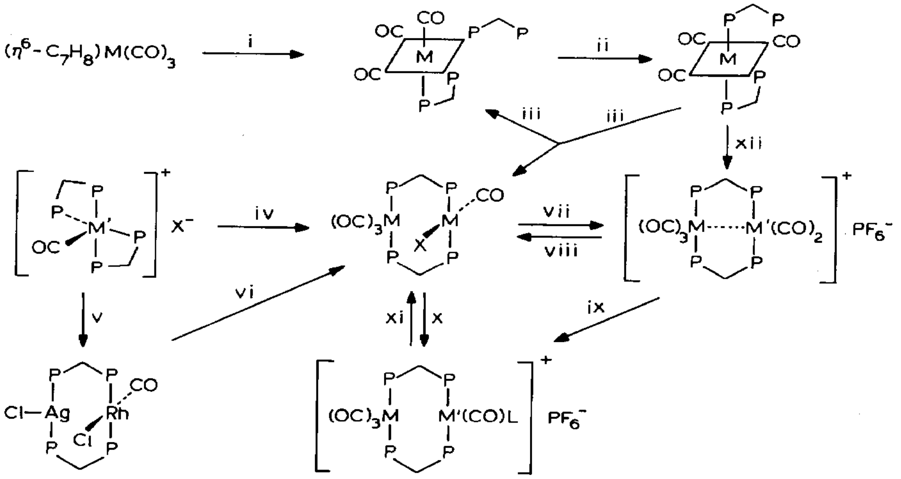
[196]

when $[RhCl(CO)_2]_2$ is added to the reaction mixture. The complex is characterized as having a polar metal-metal bond and undergoes a reversible one-electron oxidation to a product having the odd electron localized in the semi-quinone form of the catecholate ligand (ref. 419). Mercury(II) chloride oxidatively adds to the rhodium(I) complexes $[RhCl(CO)L_2]$ (L = PPh_2Et, PPh_2CH_2SPh) to give $[RhCl_2(CO)(HgCl)(PPh_2Et)_2]$ and [197] respectively (ref. 420). The *cis* stereochemistry about platinum is retained upon



[197]

reaction of *cis*$[PtCl_2(DPAM)_2]$ with $[RhCl(CO)_2]_2$ to form $[RhCl(CO)(\mu\text{-}DPAM)_2\text{-}PtCl_2]$ in which the arsenic atoms coordinate *trans* on the rhodium. Isomerization of the coordination at platinum to *trans* occurs in the presence of excess ligand (ref. 421). The synthesis of a number of heterobimetallic complexes bridged by DPM is outlined in Scheme XXXVIII (ref. 422).

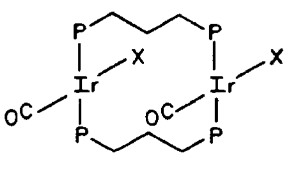


i) DPM, CH_2Cl_2, 20°C (M = Cr, Mo, W). ii) C_6H_6, 80°C, 16 h (M = Cr, Mo, W). iii) $[RhCl(CO)_2]_2$ or $[IrCl(CO)_2$(p-toluidine)] (M = Cr, Mo, W; M' = Rh, Ir). iv) $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$ (M' = Ir; X = Cl, Br, I). v) $[AgCl(PPh_3)]_4$ (M' = Rh; X = Cl). vi) $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$ (M' = Rh; X = Cl). vii) CO, PF_6^- (M = Cr, Mo, W; M' = Rh, Ir). viii) $Bu^n{}_4NX$ (X = Cl, Br; M = Cr, Mo, W; M' = Rh, Ir). ix) MeCN or PhCN (=L; M = Mo; M' = Ir). x) Bu^tNC (=L; M = Cr, Mo, W; M' = Rh). xi) $Bu^n{}_4NX$ (X = Cl; L = MeCN, PhCN; M = Mo; M' = Ir). xii) $[RhCl(CO)_2]_2$ or $[IrCl(CO)_2$(p-toluidine)], CO, NH_4PF_6 (M = Cr, Mo, W; M' = Rh, Ir).

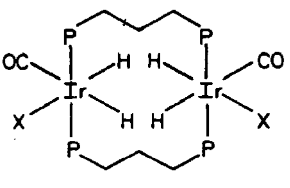
Scheme XXXVIII

The rather unstable complex $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}DPM)]$ is formed from DPM and $[cp_2Rh_2(CO)_2(\mu\text{-}CO)]$ in diethyl ether. It reacts with tin(II) and mercury (II) chlorides or with sulfur dioxide to form $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}MCl_2)(\mu\text{-}DPM)]$ (M = Sn, Hg) and $[cp_2Rh_2(\mu\text{-}SO_2)(\mu\text{-}DPM)]$ respectively. With bromine and iodine the products are $[cpRhBr_2(\mu\text{-}DPM)Rhcp(CO)Br]Br_3$ and $[cp_2Rh_2I_2(CO)\text{-}(\mu\text{-}DPM)]$ respectively but it is unreactive towards methyl iodide and diphenylacetylene (refs. 423-425). Another example of a bridging mercury halide moiety is in $[RhCl(CO)(PPh_3)(\mu\text{-}pz)(\mu\text{-}HgCl)Rh(CO)(PPh_3)]$ which is formed from $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}pz)_2]$ and mercury(II) chloride in dichloromethane. The structure determination shows the two mercury-rhodium distances to be unequal and the complex is considered to have formed by oxidative addition of a mercury-chlorine bond to one rhodium with the second rhodium then forming a donor bond to mercury (ref. 426).

Complexes [198] (X = Br, I) are prepared from $[Ir(CO)_2Br_2]^-$ and DPPP in acetone or from $[Ir_2Cl_2(CO)_2(DPPP)_2]$ and lithium iodide in benzene respectively and oxidatively add hydrogen to form [199]. The intermediate $[IrH_2Br(CO)(\mu\text{-}DPPP)_2IrBr(CO)]$ was also detected suggesting that the metal centers react independently (see also ref. 498). Attempts to prepare [198] (X = I) from the ligand and $[Ir(CO)_2I_2]^-$ gave instead [200] which added hydrogen to give [201]. Complex [201] and its bromo analog also formed when

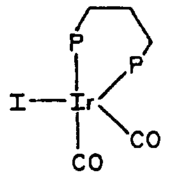


[198]

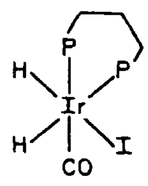


[199]

[199] was refluxed in THF containing triethylamine. With DPPE, $[IrX_2(CO)_2]^-$ (X = Br, I) gave mixtures of <u>cis</u>-$[IrX(CO)(DPPE)]$ and $[Ir(CO)(DPPE)_2]X$. The former reacted with hydrogen to form $[IrH_2X(CO)(DPPE)]$ having the same

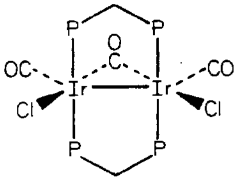


[200]

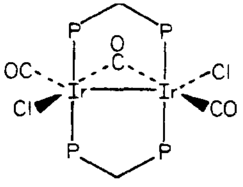


[201]

stereochemistry as [201] (refs. 427, 428). Briefly refluxing $[Ir_2(CO)_3Cl(\mu\text{-}CO)(DPM)_2]Cl$ in THF under nitrogen forms a mixture of [202] and [203]

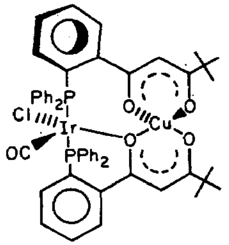


[202]

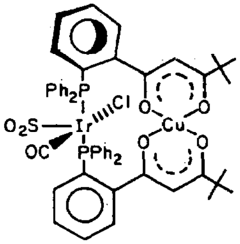


[203]

which equilibrate in solution <u>via</u> $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]Cl$ as an intermediate. Upon longer reaction, further decarbonylation occurs to give the face-to-face dimer $[IrCl(CO)(DPM)]_2$ which is converted to $[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BF_4$ by silver tetrafluoroborate (ref. 429). Addition of HacacP to solutions of $[RhCl(CO)_2]_2$ or $[IrCl(CO)_2$(p-toluidine)] forms <u>trans</u>-[MCl(CO)(HacacP)$_2$] (M = Rh, Ir). The iridium complex reacts with copper(II) heptanoate to form [204] which reversibly adds sulfur dioxide to give [205].



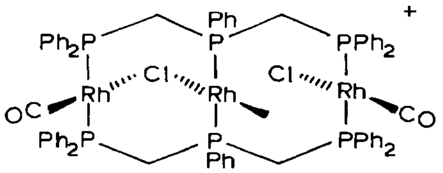
[204]



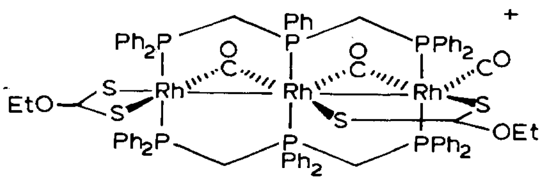
[205]

The zinc analog of [204] is formed from $[Zn(acacP)_2]$ and $[IrCl(CO)_2$(p-toluidine)] and it also adds sulfur dioxide. The electronic and ESR spectra of [204] indicate the existence of some iridium-copper interaction <u>via</u> the enolate bridge (ref. 430).

Sodium xanthate reacts with $[Rh_3(DPMP)_2(CO)_3Cl(\mu\text{-}Cl)]BPh_4$ ([206]) in ethanol to form [207]. A diethyldithiocarbamate analog was prepared

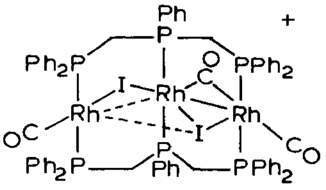


[206]



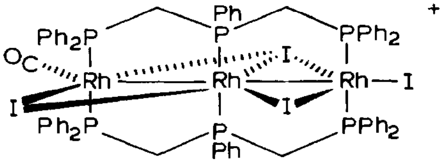
[207]

similarly. These two anions also react with $[RhCl(CO)(DPM)]_2$ to form $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S_2CR)(DPM)_2]^+$ (R = OEt, NEt$_2$) (ref. 431). Carbonylation of $[Rh_3(DPMP)_2(CO)_3I_2]BPh_4$ ([208]) forms $[Rh_3(DPMP)_2(CO)_4I_2]BPh_4$ which reverts to [208] in boiling dichloromethane but on prolonged reflux in



[208]

acetone decarbonylates further to $[Rh_3(DPMP)_2(CO)_2I_2]BPh_4$. Addition of one equivalent of iodine to [208] in dichloromethane forms $[Rh_3(DPMP)_2(CO)_3I_4]$-BPh_4 which successively loses two carbonyl ligands, the second one reversibly, to give [209]. Addition of a second equivalent of iodine to [209]



[209]

forms $[Rh_3(DPMP)_2(CO)I_6]BPh_4$ which no longer will add a carbonyl ligand (ref. 432). A full paper has appeared on the reaction of $[RhCl(CO)_2]_2$ with diphenylphosphine in benzene containing bases such as triethylamine. Addition of the phosphine (Rh/P = 1) all at once yielded $[Rh_4(CO)_4(\mu\text{-}CO)_2$-$(\mu\text{-}PPh_2)_4]$ which contains a tetrahedron of rhodium atoms with all edges bridged. Dropwise addition of the phosphine leads to initial formation of the triangular, metal-metal bonded complex $[Rh_3(CO)_5(\mu\text{-}PPh_2)_3]$ which on standing in solution slowly converts to the tetrarhodium species. In ethanol under carbon monoxide, diphenylphosphine and $[RhCl(CO)_2]_2$ initially form $[Rh_3(CO)_6(PPh_2H)(\mu\text{-}PPh_2)_3]$ which contains no metal-metal bonds and which readily converts to $[Rh_3(CO)_5(\mu\text{-}PPh_2)_3]$. This last complex is reversibly carbonylated to $[Rh(\mu\text{-}PPh_2)(CO)_x]_n$ ($x = 2$ or 3; $n = 2, 3$). A trinuclear formulation with $x = 3$ is favored (refs. 433, 434).

The complex $[Rh(OClO_3)CO(PPh_3)_2]$ is a catalyst for the hydrogenation and isomerization of soybean oil (ref. 435) while $[RhCl(CO)_2]_2$ or $[Rh(acac)$-$(CO)_2]$ in the presence of trialkylamines form catalysts for the hydroformylation of olefins and the conversion of aldehydes to alcohols. A competitive binding of the amine, carbon monoxide and the olefin to the metal is proposed (ref. 436). In related work, the effects of amines, amino acids, nitrogen-heterocycles and ureas on the [RhCl(CO)$(PPh_3)_2$]-catalyzed hydroformylation of propene have been investigated. Those of low basicity improved the yield significantly but provided only a modest increase in selectivity to n-butanal (ref. 437). Significant interest continues in [RhH(CO)$(PPh_3)_3$] as a hydroformylation catalyst. Some conversion of the triphenylphosphine ligands to propyldiphenylphosphine and benzene occurs during propylene hydroformylation and this is more significant when carbon monoxide is absent. A reversible oxidative addition of a phosphorus-phenyl bond to the metal is proposed (see also references 263, 264). This process is proposed to explain the scrambling of aryl groups on phosphorus which is observed when mixtures of [Rh(acac)(CO)(PPh_3)], [RhCl$(PPh_3)_3$] or [RhCl(CO)-$(PPh_3)_2$] and other triarylphosphines are heated in atmospheres of propylene, nitrogen, propylene plus hydrogen or hydrogen. The rate of scrambling decreases with the nature of the atmosphere used in the order listed and also decreases with time as clusters form (refs. 438, 439). The same complex hydroformylates allyl- and propenylbenzenes, specifically eugenol, safrole, isoeugenol and isosafrole. Better rates and better chemo- and regioselectivity for the allylbenzenes were obtained with $[Rh_2(\mu\text{-}SBu^t)_2\text{-}(CO)_2(P(OMe)_3)_2]$ as the catalyst. Both complexes performed comparably well with the other substrates (ref. 440). Other studies using [RhH(CO)$(PPh_3)_3$] are those on the hydroformylation of vinyl and allyl acetates (ref. 441) and of β-substituted N-vinylphthalimides. The latter was carried out in the presence of the chiral ligands DIOP and DIOCOL and while high yields were obtained with excellent regioselectivity, no asymmetric induction was observed (ref. 442). Analogs of [RhH(CO)$(PPh_3)_3$] using alkyldiphenylphosphines as ligands are also hydroformylation catalysts whose activity and selectivity are dependent on reaction conditions and particularly on the nature of the alkyl substituent on the ligand (ref. 443).

The hydrosilylation of hex-1-ene by triethoxysilane catalyzed by [Rh(acac)$(CO)_2$] has been studied in situ by infrared spectroscopy. Rhodium hydride and olefin complexes were detected and when allene was introduced, an η^3-allyl complex was seen (ref. 444). Oct-1-ene, but-1-yne, 2,3-dimethylbuta-1,3-diene and cyclohexanone are hydrosilylated in the presence of [RhCl$(PPh_3)_2$L] (L = CO, PPh_3) and the catalyst activity is enhanced by the addition of hydrogen peroxide or tert-butylhydroperoxide (ref. 445). The carbonylation of nitrobenzene to phenylisocyanate is catalyzed by $Bu^n{}_4N$-$[RhX_2(CO)_2]$ (X = Cl, Br, I), $Me_4N[Rh(SnCl_3)_2(CO)_2]$ and $[M(CO)_2(PPh_3)_2]AlCl_4$ (M = Rh, Ir) with the first series of compounds showing the highest activity (ref. 446). Both $[RhCl(CO)_2]_2$ in the presence of iodide sources and a mixture of rhodium(III) chloride, methyl iodide and triphenylphosphine form catalysts for the carbonylation of THF to lactones and of methyl acetate to acetic anhydride. The entry into the catalytic cycle is probably via $[RhI_2(CO)_2]^-$, which in the latter case is formed via an initial operation of the WGSR (refs. 447, 448). This WGSR also proceeds with $[RhCl_2(CO)_2]^-$ as the catalyst precursor but in this system attempts to effect the electrocatalytic oxidation of carbon monoxide were unsuccessful. Limited activity for this latter process was however seen in the presence of $[RhCl(PPh_3)_3]$, $[Rh(mnt)(DPPE)]^-$ and $[Rh(DPPE)_2]^+$ (ref. 449). One report of attempts to hydrogenate carbon dioxide to hydrocarbons found that $[RhCl(CO)_2]_2$ plus aluminum bromide was an effective catalyst whose activity was decreased by addition of water while addition of aluminum metal increased the yield of C_1-C_4 alkanes (ref. 450). Two final solution-phase systems are $[RhCl(CO)L_2]$ (L = triarylphosphine) which decarbonylates aroyl chlorides (ref. 451) and $[cp'_2Rh_2Cl_4]$ which reacts first with carbon monoxide in alcohols containing triethylamine to give $[cp'Rh(CO)(C(O)OR)_2]$ (R = Me, Et) and then with iodine to liberate the corresponding oxalate esters in moderate yield (ref. 452).

Addition of $[RhH(PPh_3)_3]$ to a phosphinated styrene/divinylbenzene copolymer gives supported rhodium species which under hydroformylation conditions appear to be primarily $\{Rh(CO)_2L_2\}$ moieties together with a dimer of similar empirical formula (ref. 453). Analogs of $[RhCl(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$ formed by reaction of these complexes with phosphinated polystyrene catalyze the transfer hydrogenolysis of trichloroalkanes by isopropanol to give the corresponding dichloro compounds and the hydrogenation of olefins by hydrogen transfer from formic acid (refs. 454, 455). Rhodium(III) ions incorporated into the ionic domains of sulfonated linear polystyrene films are reduced by carbon monoxide at low temperature to form trapped $\{Rh^I(CO)_2\}$ moieties. If the films are first reduced with hydrogen and then exposed to carbon monoxide the rhodium(I) carbonyls are also formed together with species containing a carbonyl group bound to one, two and several rhodium atoms. These domains appear to function as isolated reaction centers (refs. 456, 457).

The same $\{Rh^I(CO)_2\}$ moieties are also formed when rhodium metal on alumina or rhodium(III) complexes in NaY and 13X zeolites are carbonylated. In the first system under high pressure of carbon monoxide $\{Rh^I(CO)_3\}$ moieties in a low-symmetry site are also seen while in the last $[Rh_6(CO)_{16}]$ and smaller rhodium carbonyl clusters are detected as well. The variable reactivity of these with phosphines of various sizes suggests that the hexarhodium clusters are on the surface of the support and the $\{Rh^I(CO)_2\}$ species reside inside the zeolite cages (refs. 458-460). Deposition of rhodium(III) chloride by itself or mixed with manganese(II) chloride on silica followed by reduction with hydrogen forms a catalyst for the hydrogenation of carbon monoxide. The results of labelling studies using

^{13}CO and $C^{18}O$ suggest that carbon monoxide inserts into one-carbon surface species which are intermediates in the formation of both the hydrocarbon and acetaldehyde products. This insertion may be followed by the transfer of an oxygen atom from the support to give acetate which is then hydrogenated to acetaldehyde (ref. 461).

The infrared spectrum of $[Rh(acac)(CO)_2]$ in solution and in polycrystalline samples has been analyzed at various levels of ^{13}CO incorporation (ref. 462). At temperatures below 200 K slow rotation occurs about the metal-phosphorus bond in $[MCl(CO)(PXBu^t{}_2)_2]$ (M = Rh, Ir; X = H, Me, Et, Bu^n, Ph). Three rotamers are seen for all but the last pair where four are detected. The relative amounts of the various rotamers for a given ligand are independent of the metal (ref. 463). XPS studies have been reported for $[Rh(CO)_2(L_2)]BPh_4$ (L_2 = bipy, ophen and related nitrogen-donor ligands) (ref. 464) as has a determination of the secondary deuterium isotope effect in the reactions of methyl iodide and methyl triflate with $[IrCl(CO)(PPh_3)_2]$. The results support the S_N2 mechanism previously proposed for these reactions (ref. 465). Finally, two theoretical papers report on extended Hückel molecular orbital calculations to describe the bonding of carbon dioxide and carbon disulfide to transition metals, for example $[RhCl(CO_2)(diars)_2]$, $[IrClL_3(C_2O_4)]$ (L = phosphine) and $[cpRh(PMe_3)(C_2S_4)]$ (ref. 466), and on calculations of the band structure of unoxidized and partially oxidized $[IrCl(CO)_3]$ (ref. 467).

Metal Nitrosyl and Aryldiazo Complexes

Addition of bis(diphenylphosphino)amine (L) to $[Co(NO)(CO)_3]$ forms $[Co(NO)(CO)_2(L)]$ whose ^{31}P NMR spectrum indicates that the ligand may be bound through the nitrogen atom (ref. 468). Reduction of $[cp_2Co_2(\mu\text{-}NO)_2]$ with sodium amalgam in diethyl ether forms Na[cpCo(NO)] which contains a linear nitrosyl ligand and which undergoes the reactions shown in Scheme XXXIX. In its reaction with $[cpM(CO)_3X]$ (M = Mo, W; X = Cl, Br),

$$\begin{tikzcd}
 & {[cpCo(NO)(SnR_3)]} & \\
{[cpCo(\mu\text{-}NO)_2Crcp(NO)]} & {[cpCo(NO)]^-} \arrow[l, "c"'] \arrow[r, "b"] \arrow[u, "a"'] \arrow[d, "d"] & {[Ph_2Sn(Cocp(NO))_2]} \\
 & {[cpCo(\mu\text{-}NO)_2Mncp(PMe_3)]} &
\end{tikzcd}$$

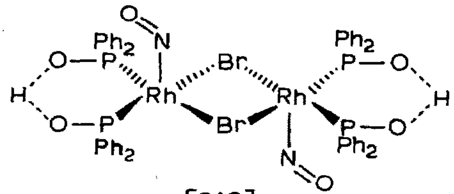
a) R_3SnCl (R = Me, Ph). b) Ph_2SnCl_2. c) $[cpCr(NO)_2Cl]$.
d) $[cpMn(NO)(CO)(PMe_3)]PF_6$.

Scheme XXXIX

$[cpM(CO)_3]^-$ is detected but no binuclear complexes were formed and the final products were $[cp_2Co_2(\mu\text{-}NO)_2]$ and $[cp_2M_2(CO)_6]$ (ref. 469). Addition of $PPN[NO_2]$ to $[YCCo_3(CO)_9]$ (Y = Me, Ph, CO_2H, Fc) forms the air-sensitive salts $PPN[YCCo_3(CO)_7(NO)]$ which are reconverted to the starting alkylidyne-nonacarbonyltricobalt complexes on protonation. The ferrocenyl complex undergoes two irreversible, one-electron oxidations (ref. 470). The photoelectron spectra of $[cp'_2M_2(\mu\text{-}CO)_2]$ (M = Co, Rh), $[cp'_2Co_2(\mu\text{-}NO)_2]$ and $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}NO)]$ support the bonding model proposed by Hoffmann in which the metal-metal interaction occurs through the bridging ligands rather than directly through a metal-metal bond (ref. 471).

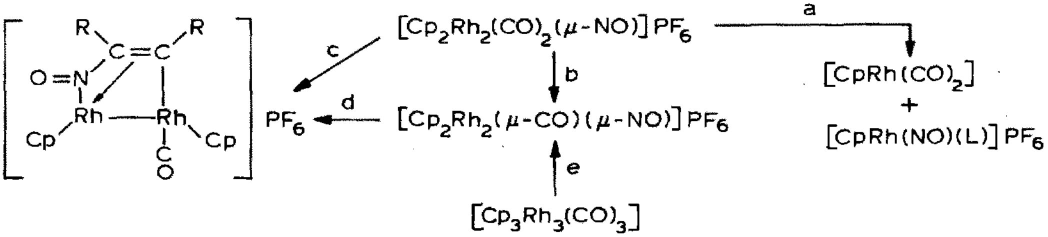
The kinetics of the oxidation of oxymyoglobin to metmyoglobin by $[Co(NO)(dmgH)_2]$ suggest that the nitrosyl ligand dissociates from the cobalt complex prior to reaction with the oxymyoglobin (ref. 472). Nitric oxide reacts with $[Co(L)X]^+$, $[Co(L)B]^{2+}$ and $[Co(L')]^{2+}$ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; X = Cl, Br, I, SCN; B = MeCN, py, H_2O. L' = meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) in acetonitrile to form $[Co(L)X(NO)]^+$, $[Co(L)B(NO)]^{2+}$ and $[Co(L')(MeCN)(NO)]^{2+}$ respectively which are proposed to be complexes of NO^- (ref. 473). Cyclic voltammetric studies on [Co(NO)(TPP)] in dichloromethane show it to undergo reversible, one-electron oxidation and reduction processes. The reduced species does not add an axial ligand but the oxidized one does to form $[Co(NO)(TPP)(L)]^+$ (L = DMF, DMSO, py) (ref. 474).

The anion in $[RhX(NO)(PPh_3)_2]_2$ (X = NO_2, NO_3) remains coordinated during reaction with carbon monoxide in acetone to form $[RhX(CO)_2(PPh_3)_2]$ but if this reaction is carried out in the presence of nitrogen-donor ligands (X = NO_3) the product is $[Rh(CO)(PPh_3)_2L]NO_3$ (L = py, γ-picoline, $MeNH_2$) or $[Rh_2(CO)_2(PPh_3)_4(\mu\text{-}bipy)](NO_3)_2$. The same cations are obtained as their perchlorate salts when the reaction is performed on $[Rh(NO)_2(PPh_3)_2]ClO_4$. Carbonylation of this last complex by itself and in the presence of triphenylphosphine yields $[Rh(NO_2)_2(NO)(PPh_3)_2]$ and $[Rh(CO)_3(PPh_3)_2]ClO_4$ respectively (refs. 475, 476). Reaction of $[Rh(NO)Br_2]_x$ with diphenylphosphine oxide yields [210] (ref. 477). Conversion of $[cpRh(CO)_2]$ into



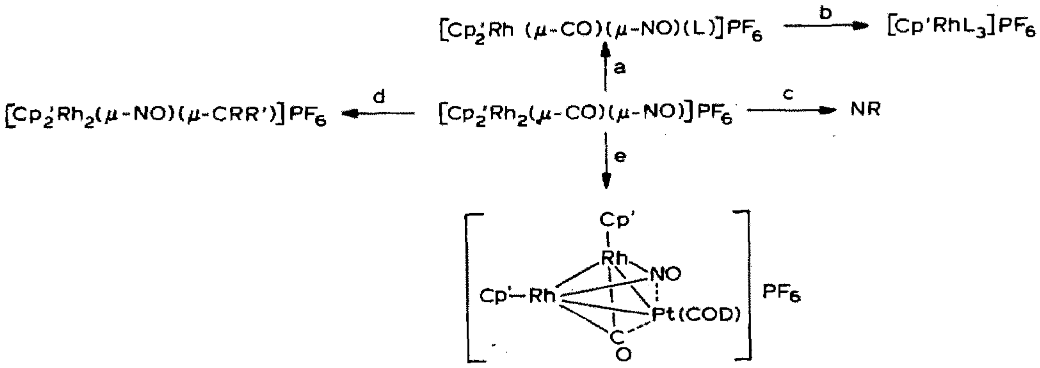
[210]

$[cp_2Rh_2(CO)_2(\mu\text{-}NO)]PF_6$ is effected by reaction with a stoichiometric quantity of nitrosyl hexafluorophosphate. Further chemistry of the product is shown in Scheme XL. The same initial reaction with $[cp'Rh(CO)_2]$ or of $[cp'Rh(CO)_2]$ with $[cp'Rh(NO)(cyoct)]PF_6$ yields $[cp'_2Rh_2(\mu\text{-}CO)(\mu\text{-}NO)]PF_6$ whose subsequent reactions are given in Scheme XLI. With excess nitrosyl hexafluorophosphate $[cp'_2Rh_2(\mu\text{-}NO)_2](PF_6)_2$ forms which can be hydrolyzed to $[cp'_2Rh_2(\mu\text{-}OPF_2)_3]PF_6$ (ref. 478).



a) L (= PPh_3, cyoct, cyclohexa-1,3-diene). b) Δ, CH_2Cl_2.
c) R_2C_2 (R = Ph, p-anisyl). d) Ph_2C_2. e) $NOPF_6$.

Scheme XL



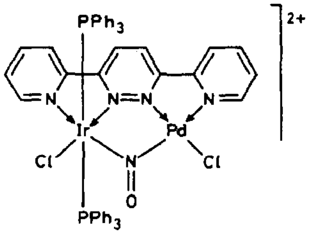
a) L (= PPh_3, $P(OMe)_3$). b) L (= $P(OMe)_3$). c) olefin.
d) $RR'CN_2$ (R = H; R' = H, Me, Ph. R = R' = Ph). e) $[Pt(COD)_2]$.

Scheme XLI

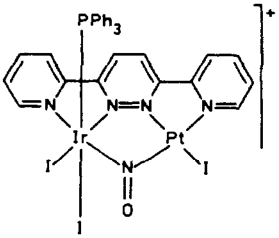
A reinvestigation of the photolysis of a dichloromethane solution of $[Ir(CO)(NO)(PPh_3)_2]$ in the presence of triphenylphosphine which was previously reported to form $[Ir(NCO)(PPh_3)_3]$ (J. C. S. Chem. Commun., (1974) 809) indicates that instead the reaction proceeds as shown in Scheme XLII (L = PPh_3) (ref. 479). The complex $[IrX(NO)(dppn)(PPh_3)_2]PF_6$ (X = Cl, Br, I) is converted to $[Ir(NO)(dppn)(PPh_3)_2](PF_6)_2$ by silver hexafluorophosphate and this reacts with $[PdCl_2(PhCN)_2]$ and $[PtI_2(COD)]$ to give [211] and [212] respectively.

$$\begin{tikzcd}
{[Ir(CO)(NO)L_2]} \arrow[r, "h\nu"] & {[Ir(CO)(NO)L_2]^*} \arrow[d] \\
{[\cdot Ir(CO)L_3]} \arrow[d, "CH_2Cl_2"] \arrow[r, shift left] & {[\cdot Ir(CO)L_2] + \cdot NO} \arrow[l, shift left, "L"'] \arrow[d, "L"] \\
{[IrCl(CO)L_2] + \cdot CH_2Cl} & {N_2O + LO}
\end{tikzcd}$$

Scheme XLII

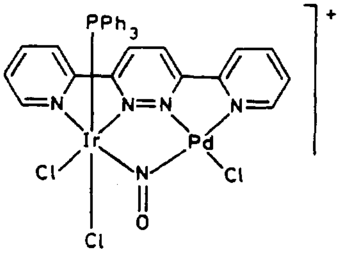


[211]



[212]

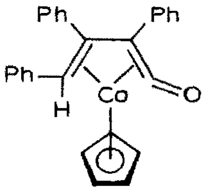
A second isomer of [212] with the phosphine ligand in an equatorial position is also formed in the latter reaction. Addition of $[PdCl_2(PhCN)_2]$ to $[IrCl(NO)(dppn)(PPh_3)_2]PF_6$ forms [213] (ref. 480).



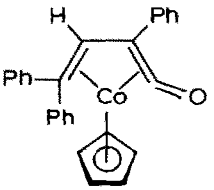
[213]

Metal Alkene Complexes

In refluxing benzene 1,2,3-triphenylcyclopropene is ring-opened by $[cpCo(CO)_2]$ to form a mixture of [214]-[216] with the inclusion of a carbonyl group. The same vinylketene ligand found in [214] forms in the reaction of the cyclopropene with $[Co_2(CO)_8]$ and the product is [217] (L = $\eta^2:\eta^2$-PhHC=C(Ph)C(Ph)=C=O) (ref. 481). Methylenecyclopropane and its tetramethyl analog displace ethylene from $[cpCo(C_2H_4)_2]$ at -78°C to form the corresponding bis(methylenecyclopropane) derivatives. In the former complex, one methylenecyclopropane ligand can be replaced by triphenylphosphine or triphenylphosphite. The same complex on heating forms a mixture of [218] -[220] while the tetramethyl analog forms [221]. With 1,1-diphenylmethylenecyclopropane $[cpCo(C_2H_4)_2]$ yields [222] plus [223]. The latter is



[214]



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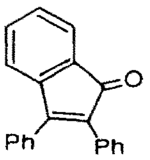
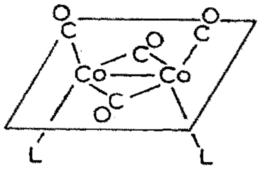
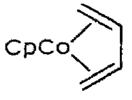


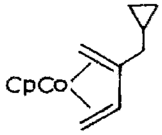
[216]



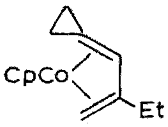
[217]



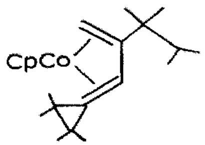
[218]



[219]

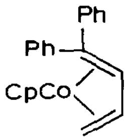


[220]

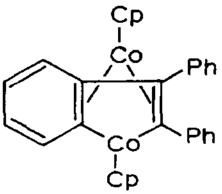


[221]

fluxional apparently via an interchange of the {cpCo} moieties (ref. 482).

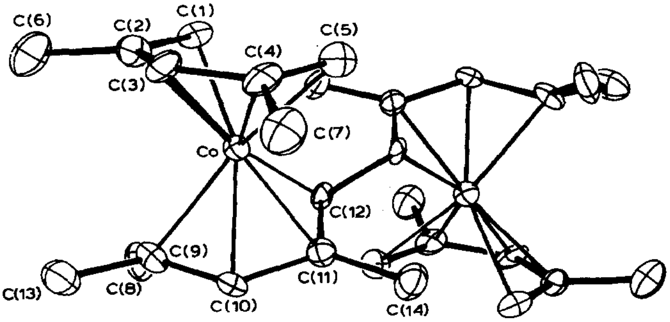


[222]

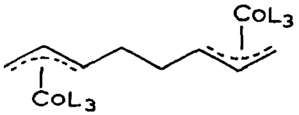


[223]

At elevated temperatures [cp_2Co] reacts with dienes to form [cpCo(diene)] (diene = duroquinone, COD, substituted cyclohexa-1,4-dienes). An η^5-to-η^1 rearrangement of one cyclopentadienyl ligand is proposed to occur prior to its displacement by the diene (ref. 483). Other dienes form [Co(diene)-$(CO)_3$]BF_4 (diene = buta-1,3-diene, isoprene) when reacted with [$Co_2(CO)_8$] and tetrafluoroboric acid etherate. The butadiene complex reacts further with that diene in nitromethane to form [(η^4-C_4H_6)$_2$Co(CO)]BF_4 (ref. 484). Reaction of anhydrous cobalt(II) chloride with two equivalents of potassium 2,4-dimethylpentadienide occurs at -78°C to form a complex formulated as [Co$(C_7H_{11})_2$] which dimerizes on standing in solution to form [224] (ref. 485). The magnesium reduction of a mixture of anhydrous cobalt(II) chloride, trimethylphosphine (L) and an olefin in THF yields [Co(olefin)L_3] (olefin = C_2H_4, C_3H_6, cyclo-C_5H_8). The same reaction with COD gives instead a mixture of [Co(COD)L_2] and [CoL_4] while with buta-1,3-diene the product is [225]. Replacement of propylene in [Co$(C_3H_6)L_3$] by bis(vinyldimethylsilyl)ether

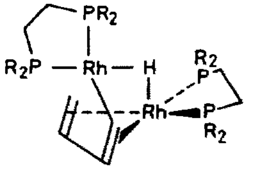


[224]

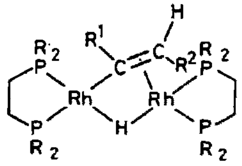


[225]

forms $[\mathrm{Co}((\mathrm{CH_2{=}CHSiMe_2})_2\mathrm{O})\mathrm{L_2}]$ (ref. 486). Buta-1,3-diene reacts readily with $[\mathrm{Rh_2(R_2P(CH_2)_2PR_2)_2(\mu\text{-}H)_2}]$ (R = $\mathrm{Pr^i}$, $\mathrm{OPr^i}$) to give [226] and [227]

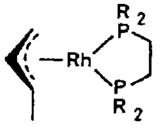


[226]

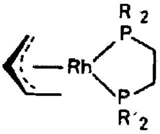


[227]

(isomeric mixture. R^1 = H; R^2 = Et. R^1 = Et; R^2 = H) respectively. On prolonged reaction with the diene, [227] is converted to the mixture of isomers [228a, b]. The formation of [226] consumes two equivalents of the



[228a]



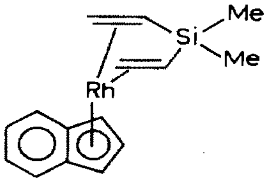
[228b]

diene with the first dehydrogenating the starting complex to give but-2-ene and an intermediate of unknown structure which then adds the second to give the product isolated (see also reference 644) (ref. 487). Addition of a catalytic amount of $[\mathrm{RhCl(C_2H_4)_2}]_2$ to a neat sample of [229] isomerizes it to [230], the first example of a 2-borolene. With larger quantities of the

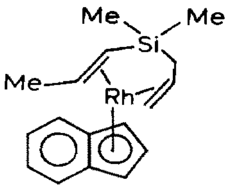
[229]

[230]

rhodium complex, $[(\eta^5\text{-}\mathrm{C_4H_4BNPr^i{}_2})_2\mathrm{Rh_2}(\mu\text{-}\mathrm{Cl})_2]$ can be isolated (ref. 488). While $[(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Rh(C_2H_4)_2}]$ forms [231] on reaction with dimethyldivinylsilane, the corresponding diallylsilane yields [232] presumably *via* an η^3-allyl hydride complex as an intermediate. However no isomerization

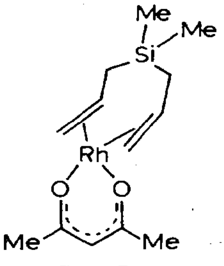


[231]

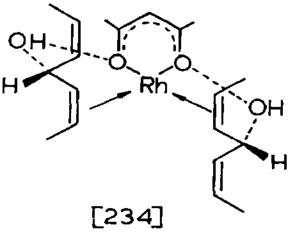


[232]

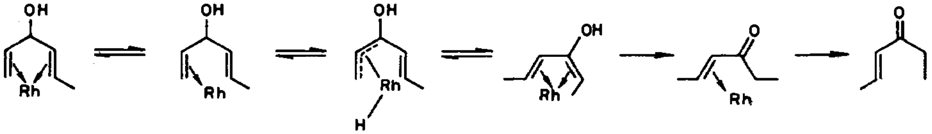
occurs on reaction of the diallylsilane with [Rh(acac)(C_2H_4)$_2$] at -78°C and [233] can be isolated. The isomerization of allyltrimethylsilane to trans-propenyltrimethylsilane is catalyzed by [(η^5-C_9H_7)Rh(C_2H_4)$_2$] but no metal complex of this silane could be isolated (ref. 489). Another reaction of [Rh(acac)(C_2H_4)$_2$] is that with carbon suboxide which gives first [Rh_2(acac)$_2$(CO)$_2$(C_2H_4)$_2$(μ-C=C=O)$_2$] and on further reaction [Rh(acac)(C_2H_4)(CO)(C_3O_2)(C_2O)]$_n$ (ref. 490). A second is that with isomers of hepta-2,5-diene to give [Rh(acac)(diene)] complexes with the (E,E) and (E,Z) isomers but [Rh(acac)(diene)$_2$] complexes with the (Z,Z) isomer. In the last, steric factors prevent the diene from chelating so only one double bond in each diene can coordinate. Hexafluoroacetylacetonate analogs were also prepared as were chelate complexes with (E)-hexa-1,4-dien-3-ol and (E,E)-hepta-2,5-dien-4-ol in which the hydroxyl groups appear to form intramolecular hydrogen bonds with the oxygen atoms of the β-diketonate ligand. A similar phenomenon appears to occur in the bis(diene) complex formed from [Rh(hfac)(C_2H_4)$_2$] and (Z,Z)-hepta-2,5-dien-4-ol ([234]). At elevated temperatures [Rh(acac)(C_2H_4)$_2$] catalyzes the conversion of (E)-hexa-1,4-dien-3-ol to (E)-hex-2-en-4-one, of (E,E)-4-acetoxyhepta-2,5-diene to (E,E)-hepta-1,3,5-triene plus (E,E)-2-acetoxyhepta-3,5-diene and of (E,Z)-4-acetoxyhepta-2,5-diene to a mixture of (E,E)- and (E,Z)-2-acetoxyhepta-3,5-diene. Proposed mechanisms for these three processes are shown in Schemes XLIII - XLV respectively (ref. 491).



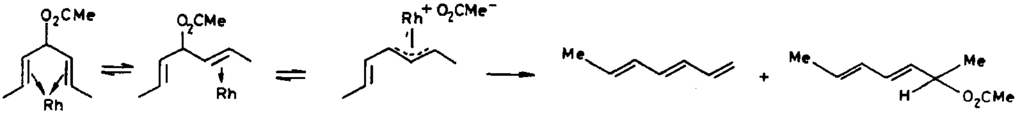
[233]



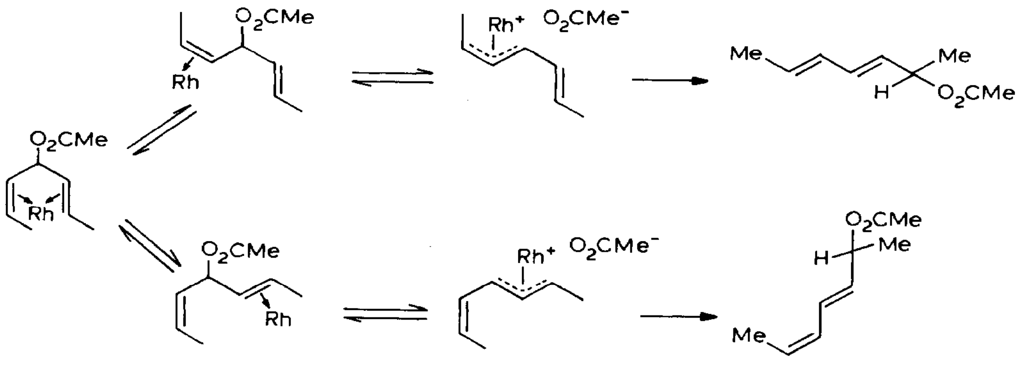
[234]



Scheme XLIII

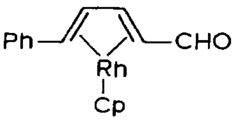


Scheme XLIV

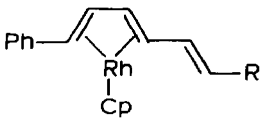


Scheme XLV

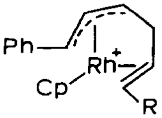
Reaction of [235] with the Wittig reagent [Ph_3PCHR]Br (R = H, Ph) and n-butyllithium forms [236] which on protonation with TFA forms [237] (ref.



[235]



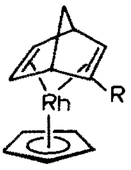
[236]



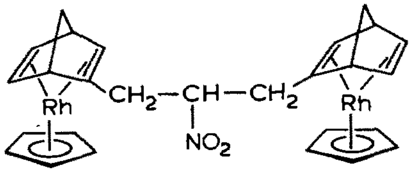
[237]

492). Reduction of [$RhCl(hexa\text{-}1,5\text{-}diene)]_2$ with potassium amalgam in neat triisopropylphosphite forms the paramagnetic complex [$Rh(P(OPr^i)_3)_4$] which on dissolution in organic solvents reacts to give [$RhH(P(OPr^i)_3)_4$]. This is reconverted to the rhodium(0) complex upon photolysis. The ESR spectrum of [$Rh(P(OPr^i)_3)_4$] has been measured and it indicates that the ligand disposition about the metal is roughly tetrahedral (ref. 493). In a continuing study of [238] (R = CH_2OH, CHO) it was found that the former was converted

into analogs having R = $CH_2CH_2NO_2$, $CH_2CH(Me)NO_2$ and $CH_2C(Me)_2NO_2$ on refluxing in nitromethane, nitroethane and 2-nitropropane respectively. Also produced in the nitromethane reaction was [239]. Complex [238] (R = CHO)

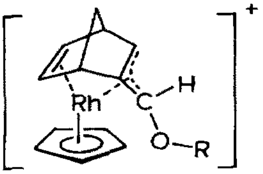


[238]



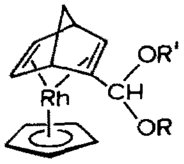
[239]

reacts with acidified alcohols to form [240] (R = Me, Et) which is converted

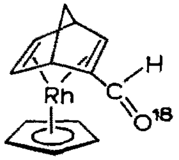


[240]

to [241] (R = R' = Me, Et) by sodium alkoxides and to [242] in the presence of $H_2{}^{18}O$ and potassium carbonate (refs. 494, 495). Some chemistry of



[241]



[242]

$[RhCl(NBD)]_2$ and $[Rh(NBD)(L_2)]ClO_4$ (L_2 = $[Fe(\eta^5-C_5H_4PBu^t{}_2)_2]$, rac-$[Fe(\eta^5-C_5H_4PPhBu^t)_2]$) is presented in Schemes XLVI and XLVII respectively. The complex at the bottom of Scheme XLVII was isolated (refs. 496, 497). The hydrogenation of [243] in methanol gives [244] (S = MeOH) in which the metal atoms appear to react independently (see also references 427, 428). Complex

[244] under hydrogen catalyzes the hydrogenation of tert-butylethylene but

$$\begin{tikzcd}
{[RhCl(NBD)]_2} \arrow[r, "a"] & {[Rh(S_2CNR_2)(NBD)]} \arrow[d, "b"] & \\
{[Rh(S_2CNR_2)L_2]} & {[Rh(S_2CNR_2)(CO)_2]} \arrow[l, "d"'] \arrow[r, "c"] & {[Rh(S_2CNR_2)L(CO)]}
\end{tikzcd}$$

a) NaS_2CNR_2 (R = Me, Et), acetone. b) CO. c) L (=$P(\underline{p}\text{-}XC_6H_4)_3$ (X = Cl, F, Me, OMe)). d) xsL (=$P(\underline{p}\text{-}XC_6H_4)_3$ (X = F, Cl)).

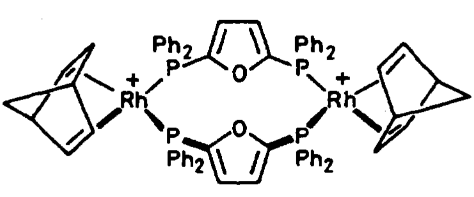
Scheme XLVI

$$\begin{tikzcd}
& {[Rh(NBD)(L_2)]^+} \arrow[d, "a"] & \\
& {[RhH_2(L_2)]^+} \arrow[dl, shift left] \arrow[dr, shift left, "a"] & \\
{[Rh_2H(L_2)_2(\mu\text{-}H)_2]^+} \arrow[ur, shift left] \arrow[dr, shift left] & & {[Rh_2H_2(L_2)_2(\mu\text{-}H)_2]^{2+}} \arrow[ul, shift left] \arrow[dl, shift left] \\
& {[Rh_2H_2(L_2)_2(\mu\text{-}H)_3]^+} \arrow[ul, shift left, "a"] \arrow[ur, shift left, "b"'] &
\end{tikzcd}$$

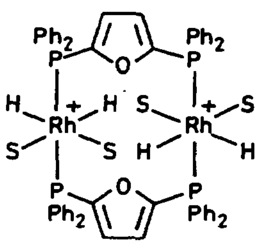
a) H_2, MeOH. b) $-H^+$, $+ H_2$.

Scheme XLVII

at a rate which is much slower than with the monomeric analogs $[RhH_2S_2(PPh_2R)_2]^+$ (S = MeOH; R = Me, 2-furyl). Only part of the difference appears to be due to electronic factors since with the monomeric complexes although the olefin hydrogenation proceeds more slowly when R = 2-furyl than when R = methyl, both are significantly faster than when [244] is the catalyst.

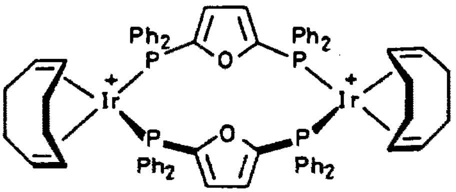


[243]

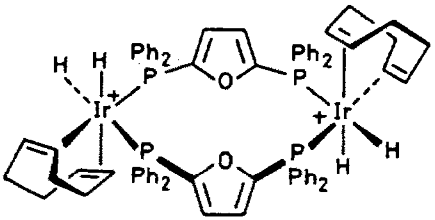


[244]

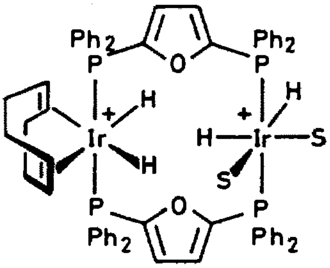
Complex [245] is prepared from $[Ir(COD)(MeOH)_2]^+$ and the diphosphine and in contrast to [243], the diolefin ligand is not hydrogenated when [245] reacts with hydrogen at -78°C. Instead [246] is formed although at room temperature a mixture of [247] - [249] is obtained. On standing [247] and [249] disappear and if COD is now added to the remaining [248] it is converted to [249] (ref. 498).



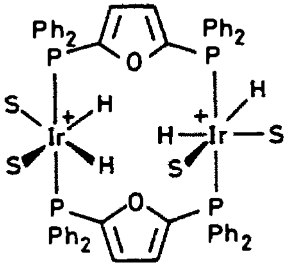
[245]



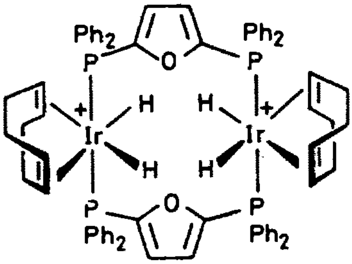
[246]



[247]

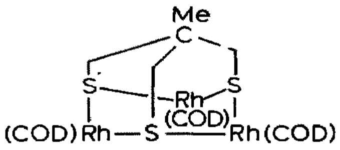


[248]

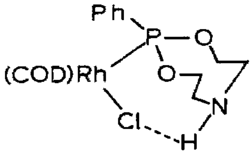


[249]

The popularity of $[RhCl(COD)]_2$ as a starting point for the synthesis of rhodium complexes continues to be high. With $Li_3[MeC(CH_2S)_3]$ it forms [250] which reacts with carbon monoxide to replace each COD ligand with two carbonyl groups. The iridium analog was prepared similarly (ref. 499). Two equivalents of the aminophosphorane [159] ($R_1 = R_2 = H$) (see also references 373, 374) initially forms [251] which rearranges to $[Rh(PNH)_2][RhCl_2(COD)]$ (PNH = tautomeric form of [159]). This is the first reported

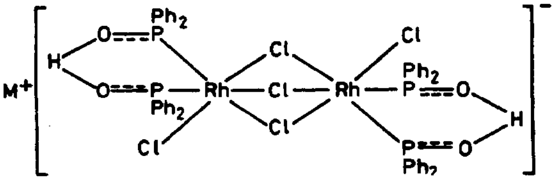


[250]



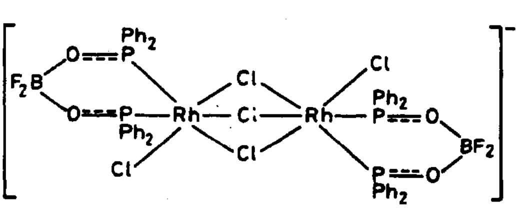
[251]

isolation of the $[RhCl_2(COD)]^-$ ion. Two more equivalents of the phosphorane convert [251] to $[Rh(PNH)_2]^+$ which was isolated as tetraphenylborate, hexafluorophosphate, tetrafluoroborate and perchlorate salts. With an excess of the phosphorane, [251] forms $[Rh(PNH)_3Cl]$ (ref. 500). Reaction of $[RhCl(COD)]_2$ with an excess of chlorodiphenylphosphine in methanol/water (7:1, v/v) followed by addition of MCl (M = Ph_4As, Ph_3bzP) forms [252] which



[252]

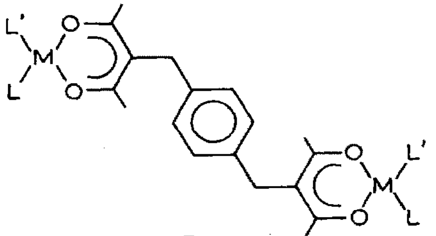
is converted to a mixture of [253] and the analog containing only one $\{BF_2\}$



[253]

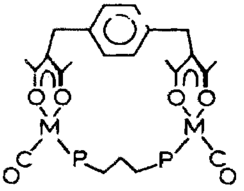
moiety by boron trifluoride etherate. By contrast in a 15:1 methanol/water mixture the chlorophosphine undergoes methanolysis in preference to hydrolysis and, following metathesis with hexafluorophosphate ion, $[RhHCl(PPh_2(OMe))_4]PF_6$ is obtained. With $[Rh(L_2)(COD)]ClO_4$ (L_2 = DPAE, bipy, $PhS(CH_2)_2SPh$), ethoxydiphenylphosphine forms $[Rh(PPh_2(OEt))_4]ClO_4$ but when L_2 = DPPE only the COD ligand can be replaced and $[Rh(DPPE)(PPh_2(OEt))_2]ClO_4$ is the product. Hydrogenation of $[RhL_2(COD)]ClO_4$ (L = PPh_3, PPh_2Me, $PPhMe_2$; L_2 = DPPE) also removes the COD ligand and addition of dialkyl phosphites forms $[RhL_2(P(OH)(OR)_2)_2]ClO_4$ (R = Me, Et) (ref. 501). In an attempt to prepare three-coordinate rhodium complexes, the bulky ligands $PX(CH(SiMe_3)_2)_2$ (L. X = H, Me, Cl) were reacted with $[RhCl(L_2)]_2$ (L_2 = $(CO)_2$, $(cyoct)_2$, COD) but in no case was the desired complex formed. Instead the products were $[RhCl(COD)L]$, $[RhCl(cyoct)(L)]_2$ and $[RhCl(CO)(L)_2]$ respectively (ref. 502). Both bridging chlorides in $[RhCl(COD)]_2$ are replaced when it reacts with an excess of lithium methylphenylphosphide and two isomers of $[Rh(\mu\text{-}PMePh)(COD)]_2$ are formed. With one equivalent of the phosphide $[Rh_2(\mu\text{-}Cl)(\mu\text{-}PMePh)(COD)_2]$ is the product. The diphenylphosphide-bridged analog can be prepared by the same route or by heating $[RhCl(COD)]_2$ and $[Rh(\mu\text{-}PPh_2)(COD)]_2$ in benzene. The success of the latter reaction was a disappointment in that it provided further evidence of the lability of phosphide bridges.

Addition of triethylphosphine to $[Rh(\mu-PPh_2)(COD)]_2$ in benzene followed by hydrogenation to remove the COD ligand forms $[Rh(\mu-PPh_2)(PEt_3)_2]_2$ which is proposed to contain a metal-metal double bond (ref. 503). Other binuclear complexes, [254] (M = Rh, Ir; L, L' = COD) are prepared from p-xylylenebis-(3-(2,4-pentandione)), $[MCl(COD)]_2$ and aqueous potassium hydroxide in ether.



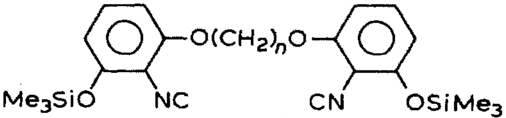
[254]

Derivatives with L = L' = CO, PPh_3 and L = CO, L' = PPh_3 are formed on reaction with appropriate quantities of the respective ligands. Complexes [254] (M = Rh, Ir; L = L' = CO) are unreactive towards hydrogen and methyl iodide but with hydrogen chloride (M = Rh) the metals are removed to form $[RhCl(CO)_2]_2$. With DPPP, [254] (M = Rh; L = L' = CO) forms [255] plus a DPPP-bridged, linear dimer and possibly higher oligomers while the iridium



[255]

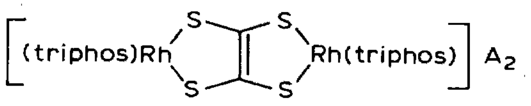
analog with L = CO and L' = PPh_3 undergoes oxidative addition of benzyl and allyl bromides at both centers (refs. 504, 505). The ligands [256] (L_2; n = 2,3) have been prepared and react with $[RhCl(COD)]_2$ in benzene followed by



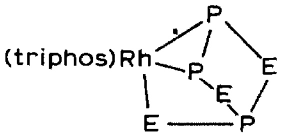
[256]

metathesis with the appropriate anion to give $[Rh(L_2)_2]A$ (A = BPh_4, PF_6). When n = 3 the complex is evidently a monomer and shows no tendency to associate in solution while when n = 2 it is formulated as a dimer with bridging ligands (ref. 506).

Reaction of $[RhCl(C_2H_4)_2]$, triphos, and carbon disulfide in benzene/THF containing sodium tetraphenylborate forms [257] (A = BPh_4) while in the absence of the tetraphenylborate $[(triphos)Rh(\eta^2-CS_2)Cl]$ is the product. This does not convert to [257] on reaction with sodium tetraphenylborate but [257] (A = BF_4, PF_6) does form when tetrafluoroboric acid or ammonium hexafluorophosphate is added. Selenium analogs of [257] (A = Cl, BF_4, PF_6) can also be formed from $[(triphos)Rh(\eta^2-CSe_2)Cl]$ and mercury(II) chloride, tetrafluoroboric acid or ammonium hexafluorophosphate respectively. It thus appears that a Lewis acid is required to cause coupling of the coordinated carbon disulfide and diselenide moieties and this proposal is supported by molecular orbital calculations. It is thought that the acid coordinates to the uncoordinated chalcogen atom in the $\{Rh(\eta^2-CE_2)\}$ (E = S, Se) moiety to convert it to {Rh-ECE}. Complex [257] (A = BF_4) undergoes a two-electron oxidation with nitrosyl tetrafluoroborate and a two-electron reduction with lithium triethylborohydride. Regeneration of [257] from the oxidized and reduced products can be effected by reaction with these same reducing and oxidizing agents respectively (refs. 507, 508). From a mixture of $[RhCl(COD)]_2$, triphos and tetraphosphorus trisulfide or its selenium analog complex [258] (E = S, Se) is obtained. However with cobalt(II) tetrafluoroborate and triphos these reagents or an arsenic analog give $[(triphos)Co(\eta^3-D_2E)]BF_4$ (D = P, As; E = S. D = P; E = Se) (see also references 743-745) (ref. 509).

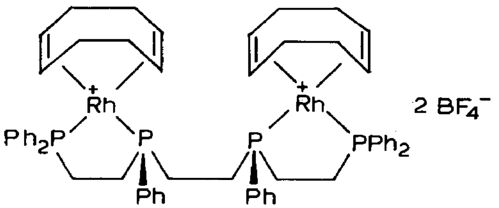


[257]



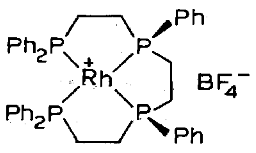
[258]

The dimers $[Rh(\mu-SC_6F_5)(COD)]_2$ are cleaved by phosphines to give $[Rh(SC_6F_5)(L)(COD)]$ (L = PPh_3, P(p-tolyl)$_3$, P(m-tolyl)$_3$) (ref. 510). Addition of meso-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane to [Rh(acac)(COD)] followed by reaction with tetrafluoroboric acid forms [259]. Reaction of [259] with hydrogen converts it to [260] which forms the oxygen adduct [261]. A mixture of the d and l isomers of the same phosphine forms



[259]

[262] which reacts with hydrogen to give rhodium metal and several complexes. The final product isolated is [263]. The same mixture of ligand



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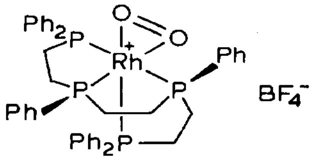
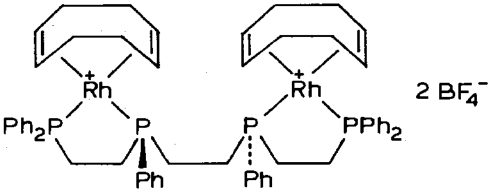
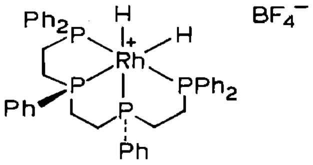


[261]

isomers when added to [Rh(NBD)$_2$]BF$_4$ initially forms [264] which then slowly

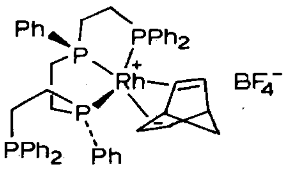


[262]

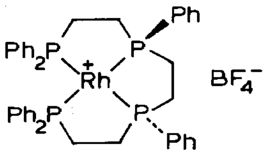


[263]

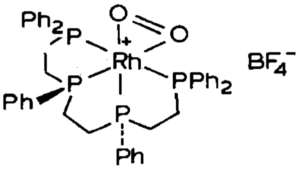
converts to [265]. Complex [265] forms adducts [266] and [267] respectively with oxygen and carbon monoxide. The analog of [259] with 1,1,4,8,11,11-hexaphenyl-1,4,8,11-tetraphosphaundecane (isomeric mixture) is prepared



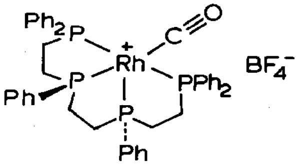
[264]



[265]

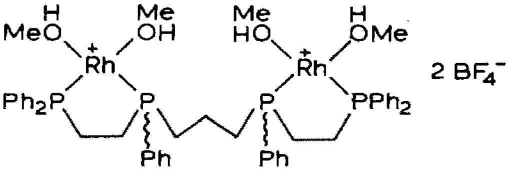


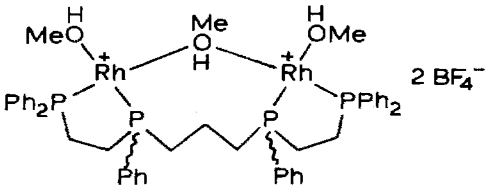
[266]



[267]

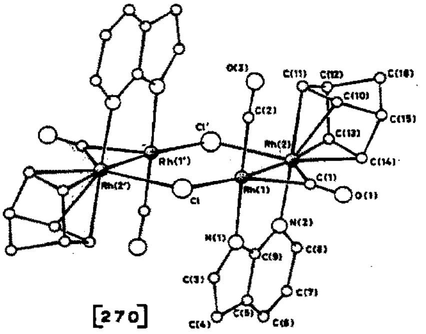
similarly but on hydrogenation in methanol the binuclear structure is maintained and [268] plus [269] form (ref. 511). Nitrosobenzenes cleave $[MCl(diene)]_2$ (M = Rh, Ir; diene = COD, NBD) to $[MCl(diene)(p\text{-}RC_6H_4NO)]$ (R =


[268]


[269]

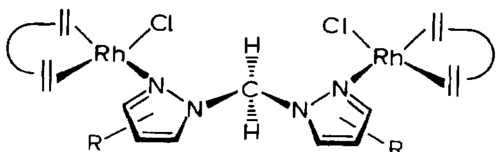
H, Me, Me_2N, Br, NO_2), but with $[RhCl(cyoct)_2]_2$ a species formulated as $[Rh_2Cl_2(cyoct)_3(PhNO)]$ is isolated in one instance. Either N- or O-coordination is possible but it was not established which. There was no reaction of the products with oxygen and while triphenylphosphine simply displaced the nitrosobenzenes, carbon monoxide caused their transformation to anilines and azoxybenzenes, possibly <u>via</u> a nitrene intermediate (ref. 512). The azulene(azul) complexes [Rh(diene)(azul)]X (diene = NBD, COD, TFB; X = ClO_4, PF_6) are formed from $[Rh(diene)_2]X$ or from $[RhCl(diene)]_2$ by initial treatment with the appropriate silver salt. The latter route also served to prepare [Ir(COD)(azul)]X. The azulene is replaced by phosphines or nitriles but carbon monoxide replaces the diene. Azulene also adds to $[cp'M(acetone)_3]X_2$ (M = Rh, Ir) to form $[cp'_2M_2(azul)_2]X_2$. The possibility that this last complex contains a coupled 4,4'-diazulene ligand is mentioned but this has not yet been established (ref. 513).

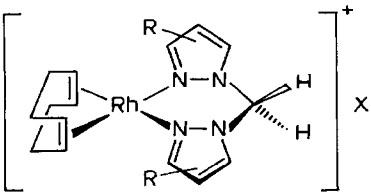
An enormous number of cationic, diene complexes of rhodium and iridium, including one report of fifty three iridium complexes derived from $[IrCl(TFB)]_2$, with predominantly nitrogen-, phosphorus- and sulfur-donor ligands has been described. These are generally of the type $[M(diene)LL']ClO_4$, $[M_2(diene)_2(\mu\text{-}L)_2](ClO_4)_2$ or $[M_2(diene)L_2(\mu\text{-}L)_2](ClO_4)_2$ (diene = NBD, COD, TFB) and in many, the diene ligand can be wholly or partially replaced by carbon monoxide and phosphines (ref. 514-517). Among the more unusual examples of this type of complex are $[Rh_4(CO)_2(NBD)_2(\mu\text{-}Cl)_2(\mu\text{-}CO)_2(\mu\text{-}az)_2]$ ([270]) which is synthesized from [RhCl(NBD)(Haz)] and $[Rh(acac)(CO)_2]$ in

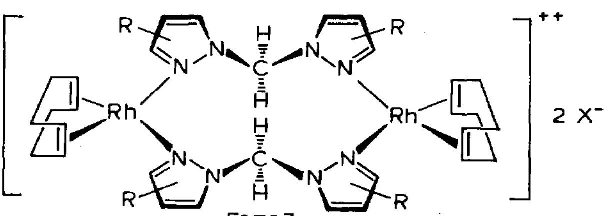


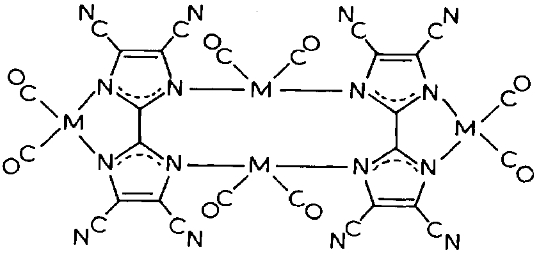
[270]

methanol (ref. 518) and [271] (R = 3,5-Me_2, 3-NH_2, 4-Br, 4-NO_2) obtained by addition of the bis(pyrazolyl)methane ligands to $[RhCl(diene)]_2$ (diene = NBD, COD, TFB). Some ionization of the chloride ligands occurs in solution. Chloride abstraction from $[RhCl(diene)]_2$ with silver perchlorate prior to addition of the ligand leads to formation of [272] which undergoes association in solution to give [273] (ref. 519). Reaction of $[MCl(COD)_2]$ (M = Rh, Ir) with $(Et_4N)_2$[Tcbiim] in refluxing acetonitrile forms Et_4N[M(COD)-(Tcbiim)] which can be carbonylated to $Et_4N[M(CO)_2(Tcbiim)]$. The iridium carbonyl complex oxidatively adds bromine to give $Et_4N[IrBr_2(CO)_2(Tcbiim)]$ while Et_4N[Ir(COD)(Tcbiim)] adds one triphenylphosphine ligand. By contrast the reaction of H_2Tcbiim with $[MCl(COD)]_2$ (M = Rh, Ir) in refluxing acetonitrile forms [M(COD)(MeCN)(μ-Tcbiim)M(COD)] which carbonylates to [274].

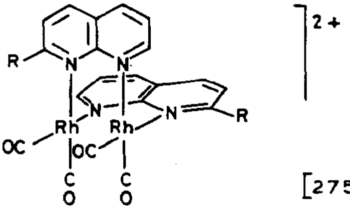

[271]


[272]


[273]

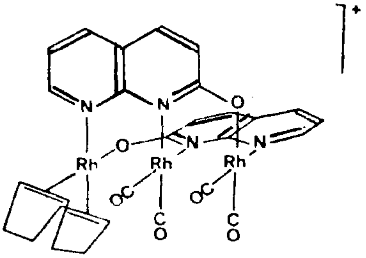

[274]

Complex [274] (M = Rh) is also formed by carbonylation of $[Rh_2(COD)_2$-(μ-Tcbiim)] which is obtained from [Rh(acac)(COD)] and H_2Tcbiim in refluxing 1,2-dichloroethane (refs. 520, 521). Cleavage of $[RhCl(diene)]_2$ (diene = NBD, COD, TFB) occurs on reaction with napy to form [RhCl(diene)(napy)] which with more ligand in acetone containing sodium perchlorate is converted to [Rh(diene)(napy)$_2$]ClO$_4$. Carbonylation of this complex forms [Rh(CO)$_2$(napy)$_2$]ClO$_4$. Iridium analogs can be formed starting with [IrCl(COD)]$_2$. Reaction of [Rh(NBD)(napy)$_2$]ClO$_4$ with [Rh(NBD)(acetone)$_2$]ClO$_4$ forms [Rh$_2$(NBD)$_2$(μ-napy)$_2$](ClO$_4$)$_2$ which carbonylates to [275] (R = H) (ref. 522). A



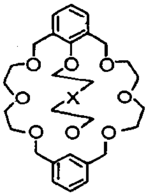
[275]

neutral analog of [275] in which the ligand is the anion of 1,8-naphthyridin-2-one is prepared by carbonylation of [Rh$_2$(diene)$_2$(μ-Onapy)$_2$] (diene = NBD, TFB) which is obtained from [RhCl(diene)]$_2$ and 1,8-naphthyridin-2-one in methanolic potassium hydroxide. Addition of [Rh(COD)(acetone)$_2$]ClO$_4$ to the dimeric carbonyl complex forms a species whose cation is thought to be



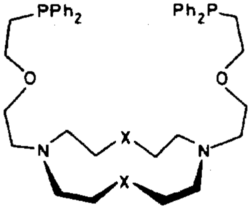
[276]

[276] (ref. 523). The anthranilate ion reacts with [RhCl(COD)]$_2$ to form [Rh(COD)(anthranilate)] with the ligand coordinated via the nitrogen atom and a carboxyl oxygen atom. With the N-phenylanthranilate ion (RCO$_2^-$) [Rh(COD)(μ-O$_2$CR)]$_2$ is formed in which the carboxylate group bridges the two metals. The complexes are catalysts for the hydrogenation of n-alkenes and dienes but their stability is poor (ref. 524). Adducts of [Rh(diene)(NH$_3$)$_2$]$^+$ (diene = COD, NBD) are formed with the crown ethers [277] (X = O, O(CH$_2$)$_2$O, OCMe$_2$CMe$_2$O, o-O$_2$C$_6$H$_4$) in which the ammine ligands hydrogen-bond to

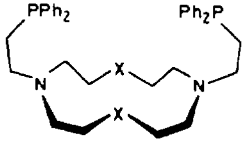


[277]

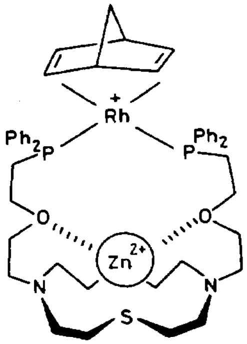
the ether oxygens and the diene ligand is partially sandwiched between the aromatic rings (refs. 525, 526). The macrocyclic ligands [278] and [279] (X = O, S) have been synthesized and their coordination behavior examined. Ligand [278] (X = S) does not form an isolable complex with $[Rh(NBD)_2]ClO_4$, although with an excess of the rhodium complex a binuclear complex of uncertain structure can be obtained, but if it is first complexed with zinc ion [280] forms. Ligand [279] (X = O) forms [281] on reaction with $[RhCl(CO)_2]_2$ while with X = S no well-defined products could be obtained. This latter ligand did however form a binuclear complex with $[RhCl(NBD)]_2$ in the presence of tetrafluoroborate ion which is proposed to contain the metals bound through phosphorus and sulfur on opposite sides of the macrocycle (ref. 527).



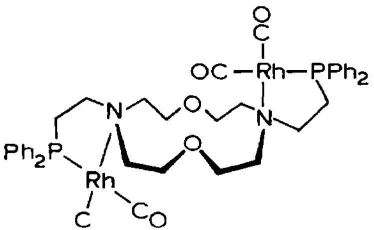
[278]



[279]



[280]



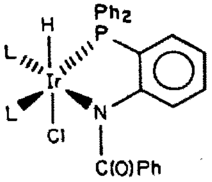
[281]

Equilibrium constants for the formation of 1:1 complexes between $[Rh_2(O_2CCF_3)_4]$ and olefins have been determined. The most stable complexes were formed with olefins bearing alkoxy substituents adjacent to the double bond (ref. 528). Among NMR studies of olefin complexes is one in which the activation energy for olefin rotation in $[cpCo(C_2H_4)_2]$ was determined (ref. 529) and another investigating the magnitude of the barriers to the interconversion of conformers of the seven-membered chelate rings in $[M(COD)(L_2)]BF_4$ and $[M(L_2)_2]BF_4$ (L_2 = DIOP, DPPB; M = Rh, Ir). As these barriers were found to be quite low it was concluded that any arguments based solely on chelate ring conformations observed in the solid state which are advanced to explain the source of the enantioselectivity observed when these complexes catalyze the asymmetric hydrogenation of prochiral olefins are tenuous at best (ref. 530). Also reported are the ^{13}C, ^{31}P and ^{103}Rh NMR spectra of a large number of rhodium complexes including [RhCl(COD)L] (L = $PCy_{3-n}Ph_n$ (n = 0-3)), [cpRh(diene)] (diene = COD, NBD), $[Rh(acac)L_2]$ (L_2 = COD, $(C_2H_4)_2$, $(CO)_2$), $[RhCl(CO)(PPh_3)_2]$ and $[RhCl(PPh_3)_3]$. A linear correlation was observed between the rhodium chemical shift and the chemical shift of the olefinic carbon atoms in the COD ligand over the first three groups of complexes. Also in the phosphine complexes the rhodium chemical shift correlates well with $^1J_{Rh-P}$ (ref. 531). Other NMR data have been reported for $[Rh_2(COD)_2(\mu\text{-pz})_2]$ and $[Rh_2(COD)(CO)_2(\mu\text{-pz})_2]$ (ref. 532).

Spectroscopic studies on $[Ir_2(COD)_2(\mu\text{-pz})_2]$ and analogs containing substituted pyrazolate ligands show that the emission quantum yield and lifetime of the $^3B_2$ excited state are significantly greater at 77 K than at room temperature. This suggests that the temperature dependence of the excited state lifetime depends primarily on variations in the rate constant for nonradiative decay. The excited state was predicted to be strongly reducing and this was confirmed by the observation that it reacts with 1,2-dichloroethane to form $[IrCl(COD)(\mu\text{-pz})]_2$ and ethylene. With dichloromethane however the product is $[IrCl(COD)(\mu\text{-pz})_2Ir(CH_2Cl)(COD)]$ (refs. 533, 534). The He(I) and He(II) photoelectron spectra of $[(\eta^5\text{-}C_5R_5)ML_2]$ (M = Co; R = H; L_2 = COD, cyclohexa-1,4-diene. R_5 = Me_4Et; L_2 = COD. M = Rh; R = H; L_2 = COD, COT, cyclohexa-1,4-diene, buta-1,3-diene. R = Me; L_2 = COD; L = C_2H_4. M = Ir; R = H; L_2 = buta-1,3-diene, isoprene) have been obtained. In the cobalt complexes the $2\pi_+$ band seems to arise largely from a metal orbital but in the others it is predominantly ligand in origin. This is interpreted to indicate that the cobalt complexes should be considered as formally Co(I)($\underline{d}^8$) while the others are M(III)($\underline{d}^6$). The difference is attributed to a strong covalent interaction of rhodium and iridium with the π orbitals of the cyclopentadienyl and diene ligands and is said to be the reason why oxidation of the cobalt complexes gives cationic, $\underline{d}^7$ complexes while with the rhodium and iridium analogs dimerization occurs to give difulvalene complexes (see also reference 699) (ref. 535). Fast-atom bombardment mass spectra have been obtained for rhodium and iridium complexes containing cumulene ligands. The primary fragmentation process appears to be cleavage of metal-ligand bonds which must be more difficult in the iridium complexes since the molecular ion peaks were more intense for these (ref. 536).

Molecular orbital calculations have been performed on $[RhH_2X(PH_3)(olefin)]$ (X = Cl, Br; olefin = C_2H_4, hex-1-ene, dodec-1-ene 2-methylpent-1-ene, *cis*- and trans-4-methylpent-2-ene) as models for intermediates in the $[RhCl(PPh_3)_3]$-catalyzed hydrogenation of olefins. Substitution of bromine for chlorine is predicted to favor migration of one hydrogen to the olefin while changing the olefin alters the formal positive charge on the metal thereby affecting the overlap population in the metal-olefin bond (ref. 537). Also studied theoretically is the hydrogenation of methyl-(Z)-α-acetamidocinnamate catalyzed by $[Rh(NBD)(DPPE)]^+$ (ref. 538).

Reaction of *o*-(diphenylphosphino)-N-benzoylaniline with $[IrClL_2]$ (L = PPh_3; L_2 = DPPE) forms a mixture of [282] and [283] which is the first example of the oxidative-addition of an N-H bond to iridium (ref. 539). Two equivalents of diphenylphosphine react with $[Ir_2(COD)_2(\mu\text{-}pz)_2]$ to form [284] in which the COD ligand attached to Ir(1) has been transformed into a cyclooctenyl group. The observation of shorter distances from the bridging ligands to Ir(1) than to Ir(2) was interpreted to suggest that the complex may be a mixed Ir(I)-Ir(III) species (ref. 540). Reaction of $[IrCl(COD)]_2$



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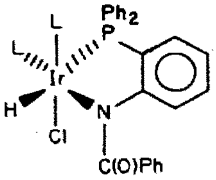

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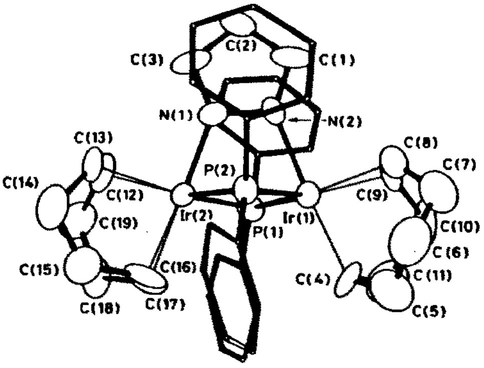
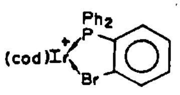
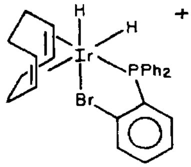


[284]

with pyrazole and triethylamine forms $[Ir(COD)(\mu\text{-}pz)]_2$ which is converted to $[Ir(CO)(PPh_3)(\mu\text{-}pz)]_2$ by successive treatment with carbon monoxide and the phosphine. This latter complex can also be formed directly from $[IrCl(CO)(PPh_3)_2]$ and sodium pyrazolate and oxidatively adds halogens to form $[IrX(CO)(PPh_3)(\mu\text{-}pz)_2IrX(CO)(PPh_3)]$ (X = Cl, Br, I). In this transformation a metal-metal bond is considered to form since the metal-metal distance contracts significantly (ref. 541). Oxidative addition of the phosphorus-hydrogen bond in a variety of dialkylphosphites and related species to the complex formed from $[IrCl(CO)(cyoct)_2]_2$ and six equivalents of dimethylphenylphosphine occurs in refluxing benzene to form *mer*-$[IrHCl(P(O)RR')(PMe_2Ph)_3]$ (R = R' = Me, Et. R = Me; R' = OMe, OEt. R = Ph; R' = OMe) (ref. 542). Reaction of $[IrCl(COD)]_2$ with *o*-bromophenyldiphenylphosphine followed by silver hexafluoroantimonate forms [285] which adds hydrogen to give [286]. A significant interaction of the bromine with the metal is indicated from the structure of [286] (Ir-Br = 2.473(4) Å) and is inferred for [285] from NMR studies. No oxidative addition of the carbon-bromine bond to the metal occurs on refluxing [285] in toluene, a result which is attributed to the electron-withdrawing nature of the COD ligand (ref. 543).



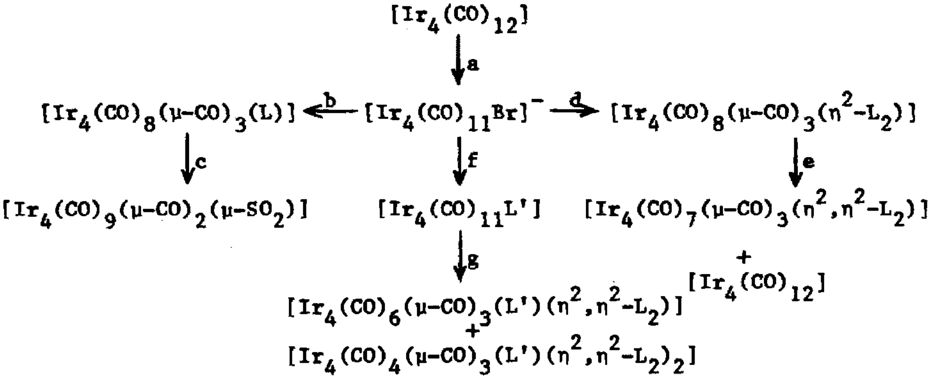
[285]



[286]

Oxidative addition of hydrogen to iridium occurs in $[Ir(COD)L_2]ClO_4$ (L = tht, trimethylene sulfide; L_2 = dth), $[Ir(COD)L_2]_2(ClO_4)_2$ (L_2 = dth, $Bu^tS(CH_2)_2SBu^t$) and $[Ir(CO)_2(L_2)]_2(ClO_4)_2$ (L_2 = $Bu^tS(CH_2)_2SBu^t$) (ref. 544). Refluxing hydrated iridium(III)chloride with Me_3TFB in ethanol forms $[IrCl(Me_3TFB)]_2$ which reacts with silver perchlorate in dichloromethane containing a wide variety of arenes to give $[(\eta^6\text{-arene})Ir(Me_3TFB)]ClO_4$ (arene = $C_6Me_{6-n}H_n$ (n = 0, 2-6), *p*-cresol, acetophenone, tetralin, naphthalene, biphenyl, indene, 9,10-dihydroanthracene). The same reaction with di- and triphenylamine gives analogous complexes where one phenyl ring of the amine is coordinated to the metal and an η^5-attachment of the tautomeric imino form of the ligand is considered to contribute significantly to the overall description of the bonding. Reaction of $[IrCl(diene)]_2$ (diene = TFB, Me_3TFB) with methanolic potassium hydroxide in the presence and absence of acetylacetone yields $[Ir(acac)(diene)]$ and $[Ir_2(\mu\text{-}OMe)_2(diene)_2]$ respectively. Both of these react with di- and triphenylamines in the presence of tetrafluoroboric acid to give tetrafluoroborate salts of the amine complexes described above (ref. 545).

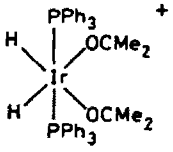
The structure of $[Ir_2(\mu\text{-}Cl)_2(PF_3)_4]$ is analogous to that of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ but with a smaller angle between the two $IrCl_2P_2$ planes. The rather short intramolecular and intermolecular Ir-Ir distances of 2.941(1) and 3.271 (Å) suggest considerable metal-metal interaction which would explain the dark color and metallic luster of the solid. By contrast neither the analog $[Ir_2(\mu\text{-}Cl)_2(PF_2NMe_2)_4]$, nor $[IrCl(PF_2NMe_2)_3]$ prepared from $[IrCl(cyoct)_2]_2$ and a stoichiometric quantity and an excess of the ligand respectively, appears to contain any significant metal-metal interaction. Also, the latter complex shows no ligand dissociation or exchange as has been observed for its rhodium analog (ref. 546). The synthesis of some olefin derivatives of $[Ir_4(CO)_{12}]$ is outlined in Scheme XLVIII (ref. 547). The



a) Br^-, CO. b) $AgBF_4$, L (= C_2H_4, norbornene), CH_2Cl_2, -30°C. c) SO_2
d) $AgBF_4$, L_2 (= NBD, COD), CH_2Cl_2, -10°C. e) warm to 0°C.
f) L' (= phosphine). g) Me_3NO, xsL_2 (= NBD, COD), THF.

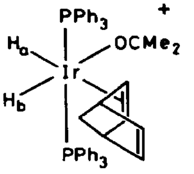
Scheme XLVIII

rates of binding of NBD and COD to [287] have been measured at 233 K and the



[287]

former was found to react much more rapidly because of its rigidity. At 213 K with NBD, formation of [288] - [290] is seen and on reaction with hydrogen [291] forms. Complex [291] partially converts to [289] plus [290] on warming, possibly *via* [292] as an intermediate. Reaction of [287] with NBD at room temperature forms $[Ir(NBD)(PPh_3)_2]^+$ and norbornene but the amount of the latter is less than the amount of iridium present initially suggesting that reductive elimination of hydrogen from $[IrH_2(NBD)(PPh_3)_2]^+$



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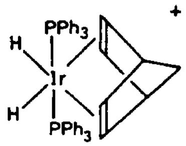

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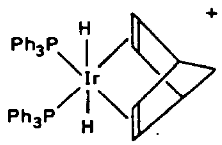

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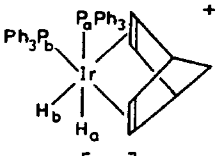

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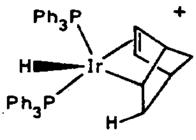
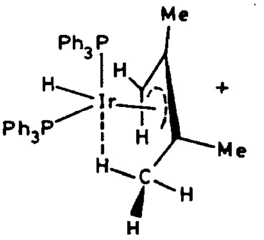
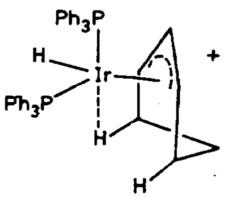


[292]

competes with hydrogenation of the diene. The same reaction with COD results in very little hydrogenation of the diene. Reaction of [287] with 2,3-dimethylbuta-1,3-diene or cyclohexa-1,3-diene forms the fluxional complexes [293] and [294] respectively. The latter was identified in solution



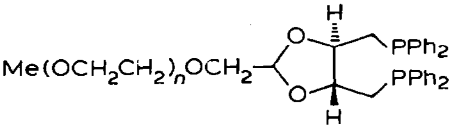
[293]



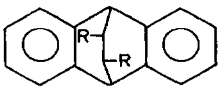
[294]

but not isolated (ref. 548). The complex $[Ir(CO)(CH_2{=}CHCN)(PPh_3)_2]ClO_4$ is thought to consist of a mixture of isomers with the acrylonitrile bound either via the double bond or via the nitrogen atom (ref. 549).

Judging from the absence of any reports on the mechanism of the asymmetric hydrogenation of prochiral olefins catalyzed by chiral transition metal complexes it would appear that at least the major mechanistic questions have now been satisfactorily answered. There remain, however, a large number of papers in this area reporting attempts to find more active and/or more selective catalysts. Unless otherwise specified in the following discussion, the catalyst precursors are prepared from $[RhCl(diene)]_2$ (diene = NBD, COD) and the ligand followed by metathesis to give $[Rh(diene)(L_2)]A$ (A = PF_6, BF_4, ClO_4). The most commonly used substrates are α-acetamidocinnamic acid, its esters and closely related prochiral olefins. Presumably with an eye on a low-cost catalyst, $[CoCl_2((-)\text{-DIOP})]$ has been synthesized and used to catalyze the hydrogenation of α-methylcrotonate. Rather extreme conditions (80 - 100°C) were required and although rates and optical yield were improved by addition of triethylamine no more than a 20% enantiomeric excess was observed (ref. 550). Similarly disappointing optical yields were obtained with catalysts containing modified DIOP-type ligands. In particular, (-)-DIOP and (S,S)-CHIRAPHOS with the phenyl groups replaced by cyclohexyl groups and the water-soluble ligand [295] (n = 5, 16) were studied

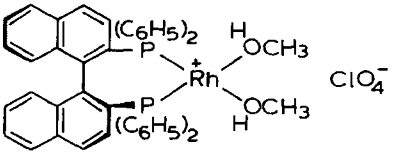


[295]

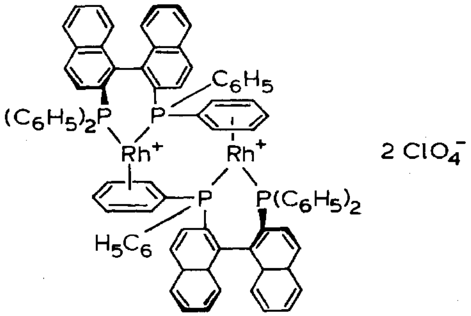


[296]

(refs. 551-554). Other modifications of DIOP such as the attachment of a bulky substituent like 1-naphthyl or 1-pyrenyl to the dioxolane ring or the substitution of one diphenylphosphino group by another diarylphosphino group to give an unsymmetrical ligand have been studied. The former has little effect on the optical yield but introduction of a $\{P(2\text{-naphthyl})_2\}$ moiety in place of one diphenylphosphino group gave a rhodium complex which afforded a better optical yield from α-acetamidocinnamic acid and dehydrodipeptides than one with DIOP itself (ref. 555). Also studied as catalyst precursors were the complexes $[Rh(NBD)(L_2)]^+$ (L_2 = PhCAPP, BPPM and DIOP). The first and second gave high optical yields of chiral oligopeptides from the corresponding dehydropeptides (ref. 556) while the second and third provided only fair optical yields in the hydrogenation of α-acetamidocinnamic acid when the catalyst was supported on charcoal (ref. 557). Some ligands based on polycyclic backbones includes [296] (R = Ph_2PCH_2) and its saturated analog (ref. 558) and (+)- and (-)-BINAP. The last ligand gave excellent optical yields and if $[Rh(NBD)((-)\text{-}BINAP)]ClO_4$ was hydrogenated in methanol in the absence of substrate a 9:1 mixture of [297] and [298] formed (ref. 559). A

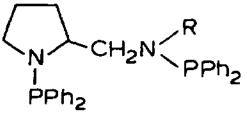


[297]



[298]

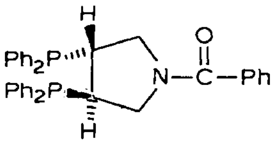
derivative of the BINAP ligand with diphenylphosphinamino substituents in place of the diphenylphosphino groups also works quite well as a chiral ligand (ref. 560), but [299] (R = bz, (S)-(-)-CHMePh, (R)-(+)-CHMePh) proved



[299]

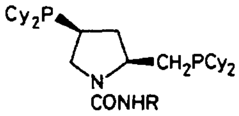
to be less successful (ref. 561).

The ligand $(Ph_2CH_2)_2NCH(Me)CO_2Me(L_2)$ when added to $[RhCl(C_2H_4)_2]_2$ in successively larger amounts forms $[Rh(C_2H_4)_2(\mu\text{-}Cl)_2Rh(L_2)]$, $[Rh_2(\mu\text{-}Cl)_2\text{-}(L_2)_2]$ and finally $[Rh(L_2)_2]Cl$. With $[RhCl(NBD)]_2$, $[Rh(NBD)(L_2)]Cl$ is formed which as a catalyst precursor gives low optical yields (ref. 562). By contrast [300] forms a catalyst giving excellent optical yields both



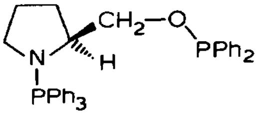
[300]

in homogeneous solution and when supported on a surface (ref. 563) but with [301] (R = Ph, cy, Bu^t) which forms a seven-membered chelate ring the



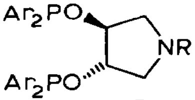
[301]

optical yields are again only moderate (ref. 564). A number of chiral phosphinaminophosphite ligands such as $Ph_2POCHRCHR'NMePPh_2$ (R = H, Ph; R' = Me, Ph, bz) and [302] have also been studied and again only fair to



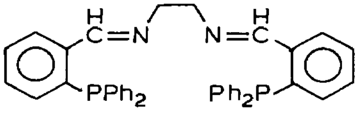
[302]

moderate optical yields were achieved (refs. 565-567). Mixed results are obtained with complexes of [303] (Ar = Ph, p-tolyl, p-anisyl; R = $(CH_2)_2NMe_2$. Ar = Ph; R = $(CH_2)_3NMe_2$, $(CH_2)_2CHMe_2$). With cinnamic acid derivatives the optical yields were fair but with dehydrodipeptides the ligands



[303]

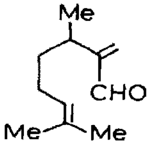
with dimethylaminoalkyl substituents gave excellent results. This was attributed to an electrostatic interaction of this substituent with the substrate which presumably favors coordination of one face of the olefin to the metal (refs. 568, 569). A diphenylphosphinite derivative of L-rhamnose provides respectable optical yields (ref. 570) but the ligands $Ph_2P(\underline{o}\text{-}RN{=}CHC_6H_4)$, $P(\underline{o}\text{-}RN{=}CHC_6H_4)_3$, $Ph_2P(\underline{o}\text{-}RNHCH_2C_6H_4)$ (R = (R)-CHMePh) and [304] were not as effective (refs. 571, 572). The complex $[Rh((-)\text{-}BINAP)(COD)]^+$ mentioned earlier catalyzes the enantioselective isomerization of



[304]

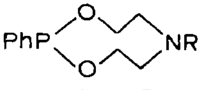
secondary and tertiary allyl amines to enimines and enamines with excellent results. The mechanism proposes binding the substrate via the allylic double bond and the nitrogen followed by an intramolecular, 1,3-hydrogen shift with an η^3-allyl complex as an intermediate. The analogous DIOP complex is not as effective (refs. 573, 574). A variety of optically active thiazolidines have been used in combination with $[RhCl(COD)]_2$ (ligand:metal = 5:1 - 9:1) for the in situ formation of catalysts for the asymmetric hydrosilylation of prochiral ketones by diphenylsilane. At sub-ambient temperatures these are said to be better than catalysts derived from chiral phosphines. The enantiomeric excess observed seemed not to require an optically pure sample of the ligand suggesting that only one diastereoisomeric complex affords a high reaction rate (ref. 575). As a step in the synthesis of optically active amines the asymmetric hydrosilylation of oximes by diphenylsilane in the presence of $[Rh(COD)((-)\text{-}DIOP)]^+$ was investigated. Unfortunately the chemical yields were not high and the optical yields were worse (ref. 576). Finally, optically active Schiff bases (L_2) derived from pyridine-2-aldehyde or pyrrole-2-aldehyde were used to form the complexes $[Rh(COD)(L_2)]^+$ for the catalysis of the hydrosilylation of prochiral ketones by diphenylsilane. Most systems gave enantiomeric excesses below 50% (ref. 577).

The complexes $[RhClL_2]$ (L = o-alkoxyphenyldiphenylphosphine) formed *in situ* from $[RhCl(cyoct)_2]_2$ or $[RhCl(C_2H_4)_2]_2$ are olefin hydrogenation catalysts with the isopropoxy ligand giving the fastest rates. Even faster rates are observed when the ligand is 2,5-diisopropoxyphenyldiphenylphosphine but bis(o-alkoxyphenyl)phenylphosphines are not as active. A transient interaction of the alkoxy group with the metal to stabilize the catalytically active species is proposed (ref. 578). Hydrogenation of methylenecyclohexanols is catalyzed by $[Rh(NBD)(L_2)]BF_4$ (L_2 = DPPB, $(PPh_3)_2$). In the case of 3-methylenecyclohexanol the predominant product is *trans*-3-methylcyclohexanol while with the 2-isomer very little selectivity is observed. The stereoselectivity in the former case is proposed to be the result of the ability of both the double bond and the hydroxyl group to coordinate to the metal (ref. 579). Two related catalyst precursors are [Rh(acac)(DPPB)] and [Rh(NBD)(DPPE)]OTs. The former efficiently catalyzes the hydrogenation of only the double bond adjacent to the aldehyde group in [305] (ref. 580) while the latter catalyzes the hydrogenation of soybean oil in acetone solution. However it is inactivated when supported on sulfonated polystyrene, possibly due to coordination of a sulfonate group or to π-complexation with a phenyl group (ref. 581).



[305]

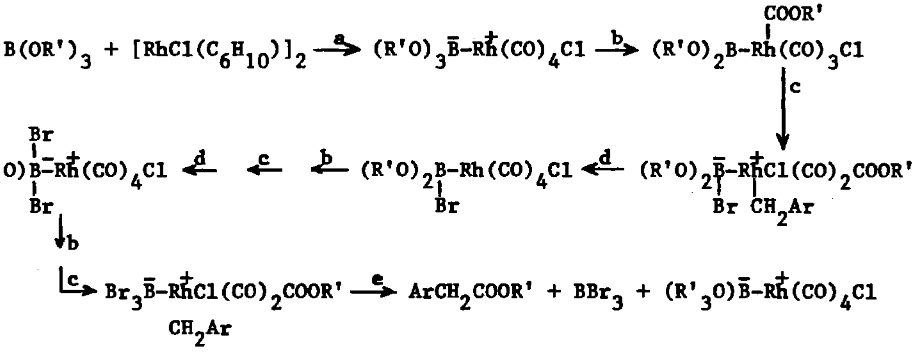
The hydrogenation of olefins, dienes and trienes is catalyzed by $[RhCl(hexa\text{-}1,5\text{-}diene)]_2$ under mild conditions in a biphasic system consisting of hexane, water and cetyltrimethylammonium bromide buffered to pH 7.6. A selective hydrogenation of α,β-unsaturated ketones can also be achieved (ref. 582). Another catalyst effective in biphasic systems for olefin hydrogenation and hydroformylation is $[RhCl(NBD)(Ph_2P(CH_2)_2NMe_3)]NO_3$ which can be prepared from $[RhCl(NBD)]_2$ and the quaternized ligand (ref. 583). The transfer hydrogenation of acetophenone and cyclohexene by acetone is catalyzed by [Rh(COD)L] and $[Rh_2(COD)_2(\mu\text{-}L_2)]$ (L and L_2 = Schiff base ligands) (ref. 584) while complexes prepared *in situ* from $[RhCl(COD)]_2$ and tributyl- or triphenylphosphine or DPM, DPPE, DPPP or DPPB catalyze the transfer hydrogenation of 2- and 4-alkylcyclohexanones by isopropanol in the presence of potassium hydroxide. The isomeric composition of the alcohol product suggests that substitution adjacent to the carbonyl group influences the stereochemical course of the reaction (refs. 585, 586). Mixtures of $[RhCl(COD)]_2$ and DPM, DPPE, DPPP or DPPB with a phosphine:metal ratio of between 0.5 and 1 form catalysts for hept-1-ene hydroformylation. The selectivity for the linear aldehyde increases as this ratio increases (ref. 587). The complex $[Rh(\mu\text{-}SC_6F_5)(COD)]_2$ was also used as the source of rhodium with the same ligands as well as with monodentate phosphines and here the selectivity to the straight chain aldehyde was enhanced by addition of triethylamine (ref. 588). Also used as hydroformylation catalysts with hex-1-ene were the complexes $[RhCl(C_2H_4)(P\text{-}N)]$ and $[Rh(P\text{-}N)_2]Cl$ (P-N = [306]



[306]

(R = H, Me)). The first complex was more active with R = Me than with R = H and less hydrogenation of the olefin occurred but the selectivity to n-heptanal was lower (ref. 589).

The carboxylation of benzyl bromides to aryl acetic acid esters by trialkylborates or trialkylaluminates in the presence of carbon monoxide is catalyzed by $[RhCl(hexa\text{-}1,5\text{-}diene)]_2$. Scheme XLIX (Ar = Ph, p-tolyl,



$$B(OR')_3 + [RhCl(C_6H_{10})]_2 \xrightarrow{a} (R'O)_3\bar{B}\text{-}\overset{+}{Rh}(CO)_4Cl \xrightarrow{b} (R'O)_2B\text{-}\overset{COOR'}{Rh}(CO)_3Cl \xrightarrow{c}$$

$$(R'O)\overset{Br}{\underset{Br}{\bar{B}}}\text{-}\overset{+}{Rh}(CO)_4Cl \xleftarrow{d} \xleftarrow{c} \xleftarrow{b} (R'O)_2\underset{Br}{B}\text{-}Rh(CO)_4Cl \xleftarrow{d} (R'O)_2\underset{Br}{\bar{B}}\text{-}\underset{CH_2Ar}{\overset{+}{Rh}}Cl(CO)_2COOR'$$

$$\xrightarrow{b}\ \xrightarrow{c} Br_3\bar{B}\text{-}\underset{CH_2Ar}{\overset{+}{Rh}}Cl(CO)_2COOR' \xrightarrow{e} ArCH_2COOR' + BBr_3 + (R'_3O)\bar{B}\text{-}\overset{+}{Rh}(CO)_4Cl$$

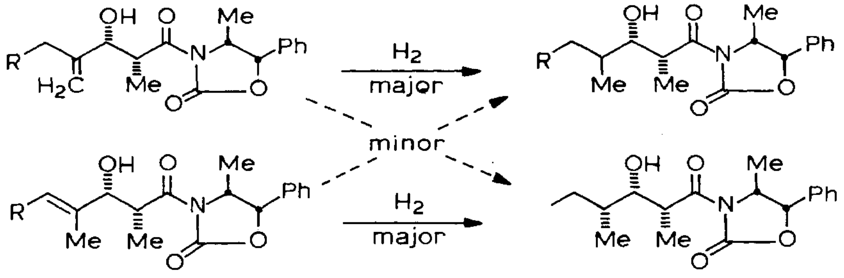
a) + CO, -hexa-1,5-diene. b) migration of OR' to a carbonyl group on Rh.
c) + $ArCH_2Br$, -CO. d) + CO, reductive elimination of $ArCH_2COOR'$.
e) + CO, + $B(OR')_3$.

Scheme XLIX

m-tolyl, 2-naphthyl, $o\text{-}BrC_6H_4$; R' = Et, Pr^n, Pr^i, Bu^n, Bu^t) is proposed in the first instance (refs. 590, 591). The same rhodium complex also serves as a catalyst precursor for the oxidation of olefins to ketones in the system O_2/H_2O/benzene/cetyltrimethylammonium bromide. In contrast to the

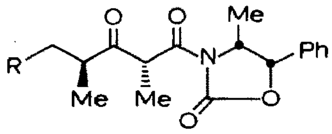
Wacker process, a variety of tetraalkylammonium ions are effective. The system is not selective for the conversion of dienes to monoketones however (ref. 592). Tests of $[RhCl(NBD)]_2$ and $[RhCl(PPh_3)_3]$ as catalysts for the addition of ethyldiazoacetate to allylamines showed that they were ineffective (ref. 593). Mixtures of $[Rh(acac)(C_2H_4)_2]$ with triethylphosphine or $[Rh(diene)(PPh_3)_2]BPh_4$ (diene = COD, NBD) but not $[RhPh(PPh_3)_3]$ are catalyst precursors for the reaction of buta-1,3-diene with carbon dioxide to form 2-ethylundeca-2,4,9-trien-4-olide. A trimerization of the diene on rhodium followed by reaction with carbon dioxide is proposed (ref. 594). The reaction of ethanol with the siloxane oligomer $Me_3SiO(SiHMeO)_nSiMe_3$ ($n \sim 50$) is catalyzed by various rhodium and iridium complexes such as $[RhH(SiEt_3)Cl(Ph_2P(CH_2)_2Si(OEt)_3)_2]$ and $[IrH(SiEt_3)Cl(cyoct)(S(CH_2)_3Si(OEt)_3)]$ which can be anchored to silica surfaces. However serious leaching of the metal from the support occurs during the reaction and since tracer studies indicate that the ligands are also lost it appears that the complexes did not become adequately anchored. Possibly, therefore, the observed catalysis may be due to species in solution rather than the anchored complexes. With macroreticular polystyrene functionalized with diphenyl- or diethylphosphino or diphenylarsino groups as the support for related iridium complexes similar problems were encountered (refs. 595, 596). It has also been reported that rhodium phosphine complexes supported on layered, zirconium phosphonates are active for propylene hydroformylation (ref. 597).

A comparison of $[M(NBD)(DPPB)]^+$ (M = Rh, Ir) and $[Ir(COD)(py)(Pcy_3)]^+$ as catalysts for the hydrogenation of acyclic allylic alcohols at 640 psi hydrogen pressure shows a 90% stereoselectivity in the conversions of Scheme L (R = Me, Pr^i, Ph) with the rhodium complex but this is significantly less with the iridium complexes. At low hydrogen pressure the stereoselectivity is poor with all three complexes due to a competing isomerization of the substrates. Under these conditions the rhodium system also forms significant quantities of [307]. The rate-determining step is proposed to be oxidative-addition of hydrogen at low pressure and substrate coordination at



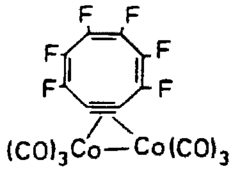
Scheme L

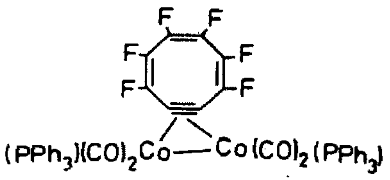
high pressure. For the second iridium complex an increase in stereoselectivity is observed with decreasing catalyst concentration suggesting the presence of more than one catalytically active species at the higher concentrations with these being less selective (refs. 598, 599). A mixture of $[IrCl(COD)]_2$ and tris(o-anisyl)phosphine catalyzes the selective hydrogenation of the ketone group in hex-5-en-2-one by hydrogen transfer from isopropanol (ref. 600) while $[Ir(pz)(COD)(PPh_3)]$ or $[Ir(pz)(COD)]_2$ plus triphenylphosphine in acetone catalyzes some hydroformylation of hept-2-yne. Hydrogenation is the major reaction however (ref. 601).

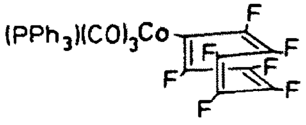

[307]

Metal Alkyne Complexes

A low yield of [308] is obtained from octafluorocyclooctatetraene and $[Co(CO)_4]^-$ while with $[Co(CO)_3(PPh_3)]_2$ the analog [309] forms in better yield. In [308] the C_8F_6 ring is tub-shaped but in [309] it is nearly planar. No reason for the difference is apparant. Complex [309] is also formed together with [310] from reaction of octafluorocyclooctatetraene with $[Co(CO)_3(PPh_3)]^-$ and since reaction of isolated [310] with $[Co(CO)_3(PPh_3)]^-$ does not form [309] these two complexes must form independently (ref. 602). In DME solution at 65°C $[Co_2(CO)_8]$ reacts with acetylene and carbon monoxide to form low yields of benzoquinone and [311] together with traces of [312] - [315]. The formation of [311] is thought to occur by the dimerization of


[308]


[309]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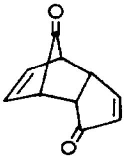
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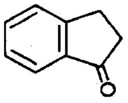
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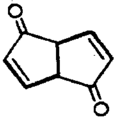
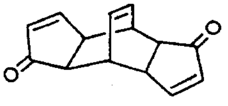

[313]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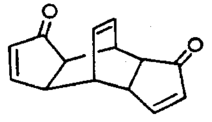
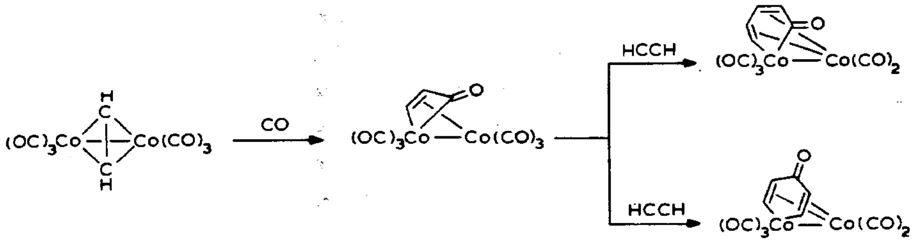
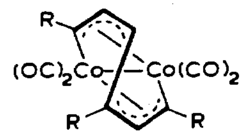

[315]

cyclopentadienone generated according to Scheme LI, [312] by decarbonylation



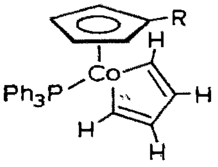
Scheme LI

of [311] and [313] possibly from [316] (R = H). The last two probably do

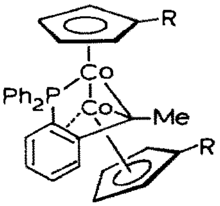


[316]

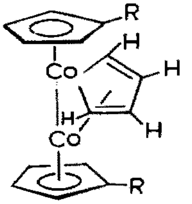
not form directly in metal-centered processes (ref. 603). The gas-phase ion-molecule reactions of NH_3^+, $MeNH_2^+$ and CH_4^+ with $[Co_2(CO)_6(acetylene)]$ (acetylene = HC≡CR (R = CH_2OH, CMe_2OH, CH_2NMe_2, Ph), R_2C_2 (R = Ph, Me, CO_2Me)) have been investigated. In the first group the ion adds to the acetylene (except for HC≡CPh) while in the latter group addition occurs at the metal (refs. 604, 605). Acetylenes are cleaved on reaction with $[cpCo(CO)_2]$ in refluxing dodecane to yield the bis(alkylidyne) complexes $[cp_3Co_3(\mu_3\text{-CR})(\mu_3\text{-CR}')]$ (R = R' = Ph, Fc. R = H; R' = Ph, $SiMe_3$, Fc). An analog with R = $SiMe_3$ and R' = I was prepared from iodine and $[cp_3Co_3(\mu_3\text{-CSiMe}_3)(\mu_3\text{-CH})]$. Those with R = R' = Ph and with R = H and R' = Ph, $SiMe_3$ are oxidized to monocations by silver hexafluorophosphate while with R = H and R' = Fc a stepwise oxidation to mono- and dications can be accomplished. The same reaction with $[cp_3Co_3(\mu_3\text{-CFc})_2]$ forms an equilibrium mixture of mono-, di- and trications. Not all the cations react with nucleophiles but those that do reform the neutral clusters. Cyclic voltammetric studies of the clusters at a platinum electrode reveal a reversible, one-electron oxidation step, and an irreversible, one-electron reduction. The second oxidation step is irreversible. At a mercury electrode the electrochemical behavior is complicated by reaction of the complexes with the electrode surface. The redox chemistry appears to be dominated by π-interactions between the alkylidyne fragment and the metal cluster and the Fc derivatives display class II mixed valence ion behavior (ref. 606). Low yields of [317] - [319] (R = H, COMe, CO_2Me) are formed from $[(\eta^5\text{-}C_5H_4R)Co(PPh_3)_2]$ and acetylene in benzene at room temperature. The second product is thought to be formed from an intermediate vinylidene complex (ref. 607).



[317]

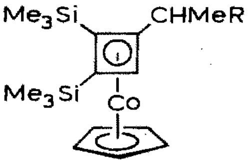


[318]

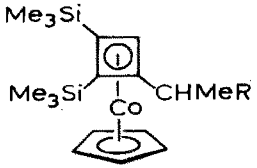


[319]

The use of $[cpCo(CO)_2]$ to mediate cyclization and cocyclization reactions of acetylenic compunds continues to be popular. Heating the complex with several but-1-ynes in BTMSA forms a diastereoisomeric mixture of [320] and [321] (R = OH, $OSiMe_3$, OMe, Ph). Flash-vacuum-pyrolysis of [321] (R = OH) at 520°C causes a 15% diastereoisomerization to [320] (R = OH) while at 580°C the conversion occurs to a greater extent and [322] plus [323] also are formed. On the other hand flash-vacuum-pyrolysis of [320] (R = OH) causes a 34% conversion to [321] (R = OH); the other analogs of [320] also



[320]



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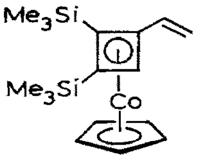

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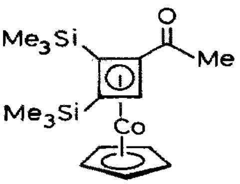
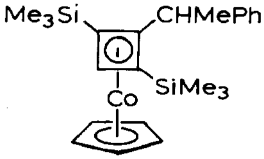


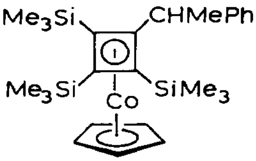
[323]

are extensively diastereoisomerized under these conditions. With [320] (R = Ph) [324] is also formed. Cocyclization of BTMSA with $Me_3SiC{\equiv}CCHMePh$ occurs



[324]

in refluxing BTMSA in the presence of $[cpCo(CO)_2]$ to form [325] together with [326] and other, as yet unidentified products. Under acidic conditions



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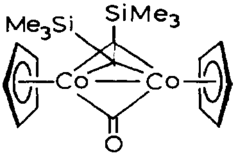
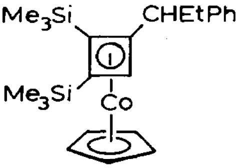
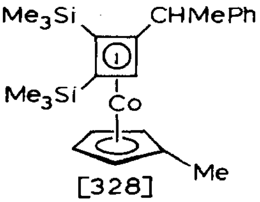


[326]

[325] is selectively converted to [324]. To explore the mechanism of the interconversion of complexes [320] and [321] several crossover experiments were performed. First [327] and [328] and their respective diastereoisomers

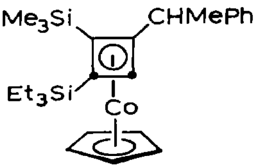


[327]

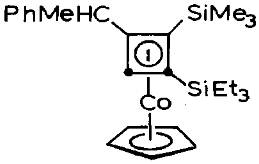


[328]

were prepared in the same fashion as for [320] and [321] and separated. Flash-vacuum-pyrolysis of mixtures of these showed the same diastereoisomerization as before but no crossover occurred indicating that the process is intramolecular. Second, the $[cpCo(CO)_2]$-mediated cocyclizations of $Me_3SiC{\equiv}CCHMePh$ with $Me_3SiC{\equiv}CH$ and of $Et_3SiC{\equiv}CCHMePh$ with $Me_3SiC{\equiv}CH$ gave the pairs of complexes [329] plus [330] and [331] plus [332] respectively.

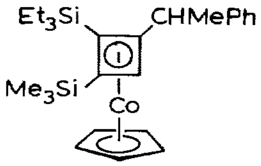


[329]



[330]

Flash-vacuum pyrolysis of [329] formed [332] while [330] converted to [331] thereby ruling out the intermediacy of a metallacyclic intermediate.



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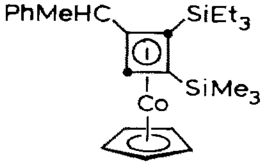
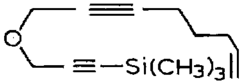


[332]

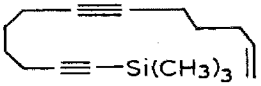
Finally, when [329] containing ^{13}C labels as indicated by the bold dots was pyrolyzed the labelled atoms in [332] were no longer bonded together suggesting that the diastereoisomerization in these systems occurs *via* a reterocyclization (ref. 608). In continuing studies of [cpCo(CO)$_2$]-mediated



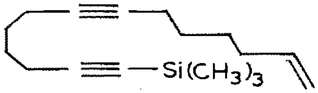
[333]

[334]

routes to fused-ring molecules, the [2+2+2] cycloaddition of [333] gave only [334] while those of [335] and [336] gave [337] and [338] respectively



[335]



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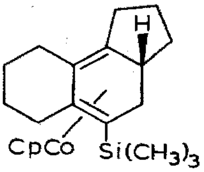

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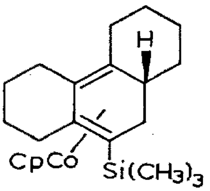
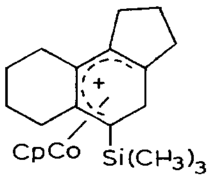


[338]

together with the *endo*-H isomers of each. Reaction of [337] with trityl hexafluorophosphate formed [339] which on further treatment with methyllithium or potassium carbonate gave [340] and [341] respectively (ref. 609). Generation of a steroid nucleus occurs efficiently on refluxing [342] with [cpCo(CO)$_2$] in isooctane whereupon [343] and [344] are formed (ref. 610).



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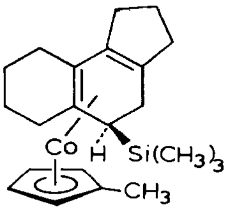
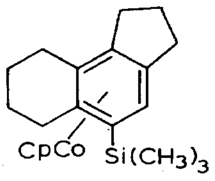
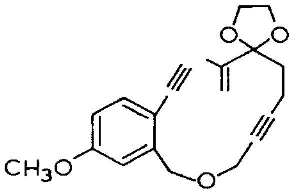


[340]

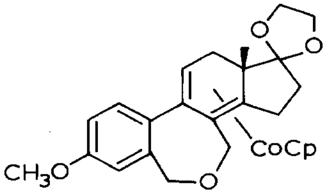


[341]

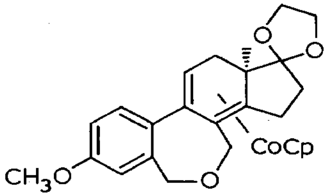
Even the tetrasubstituted double bond in 7,8-dimethyltetradec-7-en-1,13-diyne can be involved in the [2+2+2] cycloaddition to form [345] (ref. 611).



[342]



[343]



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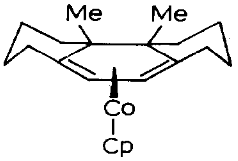

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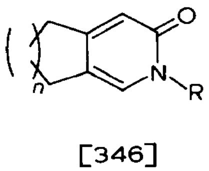

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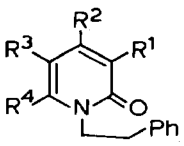
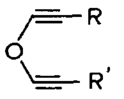


[347]

Other uses of $[cpCo(CO)_2]$ are to mediate the cocyclizations of alkynes with isocyanates and with nitriles. In the first system, α,ω-diynes and 1-phenylbutyne combine with isocyanates to give the pyridones [346] ($n = 1$; $R = Ph$. $n = 2$; $R = PhCH_2CH_2$) and [347] ($R_1 = R_4 = Ph$; $R_2 = R_3 = Et$ as the major regioisomer). In the former reaction, the initial step is proposed to be formation of a cobaltacyclopentadiene by a coupling of the alkyne functions. The isocyanate function is then incorporated subsequently (ref. 612). In the latter reaction, [348] ($R = SiMe_3$; $R' = SiMe_3$, CO_2Et) couples with acetonitrile to form [349] and [350] respectively (ref. 613). Another study of the α,ω-diyne-nitrile cocyclization also used $[Co_2(CO)_8]$ as a catalyst and found that bulky groups on the diyne were required for the process to be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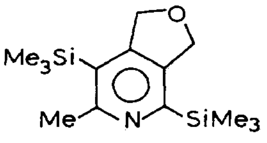
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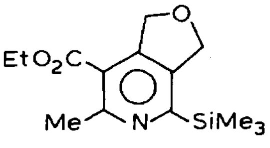
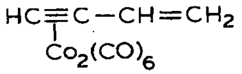

[350]

successful (ref. 614). Also of continuing interest is the use of $\{Co_2(CO)_6\}$ moieties to stabilize propargyl cations and to direct the reactions of enynes. Thus [351] reacts with acyl tetrafluoroborates followed by addition of a trimethylsilyl enol ether or a ketone to form species such as [352] (R = H; R^1 = Me, Ph, *cyclo*-C_3H_6; R, R^1 = $(CH_2)_4$; R^2 = Pr^iCH_2CO, MeCH=CHCO,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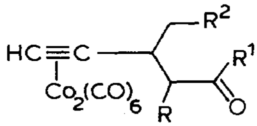
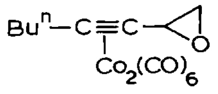

[352]

cyclo-C_3H_5CO, Bu^t) which can be demetallated and hydrated to generate an additional keto group (refs. 615, 616). The epoxide rings in [353] and [354] undergo nucleophilic attack at the carbon adjacent to the alkyne function. With methanol in the presence of tetrafluoroboric acid etherate these form [355] and [356]. Complex [356] is obtained as a 1:1 mixture of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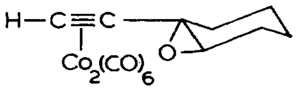
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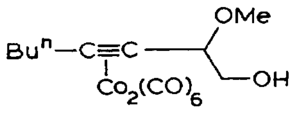
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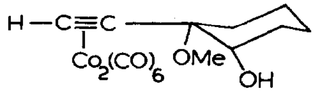
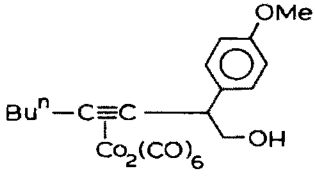

[356]

cis and *trans* isomers which contrasts with the almost exclusive formation of the *trans* isomer in the absence of the $\{Co_2(CO)_6\}$ moiety which indicates that the presence of the electron-releasing $\{(alkyne)Co_2(CO)_6\}$ substituent exerts a significant syn selectivity. Reaction of [355] with methoxybenzene under acidic conditions forms a mixture of [357] and [358] as the major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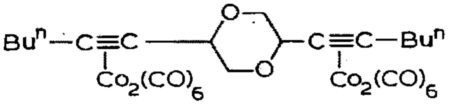
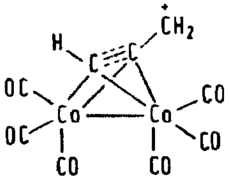

[358]

products (ref. 617). Reaction of [359] with propionic acid gives [360]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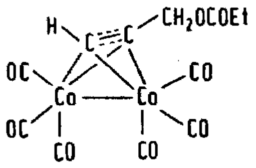
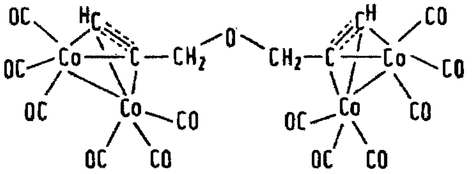

[360]

while with $[Co_2(CO)_6(HC{\equiv}CCH_2OH)]$ and 2-substituted thiophenes the products are [361] and [362] (R = $(CH_2)_2CO_2Me$, CH_2CO_2Me, H) respectively (ref. 618).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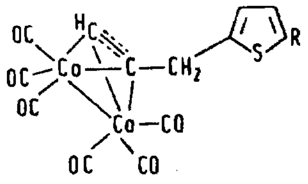
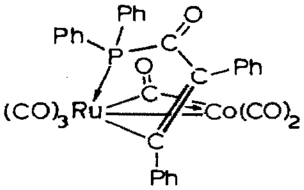

[362]

Allylpropargyl ethers (L) form cobalt complexes $[Co_2(CO)_6L]$ which on heating at 60°C under carbon monoxide provide moderate yields of 3-oxabicyclo-[3.3.0]oct-6-en-7-ones (ref. 619).

The room temperature reaction of diphenylacetylene with $[RuCo(CO)_7(\mu\text{-}PPh_2)]$ forms [363] which loses a carbonyl ligand on heating to give [364]. Regeneration of [363] from [364] and carbon monoxide did not occur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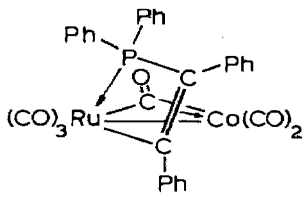
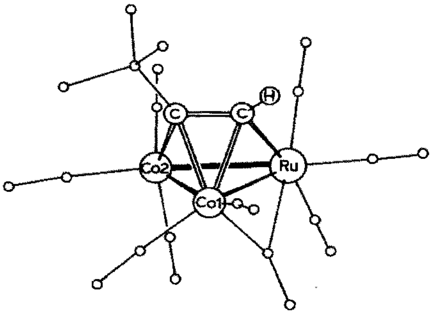

[364]

however (ref. 620). A cluster-centered acetylene-vinylidene rearrangement occurs when the product formed from tert-butylacetylene and $[RuCo_2(CO)_{11}]$

([365]) is refluxed in hexane to form [366] (ref. 621). Coupling of



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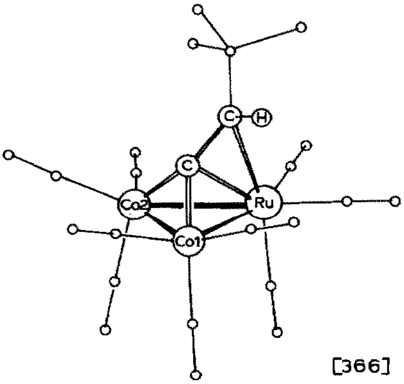
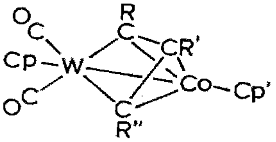


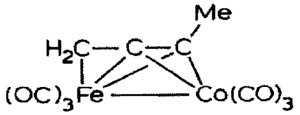
[366]

acetylenes with the bridging carbyne moiety in [cp'(CO)Co(μ-CR)Wcp(CO)$_2$] occurs in refluxing toluene with the formation of [367] (R = p-tolyl; R' =



[367]

R" = Ph, Me; R' = Me, R" = Ph; R' = Ph; R" = Me; R' = Bu^t, R" = H) (ref. 622). Complex [368] reacts with hydrogen at 60°C to form a variety of



[368]

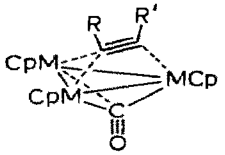
hydrocarbons but the largest fraction consists of butene isomers. Also formed is [Fe(CO)$_5$], [Co$_2$(CO)$_8$] and metallic iron and cobalt. It is proposed that the iron-carbon σ-bond is retained until late in the reaction (ref. 623). Acetylenes replace two carbonyl ligands in [CoMn(CO)$_9$] to form [CoMn(CO)$_7$(μ-RC$_2$R')] (R = R' = Et, Ph. R = Me; R' = Et, Ph) which decomposes in polar solvents to form [Co$_2$(CO)$_6$(μ-RC$_2$R')] as the major product (ref. 624).

An electron-transfer chain catalyzed substitution of the three carbonyl groups on one cobalt in [Co$_2$(CO)$_6$(μ-HFB)] by ttas occurs upon electrochemical reduction in the presence of the ligand. In the product,

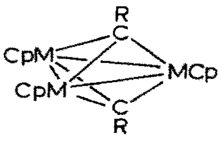
$[(ttas)Co(\mu\text{-}HFB)Co(CO)_3]$, one of the remaining carbonyl groups is semi-bridging (ref. 625). In related work, the complexes $[Co_2(CO)_6(\mu\text{-}R_2C_2)]$ (R = Ph, Bu^t) also undergo electron-transfer chain catalyzed substitution by phosphine and arsine ligands at low temperature but are also cleaved to the radicals $[\cdot Co(R_2C_2)(CO)_{3-x}L_x]$ (x = 1; R = Ph, Bu^t; L = CO, PBu^n_3, $P(OMe)_3$; R = Ph, L = Pcy_3, PPh_3, $P(OPh)_3$, $AsPh_3$. x = 2; R = Ph; L = $P(OMe)_3$, $P(OEt)_3$, ½DPPE, ½DPAE, ½ARPHOS. x = 3; R = Ph; L = $P(OMe)_3$). The species $[\cdot Co(Ph_2C_2)(CO)(P(OMe)_3)_2]$ is fluxional (ref. 626). Hydrocyanation of acetylenes to give first unsaturated nitriles and ultimately saturated, secondary nitriles can be effected by cobalt(II) salts in the presence of up to five equivalents of cyanide ion and hydrogen. The formation of $[(acetylene)Co(CN)_4]^{3-}$ which can be hydrogenated to a vinyl cobalt cyanide complex is proposed (ref. 627).

Carbon-13 NMR spectra of the stabilized, propargyl cations $[Co_2(CO)_6(\mu\text{-}R''C_2CRR')]^+$ (R' = R = H; R'' = H, Me. R' = R'' = H; R = Me, Ph. R = R' = Me; R'' = H) have been measured in liquid sulfur dioxide. The carbon atoms appear somewhat deshielded as compared with what is found for the parent $[Co_2(CO)_6(\mu\text{-}R''C_2CRR'OH)]$ complexes but are much more highly shielded than is found for the uncomplexed carbocations. This attributed to a significant electron-donating ability of the $\{Co_2(CO)_6\}$ moiety (ref. 628). Proton NMR spectra of the ^{13}C-enriched acetylene complexes $[Co_2(CO)_6(\mu\text{-}C_2H_2)]$ and $[Co_4(CO)_{10}(C_2H_2)]$ have been obtained to measure $^1J_{C-C}$, $^1J_{C-H}$ and $^2J_{C-H}$ in the acetylene ligand. The trends in these values parallel the rehybridizations of the carbon atoms but are not directly related to the expected reductions in the carbon-carbon bond order (ref. 629). Rotational correlation times for $[Co_2(CO)_6(C_2H_2)]$ and [368] have been obtained by carbon-13, T_1 measurements. Also measured were the ^{17}O NMR spectra of the carbonyl groups to obtain values for the ^{17}O electric quadrupole coupling constants. It was suggested that these values could help in assigning ^{17}O NMR resonances in these types of complexes (ref. 630). The relative importance of σ- and π-bonding of acetylenes to cobalt in $[Co_2(CO)_6(RC_2R')]$ (R, R' = various alkyl or aryl groups or H) has been explored by correlating changes in $\nu_{C\equiv C}$ and $\nu_{C\equiv O}$ with variations in the acetylene substituents (ref. 631).

Photolysis of $[cp_3M_3(CO)_3]$ in the presence of diarylacetylenes forms [369] (M = Rh, Ir; R = R' = Ph. M = Rh; R = Ph, R' = *p*-tolyl) which converts to [370] on flash-vacuum-pyrolysis. In the case of the unsymmetrical

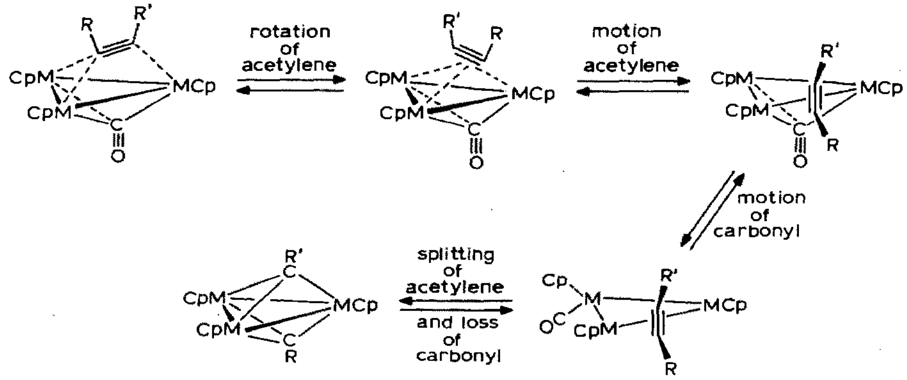


[369]

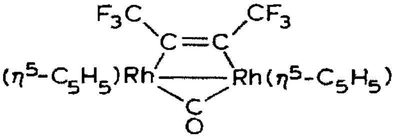


[370]

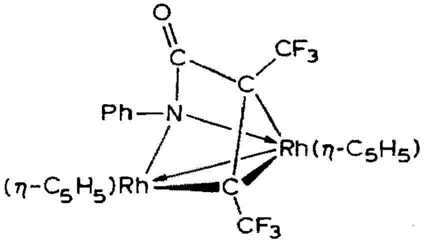
acetylene no metathesis is observed and molecular orbital calculations suggest the reaction proceeds as shown in Scheme LII (ref. 632). Addition of phenylisocyanate or phenyl azide to [371] forms [372]. Analogs were also formed from methyl- and *tert*-butylisocyanate and from benzoyl- and *p*-toluenesulfonylazide (ref. 633). The formation of hydroquinone from acetylene and carbon monoxide in aqueous THF is catalyzed by [RhCl(CO)-$(PR_3)_2$] (R = Ph, *p*-tolyl, *p*-anisyl) (ref. 634). Extended Hückel calculations on the oxidative addition of hydrogen or acetylene (to give a dimetallated olefin) to a series of binuclear complexes of rhodium and iridium indicate that a concerted, thermal reaction should occur more readily when the metals formally have the $\underline{d}^7$ configuration than when they are $\underline{d}^8$ since a HOMO-LUMO crossing occurs on the reaction coordinate in the latter case. For the $\underline{d}^8$ systems either formation of a diradical followed by rearrangement or a two-step process involving oxidative addition to each metal individually can circumvent this barrier. The latter pathway is preferred (ref. 635).



Scheme LII

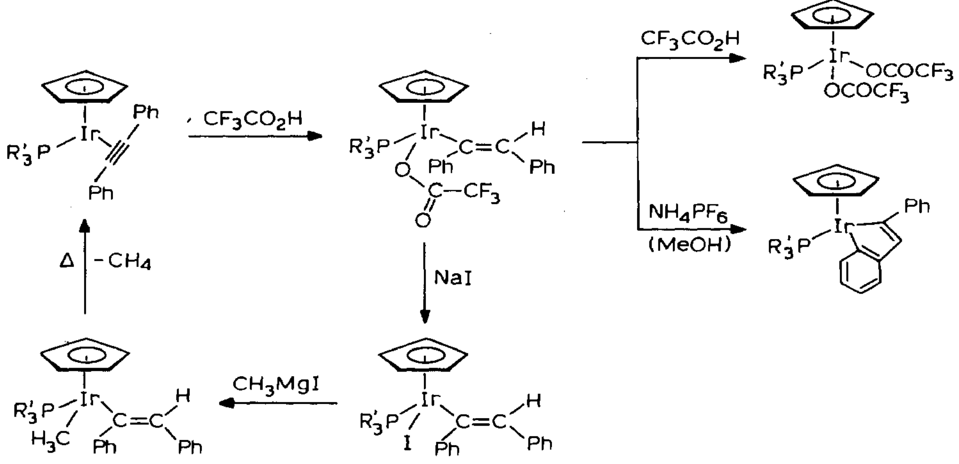


[371]



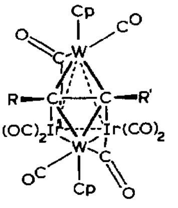
[372]

In refluxing benzene diphenylacetylene adds to $[Ir(CO)_2(PPh_3)]_2$ to form $[Ir_2(CO)_4(PPh_3)_2(\mu\text{-}Ph_2C_2)]$ with a structure like that of the cobalt analog (ref. 636). *In situ* formation of $[IrClL_2]$ (L = PPr^{i}_{3}) from $[IrCl(cyoct)_2]_2$ and four mols of the phosphine followed by addition of acetylenes forms *trans*-[IrClL$_2$(R$_2$C$_2$)] (R = H, Me, Ph). With phenylacetylene some oxidative addition occurs to also form [IrH(C$_2$Ph)ClL$_2$] which adds pyridine *trans* to the hydride ligand. Reaction of [IrClL$_2$(Ph$_2$C$_2$)] with sodium cyclopentadienide forms [cpIrL(Ph$_2$C$_2$)] some of whose chemistry is outlined in Scheme LIII (R' = Pr^i). Reaction of [cpIrL(Ph$_2$C$_2$)] with halogens forms [cpIrX$_2$L]



Scheme LIII

(X = Br, I). The iodo complex is converted to [cpIrMe$_2$L] by methylmagnesium iodide while the bromo complex can also be formed from [cpIr(O$_2$CCF$_3$)$_2$L] and 2,2-diphenylethenylmagnesium bromide (ref. 637). In refluxing dichloromethane acetylenes react with [cp$_2$W$_2$Ir$_2$(CO)$_{10}$] to form [373] (R = R' = Ph, *p*-tolyl, CF$_3$, CO$_2$Et. R = Ph; R' = Me, CO$_2$Et). With diphenylacetylene significant amounts of [374] also form implying scission of the carbon-carbon triple bond can occur. Bridge-terminal exchange of carbonyl ligands occurs in [373] (ref. 638).



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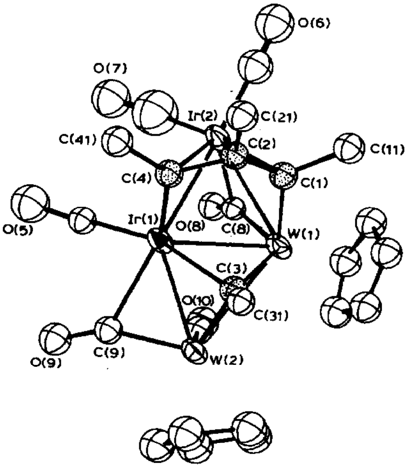
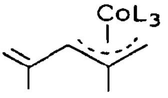


[374]

Metal π-allyl Complexes

Photolysis of a mixture of $[cpCo(CO)_2]$, allyl alcohol and tetrafluoroboric acid in diethyl ether affords a moderate yield of $[cpCo(CO)(\eta^3-C_3H_5)]BF_4$. The same reaction with buta-1,3-diene in place of the alcohol forms $[cpCo(CO)(\eta^3\text{-3-methylallyl})]BF_4$ (ref. 639). In contrast to the results described in reference 485 when anhydrous cobalt(II) chloride is reduced with zinc in THF in the presence of potassium 2,4-dimethylpentadienide and triethylphosphine the product is $[(\eta^5-2,5-Me_2C_5H_5)Co(PEt_3)_2]$. However reaction of $[CoCl(PEt_3)_3]$ with potassium 2,5-dimethylpentadienide alone in THF forms a mixture of [375] and [376] (L = PEt_3) which interconvert in



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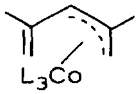
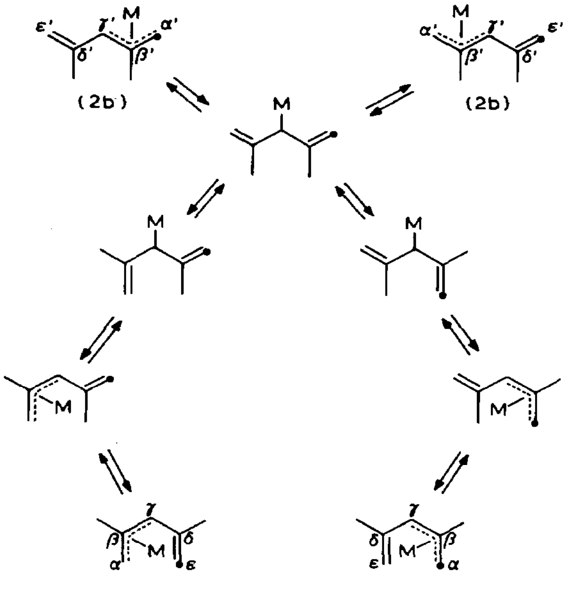


[376]

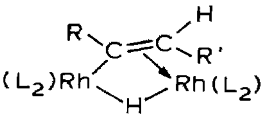
solution as shown in Scheme LIV (ref. 640). Under 95 atm pressure of syngas $[(\eta^3-C_4H_7)Co(CO)_3]$ and $[(\eta^4-C_4H_6)Co_2(CO)_4]$ are formed from $[Co_2(CO)_8]$ and buta-1,3-diene at 80°C but if tri-n-butylphosphine (L) is present the



Scheme LIV

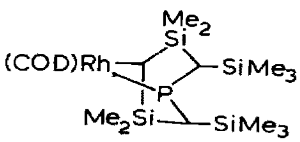
products are $[(\eta^3-C_4H_7)Co(CO)_2L]$ and $[Co_2(CO)_6L_2]$. In the second instance the allyl moiety is more labile than in the first and slow hydrogenation and hydroformylation of the diene also occurs. At temperatures above 100°C $[(\eta^3-C_3H_7)Co(CO)_3]$ forms a carbonyl-free species which catalyzes the oligomerization of the diene (ref. 641). The product of the lithium aluminum hydride reduction of $[(\eta^3\text{-}C_8H_{13})Co(COD)]$ effectively desulfurizes dibenzothiophene, a process which is inhibited by the addition of bipy (ref. 642). The same species and related complexes function as catalysts for the hydrogenation of carbon monoxide and produce little alcohol but they are rapidly deactivated. Mixed rhodium-cobalt analogs are more effective than rhodium complexes alone for hydrocarbon production and particularly active species are formed on addition of $[Fe(CO)_5]$ to the cobalt catalysts (ref. 643).

Reaction of $[(\eta^3\text{-}C_3H_5)Rh(COD)]$ and its 3-methyl analog with 1,2-bis(diisopropylphosphino)ethane (L_2) forms $[(\eta^3\text{-}C_3H_4R)Rh(L_2)]$ (R = H, Me) which is slowly converted to $[Rh_2(L_2)_2(\mu\text{-}H)_2]$ on reaction with hydrogen. This dihydride reacts with ethylene propylene and pent-1-ene to give [377] (R = R' = H. R = H, R' = Me; R = Me, R' = H. R = H, R' = Bu^n; R = Bu^n, R' = H).



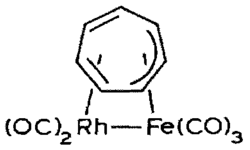
[377]

The same reaction with hex-1-ene gives analogous vinyl hydride complexes plus one equivalent of hexane. The excess olefin was recovered as a mixture of cis- and trans-hex-2-ene. The isomerization appeared to occur during the reaction (see also reference 487) (ref. 644). Reaction of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Rh(COD)]$ with di-tert-butylphosphine at room temperature forms $[(\eta^3\text{-}2\text{-}MeC_3H_4)Rh(PBu^t{}_2H)(COD)]$ which reacts further with more ligand at 65°C to give $[(\eta^3\text{-}2\text{-}MeC_3H_4)Rh(PBu^t{}_2H)_2]$. The dicyclohexylphosphine analog of the second complex is obtained as the product when this ligand is used in the first reaction. Also, $[(\eta\text{-}2\text{-}MeC_3H_4)Ir(COD)]$, prepared in situ, adds di-tert-butylphosphine at -78°C and on warming $[(\eta^3\text{-}2\text{-}MeC_3H_4)Ir(PBu_2{}^tH)(COD)]$ is obtained. By contrast, the original reaction with bis(bis(trimethylsilyl)methyl)phosphine yields [378] plus methane and isobutene. The differences in the

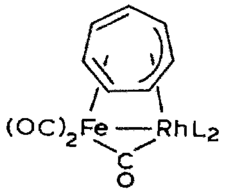


[378]

course of the reactions are attributed to the differences in the bulk of the ligands used (ref. 645). A reversal in the mode of the attachment of the C_7H_7 ring in [379] occurs on reaction with phosphines to form [380] (L_2 =

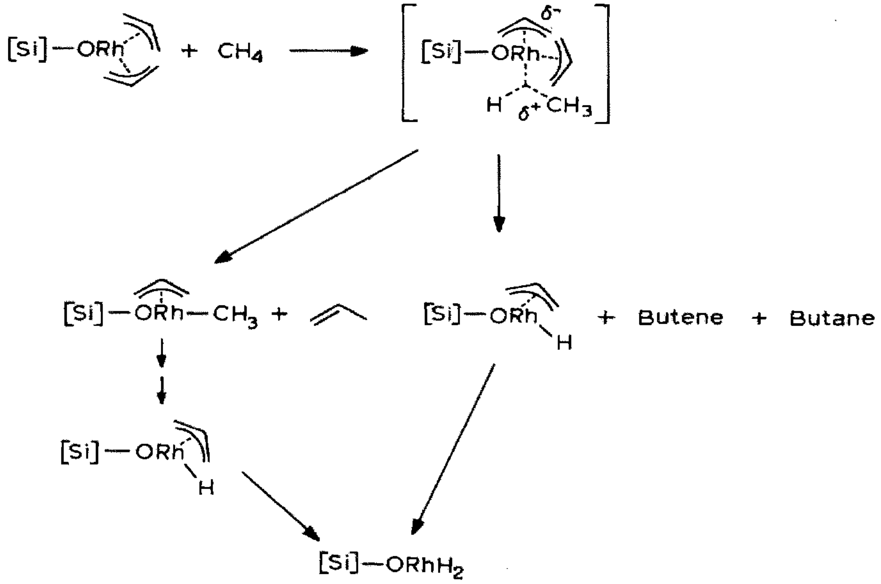


[379]

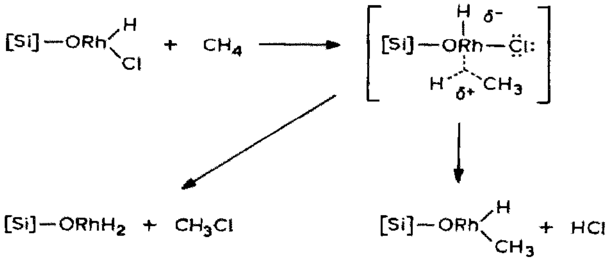


[380]

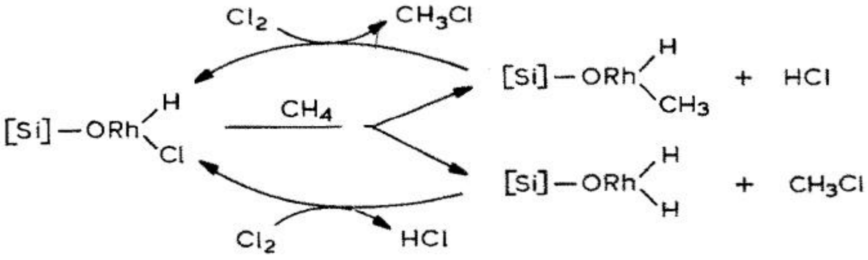
(PMe$_3$)$_2$, DPM, DPPE, dmpe) (ref. 646). At 100°C {(η^3-C$_3$H$_5$)$_2$Rh} moieties attached to a silica surface slowly react with methane to give propene, butene and butane as outlined in Scheme LV. Also studied was the methanation of silica-supported {RhHCl} moieties and the use of this species to catalyze the chlorination of methane. Schemes LVI and LVII respectively are proposed for these processes (ref. 647). In related work the kinetics of hydrogen-deuterium exchange in alkanes catalyzed by the supported allylrhodium species were studied and the results suggested that electrophilic attack on a carbon-hydrogen bond of the alkane by the catalyst occurs. Once



Scheme LV



Scheme LVI

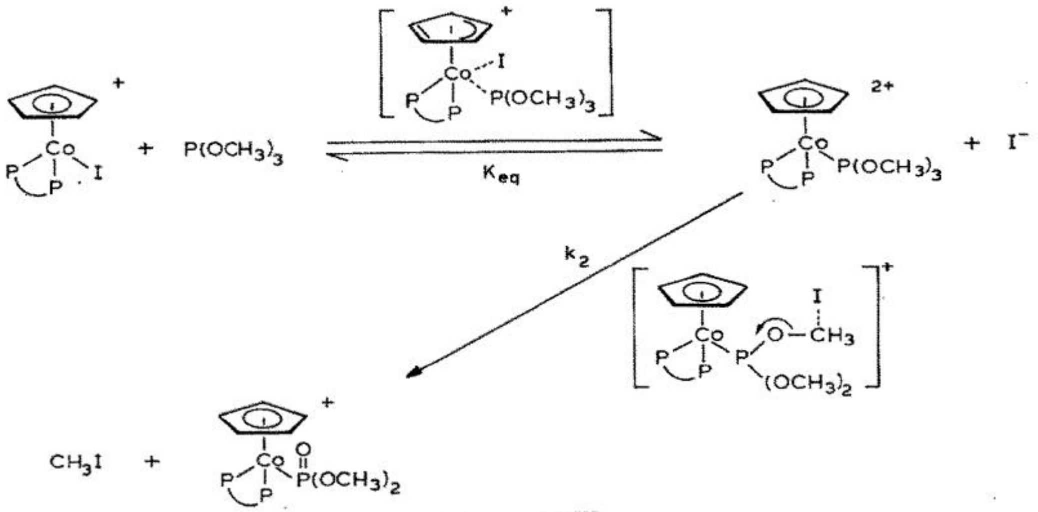


Scheme LVII

the system has been running for some time, alkene is also present and then electrophilic attack on a carbon-hydrogen bond of the alkene is preferred. Steric factors are thought to be important in the rate-determining step (ref. 648).

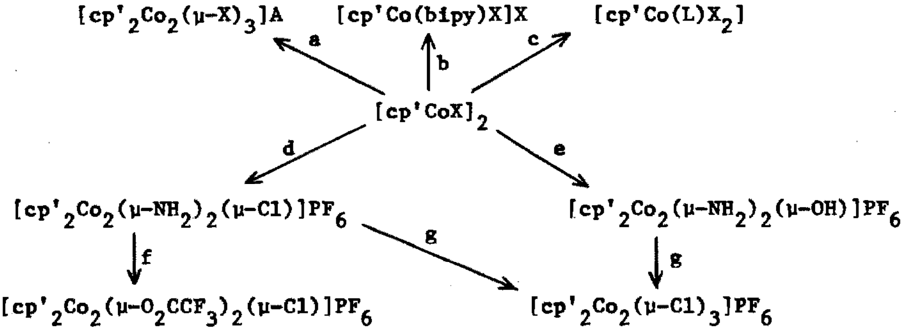
Metal Carbocyclic Complexes

Further work has been reported on attempts to assess the effect of steric and electronic factors on the course of the Arbusov reaction of trimethylphosphite coordinated to cobalt for which Scheme LVIII ($\widehat{PP}$ = DPPE and related ligands) has been proposed. The rate of replacement of halide in $[cpCo(DPPE)X]^+$ (X = Cl, Br, I) by trimethyl- and triethylphosphite is in the order I>Br>Cl which is the expected order for halide as a leaving group from a cobalt(III) center. Also, the proposed intermediate, $[cpCo(DPPE)(P(OMe)_3)](BF_4)_2$, has been synthesized by treatment of [cpCo(DPPE)I]I with silver tetrafluoroborate in acetonitrile followed by addition of the phosphite. It is converted to the final product, $[cpCo(DPPE)(P(O)(OMe)_2)]BF_4$ on reaction with halide ion at rates which are comparable to those observed for the overall reaction. These and related results are interpreted to support



Scheme LVIII

the mechanism of Scheme LVIII. It appears that the first step (replacement of iodide) is associative in character since it does not occur with bulky ligands. Replacement of DPPE by ligands having different electronic properties also affects the rate, indicating this factor is also important. Perhaps the most interesting result, obtained from the reactions of $[cpCo(DPPE)(P(OMe)_3)]^{2+}$ with nucleophiles, is the observation that the overall rate of formation of the Arbusov product is not greatly affected by the strength of the nucleophile which contrasts with the conventional view that the strength of the nucleophile controls the rate of the Arbusov reaction (refs. 649, 650). Reaction of $[cp'Co(CO)I_2]$ with sodium catecholate forms $[cp'Co(1,2\text{-}O_2C_6H_4)]$ (ref. 651). Some chemistry of the cobalt(II) dimers $[cp'CoX]_2$ (X = Cl, Br, I, NH_2) is outlined in Scheme LIX (ref. 652). The



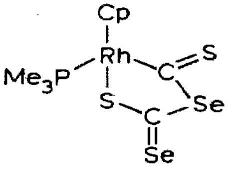
a) FeX_3 (X = Cl, Br) then PF_6^- (= A); FeI_3 (X = I, A = I).
b) bipy (X = Cl, Br, I). c) L (= CO; X = Cl, Br. = py; X = Cl).
d) $FeCl_3$ (X = NH_2) then PF_6^-. e) $Fe_2(SO_4)_3$ (X = NH_2) then PF_6^-.
f) TFA. g) HCl.

Scheme LIX

corresponding cobalt(III) dimer $[cp'Co_2Cl_4]$ forms the arene complexes, $[cp'Co(\eta^6\text{-arene})](PF_6)_2$ (arene = C_6H_6, C_6H_5Me, C_6Me_6, mesitylene) on reaction with aluminum(III) chloride and the arene followed by addition of hexafluorophosphate ion while in aqueous solution the dimer forms $[cp'Co_{(aq)}]^{2+}$ at pH<5 and $[cp'_2Co_2(\mu\text{-}OH)_3]^+$ at pH>9. The arene complexes and their cyclopentadienyl analogs have been studied electrochemically in propylene carbonate solution. Two reversible, one-electron reduction steps are observed. INDO-SCF molecular orbital calculations on the reduced species suggest that there is significant covalent character in the metal-ring bonding (refs. 653, 654).

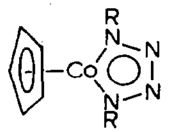
Addition of thiocyanogen or sulfur(II) cyanide to $[cp'CoL_2]$ forms $[cp'CoL(X)(NCS)]$ (L = CO, C_2H_4; X = CN, NCS) (ref. 655). Reaction of $[cpCo(PMe_3)_2]$

at -10°C with CSSe forms a mixture of $[cpCo(PMe_3)(\eta^2\text{-}SeC{=}S)]$, $[cpCo(CS)(PMe_3)]$ and $[cpCo(PMe_3)(Se_2C{=}S)]$. Triphenylphosphine abstracts selenium from the first complex to generate the second. The same reaction at 50°C with the phenyldimethylphosphine and trimethylphosphite analogs forms only thiocarbonyl and thiodiselenocarbonate products while with $[cpRh(PMe_3)(C_2H_4)]$ the initial product is $[cpRh(PMe_3)(\eta^2\text{-}SeC{=}S)]$ which is converted to $[cpRh(PMe_3)(CS)]$ by triphenylphosphine and to [381] by more CSSe. Similarly

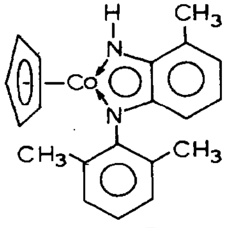


[381]

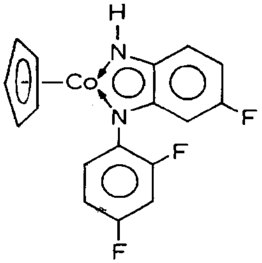
$[cpCoL_2]$ (L = PMe_3, $P(OMe)_3$) reacts with carbon disulfide and carbon diselenide to form $[cpCo(\eta^2\text{-}CS_2)(P(OMe)_3)]$ and $[cpCo(\eta^2\text{-}CSe_2)(PMe_3)]$. The latter complex forms a mixture of $[cpCo(PMe_3)(CSe)]$ and $[cpCo(PPh_3)(CSe)]$ on reaction with triphenylphosphine (ref. 656). In related work, $[cpCoI_2L]$ (L = PEt_3, $PPr^n{}_3$, $PBu^n{}_3$, PMe_2Ph, $PMePh_2$, PPh_3, $PPh(OPh)_2$, $P(OPh)_3$, $AsMe_2Ph$, CNR (R = Bu^t, cy, bz)) and sodium trithiocarbonate form $[cpCo(L)(S_2C{=}S)]$ in higher yield than does the reaction of carbon disulfide with $[cpCo(CO)L]$ since this latter reaction also forms three other products (see also 1983 Annual Survey, reference 662). Reaction of $[cpCo(L)(S_2C{=}S)]$ (L = $PBu^n{}_3$) with methyl iodide forms a mixture of $[cpCo(L)(S_2CSMe)]I$ plus $[cpCo(I)(S_2CSMe)]$ while with mercury(II) halides the product is $[cpCo(L)(CS_3{\cdot}nHgX_2)]$ (n = 1; X = Cl. n = 2; X = Br, I). The dithiocarbonates, $[cpCo(L)(S_2C{=}O)]$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PPh_2cy, $PBu_3{}^n$, $P(OPh)_3$, $PPh(OPr^i)_2$) can be obtained from $[cpCoI_2(L)]$ and sodium methyl- or ethylxanthate in ethanol/dichloromethane. These were unreactive towards methyl iodide, benzyl bromide or 1,2-dibromoethane but when L = $PMePh_2$ methylation to $[cpCo(PMePh_2)(S_2COMe)]^+$ could be achieved with methyl fluorosulfonate (ref. 657). Using an ion plasma technique, $[cpCo(CO)_2]$ can be converted to $[cp_3Co_3(CO)_3]$ (ref. 658). Other reactions of $[cpCo(CO)_2]$ includes that with organic azides to form the tetraazadiene complexes [382] (R = $2,6\text{-}Me_2C_6H_3$, $2,4\text{-}F_2C_6H_3$). Photolysis of the former forms [383] while the latter is converted to a mixture of [384] and [385]. A dinitrene intermediate, $[cpCo(-\ddot{N}R)_2]$, is proposed. A series of the tetraazadiene complexes ([382] (R = Me, Ph, $2,6\text{-}Me_2C_6H_3$, $2,4\text{-}F_2C_6H_3$, C_6F_5)) have been reduced to the corresponding monoanions by sodium amalgam and their electronic absorption spectra measured. The reductions have also been performed electrochemically and found to be quasi-reversible with the reduction potentials varying with



[382]



[383]



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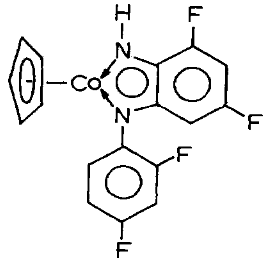
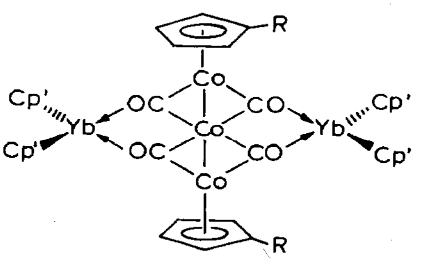


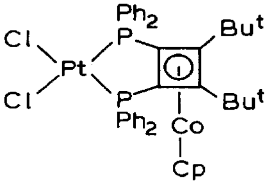
[385]

the substituents on nitrogen. When R = Ph the anion was isolated as the sodium dibenzo-18-crown-6-salt. ESR spectra of the anions suggest the odd electron is located primarily on the metal but is partially delocalized in a π* orbital of the CoN_4 ring (refs. 659, 660). Phosphorus(III) pseudohalides and halogens oxidatively add to $[cp'Co(CO)_2]$ to form $[cp'Co(CO)X(PX_2)]$ (X = CN, NCO, NCS) and $[cp'CoCl(\mu\text{-}Cl)]_2$ or $[cp'Co(CO)X_2]$ (X = Br, I) respectively. The last can be converted to $[cp'CoX(\mu\text{-}X)]_2$ in petroleum ether at 100-120°C and all three dimers on contact with potassium hydroxide in isopropanol form $[cp'_2Co_2X_2(\mu\text{-}H)(\mu\text{-}X)]$ (X = Cl, Br, I) (refs. 661, 662). Coordination of $\{cp'_2Yb\}$ moieties to the oxygen atoms of carbonyl groups occurs when $[cp'_2Yb(Et_2O)]$ reacts with $[(\eta^5\text{-}C_5H_4R)Co(CO)_2]$ (R = H, Me, $SiMe_3$) to form [386]. The central cobalt atom has the unusual hexagonal



[386]

planar coordination (ref. 663). An interesting example of alkyne coupling mediated by [cpCo(CO)$_2$] is that of cis-[PtCl$_2$(Ph$_2$PC≡CBu^t)$_2$] under photolytic conditions which forms [387] (ref. 664). The slow addition of dihydrofulvalene in THF/heptane to a refluxing solution of [Co$_2$(CO)$_8$] in dichloromethane forms [388] (ref. 665).



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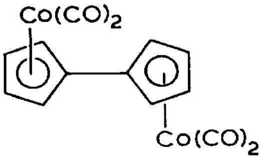
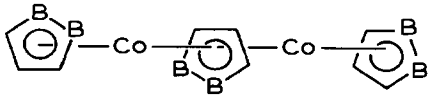


[388]

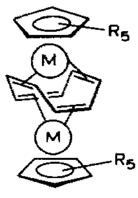
Oxidation of the borazole complexes [(η^5-C$_3$H$_3$B(Me)NR)$_2$Co] (R = Me, Bu^t, SiMe$_3$) with the requisite amount of iodine forms [(η^5-C$_3$H$_3$B(Me)NR)$_2$Co]I$_n$ (n = 3, 5). Hexafluorophosphate salts were obtained by oxidation with ferricinium hexafluorophosphate. The same complexes, including the two rotational isomers of the trimethylsilyl complex, were also studied electrochemically. A reversible, one-electron oxidation step was seen in all cases except when R = SiMe$_3$ where some substitution of the trimethylsilyl group by an alkyl group of the tetraalkylammonium cation of the supporting electrolyte also occurred. The observation that the oxidations occurred at a higher potential than for [cp$_2$Co] was attributed to the "slipped" coordination of the borazole rings (refs. 666, 667). Molecular orbital calculations on the band structures of polydecker sandwich complexes including [389] have been performed to explore the possibility of one-dimensional conductor behavior. For [389] in particular, injection of a charge carrier was necessary and then the conduction pathway was via diffuse ligand states (ref.



[389]

668). Addition of two equivalents of sodium tetraphenylborate to a methanol solution of $[CoCl(PMe_3)_3]$ formed a mixture of $[Co(PMe_3)_4]BPh_4$ and $[Co(\eta^6\text{-}C_6H_5BPh_3)(PMe_3)_2]$ (ref. 669). A mixture of $[cp_2Co]$ and $[cpCo(\eta^4\text{-}C_5H_5Me)]$ is formed when $[cp_2Co]Cl$ reacts with methyllithium in diethyl ether but in THF at -80°C only the latter is obtained. The ethyl analog is obtained similarly with ethyllithium. A quantitative yield of the former results on reaction with methylmagnesium iodide or ethylmagnesium bromide. On the other hand no reduction occurs with ethylaluminum dichloride or diethylaluminum chloride; $[cp_2Co]AlEt_nCl_{4-n}$ (n = 1, 2) is formed instead. Reaction of $[cp_2Co]Cl$ with sodium alkoxides in the appropriate alcohol forms $[cp_2Co]X{\cdot}nHX$ which is in equilibrium with $[cpCo(\eta^4\text{-}C_5H_5X)]$ (X = OMe, OEt). The latter (X = OBu^t, Pcy_2) is formed directly with potassium tert-butoxide or lithium dicyclohexylphosphide. Various organolithium or Grignard reagents attack the metal in $[cpCo(\eta^3\text{-}C_3H_5)Br]$, however, to form $[cpCo(R)(\eta^3\text{-}C_3H_5)]$ (R = Me, Et, vy, Ph, bz, CH_2SiMe_3). In the vinyl complex, coupling of the allyl and vinyl groups occurs on standing at room temperature to form (E)- and (Z)-isomers of $[cpCo(\eta^4\text{-}CH_2CHCHCH_2Me)]$ (ref. 670). Treatment of $[cpCo(\eta^4\text{-}exo\text{-}RC_5H_5)]$ with 5N sulfuric acid in THF forms $[cpCo(\eta^5\text{-}C_5H_4R)]$ (R = Me, Et, Pr^i, Bu^t, cy, bz) indicating that the acid is functioning as a hydride acceptor (ref. 671).

Electrochemical studies on [390] (M = Co, R = Me; M = Rh, R = H) reveal the presence of a two-electron oxidation process which is quasi-reversible for cobalt and irreversible for rhodium. These oxidations are chemically reversible however. Bulk electrolysis of the rhodium complex or oxidation with two equivalents of silver hexafluorophosphate produces isolable quantities of the dication whose structure is [391]. The C_8 ring has now become



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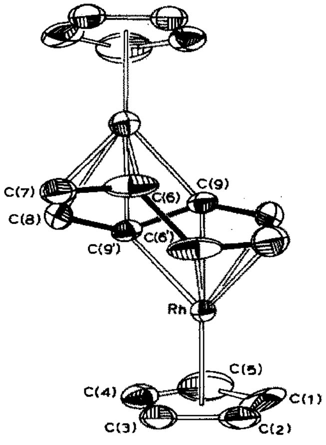
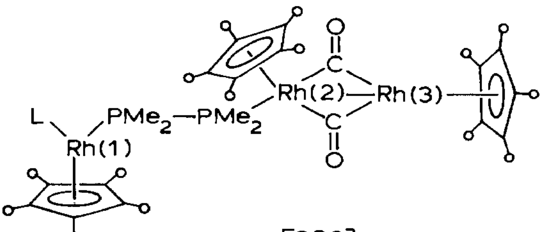


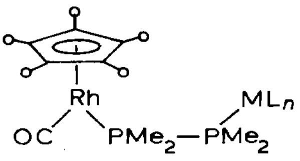
[391]

twisted so that five atoms are now within bonding distance of each metal. In this instance it is felt that the change in the ring conformation occurs after electron transfer while for the cobalt complex this is proposed to accompany the electron transfer (ref. 672). Addition of di- and triolefins to $[(\eta^6\text{-}C_6Me_6)_2Co]^+$ in propylene carbonate forms $[(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}L_2)]^+$ (L_2 = NBD, COD, cyclohexa-1,4-diene, cycloheptadiene, cycloheptatriene, COT), all of which undergo reversible, one-electron reduction (ref. 673). Molecular orbital calculations on $[cpCo(\eta^4\text{-}C_4H_4)]$ and $[cpCo(\eta^4\text{-}C_4H_4CO)]$ suggest that the {cpCo} moiety is bound more strongly to the second ligand in the first complex. Inclusion of configuration interaction significantly improves the predicted stability (ref. 674). Correlations have been made between ^{13}C and ^{59}Co NMR spectral parameters for $[(\eta^5\text{-}C_5H_{5-n}R_n)Co(COD)]$ (n = 1; R = Me, Bu^t, $SiMe_3$, Ph, MeC(O). n = 2; R = $(CH_2)_3$. n = 5; R = Me) and their catalytic activity for the cocyclization of acetylene with nitriles to form 2-substituted pyridines. The catalytic activity appears to increase as the electron density on the metal decreases as indicated by the NMR results. It is therefore suggested that such NMR data might be useful as a predictor of catalytic activity (ref. 675). ESR data are reported for cobalt(0) and -(II) arene complexes (ref. 676) as are infrared spectra of the unstable products from the cocondensation of cobalt atoms with benzene or toluene which are thought to be mono- and bis(arene) cobalt complexes (ref. 677). Inelastic neutron scattering spectra of $[(\eta^5\text{-}C_5D_5)_2Co]$ suggest that a dynamic Jahn-Teller effect and vibronic coupling are important in a description of the ground state (ref. 678). Copolymerization of $[cpCo(CO)_2]$ with the ethylene, acetylene and ethane can be achieved in a plasma system (ref. 679). Silica or alumina treated with potassium cyanide complexed by dibenzo-18-crown-6 are reported to be suitable stationary phases for the chromatography of the products of photolysis of $[cpCo(CO)_2]$ in the presence of the crown-complexed potassium cyanide (ref. 680).

Addition of $[cp'Rh(L)(PMe_2PMe_2)]$ (L = CO, C_2H_4) to $[cp'_2Rh_2(\mu\text{-}CO)_2]$ forms [392] while with $[ML'_n(CO)]$ (L = CO; ML'_n = cpM'(CO) (M' = Co, Rh), $cpMn(CO)_2$, $cpMeMn(CO)_2$) the products are [393] (ref. 681). Reaction of

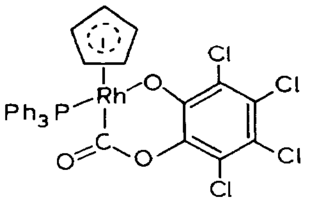


[392]

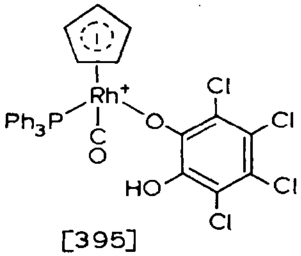


[393]

$[cpRh(CO)(PPh_3)]$ with 3,4,5,6-tetrachloro-o-benzoquinone forms [394] which is converted to [395] by tetrafluoroboric acid etherate. Loss of carbon monoxide occurs on dissolving [395] in dichloromethane to form $[cpRh(\underline{o}\text{-}O_2C_6Cl_4)(PPh_3)]$. The analog of [394] with a carbonyl in place of

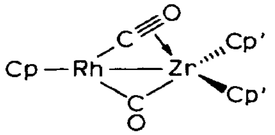


[394]



[395]

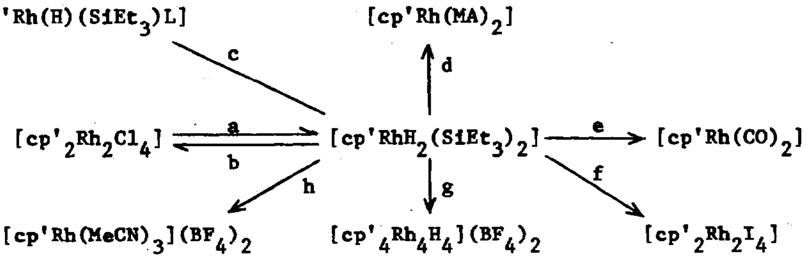
the phosphine was also synthesized as were pentamethylcyclopentadienyl analogs of both. The carbonyl complexes lose two molecules of carbon monoxide in dichloromethane solution to give $[(\eta^5\text{-}C_5R_5)Rh(\underline{o}\text{-}O_2C_6Cl_4)]$ (R = H, Me). Cyclic voltammetric studies on $[(\eta^5\text{-}C_5R_5)Rh(\underline{o}\text{-}O_2C_6Cl_4)(L)]$ (R = H, Me; L = PPh_3) show two, one-electron oxidation processes, the first of which is reversible. The analogs with R = H; L = $AsPh_3$, $P(OPh)_3$ and R = Me; L = $AsPh_3$ behave similarly but the interpretation is complicated due to ligand dissociation. Oxidation of the complexes (R = H; L = PPh_3, $AsPh_3$, $P(OPh)_3$, py. R = Me; L = PPh_3, $AsPh_3$) with silver hexafluorophosphate yields isolable salts of the monocations which are paramagnetic with the unpaired electron localized primarily on the catecholate ligand (ref. 682). Hydrogen loss occurs on reaction of $[cp'_2ZrH_2]$ with $[cpRh(CO)_2]$ and the product is [396].



[396]

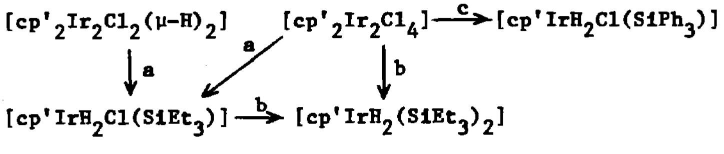
This can also be obtained from $[(cp'_2Zr(N_2))_2N_2]$. On the other hand if $[cpM(CO)_2]$ (M = Co, Rh) is reacted with $[cp'_2ZrHX]$ (X = F, Cl), the product is $[cp(CO)M{=}CHOZrcp'_2X]$ containing a zirconoxycarbene ligand bound to cobalt or rhodium (ref. 683). Lewis acid-base adducts $[cpRhL(L')(AlR_3)]$ (L = L' = PMe_3, PMe_2Ph, PEt_3; R = Me. L = L' = PMe_3; R = Et. L = PMe_3; L' = C_2H_4; R = Me) are formed from $[cpRhL(L')]$ and the aluminum alkyls. In the last instance as well as in the case of the triethylphosphine complex an equilibrium mixture of product and starting materials forms. Similar adducts are formed with alkyl aluminum halides, for example [cpRh(PMe$_3$)$_2$-AlClMe(μ-Cl)AlClMe$_2$] from [cpRh(PMe$_3$)$_2$] plus one mol of [Al$_2$Me$_4$Cl$_2$] and [cpIr(C$_2$H$_4$)(AlEt$_2$I)] from [cpIr(C$_2$H$_4$)$_2$] and one half mol of [Al$_2$Et$_4$I$_2$]. Surprisingly however the acidic complexes [cpMH(L)(PMe$_3$)]A (M = Co, Rh; L = PMe$_3$; A = PF$_6$. M = Rh; L = C$_2$H$_4$; A = BF$_4$) are not deprotonated by hexamethyldialuminum. The first two undergo simple replacement of hydride by methyl to give [cpM(Me)(PMe$_3$)$_2$]PF$_6$ while in the last the ethyl tautomer is trapped as [cpRh(Me)(Et)PMe$_3$] (ref. 684). Reaction of pyrazole with [cp'$_2$Rh$_2$(μ-OH)$_3$]ClO$_4$ in methanol forms [cp'$_2$Rh$_2$(μ-OMe)$_2$(μ-pz)]ClO$_4$ which reacts further with pyrazole in aqueous perchloric acid to give [cp'$_2$Rh$_2$-(pzH)$_2$(μ-OH)$_2$](ClO$_4$)$_2$. This last complex can be got directly if the original reaction is run in aqueous perchloric acid. Analogs with 2,5-dimethylpyrazole were also prepared. Reaction of either of the pyrazoles with [cp'Rh(acetone)$_3$](ClO$_4$)$_2$ in the presence of potassium hydroxide forms [cp'$_2$Rh$_2$(μ-OH)(μ-pz)$_2$]ClO$_4$ (ref. 685). More examples of cationic rhodium-arene complexes containing diolefin ligands have been reported. Formation of [Rh(L$_2$)(acetone)$_x$]ClO$_4$ (L$_2$ = COD, TFB, Me$_3$TFB) by halide abstraction from [RhCl(L$_2$)]$_2$ with silver perchlorate in the presence of a stoichiometric quantity of arenes produces [(η^6-arene)Rh(L$_2$)]ClO$_4$ (L$_2$ = COD, TFB, Me$_3$TFB; arene = biphenyl, diphenylmethane. L$_2$ = COD; arene = tetralin, indene, fluorene, dihydroanthracene, carbazole). A second {RhL$_2$$^+$} moiety can be added to the uncomplexed ring in the diphenylmethane complex to give [(L$_2$)Rh-(η^6-C$_6$H$_5$)CH$_2$(η^6-C$_6$H$_5$)Rh(L$_2$)](ClO$_4$)$_2$. The complex [Au(PPh$_3$)(carbazole)] will also add {LRh^{n+}} (L = COD; n = 1. L = cp'; n = 2) moieties to one or both aromatic rings (refs. 686, 687).

Halide abstraction from [cp'RhCl$_2$]$_2$ by silver salts in acetonitrile forms [cp'Rh(MeCN)$_3$]$^{2+}$ which reacts with two heteropolytungstate anions to form [cp'RhSiW$_9$Nb$_3$O$_{40}$]$^{5-}$ and [cp'Rh(*cis*-Nb$_2$W$_4$O$_{19}$)]$^{2-}$. In the first complex, a covalent attachment of the {cpRh^{2+}} moiety to a {NbW$_2$} site is proposed. The second complex is obtained as a mixture of three diastereoisomers by the route just mentioned but only two of these are formed if the heteropolytungstate is reacted directly with [cp'RhCl$_2$]$_2$ in dichloromethane. A crystal structure study of the three-component mixture showed the {cp'Rh} moiety to be bound to three adjacent bridging oxygen atoms of a disordered heteropolytungstate ion. With the aid of ^{17}O NMR studies it was proposed that the diastereoisomers in the two-component mixture have the rhodium atom adjacent to one and both niobium atoms respectively while the third diastereoisomer found in the three-component mixture has the rhodium on the opposite side of the cage from the niobium atoms (refs. 688, 689). The synthesis and chemistry of the formally rhodium(V) complex [cp'RhH$_2$(SiEt$_3$)$_2$] and its iridium analog are shown in Schemes LX and LXI respectively. Reaction of [cp'$_2$Rh$_2$Cl$_4$] with triphenylsilane in refluxing 1,2-dichloroethane forms a mixture of [cp'RhH$_2$(SiPh$_3$)$_2$] and [cp'RhH$_2$(SiPh$_3$)(SiClPh$_2$)]. The formation of [cp'MH$_2$(SiEt$_3$)$_2$] (M = Rh, Ir) is proposed to occur as shown in Scheme LXII (refs. 690, 691). As might be anticipated from these results, [cp'$_2$Rh$_2$Cl$_4$] in 1,2-dichloroethane is a catalyst precursor for the hydrosilylation of



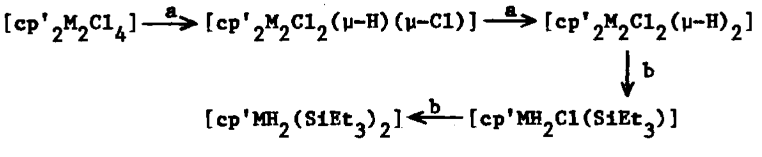
a) Et_3SiH, Et_3N, 25°C, $C_2H_4Cl_2$. b) HCl. c) L (= PPh_3, PEt_3, $P(OMe)_3$).
d) MA, 80°C, C_6H_6. e) CO, 10 atm, 90°C. f) I_2, 80°C, C_6H_6.
g) HBF_4, C_6H_6/MeCN. h) $AgBF_4$, MeCN.

Scheme LX



a) $HSiEt_3$, CH_2Cl_2. b) $HSiEt_3$, NEt_3, 80°C, C_6H_6. c) Ph_3SiH, MeCN.

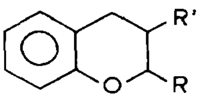
Scheme LXI



a) +Et_3SiH, -Et_3SiCl. b) +Et_3SiH, -HCl.

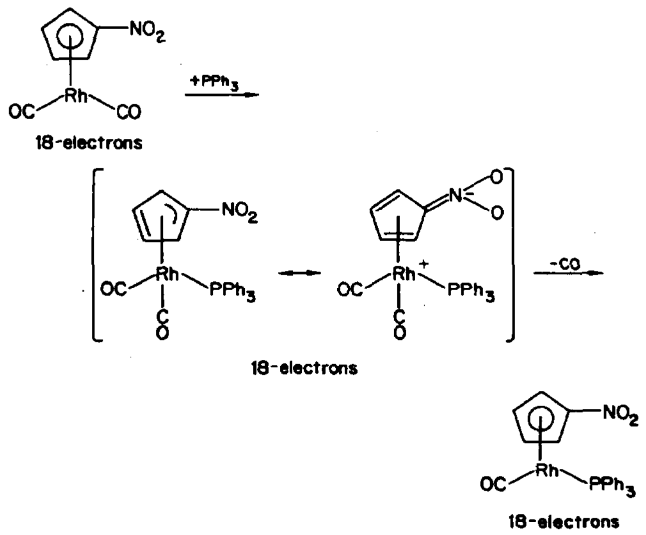
Scheme LXII

hex-1-ene by triethylsilane. Besides the expected *n*-hexyltriethylsilane some (E)-hex-1-enyltriethylsilane is also formed. A significant selectivity to the latter product can be achieved at lower temperatures with a high olefin/silane ratio. No evidence was found for a radical pathway (ref. 692). The dimers [cp'$_2$M$_2$Cl$_4$] (M = Rh, Ir) and [cp'$_2$Rh$_2$(μ-OH)$_3$]Cl are catalyst precursors for the hydrogenation of cyclohexanone to cyclohexanol by hydrogen transfer from methanol (ref. 693). Also, [(η^6-C_6H_6)Rh-(η^5-C_5Et_4Me)](PF$_6$)$_2$ is a catalyst precursor for the cyclization of 3-(2-fluorophenyl)propanols to [397] (R = H; R' = H, CH$_2$OH, *o*-FC$_6$H$_4$CH$_2$. R = Me; R' = H) in acetone/nitromethane at 80°C (ref. 694).



[397]

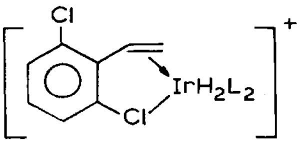
The kinetics of the reaction of triphenylphosphine with [(η^5-$C_5H_4NO_2$)-Rh(CO)$_2$], [(η^5-$C_5H_4PPh_3$)Rh(CO)$_2$]$^+$, [(η^5-C_9H_7)Rh(CO)$_2$] and [(η^5-C_9Me_7)-Rh(CO)$_2$] have been studied. The reactions are first order in each reactant and an analysis of the data indicates the reactions proceed exclusively by an associative process involving an η^5-to-η^3 slippage of the cyclopentadienyl or indenyl ring as shown in Scheme LXIII. This process is enhanced



Scheme LXIII

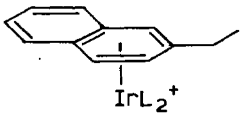
by the presence of an electron-withdrawing group on the ring. The observation that the indenyl complexes react several orders of magnitude faster than the cyclopentadienyl species despite the absence of such groups is explained by a stabilization of the "ring-slipped" transition state due to a complete aromatization of the six-membered ring when the five-membered ring is bound in an η^3 fashion (ref. 695). Photolysis of [(η^5-C_5R_5)M(CO)$_2$] (M = Rh, Ir; R = Me. M = Ir; R = H) in a methane matrix forms [(η^5-C_5R_5)M(H)Me(CO)] by oxidative addition of a carbon-hydrogen bond of the methane. In argon or nitrogen matrices very little formation of photoproducts is observed while in a carbon monoxide matrix [(η^3-C_5R_5)Ir(CO)$_3$] is detected. The results are interpreted to indicate that the primary photoprocess forms [(η^3-C_5R_5)M(CO)$_2$] rather than [(η^5-C_5R_5)M(CO)] (ref. 696). An accurate structural study of [cp'Rh(CO)$_2$] shows it to be essentially identical to its cobalt analog and to have a significant asymmetry in the π-electron density in the pentamethylcyclopentadienyl ring. This is interpreted to indicate that of the two e_1 molecular orbitals of the ring, one contributes more to the binding to the metal than does the other and this proposal is supported by molecular orbital calculations using the Fenske-Hall method. This is probably the reason why, in the photoelectron spectra of [cpM(CO)$_2$] and [cp'M(CO)$_2$] (M = Co, Rh), the valence ionization from the e_1 orbitals of the ring show a much greater splitting in the rhodium complexes than in the cobalt analogs although the difference is also attributed to electron relaxation effects in the excited state of the positive ions formed (refs. 697, 698). Other workers have also obtained photoelectron spectra for [cp'M(CO)$_2$] (M = Co, Rh, Ir) as well as for [cp'IrMe$_2$(DMSO)] and [cp'IrMe$_4$]. For the first three the HOMO appears to have more ring-carbon character for rhodium and iridium than for cobalt which is consistent with their differing behavior on oxidation (see also reference 535) and the relative ease with which they undergo carbonyl substitution by Lewis bases which, as discussed earlier, involves a ring-slip. For the iridium complexes, the first ionization energy increases only slightly with increasing oxidation state. The evident ability of the $\{cp'Ir\}$ moiety to exist in a variety of formal oxidation states is attributed to the electron-donating ability of the pentamethylcyclopentadienyl group which allows the d orbitals to maintain energies and overlap properties conducive to covalent bond formation (ref. 699). Calculations on the activation of hydrogen-hydrogen and carbon-hydrogen bonds by metal fragments including d^8, $\{ML_4\}$ and $\{cpML\}$ moieties by the extended Hückel technique suggest that successful reaction requires coordinative unsaturation and that σ-to-metal electron transfer dominates the early stage of the reaction. For carbon-hydrogen bond activation, steric effects are also important (ref. 700).

The original reaction of $[IrH_2S_2L_2]A$ (L = PPh_3; S = acetone; A = BF_4) with alkanes in 1,2-dichloroethane in the presence of tert-butylethylene as a hydrogen acceptor showed carbon-hydrogen bond activation occurred to a moderate extent with cyclopentane, cycloheptane and cyclooctane but many other alkanes failed to react. It has now been found that the iridium complex can also react with the solvent to form $[Ir_2H_2L_4(\mu\text{-}Cl_2)(\mu\text{-}X)]BF_4$ (X = H, Cl). Much better yields of C-H oxidative addition products are obtained when run in the neat alkane despite the very low solubility of the starting complex. Thus although the original system showed no reactivity towards cyclohexane, the new one (A = SbF_6) did and $[(\eta^5\text{-}C_6H_7)IrHL_2]A$ (5%), $[(\eta^6\text{-}C_6H_6)IrL_2]A$ (45%) and benzene (32%) were formed (ref. 701). In a stoichiometric reaction, $[IrH_2S_2L_2]^+$ also hydrogenates styrene to form $[(\eta^6\text{-}C_6H_5Et)IrL_2]^+$ but this product is not observed when excess styrene is present. Similarly allylbenzene is first isomerized to propenylbenzene and then is hydrogenated to finally form $[(\eta^6\text{-}C_6H_5Pr^n)IrL_2]^+$. With 2,6-dichlorostyrene the intermediate [398] is detected which on heating also converts to



[398]

$[(\eta^6\text{-}C_6H_3Cl_2Et)IrL_2]^+$. This neighboring group effect is suggested to have implications for asymmetric catalysis. In an extension of this work the iridium hydride (A = SbF_6) reacted with 2-vinylnaphthalene at -30°C to first give [399] which converted to [400] on warming although there appeared to be



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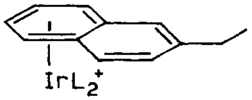
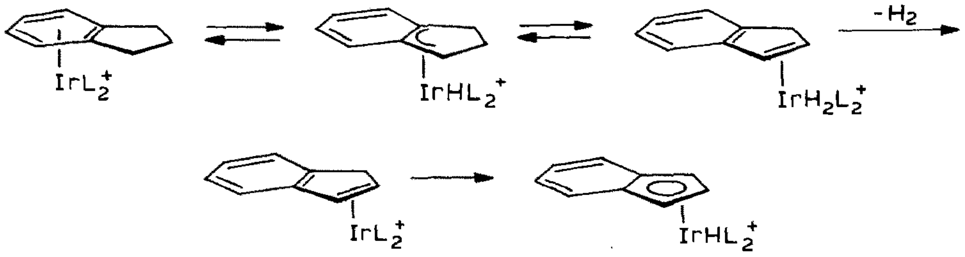


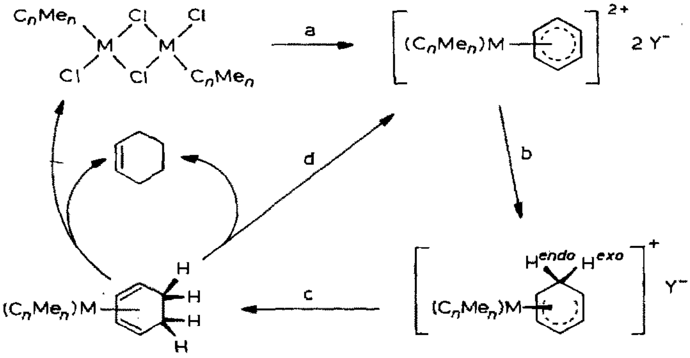
[400]

a tendency to slip to an η^4-coordination. At 40°C the iridium hydride hydrogenates the double bond in the five-membered ring of indene to form $[(\eta^6\text{-}C_9H_{10})IrL_2]^+$ and on heating is converted into $[(\eta^5\text{-}C_9H_7)IrHL_2]^+$ as proposed in Scheme LXIV (refs. 702, 703). The first case of carbon-carbon bond cleavage in an alkane by a transition metal complex in a homogeneous system is found in the reaction of $[IrH_2S_2L_2]SbF_6$ (S = acetone, L =



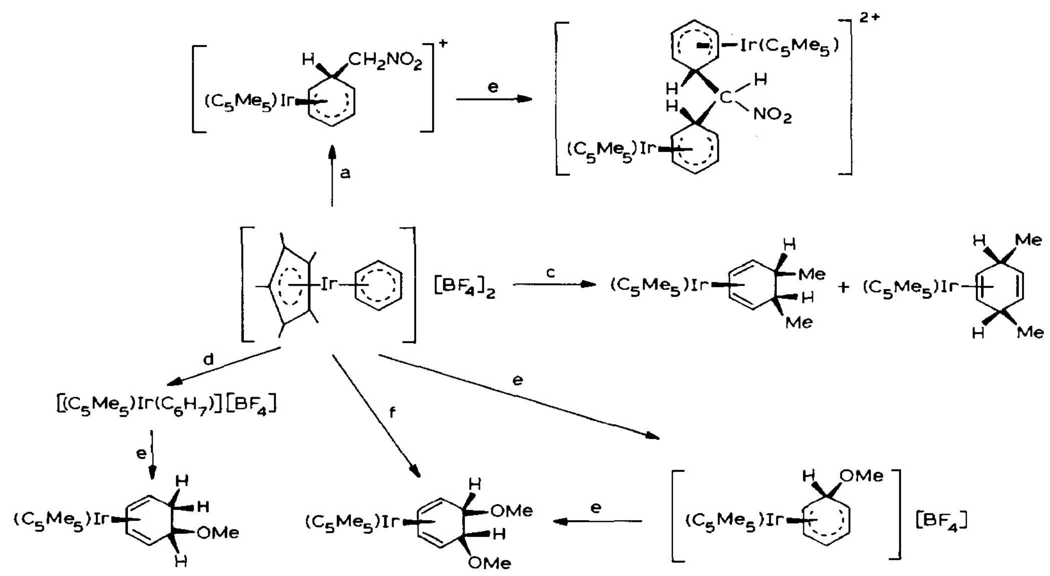
Scheme LXIV

P(p-$FC_6H_5)_3$) with 1,1-dimethylcyclopentane in the presence of tert-butylethylene. First formed is $[(\eta^4\text{-}C_5H_4Me_2)IrL_2]^+$ which on further heating converts to $[(cpMe)IrMeL_2]^+$. The intermediate can also be formed from the dihydride and 5,5-dimethylcyclopenta-1,3-diene. The original reaction takes a different course when the alkane is 1,1-dimethylcyclohexane. Here the only product obtained is $[(\eta^5\text{-}C_6H_5Me_2)IrHL_2]^+$ which does not undergo carbon-carbon bond cleavage on heating presumably because there is no vacant coordination site on the metal. As before the same complex can also be got from the dihydride and 6,6-dimethylcyclohexa-1,4-diene. In the first reaction, the formation of the intermediate diene complex is thought to involve oxidative addition of secondary carbon-hydrogen bonds and the eventual carbon-carbon bond cleavage is thought to be driven by the considerable stability of the methylcyclopentadienyl complex that is the final product (ref. 704). Full details of the hydrogenation of benzene to cyclohexene mediated by $[cp'_2M_2Cl_4]$ (M = Rh, Ir) have now been published. This is outlined in Scheme LXV (n = 5). Analogous systems using toluene, tert-butylbenzene, methoxybenzene and chlorobenzene behave similarly. Some further chemistry of $[cp'Ir(\eta^6\text{-}C_6H_6)]^{2+}$ is outlined in Scheme LXVI (refs. 705, 706).



a) i) $AgBF_4$, acetone; ii) evaporate; iii) C_6H_6, $BF_3\cdot 2H_2O$. b) $NaBH_4$, H_2O. c) $NaH_2Al(OC_2H_4OMe)_2$, toluene. d) HBF_4, C_6H_6. e) HCl.

Scheme LXV

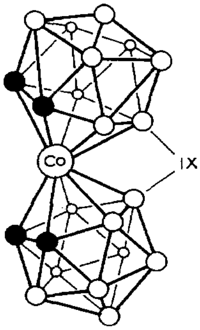


a) MeNO$_2$, base. b) [cp'Ir(η^6-C_6H_6)]$^{2+}$, base. c) MeLi. d) NaBH$_4$, H_2O.
e) 1 NaOMe. f) 2 NaOMe

Scheme LXVI

Metallaborane and -carbaborane Complexes

Careful fractional sublimation of 2-[cpCoB$_4$H$_8$] converts it into the 1-isomer in much better yields than has previously been reported. The proton, ^{13}C and ^{11}B NMR spectra of this and its pentamethylcyclopentadienyl analog have been measured (ref. 707). The J-correlated, two-dimensional ^{11}B-^{11}B NMR spectra of [2-Et-CoB$_4$H$_8$] and [(η^5-C_5R_5)CoB$_9$H$_{13}$] (R = H, Me) have been used to determine ^{11}B-^{11}B couplings and thereby the boron-boron connectivities (ref. 708). Addition of [cp$_2$Co]$^+$ to [$B_{12}H_{12}$]$^{2-}$ forms [(cp$_2$Co)$_2$-$B_{12}H_{12}$] but whether this is a cobaltaborane or simply the cobalticinium salt of [$B_{12}H_2$]$^{2-}$ is not clear (ref. 709). Refluxing Cs[8-I-$C_2B_9H_{10}$CoC$_2B_9H_{11}$] with aluminum(III) chloride in benzene forms [401] (X = I) which contains an



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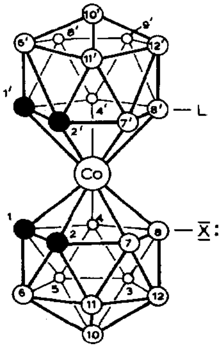
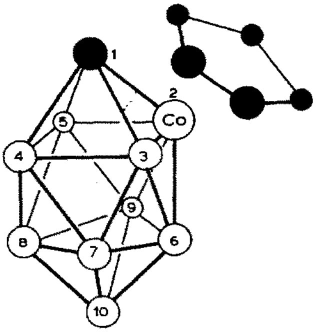


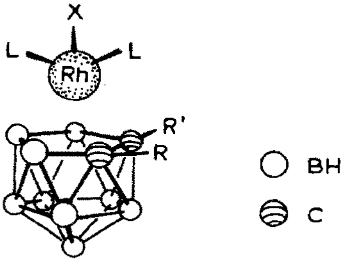
[402]

iodonium bridge. The bridge is cleaved by Lewis bases to form [402] (L = Me$_2$S, py, Me$_3$N, NH$_3$). The analogous bromo complexes were also formed but the former is less stable than its iodo counterpart (ref. 710). Reaction of [4-CB$_8$H$_{14}$] with cyclopentadiene and hydrated cobalt(II) chloride in ethanolic potassium hydroxide forms [403] (ref. 711). Further reports on the use of zone melting for the separation of mixtures of Cs[(B$_9$C$_2$H$_{11}$)$_2$Co] Cs$_2$[(B$_9$C$_2$H$_{11}$)$_2$Co$_2$(B$_9$C$_2$H$_{10}$)] and Cs$_3$[(B$_9$C$_2$H$_{11}$)$_2$Co$_3$(B$_9$C$_2$H$_{10}$)$_2$] have appeared as has a report of the synthesis of K[(B$_9$C$_2$H$_{11}$)$_2$Co] by the electrolysis of K[B$_9$C$_2$H$_{12}$] in DMSO at a cobalt anode (refs. 712, 713).



[403]

In the past few Annual Surveys a considerable number of preliminary reports from the Hawthorne group on the chemistry and catalytic properties of a series of rhodacarbaboranes have been covered. This year complete details of much of this work have been published. In refluxing ethanol or at room temperature in methanol [RhCl(PPh$_3$)$_3$] reacts with [nido-7,8-CRCR'-B$_9$H$_{10}$]$^-$ to form the closo complexes [404] (X = H; R = R' = H; L = PPh$_3$, PEt$_3$, PMe$_2$Ph, ½DPPE. X = H; R = H; R' = Me, Ph, Bu^n; L = PPh$_3$. X = H; R = R' = D; L = PPh$_3$. X = D; R = R' = H; L = PPh$_3$). From the appropriate examples of [404], analogs with X = Cl; R = R' = H; L = PPh$_3$, PMe$_2$Ph could also be formed on reaction with hydrogen chloride in wet chloroform. From the corresponding 7,9 and 2,9 isomers of the nido carbaborane anion [405] (X = H; R = H, Me, Ph; L = PPh$_3$. X = H; R = H; L = PMe$_2$Ph, PEt$_3$) and [406] respectively could be prepared in similar fashion. The series of complexes [404] with X = D were prepared from the carbaborane which contained



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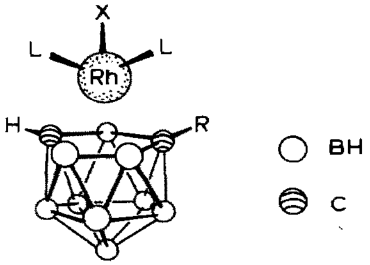

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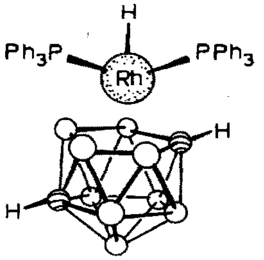
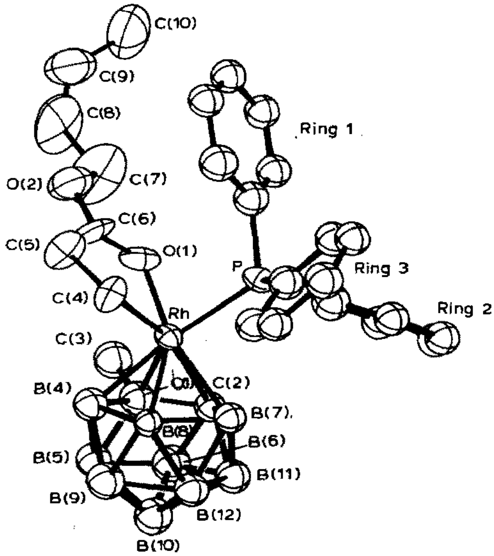


[406]

deuterium in the bridging position on the face thereby supporting the original proposal that this is the source of the hydride ligand on the metal. Complex [404] (X = H; L = PPh_3; R = H; R' = Me) could be resolved but the separate diastereoisomers gave very low optical yields when used to catalyze the hydrogenation of ethyl-α-phenylacrylate. On a preparative scale and in the absence of hydrogen, insertion of the olefin into the rhodium-hydrogen bond occurred to form [407]. Complexes [404] (X = H; L = PPh_3; R = R' = Me; R = H; R' = Me, Ph) on standing in solution undergo some reaction to transfer one phosphine ligand to the carbaborane cage. These same species can also be got from $[RhCl(PPh_3)_3]$, excess phosphine and the appropriate nido carbaborane in aqueous tetrafluoroboric acid (ref. 714). It was observed in the original syntheses of [404] (X = H; L = PPh_3; R,R' = o-xylylene) that the prolonged reaction times required led to the formation of several byproducts. Subsequently it was discovered that a much cleaner route was the reaction of $[RhCl(PPh_3)_3]$ with M[nido-7,8-$CRCR'B_9H_{10}$] (M = Cs, Tl; R,R' = o-xylylene) in benzene containing a little ethanol. The same reaction with other carbaboranes (R = Me, Ph; R' = Me. R,R' = $(CH_2)_3$) however forms the exo-nido complexes [408]. The similar species [409]



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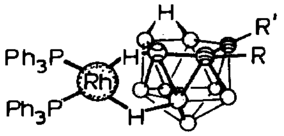
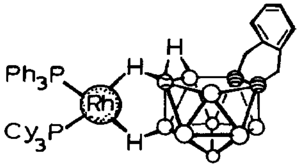
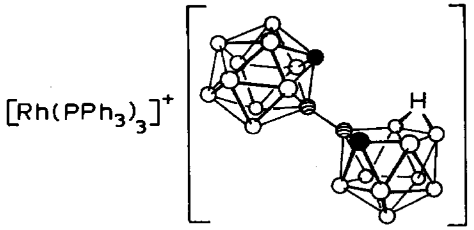


[408]



[409]

results when [404] (X = H; L = PPh$_3$; R,R' = *o*-xylylene) reacts with tricyclohexylphosphine. In fact both this example of [404] and [408] (R = R' = Me) appear to exist in solution as a mixture of *closo* and *exo*-*nido* isomers. On the other hand, when the same reaction used to form [408] is performed with the carbaborane whose substituents are R = H and R' = 1'-[*closo*-1',2'-$C_2B_9H_{10}$] complex [410] forms instead. Analogous ionic complexes [Rh(PEt$_3$)$_4$]-[*nido*-7,8CRCR'B_9H_{10}] are formed when [408] - [410] are reacted with excess triethylphosphine. Heating these salts causes loss of phosphine and the formation of either [404] (X = H; L = PEt$_3$; R, R' = $(CH_2)_2$, *o*-xylylene) or the new isomer [411] (R = Me, Ph; R' = Me. R = H; R' = 1'-[*closo*-1',2'-$C_2B_9H_{10}$]). Complexes [408] and [409] also react with carbon monoxide and



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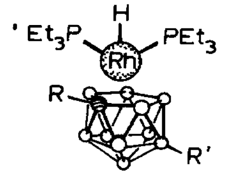
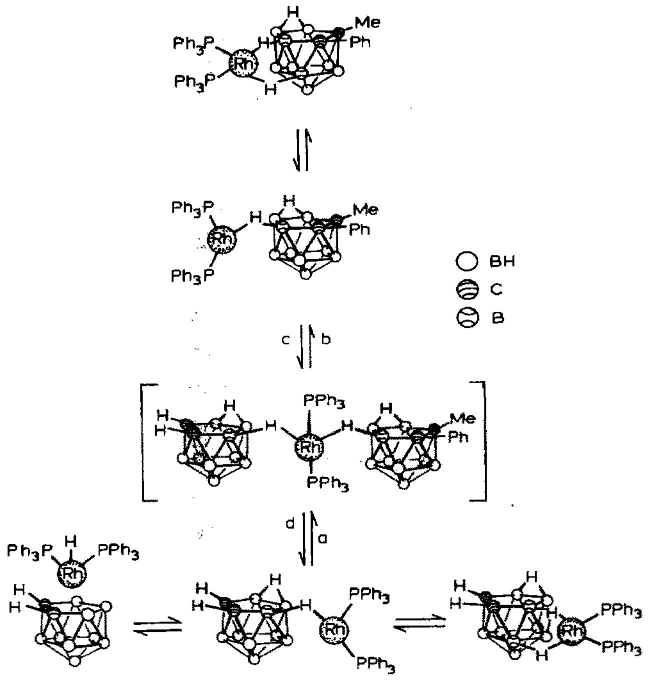


[411]

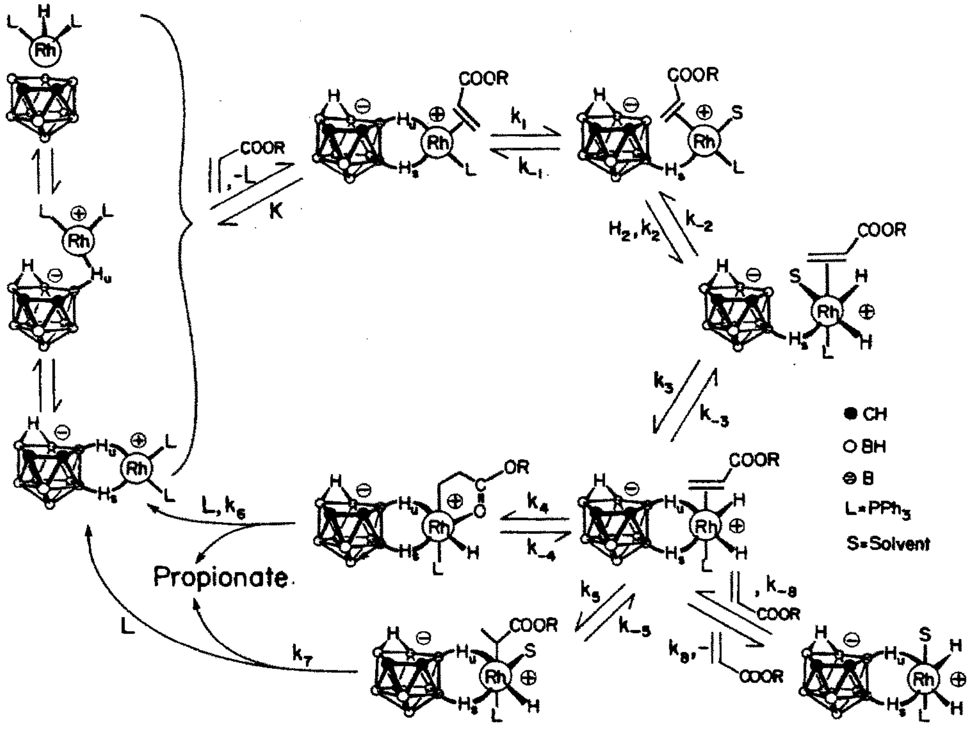
hydrogen to form [Rh(CO)$_3$(PPh$_3$)$_2$][*nido*-7,8-CRCR'B_9H_{10}] and [RhH$_2$(PPh$_3$)$_2$]-[*nido*-7,8-CRCR'B_9H_{10}] respectively. In the latter complexes the Rh-H-B bridges appear to be retained (ref. 715). As has been reported in previous Annual Surveys the {RhH(PPh$_3$)$_2$} moiety in [404] - [406] (X = H; L = PPh$_3$) can be made to transfer to a different [*nido*-CRCR'B_9H_{10}]$^-$ unit to form new *closo* complexes. The ease of the reaction varies with the degree of substitution on the carbon atoms and their position in the cage and was found to be 7,8-disubstituted > 7,8-monosubstituted > 7,8-unsubstituted > 7,9-unsubstituted ∿ 2,9-unsubstituted. The reaction is proposed to proceed *via* *exo*-*nido* species as shown in Scheme LXVII for one example. An alternative process is one in which an $\{Rh(PPh_3)_2^+\}$ moiety transfers directly from one exo-nido



a) + [nido-7,8-CMeCPhB$_9$H$_{10}$]$^-$. b) − [nido-7,8-CHCHB$_9$H$_{10}$]$^-$.
c) + [nido-7,8-CHCHB$_9$H$_{10}$]$^-$. d) − [nido-7,8-CMeCPhB$_9$H$_{10}$]$^-$.

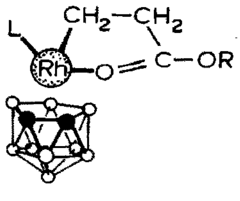
Scheme LXVII

species to the new cage to initially form a new exo-nido complex which then collapses to the closo form (ref. 716). Complexes [404] − [406] (X = H; L = PPh$_3$; R = R' = H) and [408] (R = R' = Me) have been studied as catalyst precursors for olefin hydrogenation. Since the first and last both show approximately the same degree of hydrogenation vs isomerization of hex-1-ene, it is proposed that both form the same active intermediate. This is proposed to be the species at the bottom center of Scheme LXVII in which the metal is coordinatively unsaturated and therefore able to coordinate the olefin. The remainder of the hydrogenation process as well as the isomerization are presumed to occur by well-established routes, the former by oxidation addition of hydrogen to the metal followed by stepwise hydrogen transfer to the olefin and the latter via η^3-allyl hydride intermediates. When the olefin is 1-butylacrylate the course of the catalytic reaction is somewhat different and depends on the complex used as the catalyst precursor. With [404] (X = H; L = PPh$_3$; R = R' = H) and [406] catalytic



Scheme LXVIII

hydrogenation occurs as indicated in Scheme LXVIII (R = 1-butyl). The only difference between this proposed pathway and that discussed just above is the coordination of the ester oxygen that is suggested to occur between the two hydrogen transfer steps. Again it appears that despite the fact that [412] and [413] (R = 1-butyl) can be formed from this example of [404] and



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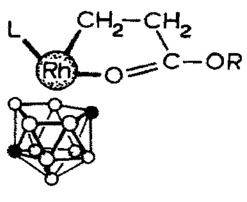

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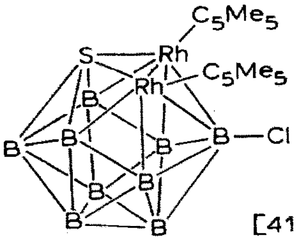
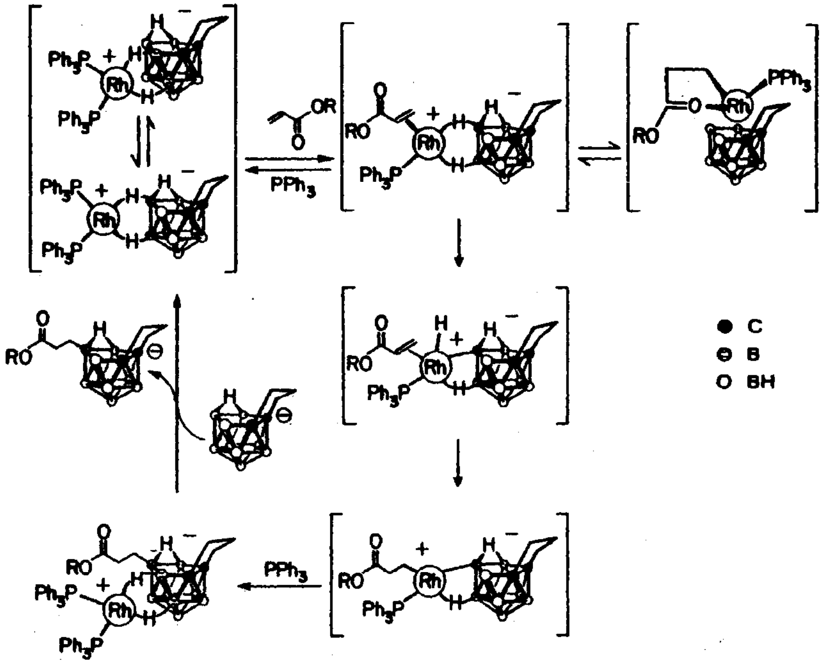


[414]

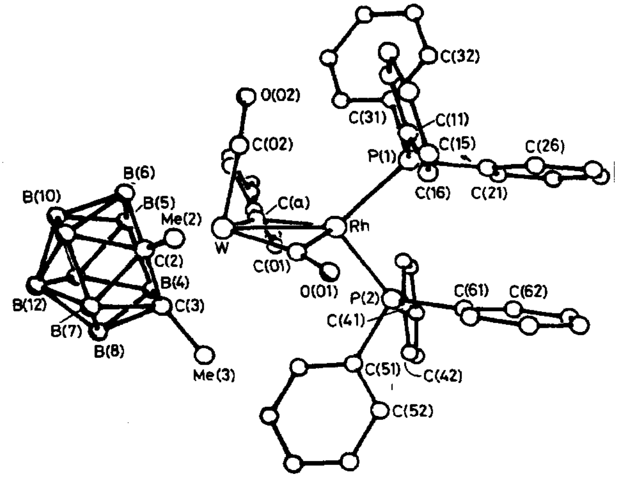
[406] respectively in the absence of hydrogen the hydride ligand originally on the rhodium does not become involved in the catalysis. Thus if [412] and [413] form under catalytic conditions, they must do so reversibly as they are not on the reaction coordinate for the catalytic hydrogenation. Also it appears that none of the boron-hydrogen bonds becomes involved in the catalysis. If, however, the *exo-nido* complex [408] (R,R' = $(CH_2)_3$) is reacted with 1-butylacrylate in the absence of hydrogen, the olefin inserts into a boron-hydrogen bond as suggested in Scheme LXIX (R = 1-butyl) to form

the product shown on the lower left of the scheme (refs. 717-720). Reaction of [RhCl(PPh$_3$)$_3$] with [*nido*-H$_3$NCB$_{10}$H$_{12}$] in the presence of tetra-*n*-butylammonium hydroxide forms Bu$_4$N[*closo*-2,2-(PPh$_3$)$_2$-2-H-1-NH$_2$-2,1-RhCB$_{10}$H$_{10}$] which on refluxing in methanol dimerizes to form an anionic complex with an {Rh-H-Rh} moiety present (ref. 721). In refluxing THF, [cp'RhCl$_2$]$_2$ reacts with Cs[*arachno*-6-SB$_9$H$_{12}$] to form at least six products with the major one identified as [414] (ref. 722).



Scheme LXIX

Addition of Na$_2$[7,8-C$_2$Me$_2$B$_9$H$_9$] to [W(≡CR)Br(CO)$_4$] (R = *p*-tolyl) in THF at −40°C followed by warming to room temperature forms [W(≡CR)(CO)$_2$(η-C$_2$Me$_2$B$_9$H$_9$)]$^-$ which reacts with [RhCl(PPh$_3$)$_3$] or [Rh(COD)(PPh$_3$)$_2$]BF$_4$ in dichloromethane to form [415]. With [Rh(NBD)(PPh$_3$)$_2$]BF$_4$, however, the tungsten complex forms [416] in which the NBD has been isomerized to a nortricyclane moiety and become attached to the carbaborane cage in what is suggested to be a metal-promoted hydroboration. Both [415] and [416] are fluxional by a process which seems to involve bridge-terminal exchange as well as possibly a rotation of the {Rh(PPh$_3$)$_2$} moiety about the metal-metal axis (ref. 723). Reaction of Et$_4$N[*nido*-B$_9$H$_{12}$] with [IrCl(CO)(PMe$_3$)$_2$] in dichloromethane forms



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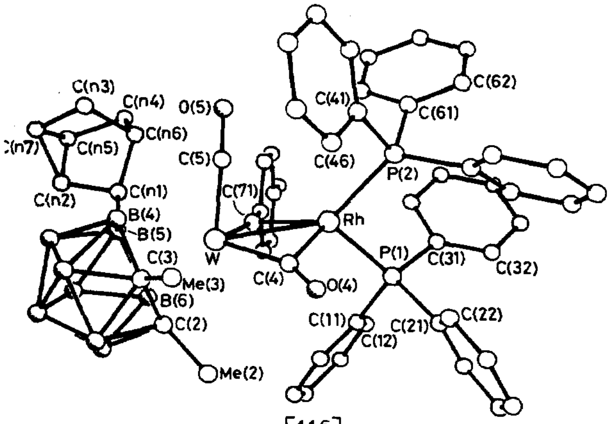
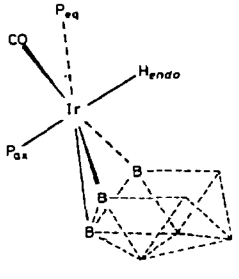


[416]

[417] together with smaller amounts of [418] plus [*nido*-6-H-6,6-(PMe$_3$)$_2$-6-IrB$_9$H$_{13}$] and traces of [419] plus [*arachno*-1-(CO)-1,1-(PMe$_3$)$_2$-1-IrB$_4$H$_9$]



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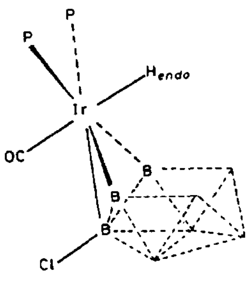

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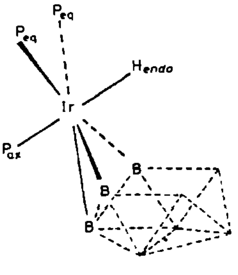
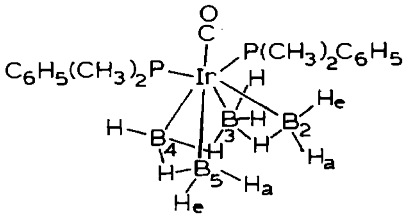
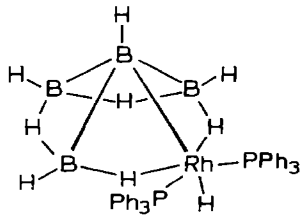


[419]

(ref. 724). Reaction of [IrCl(CO)(PMe$_2$Ph)$_2$] with K[B$_4$H$_9$] in THF/dichloromethane at -18°C forms [420] while under the same conditions [RhCl(PPh$_3$)$_3$] gives [421] (ref. 725). Under hydrogen, maleic anhydride reacts with



[420]



[421]

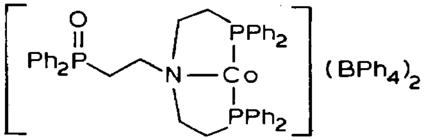
$[Ir(\sigma\text{-carb})(CO)(PhCN)(PPh_3)]$ (σ-carb = $7\text{-Ph-}1,7\text{-}C_2B_{10}H_{10}$) to form $[Ir(\sigma\text{-carb})H(\overline{CHCH_2C(O)OC}(O))(CO)(PhCN)(PPh_3)]$. The reductive elimination of succinic anhydride has been studied in 1,2-dichloroethane solution. Since excess benzonitrile retards the rate and replacement of the nitrile by a second carbonyl group stops the reaction altogether, it was proposed that the nitrile dissociates and then reductive elimination occurs followed by reattachment of the nitrile (ref. 726). In refluxing toluene $[\underline{closo}\text{-}3,3\text{-}(PPh_3)_2\text{-}3\text{-H-}1\text{-R-}3,1,2\text{-}IrC_2B_9H_{10}]$ (R = Me, Ph) rearranges to $[\underline{closo}\text{-}2,2\text{-}(PPh_3)_2\text{-}2\text{-H-}8\text{-R-}2,1,8\text{-}IrC_2B_9H_{10}]$ with the latter rearranging more rapidly. When R = H, no rearrangement occurs suggesting that relief of steric strain provides at least part of the driving force (ref. 727).

Miscellaneous Complexes

As in previous Annual Surveys, this section includes papers which cannot be satisfactorily included in the other sections but which nonetheless are likely to be of interest to organometallic chemists. This year has seen an upsurge of studies on ion-molecule reactions in the gas phase using ion cyclotron resonance, fourier transform mass spectrometry and related techniques. Both bare metal ions as well as ionized metal carbonyl and metal alkyl fragments have been used in combination with a wide range of cyclic, acylic and functionalized hydrocarbons. Bond dissociation energies for $\{Rh\text{-}H\}^+$ and $\{Rh\text{-}CH_3\}^+$ have been determined with the latter being ca 5 kcal/mol greater, a difference attributed to a resonant charge stabilization of Rh^+ by the methyl ligand. The bonds to rhodium are considered to be largely covalent with the metal using largely d-type orbitals (ref.728). With toluene, Co^+ simply forms an adduct but Rh^+ causes dehydrogenation. Using $C_6H_5CD_3$ the products are $\{RhC_7H_5D\}^+$ plus D_2 and $\{Rh(C_7H_4D_2)\}^+$ plus HD in a seven-to-three ratio. Hydrogen adds readily to $\{Rh(C_7H_6)\}^+$ and no H/D exchange occurs if deuterium is added. Since a separate study has shown that $\{C\text{-}Rh(\eta\text{-}C_6H_6)\}^+$ does not add hydrogen, the $\{Rh(C_7H_6)\}^+$ formed here from toluene must have a different structure such as $\{Rh\text{-}CHPh\}^+$ or $\{Rh(\eta\text{-}\underline{cyclo}\text{-}C_7H_6)\}^+$ or possibly an equilibrium mixture of the two. With cycloheptatriene Rh^+ forms $\{Rh(C_7H_6)\}^+$ together with some products derived from cleavage of carbon-carbon bonds while Co^+ proceeds mainly by the second pathway. Both ions react with NBD to form two- and five-carbon fragments bound to the metal, possibly via an initial retro Diels-Alder reaction (refs. 729, 730). The primary process in the reaction of $\{CoMe\}^+$ with acylic alkanes, like that with $\{CoH\}^+$, is insertion into a carbon-hydrogen bond and elimination of methane. The remaining fragments on the metal undergo β-hydrogen abstraction processes to form hydrogen and ultimately $\{Co(allyl)\}^+$. Small to moderate amounts of hydride abstraction occur initially also. With cycloalkanes insertion into a carbon-carbon bond occurs in the strained molecules cyclopropane and cyclobutane while with higher members of the series insertion into carbon-hydrogen bonds is again observed to be the primary process. The initial products in the first instances is a metallacycle (refs. 731, 732). While $\{Co_2\}^+$ is unreactive towards alkanes, $\{Co_2(CO)\}^+$ is quite reactive and inserts into carbon-hydrogen bonds to form dehydrogenated hydrocarbon complexes without loss of the carbonyl ligand. A possible reason for the difference in reactivity is that the carbonyl-free cobalt atom in $\{Co_2(CO)\}^+$ bears a partial positive charge as a result of a polarization of the metal-metal bond by the carbonyl ligand and thereby is able to form stronger cobalt-carbon bonds (ref. 733). Cobalt ions react with $[Fe(CO)_5]$ to form predominantly $\{CoFe(CO)_3\}^+$ while iron ions and $[Co_2(CO)_8]$ generate mainly $\{FeCo_2(CO)_5\}^+$. Collisional activation of the primary products ultimately forms $\{FeCo\}^+$ and $\{FeCo_2\}^+$ respectively. The former reacts with benzene to first form $\{Co(C_6H_6)\}^+$ and atomic iron, a process which was used to estimate the bond dissociation energy of the bimetallic ion. The second is unreactive towards methane, ethane and neopentane but with propane and isomeric butanes insertion into carbon-hydrogen bonds is observed. In contrast to Fe^+ or Co^+ by itself little if any insertion into carbon-carbon bonds occurs (refs. 734, 735).

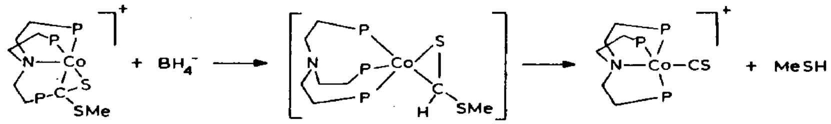
What is effectively a carbon monoxide abstraction occurs when Co^+ reacts with cyclic or acylic ketones and with aldehydes. For example cyclopentanone gives $\{Co(\eta^4\text{-}C_4H_6)\}^+$ plus $\{Co(CO)\}^+$ while cyclobutanone and acetaldehyde give primarily $\{Co(CO)\}^+$ plus $\{Co(C_3H_6)\}^+$ or methane respectively. With larger molecules a larger variety of products is seen because of the larger number of reaction points in the longer alkyl chains but the initial step still appears to be predominantly insertion into a carbon-carbon bond adjacent to the carbonyl group. By contrast, cobalt atoms react with acetaldehyde, at least partially by insertion into the aldehyde carbon-hydrogen bond (refs. 736-739). Cobalt ions also react with n-propylamine by insertion into the carbon-carbon bond adjacent to nitrogen as the primary process. The absence of products which would arise from an insertion into the carbon-nitrogen bond was attributed to the expectation that the cobalt-nitrogen bond which would be formed would be too weak to provide a driving force for reaction at that point (ref. 740). Finally, the reactions of Co^+, $\{Co(CO)_x\}^+$ (x = 1,2) and $\{Co(NO)(CO)_x\}^+$ (x = 0-3), formed by ionization and fragmentation of $[Co(NO)(CO)_3]$, with nitroalkanes, 1,4-dihalobutanes and 4-halobutanols have been studied. In the first instance Co^+ and $\{Co(CO)\}^+$ are quite reactive and form a variety of products while $\{Co(NO)\}^+$ is less reactive. In the last case insertion into a carbon-hydrogen bond is slightly preferred over a carbon-oxygen bond and $\{Co(\eta^4\text{-}C_4H_6)\}^+$ is often seen. Carbon-carbon bond insertion also occurs with Co^+ preferring the central carbon-carbon bond while $\{Co(CO)\}^+$ attacks the one adjacent to the hydroxyl group (refs. 741, 742).

Addition of triphos and E_4X_3 (E = P; X = S, Se. E = As; X = S) to solutions of hydrated cobalt(II) tetrafluoroborate forms [(triphos)Co(η^3-E_2X)]BF_4 (see also reference 509). This complex (E = P, As; X = S) can function as a ligand and on reaction with $[Pt(C_2H_4)(PPh_3)_2]$ forms [(triphos)Co(μ-η^3-η^2-E_2S)$Pt(PPh_3)_2$]BF_4 in which the platinum binds to sulfur and one of the two pnicogen atoms (refs. 743-746). Reaction of [Co(triphos)(NCS)] with Na_2X_4 (X = S, Se) forms [Co(triphos)(X_4)]. This complex with X = S can also be formed from the thiocyanate complex by reaction with sodium hydrogen sulfide (to first give [Co(triphos)$(SH)_2$]) and then with elemental sulfur. On the other hand the thiocyanate complex and sodium sulfide gives [Co(triphos)$(SNa)_2$] (ref. 747). Reduction of carbon dioxide occurs when $[CoH(np_3)]$ is reacted with it in THF containing crown ether-complexed sodium ions. Subsequent addition of tetraphenylborate ion forms a mixture of $[Co(CO)(np_3)]BPh_4$ and [422]. The rhodium analog reacts similarly but no



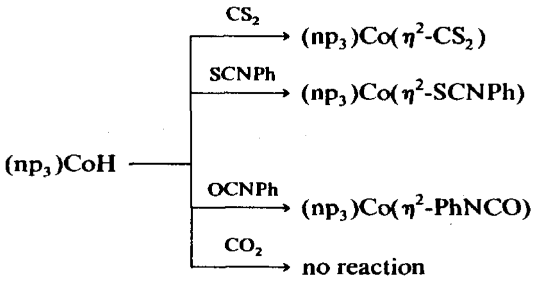
[422]

reaction is observed in the absence of sodium (ref. 748). The synthesis of $[Co(CS)(np_3)]BPh_4$ is proposed to occur as shown in Scheme LXX. Also studied



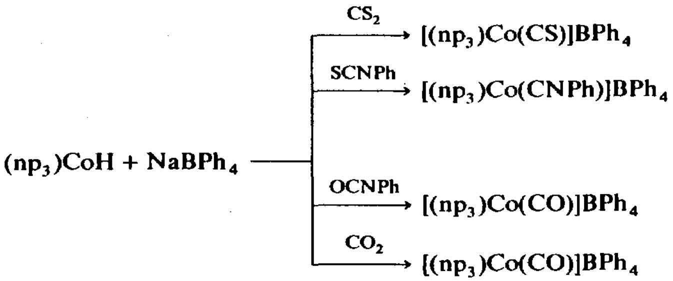
Scheme LXX

was some chemistry of $[Co(H)(np_3)]$ which is outlined in Schemes LXXI and



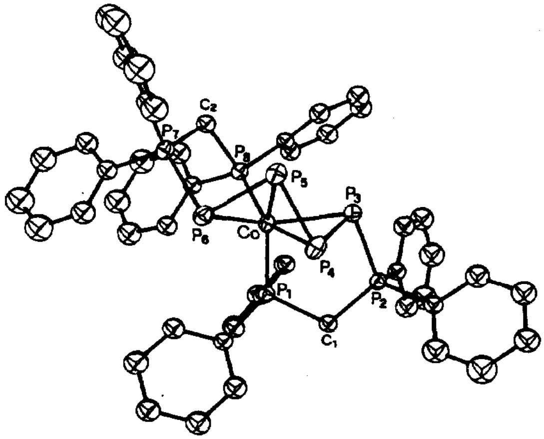
Scheme LXXI

LXXII. A third route to the thiocarbonyl complex is reaction of [(np_3)Co-(η^2-SCNPh)] with methyl methanesulfonate and sodium tetraphenylborate. Two other reactions of [Co(H)(np_3)] are with methyl triflate and tetrafluoroboric acid which form [Co(np_3)]X (X = SO_3CF_3, BF_4) and methane or hydrogen respectively (ref. 749).



Scheme LXXII

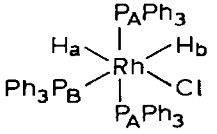
The paramagnetic cobalt(II) hydride complex [CoH$(PPh_3)_3$$(NCBH_3)$] is formed from hydrated cobalt(II) perchlorate, triphenylphosphine and sodium cyanoborohydride in ethanol and rapidly decomposes in solution (ref. 750). An opening of the P_4 molecule occurs on reaction with [Co$(H_2O)_6$]$(BF_4)_2$ and DPM in refluxing THF/Bu^nOH to form [423]. This reacts with [W$(CO)_6$] to



[423]

attach a $\{W(CO)_5\}$ moiety to one phosphorus atom (ref. 751). Reaction of $[CoCl_2(PPh_3)_2]$ with $[Pd(SiMe_3)_2]$ in THF forms $[Co_4(\mu_3\text{-}Pd)_4(PPh_3)_4]$ which can be reversibly oxidized to mono- and dicationic complexes. Reaction with halogens, carbon tetrachloride and acetyl chloride forms $[CoX_2(PPh_3)_2]$ (X = Br, I), $[Co_4(\mu_3\text{-}PPh)_4(PPh_3)_4]Cl$ and $[Co_4(\mu_3\text{-}PPh)_4(PPh_3)_4][CoCl_3(PPh_3)]$ respectively (ref. 752). Laser flash photolysis of $[CoH(PPh(OEt)_2)_4]$ forms the transient species $[CoH(PPh(OEt)_2)_3]$ which can then add the liberated ligand or olefins if the latter are also present. The kinetics of the recombination reaction have been studied (refs. 753, 754). An adduct of unspecified structure can be formed between $[cp_2ReH]$ and anhydrous cobalt(II) chloride or bromide (ref. 755). In toluene solution, bis(trifluoromethansulfonyl)methane reacts with $[MHL_4]$ (M = Co, Ir; L = PPh_3, ½DPPE) to form *cis*-$[MH_2L_4](HC(SO_2CF_3)_2)$. However with the rhodium analog, reductive elimination of hydrogen occurs subsequently and the product isolated is $[Rh(PPh_3)_3](HC(SO_2CF_3)_2)$. This last complex is a catalyst precursor for the cyclotrimerization of HFB and the hydroformylation of olefins. It will also add a carbonyl ligand (ref. 756).

The product of the reaction of hydrogen sulfide with $[RhCl(PPh_3)_3]$ which was originally considered to be monomeric has now been shown to be the dimer $[Rh_2H_2Cl_2(PPh_3)_4(\mu\text{-}SH)_2]$. With $[IrCl(CO)(PPh_3)_2]$ however *cis*-oxidative addition occurs to give the monomeric $[IrH(SH)Cl(CO)(PPh_3)_2]$ (ref. 757). The kinetics of the reaction of $[RhH_2ClL_2]$ (L = PPh_3, P(*p*-tolyl)$_3$, P(*p*-anisyl)$_3$, $P(p\text{-}XC_6H_4)_3$ (X = F, Cl)) with styrene and of the triphenylphosphine complex with *p*-substituted styrenes have been measured to assess the effect of electronic factors on the hydrogenation reaction. The results suggest that the extent of π-backbonding available to the olefin is the dominant factor affecting the binding of the olefin but the rate of hydrogen transfer to the olefin is affected in the opposite sense so that the overall effects of changing the electronic properties of these triarylphosphine ligands on the rate of hydrogenation are very small (ref. 758). In a study of the stereochemistries of possible intermediates in the $[RhCl(PPh_3)_3]$-catalyzed hydrogenation of olefins, magnetization transfer experiments (^1H and ^{31}P NMR) were performed on *cis*$[RhH_2Cl(PPh_3)_3]$ ([424]). Initially these experiments indicated an exchange process in which only Ph_3P_B reversibly dissociates as has been previously proposed. However in the presence of a twelve-fold excess of phosphine magnetization transfer was observed between the Ph_3P_B and Ph_3P_A sites indicating an equilibration of the two phosphorus environments. It was suggested that the initially formed five-coordinate species, [425], can isomerize to [426]. Intermediate [426] is considered more likely to be the active catalytic intermediate than is [425] since on addition of the olefin [427] rather than [428] would form which has the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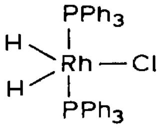
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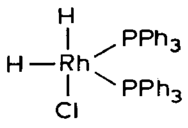
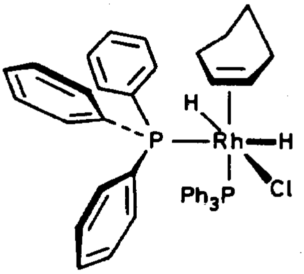

[426]

advantage of being less sterically encumbered and having one hydride trans to a phosphine which will tend to weaken that metal-hydrogen bond. In support of this proposal it is noted that rhodium hydride complexes containing a chelating diphosphine ligand which would force configuration [426] show rapid transfer of hydrogen to an olefin while those containing a rigidly enforced trans disposition transfer the hydrogen much more slowly (see also reference 498) (ref. 759). Two reversible, one-electron reductions are seen for $[Rh(PPh_3)_3(DME)]ClO_4$ in DME solution and the rhodium(0) intermediate can also dimerize to form $[Rh(PPh_3)_n]_2$ (n = 2, 4) (ref. 760). The electroreduction of carbon dioxide to formate is catalyzed by $[Rh(DPPE)_2]Cl$. The source of the hydrogen in the formate product appears to be the acetonitrile solvent. Scheme LXXIII outlines the proposed major pathway (ref. 761). The low temperature reaction of thiirane S-oxide with $[MCl(PPr^{i}_3)_3]$ (M = Rh, Ir) forms trans-$[MCl(SO)(PPr^{i}_3)_2]$ in which the {M-S=O} moiety is non-linear (ref. 762).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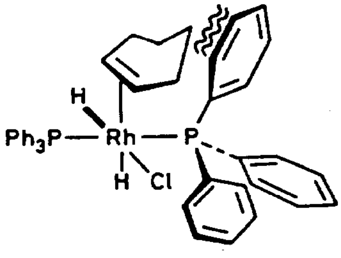

[428]

$$\begin{tikzcd} {[\mathrm{Rh(DPPE)_2}]^+} \arrow[r, "e^-"] & {[\mathrm{Rh(DPPE)_2}]} \arrow[r, "CO_2"] & {[\mathrm{Rh(DPPE)_2(CO_2)}]^+} \arrow[dl, "MeCN"] \\ & {\cdot CH_2CN + HCOO^- + [\mathrm{Rh(DPPE)_2}]^+} & \end{tikzcd}$$

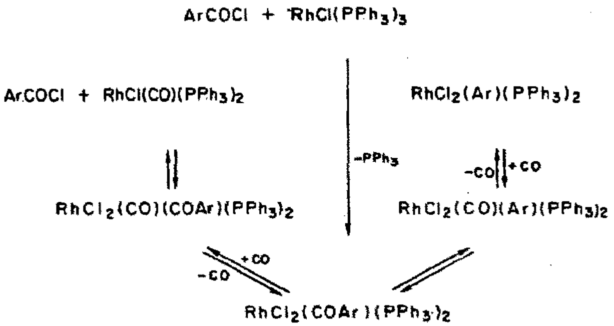
Scheme LXXIII

Sodium azide reacts with $[IrCl_3(PPh_3)_3]$ in hot 2-methoxyethanol to form *cis*-$[IrH_2(N_3)(PPh_3)_3]$ in which the hydride ligands derive from the solvent. Reductive elimination of hydrogen occurs on photolysis and reformation of the dihydride occurs in the dark (ref. 763). The iridium hydrides *mer*-*trans*-$[IrHCl_2L_3]$ (L = PMe_2Ph, PEt_2Ph, PEt_3) and *mer*-*cis*-$[IrH_2Cl(PEt_3)_3]$ add to $[Rh(DPPE)(acetone)_2]BF_4$ forming $[(DPPE)Rh(\mu\text{-}H)(\mu\text{-}Cl)IrClL_3]BF_4$ and $[(DPPE)Rh(\mu\text{-}H)(\mu\text{-}Cl)IrH(PEt_3)_3]BF_4$ however *mer*-*cis*-$[IrHCl_2(PMe_2Ph)_3]$ forms $[(DPPE)Rh(\mu\text{-}Cl)_2IrH(PMe_2Ph)_3]BF_4$. In all instances no isomerization occurs at the iridium center. The first adducts are disrupted by carbon monoxide, acetonitrile and sodium tetraphenylborate to form in each case *mer*-*trans*-$[IrHCl_2L_3]$ plus $[Rh(CO)_3(DPPE)]BF_4$, $[Rh(DPPE)(MeCN)_2]BF_4$ and $[Rh(DPPE)(\eta^6\text{-}C_6H_5BPh_3)]$ respectively (ref. 764). Several other adducts of iridium hydrides have been reported including those of *mer*-$[IrH_3L_3]$ (L = PPh_3, PMe_2Ph) with $[(L')M(S)]^+$ (L' = PPh_3, PEt_3; M = Ag, Au; S = solvent) to form $[L'M(\mu\text{-}H)IrH_2(PPh_3)_3]^+$ (ref. 765) and with one half mol of $[Cu(MeCN)_4]PF_6$ in THF at -70°C followed by warming to give the nonfluxional complex $[(PMe_2Ph)_3HIr(\mu\text{-}H)_2Cu(\mu\text{-}H)_2IrH(PMe_2Ph)_3]PF_6$ in which the *mer* configuration is retained about both iridium centers. The same reaction with *fac*-$[IrH_3(PMe_2Ph)_3]$ gives the analogous adduct with each iridium retaining the *fac* configuration. No conversion of the latter into the former was noted. The silver analog of the latter complex was also prepared from *fac*-$[IrH_3(PMe_2Ph)_3]$ and silver tetrafluoroborate. Despite the stereochemical rigidity about the iridium centers, both the silver and copper adducts with *fac*-$[IrH_3(PMe_3Ph)_3]$ show fluxional behavior in solution. This must be due to stereochemical non-rigidity in the coordination sphere of the copper and silver atoms (ref. 766). Refluxing $[IrCl_4(PMe_2Ph)_2]$ in THF followed by addition of lithium aluminum hydride and workup in the presence of air and moisture yields $[Ir_2H_4(PMe_2Ph)_4(\mu\text{-}H)_2]$ in which the phosphine ligands are *cis* to one another in the centrosymmetric complex (ref. 767). Tetrafluoroboric acid in acetonitrile converts $[IrH_5(PPh_3)_2]$ to $[IrH_2(MeCN)_2(PPh_3)_2]BF_4$ (ref. 768). Oxidation of the disulfur ligand in $[Ir(S_2)(DPPE)_2]PF_6$ with *m*-chloroperoxybenzoic acid occurs stepwise to form $[Ir(S_2O)(DPPE)_2]PF_6$ and then $[Ir(S_2O_2)(DPPE)_2]PF_6$. Only one diastereoisomer is formed in each case. Only the first oxidation could be accomplished with $[Ir(S_2)(DPPE)_2]Cl$, possibly because oxidation of the counterion interferes. At -10°C $[Ir(Se_2)(DPPE)_2]Cl$ is oxidized similarly to $[Ir(Se_2O)(DPPE)]_2Cl$ but on warming it reverts to the starting complex. The second oxidation could not be achieved and use of other acids led only to decomposition. Attempts to generate $[Ir(EO)(DPPE)_2]^+$ from $[Ir(E_2O)(DPPE)_2]^+$ (E = S, Se) by reaction of the first with triphenylphosphine or the second with thiols were unsuccessful. A final attempt using $[Ir(DPPE)_2]^+$ and the episulfoxide of <u>trans</u>-stilbene formed $[Ir(S_2O)(DPPE)_2]^+$ instead (ref. 769).

Another method to distinguish between homogeneous and heterogeneous catalysis has been proposed. This is based on relative reactivities of the catalyst species towards polymeric substrates such as pendant styrene functionalities on soluble and cross-linked polymers. It is proposed that homogeneous catalysts should be significantly more active in hydrogenating the olefin functionalities and this is supported by studies using $[RhCl(PPh_3)_3]$ and $[Ir(COD)L_2]PF_6$ (L = phosphine). On the other hand, $[cp'RhCl_2]_2$ seems to behave more like a heterogeneous system since it effects significant hydrogenation of polymer-bound arene functionalities. In contrast to the results using the test proposed by Crabtree (1983 Annual Survey, reference 603) this one suggests that the $[RhCl_3py_3]/NaBH_4$ catalyst system is homogeneous (ref. 770). A number of catalytic systems reported include that formed from cobalt(II) chloride, (+)-neomenthyldiphenylphosphine and sodium borohydride which catalyzes the hydrogenation of N-acetyl-α-aminocinnamic acid with a moderate optical yield (ref. 771), $[CoX(PPh_3)_3]$ (X = Cl, Me) which catalyzes hydrogen transfer from Grignard reagents to diphenylacetylene by what is characterized as a stepwise, radical process (ref. 772) and $[CoCl(PPh_3)_3]$ for the coupling of benzylic halides, the dehalogenation of <u>vic</u>-dihalides to olefins and the reductive coupling of allylic halides to form 1,5-dienes with retention of configuration about the carbon-carbon bond adjacent to the halogen substituent (ref. 773). Two other cobalt systems are the photoassisted catalysis of hydrogen transfer from secondary alcohols to ketones in the presence of $[CoH(PPh(OEt)_2)_4]$ (see also references 753, 754) (ref. 774) and $[CoH_3(PPh_3)_3]$ which can cleave carbon-oxygen bonds in allylic phenyl carbonates to form $[Co(OPh)(PPh_3)_3]$, propylene and carbon dioxide. Similar behavior is noted for $[RhH(PPh_3)_4]$ which also cleaves allylic carbon-sulfur bonds in allylic and alkenyl sulfides to form olefins and $[Rh(\mu\text{-}SR)(PPh_3)_2]_2$ and, in the presence of two equivalents of tri-<u>n</u>-butylphosphine, catalyzes the transfer of an allylic group from allylic carbonates to a variety of carbon nucleophiles (refs. 775-777). Another application of $[RhH(PPh_3)_4]$ is to catalyze the isomerization of α-, β- and γ-silylated alcohols to acylsilanes and α- or β-silyl ketones respectively (ref. 778).

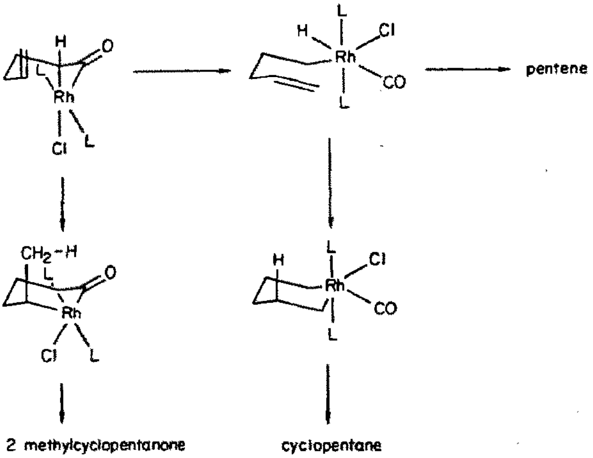
Much attention continues to be paid to $[RhCl(PPh_3)_3]$ and its analogs as catalysts. In one extensive study to establish optimum conditions for hydrogenation catalysis it was found that the activity increased with increasing basicity of the triarylphosphine ligands, that compounds of the type $[RhL_2S_2]^+$ (L = phosphine, S = solvent) were superior to neutral complexes and that in this latter group use of a chelating diphosphine was preferred over monodentate phosphines since it would give a cis complex (see also reference 759). The higher activity of the cationic complexes was attributed to their enhancing the susceptibility of the coordinated olefin to attack by the first hydride which transfers from the metal. Also, in the cationic diphosphine complexes the activity increased as the length of the ligand backbone increased presumably because the increased flexibility makes it easier to attain the preferred transition-state geometry (ref. 779). A related study explored the effects of using o-substituted triphenylphosphine ligands. The rate of catalytic hydrogenation was accelerated when one aryl ring contained an alkoxy, a dialkylamino or an alkylthio substituent which can presumably interact weakly with the metal (ref. 780). Catalytic applications of [$RhCl(PPh_3)_3$] include the stereoselective hydrogenation of tetrahydronaphthalenes to their octahydro derivatives (ref. 781) and the regiospecific deuteration of methyl 3-(benzoyloxy)-2-butenoate. The (Z)-olefin gives a 91.5% yield of the (RR,SS) butanoate while the (E)-olefin gives an 84.4% yield of the (RS,SR) species implying the major mode of addition of deuterium is syn (ref. 782). Also [$RhClL_3$] (L = sulfonated triphenylphosphine) can be supported on a basic ion exchange resin to form a heterogenized, olefin hydrogenation catalyst (ref. 783) while [$RhCl(PPh_3)_3$] catalyzes the selective hydrogenation of the heterocyclic ring in polynuclear heteroaromatics such as quinoline, acridine, phenanthridine, benzothiophene and benzoquinolines. The first step is suggested to be the reduction of the carbon-nitrogen double bond (ref. 784). Further applications are in the hydrogenation of allyl alcohol where a kinetic study showed inhibition by substrate at high concentration (ref. 785), the hydrogen transfer hydrogenation of α,β-unsaturated carbonyl compounds to their saturated counterparts by N-propyl-1,4-dihydronicotinamide (ref. 786) and the hydrogenation of cyclopropene units in esters of cyclopropene fatty acids (ref. 787). In related work, the kinetics of hydrogenation of unsaturated fatty acids catalyzed by [$RhClL_3$] (L = sulfonated triphenylphosphine) have been studied and several reaction pathways appear to exist (ref. 788). Both [$RhClL_3$] and [$RhHL_4$] (L = PPh_3) have been used as catalyst precursors in related systems (ref. 789) while [$RhCl(L_3)$] (L_3 = bis(2-diphenylphosphinoethyl)amine) and several related rhodium complexes of DPPE, DPPP and DPPB catalyze the hydrogenation of terminal olefins (ref. 790, 791). Also [$RhCl(PPh_3)_3$] is effective for the selective hydrogenation of emulsion nitrile rubbers (ref. 792).

The mechanism of the reaction of [$RhCl(PPh_3)_3$] with aroyl chlorides proposed earlier (Scheme LXXIV) has been given more support by the results of ^{13}CO labelling experiments. Thus heating a mixture of [$RhCl(CO)(PPh_3)_2$], benzoyl chloride and ^{13}CO at 90°C for 24 h produced a 5.4% enrichment in the



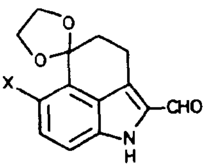
Scheme LXXIV

recovered benzoyl chloride and no chlorobenzene was detected. Using benzoyl chloride highly enriched in carbon-13 at the acyl carbon and unlabelled [$RhCl(CO)(PPh_3)_2$] in the same experiment over half the [$RhCl(CO)(PPh_3)_2$] recovered contained ^{13}CO. The slow step of this part of the scheme appears to be the oxidative addition of the benzoyl chloride to the metal and the high temperatures generally required for decarbonylation of aroyl halides seems to be due to a large activation energy for the formation of [$RhCl_2(CO)Ar(PPh_3)_2$] (ref. 793). The same group has also reported experiments to detect alkyl rhodium hydride intermediates postulated earlier to be formed in the decarbonylation of aldehydes by [$RhCl(PPh_3)_3$]. Thus the formation of pentene, cyclopentane and 2-methylcyclopentanone from its reaction with 5-hexenal suggest the processes in Scheme LXXV (L = PPh_3) which could



Scheme LXXV

reasonably be expected to follow an oxidative addition of the aldehyde carbon-hydrogen bond to the metal. Further support for this process is provided by the observation that decarbonylation of *o*-allylbenzaldehyde yields allylbenzene and indane in a 1:4 ratio while *endo*-5-norbornene-2-carboxaldehyde is converted to nortricyclene. Reaction of the *exo* isomer of this last aldehyde gives norbornene, however, presumably because geometric constraints prevent the double bond from interacting with the metal. These results suggest that with the endo isomer, the postulated alkyl rhodium hydride is trapped by a homoallylic rearrangement and that the alkyl hydride intermediate is formed with retention at carbon (ref. 794). Decarbonylation of [429] (X = H, OMe) to [430], an ergoline synthon, is accomplished using $[Rh(DPPP)_2]Cl$ in boiling xylene. The reaction is also successful with simpler indole-2-carboxaldehydes (ref. 795). Pentafluorostyrene and trifluoropropene can be hydrosilylated by a variety of silanes in the presence of $[RhCl(PPh_3)_3]$. With triethyl-, trichloro- and dimethylethylsilane a mixture of trans-$RCH=CHSiR'_3$ ($R = CF_3, C_6F_5$; $R'_3 = Et_3, Cl_3, Me_2Et$) and the



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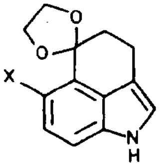
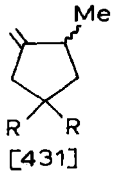


[430]

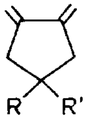
saturated analog are formed but in the remaining cases ($R'_3 = Me_2Ph, Me_2Cl, MeCl_2$) only the vinyl silane was formed. Here it was presumed that a monomeric silylalkyl rhodium hydride intermediate was formed which could either reductively eliminate alkane or undergo β-hydrogen abstraction to form the olefin (ref. 796). On the other hand a second study of the hydrosilylation reaction showed that the proportion of vinyl silane formed increased as the catalyst concentration was increased above 10^{-4} M. It was suggested that at the higher concentrations a dimeric rhodium complex formed which was responsible for formation of the vinyl silanes (ref. 797). The addition of trimethylsilyl groups derived from hexamethyldisilane to allylic esters to form allyl silanes is also catalyzed by $[RhCl(PPh_3)_3]$ (ref. 798).

Cyclization of 4,4-disubstituted hepta-1,6-dienes to [431] (R = C(O)Me, C(O)Ph, CO_2Et) occurs reasonably cleanly in acidified chloroform in the

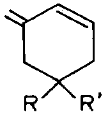


[431]

presence of $[RhCl(PPh_3)_3]$ but with longer chain α,ω-dienes a greater variety of products resulted. On the other hand in refluxing acetonitrile some of the same 1,6-dienes when brominated in the 2-position are cyclized preferentially to [432] over [433] (R = R' = C(O)Me. R = Me; R' = C(O)Ph. R, R'



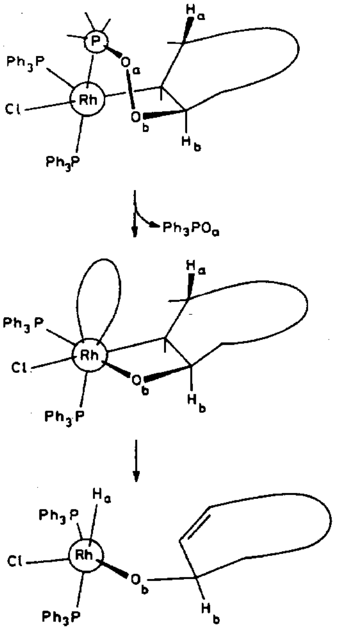
[432]



[433]

= 2,2'-biphenylyl) (refs. 799, 800). Other applications of $[RhCl(PPh_3)_3]$ are as a catalyst for the isomerization of N-allylimines to 2-aza-1,3-dienes (ref. 801) and the conversion of aryl iodides to arenes by 1-benzyl-1,4-dihydronicotinamide (ref. 802). The photolytic generation of hydrogen from isopropanol following an oxygen pretreatment is catalyzed by a variety of rhodium(I) complexes, the most active of which are $[RhClL_3]$ (L = $P(OPh)_3$, PPh_3) (ref. 803).

Two conflicting proposals concerning the mechanism of olefin oxidation catalyzed by $[RhCl(PPh_3)_3]$ have appeared. In the first the appearance of cyclooct-2-en-1-ol and triphenylphosphine oxide at comparable rates during the oxidation of cis-cyclooctene suggested a cooxygenation process involving attack of a coordinated dioxygen at a vinylic center and subsequent reaction as depicted in Scheme LXXVI. This mechanism imposes rigid stereochemical



Scheme LXXVI

requirements and support for it is claimed from the observation that with trans-cyclooctene, the only alicyclic product is cyclooctanone (ref. 804). On the other hand, in the rhodium-catalyzed oxidation of oct-1-ene to octan-2-one in ethanol, labelling studies indicate that significant exchange of hydrogen atoms between olefin and solvent occurs. The results were interpreted with a mechanism involving a peroxymetallocycle intermediate which decomposed without the occurrence of β-hydride abstraction (ref. 805). Oxidation of cyclohexene is catalyzed by $[RhClL_3]$, $[RhCl(CO)L_2]$ ($L = PPh_3$) and $[RhCl(C_2H_4)_2]_2$ and the addition of cumyl hydroperoxide eliminates the induction period which is otherwise observed. The main product is cyclohexylhydroperoxide and about one third of it is proposed to derive from a radical path (ref. 806). Catalyst precursors for oct-1-ene oxidation by *tert*-butylhydroperoxide include $[RhHCl_2(PPh_2Bu^n)_3]$ and related rhodium(III) complexes. No mechanistic information was provided (ref. 807).

Tertiary phosphine complexes of rhodium are said to catalyze the cooligomerization of carbon monoxide and olefins to form polymeric ketones and keto esters (ref. 808) A codimerization of buta-1,3-diene and 1-acetoxyocta-2,7-diene to give various dodecatriene isomers is catalyzed by rhodium(III) complexes. The catalyst is poisoned by phosphines and even dinitrogen. Addition of allylic chlorides enhances the activity (ref. 809). Iridium(I) complexes containing bipy, ophen and their derivatives as ligands catalyze the transfer hydrogenation of α,β-unsaturated carbonyl compounds by alcohols. Although α,β-unsaturated ketones are converted to saturated ketones, α,β-unsaturated aldehydes are hydrogenated to saturated alcohols (ref. 810). The Crabtree mechanism is proposed to be operative in the $[IrH_5L_2]$-catalyzed ($L = PPr^i_3$, $P(p\text{-}FC_6H_4)_3$) dehydrogenation of cyclooctane to cyclooctene in the presence of *tert*-butylethylene (ref. 811).

A copolymer of methyl methacrylate and 1-isopropenyl-(3)-1,2-dicarbaundecaborate salts provides a support for $\{RhCl(PPh_3)_2\}$ moieties which can catalyze olefin hydrogenation and isomerization (ref. 812). Mixtures of Rh_2O_3 and Ph_3E (E = N, P, As, Sb) are somewhat active for the catalysis of dodec-1-ene hydroformylation. At high loadings only triphenylphosphine and triphenylarsine gave more than trace conversions and triphenylbismuth was totally inactive. At lower loadings triphenylstibine also gave modest conversion (ref. 813). Rhodium zeolites catalyze the homologation of methanol to methyl acetate by carbon monoxide. The active sites appear to contain rather small numbers of rhodium atoms since the activity falls sharply when conditions promoting significant agglomeration of metal atoms are employed (ref. 814). Studies of the catalytic or stoichiometric homologation of olefins by rhodium on silica suggest that the mechanism of carbon-carbon bond formation is the same as in Fischer-Tropsch systems implying that it occurs *via* combination of $\{CH_x\}$ fragments on the surface (ref. 815). On rhodium and iridium films 2,2,4,4-tetramethylpentane is both cyclized to

1,1,3,3-tetramethylcyclopentane and isomerized to 2,2,4- and 2,2,5-trimethylhexane. A single metal center is proposed to be involved in each process (ref. 816).

A valence bond treatment of complexes of cobalt, rhodium and iridium among others containing metal-metal bonds and carbonyl, phosphine, olefin, alkyl and related ligands predicts these bonds to have unit bond order with bond lengths equal to twice the appropriate covalent radius previously determined by the author. Good agreement between predicted and observed values is reported (ref. 817).

List of Abbrevations

acac = acetylacetonate
ARPHOS = 1-diphenylphosphino-2-diphenylarsinoethane
az = 7-azaindolate
BAE = bis(acetylacetone)ethylenediiminato
bdpp = bis(3-diphenylphosphinopropyl)phenylphosphine
(-)-BINAP = (S)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
bipy = 2,2'-bipyridine
BPPM = (2S,4S)-N-*tert*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine
br = 1,3-diisocyanopropane
BTMSA = bis(trimethylsilyl)acetylene
bz = benzyl
bzac = benzoylacetonato
(S,S)-CHIRAPHOS = (S,S)-2,3-bis(diphenylphosphino)butane
COD = cycloocta-1,5-diene
COT = cycloctatetraene
cp = cyclopentadienyl
cp' = pentamethylcyclopentadienyl
cpMe = methylcyclopentadienyl
cy = cyclohexyl
cyoct = cyclooctene
cyttp = bis(3-dicyclohexylphosphinopropyl)phenylphosphine
dbm = dibenzoylmethanato
dct = dibenzo[a,e]cyclooctatetraene
diglyme = bis(2-methoxyethyl)ether
DIOCOL = 2,3-O-(5'α-cholestan-3',3'-ylidene)-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane

DIOP = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DMAD = dimethylacetylenedicarboxylate
DME = dimethoxyethane
DMF = N,N-dimethylformamide
dmgH = dimethylglyoximate
dmpe = 1,2-bis(dimethylphosphino)ethane
DMSO = dimethylsulfoxide
DPAE = 1,2-bis(diphenylarsino)ethane
DPAM = diphenylphosphinodiphenylarsinomethane
dpgh = diphenylglyoximate
DPM = bis(diphenylphosphino)methane
DPMP = bis(diphenylphosphinomethyl)phenylphosphine
DPPB = 1,4-bis(diphenylphosphino)butane
DPPE = 1,2-bis(diphenylphosphino)ethane
dppn = 3,6-bis(2'-pyridyl)pyridazine
DPPP = 1,3-bis(diphenylphosphino)propane
dth = 2,5-dithiahexane
en = ethylenediamine
EXAFS = extended x-ray absorption fine structure
Fc = ferrocenyl
glyme = 2-methoxyethyl methyl ether
HacacP = *o*-(diphenylphosphinobenzoyl)pinacolone
Haz = 7-azaindole
hfac = hexafluoroacetylacetonato
HFB = hexafluorobut-2-yne
H_2Tcbiim = 4,4',5,5'-tetracyano-2,2'-biimidazole
MA = maleic anhydride
7-Me-salen = N-(2-aminoethyl)-7-methylsalicylaldiminato
Me_3TFB = trimethyltetrafluorobenzobarrelene
mnt = maleonitrile dithiolate
napy = 1,8-naphthyridine
NBD = bicyclo[2.2.1]heptadiene
np_3 = tris(2-(diphenylphosphino)ethyl)amine
OEP = octaethylporphyrin
Onapy = anion of 1,8-naphthyridin-2-one
ophen = 1,10-phenanthroline
oq = 8-oxoquinolinate
oTs = *p*-toluenesulfonate
Ph-CAPP = (2S,4S)-N-(N-phenylcarbamoyl)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine

PNP = 2-[bis(diphenylphosphino)methyl]pyridine
PPN = bis(triphenylphosphine)iminium cation
py = pyridine
pz = pyrazolate
pzH = pyrazole
salen = N,N'-ethylenebis(salicylaldiminato)
saloph = N,N'-*o*-phenylenebis(salicylaldiminato)
syngas = synthesis gas (H_2/CO)
Tcbiim = 4,4',5,5'-tetracyano-2,2'-biimidazolate
TCNQ = tetracyanoquinodimethane
TFA = trifluoracetic acid
tfac = trifluoroacetylacetonate
TFB = tetrafluorobenzobarrelene
THF = tetrahydrofuran
tht = tetrahydrothiophene
TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene
tms = trimethylene sulfide
TPM = tris(diphenylphosphino)methane
TPP = tetraphenylporphyrin
triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane
ttas = bis(*o*-dimethylarsinophenyl)methylarsine
UPS = ultraviolet photoelectron spectroscopy
vdiphos = *cis*-1,2-bis(diphenylphosphino)ethylene
vy = vinyl
WGSR = water-gas-shift reaction
XPS = x-ray photoelectron spectroscopy

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