COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1982*

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CONTENTS

Introduction

The format used previously will be retained with articles appearing in less-available journals being covered in abstract form and so-indicated in the list of references. Papers reporting only the results of crystal structure determinations are not included. Abbreviations for ligands will be explained following their initial occurrance save for the cyclopentadienyl (η^5-C_5H_5) group and its pentamethyl analog (η^5-C_5Me_5) for which the abbreviations "cp" and "cp'" are given here.

This year saw the publication of a monumental treatise on organometallic chemistry of which one volume is devoted to the cobalt group (ref. 1). Two other

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* No reprints available. Previous Survey, J. Organometal. Chem., 242(1983)241.

books also contain considerable material on cobalt, rhodium and iridium (refs. 2,3). Three general reviews contain some material on organometallic complexes of the cobalt groups (refs. 4-6). More specialized reviews cover σ-bonded metal-carbon complexes of this group (ref. 7), the reductive elimination of alkanes from metal alkyl hydrides (ref. 8), the chemistry of alkyl-cobalt complexes (ref. 9) and metal alkynyl compounds (ref. 10). Methylene-bridged metal complexes (ref. 11) and iridium formyls (ref. 12) are reviewed as are the determination of metal-carbon bond strengths in alkyl cobaloximes (ref. 13) and the synthesis of organocobalt complexes as models for vitamin B_{12} (ref. 14).

Other reviews deal with the photophysical properties of binuclear rhodium(I) isocyanide complexes (ref. 15), the catalysis of the carbonylation of benzyl alcohols and acetates (ref. 16) and the combination of trialkyl silanes and carbon monoxide with oxygenated compounds by cobalt complexes (ref. 17) and the rhodium carbonyl-catalyzed hydrogenation of carbon monoxide, dinitrogen and isocyanides (ref. 18). The electrochemistry of clusters (ref. 19), the interaction of carbon dioxide, carbon disulfide and carbonyl sulfide with rhodium and iridium complexes (ref. 20), the reactivity of thiolate-bridged dimers of rhodium and iridium (ref. 21), the chemistry and catalytic applications of $[RhH(CO)(PPh_3)_3]$ (ref. 22), the thermochemistry of oxidative addition to d^8 iridium complexes (ref. 23) and the synthesis of diazabutadiene complexes (ref. 24) have also been reviewed.

The mechanism of asymmetric hydrogenation has been reviewed (ref. 25) as has the use of rhodium complexes of ferrocenyl phosphines for the same purpose (refs. 26, 27). Also covered are cobalt-mediated carbon-carbon bond formation and cleavage (ref. 28), the synthesis of functionalized cyclopentadienyl complexes (ref. 29), cobalt π-complexes of silacyclopentadiene and silacyclohexadiene (ref. 30) and metal arene compounds (ref. 31).

Finally, metallaboranes (ref. 32), silicon-transition metal complexes (ref. 33), compounds of η^3-P_3 and η^1-P_4 ligands (ref. 34) and the reactivity of dinitrogen complexes (ref. 35) have been reviewed.

Dissertations

One dissertation reports the formation of alkyl-bridged complexes by the action of alkyllithiums on $[MCl(diene)]_2$ (M = Rh, Ir; diene = cycloocta-1,5-diene (COD), norbornadiene (NBD)) (ref. 36) while four more deal with the chemistry of alkyl cobaloximes and related complexes (refs. 37-40). The chemical and spectroscopic properties of binuclear rhodium and iridium complexes containing bridging diisocyanides are discussed in three dissertations (refs. 41-43). Two studies of $[HCo(CO)_4]$ concern molecular orbital calculations using the Xα-CW method (ref. 44) and its acidity and reactions with olefins (ref. 45).

The catalysis of ketone and alcohol oxidation by $[Rh_6(CO)_{16}]$ (ref. 46), the nature of species resulting from supporting $[Rh(CO)_2Cl]_2$ on inorganic oxides (ref.

47), and the synthesis and chemistry of the complexes $[RhClBr(CO)(Ph_2P(CH_2)_n$-$P(CH_2Ph)Ph_2)]$ (n = 2-4) (ref. 48) and $[RhL(cyttP)]^+$ (cyttP = $PhP(CH_2CH_2CH_2Pcy_2)_2$ (cy = cyclohexyl)) (ref. 49) have also been reported. Further dissertations report the reactions of $[M(CO)Cl(PPh_3)_2]$ (M = Rh, Ir) with oxiranes and cyclobutenes (ref. 50), a determination of the kinetic isotope effect in the oxidative addition of hydrogen to $[Ir(CO)Cl(PPh_3)_2]$ (ref. 51), the kinetics and mechanisms of reactions of [IrCl(am)(COD)] (am = substituted pyridines) (ref. 52), the reactions of carbon dioxide, carbon disulfide and carbonyl sulfide with $[RhH(PPh_3)_4]$ and $[Ir(CO)ClL_2]$ (L = tertiary phosphine) (ref. 53) and the use of $[Rh(COD)L_2]PF_6$ (L = tertiary phosphine) as catalysts for the isomerization, hydrogenation and hydrocyanation of olefins (ref. 54).

Two reports appear on the use of $[Rh(diene)(PPh_3)_2]PF_6$ (diene = COD, NBD) intercalated in mica type silicates as catalysts for olefin hydroformylation and hydrogenation (refs. 55, 56) while a third concerns the use of similarly supported complexes containing chiral phosphine ligands as catalysts for asymmetric hydrogenation (ref. 57). Also reported is the use of $[Rh(NBD)(L)_2]^{3+}$ (L = $Ph_2PCH_2CH_2NMe_3{}^+$) as a water-soluble hydrogenation catalyst (ref. 58) and the hydroacylation of ethylene with unsaturated aldehydes catalyzed by $[Rh(acac)(C_2H_4)_2]$ (acac = acetylacetonate) (ref. 59).

The synthesis and reactivity of η^3-cyclobutenoyl cobalt carbonyl complexes is the subject of a further dissertation (ref. 60) and three more concern the use of $[cpCo(CO)_2]$ to mediate the oligomerization and cooligomerization of acetylenes (refs. 61-63). Also concerned with acetylene chemistry is a study of the rearrangement of propargylic esters and alcohols mediated by $[Rh(CO)_2Cl]_2$ (ref. 64).

A number of studies on cyclopentadienyl complexes are available including those on cyclopentadienyl cobalt tetraazadiene complexes (ref. 65), the synthesis and electrochemical characterization of $[cp'_2Co]$ (ref. 66), the chemistry of $[cpCoMe_2$-$(PPh_3)]$ and related complexes (ref. 67), the stereochemistry of ligand substitution in cyclopentadienyl rhodium complexes (ref. 68) and the results of molecular orbital calculations on $[cpM(CO)_2]$ (M = Co, Rh) (ref. 69). The synthesis of unstable cobalt arene complexes by the metal vapor technique has also been reported (ref. 70).

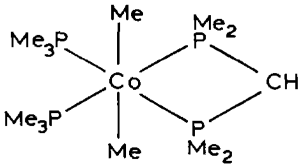
Three dissertations report on cobalt (ref. 71) and rhodium and iridium carbaboranes (refs. 72, 73).

Finally there are reports on the preparation of bicarbonate and peroxycarbonate complexes of cobalt and iridium (ref. 74), of the cubane type complexes M_4X_4 (M = cpCo, $Co(CO)_3$; X = P, As, Sb, Bi) (ref. 75) and of the compounds $[Ir_2H_5(dppp)_2]^+$ and $[Ir_3H_7(dppp)_3]^{2+}$ (dppp = $Ph_2P(CH_2)_3PPh_2$)(ref. 76).

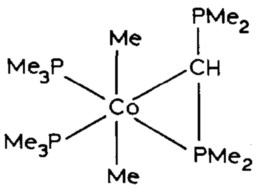
Metal Carbon σ-bonded Complexes

Acylation of imines at nitrogen by $[MeC(O)Co(CO)_4]$ generated *in situ* from $[Co_2(CO)_8]$, carbon monoxide, methyl iodide and lithium triethylborohydride yields β-keto amides. Reduction to the corresponding amine also occurs to a limited extent. The observation of some PhC(O)CHPhNPhC(O)Et when PhC(O)C(Ph)=NPh is the substrate and its increased yield in the absence of methyl iodide implicates the involvement of the triethylborohydride ion but mechanistic details are lacking (ref. 77).

Dissolution of $Li_2[CoPh_4]\cdot 4THF$ (THF = tetrahydrofuran) in THF or benzene yields $Li_4[Co_2Ph_4]\cdot 4THF$ which is converted to $Li_4[CoPh_3]\cdot 5THF$ on reaction with phenyllithium and to cobalt(II) iodide and biphenyl by iodine. Homolysis of cobalt-carbon bonds is proposed to occur in the first reaction (ref. 78). Alkylation of $[Co(L_4)Cl]$ (L_4 = tetraphenylporphyrin (TPP), octaethylporphyrin (OEP)) with phenyllithium produces $[CoPh(L_4)]$. Further treatment with trifluoroacetic acid in dichloromethane followed by decomposition with aqueous ammonia liberates the N-phenyl-substituted porphyrin. Labelling studies show that the migration of the phenyl group occurs intramolecularly (ref. 79). Aryl Grignard reagents react with $[CoCl_2L_2]$ to yield $[CoR_2L_2]$ (L = $PEtPh_2$; R = 2,6-$C_6H_3Cl_2$, 2,4,6-$C_6H_2Cl_3$, 2,3,5,6-C_6HCl_4, C_6Cl_5. L = PEt_2Ph, PEt_3; R = 2,4,6-$C_6H_2Cl_3$, C_6Cl_5. L = pyridine (py), β-picoline, γ-picoline, 3,5-lutidine; R = C_6Cl_5. L_2 = 1,2-bis(diphenylphosphino)-ethane (diphos), 2,2'-bipyridyl (bipy); R = C_6Cl_5). The majority of the products appear to be air-stable but for the less-electronegative aryl groups thermal decomposition occurs in refluxing benzene and acceleration in the presence of oxygen was noted. For L = phosphine, biaryls predominated while for L = nitrogen donor polychlorobenzenes were the major products. A mechanism involving initial loss of L followed by reductive elimination from the resulting three-coordinate species was proposed (refs. 80, 81). Treatment of *mer*-$[CoMe_2Br(PMe_3)_3]$ with $Li[CH(PMe_2)_2]$ yields [1] which rearranges to [2] on phosphine substitution by PMe_2Ph. The related complex [3] results from reaction of *mer*-$[CoMe_2Br(PMe_3)_3]$ with $Li[CH_2PMe_2]$ (ref. 82).



[1]



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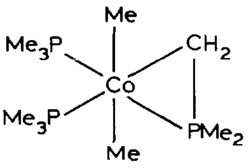
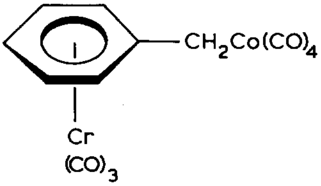


[3]

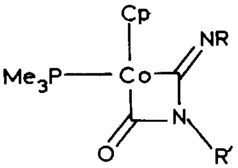
The benzyl chlorides RCH_2Cl (R = Ph, *o*-tolyl, *m*-tolyl, *p*-tolyl, *p*-anisyl, 3,4-$(MeO)_2C_6H_3$, *p*-ClC_6H_4, 2,6-$C_6H_3Cl_2$) form η^3-benzylcobalt tricarbonyl complexes with $Na[Co(CO)_4]$ in ether. All but the last two were isolated and could be converted to $[RCH_2Co(CO)_3(PPh_3)]$ on reaction with triphenylphosphine at 0° C. The full set of η^3-benzyl complexes, on reaction with carbon monoxide, yielded a mixture of $[RCH_2Co(CO)_4]$ and $[RCH_2C(O)Co(CO)_4]$. Flushing with argon at 0° C reversed the process while treatment with triphenylphosphine at room temperature gave the acyls $[RCH_2C(O)Co(CO)_3(PPh_3)]$. These same complexes could also be generated by carbonylation of $[RCH_2Co(CO)_3(PPh_3)]$ (R = Ph, p-tolyl, o-tolyl, p-anisyl, $3,4-(MeO)_2C_6H_3$), a reaction which could be reversed by refluxing in benzene. In solution the η^3-benzyl complexes appear to polymerize on standing. By contrast, $[(\eta^6-C_6H_5CH_2Cl)Cr(CO)_3]$ reacts with $Na[Co(CO)_4]$ to yield [4] (ref. 83).



[4]

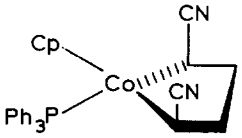
The use of the reaction of iodine in methanol to determine the nature of alkyl- or acyltetracarbonyl cobalt species in solution may not be very accurate since even when the absence of acyl species can be demonstrated by infrared spectroscopy, carbonylation products result. Thus decomposition of $[EtO_2CCH_2Co(CO)_4]$ by this reagent yields $MeCO_2Et$, ICH_2CO_2Et and $MeO_2CCH_2CO_2Et$. It is proposed that the methanol functions as a base to promote insertion of carbon monoxide into the cobalt-carbon bond before cleavage by iodine occurs. Also, the fact that large quantities of ethyl acetate are observed when iodine is added in the absence of methanol suggests that radical processes can be involved (ref. 84).

Isocyanates couple with $[cpCo(PMe_3)(CNR)]$ to give [5] (R = Me; R' = p-tolyl. R



[5]

= Ph; R' = Me). An analogous reaction occurs with isothiocyanates (ref. 85). A full report has now appeared on the reaction of $[cpCoPh(PPh_3)_2]$ with acrylonitrile. The adduct $[cpCo(PPh_3)(CH_2=CHCN)]$ can be identified in solution and on refluxing with excess nitrile in the presence of hydroquinone yields the isomeric metallacycles [6] and [7] (ref. 86). Complex [8] reacts with silver tetrafluoroborate



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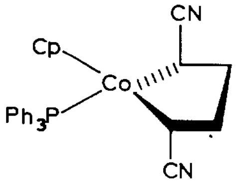
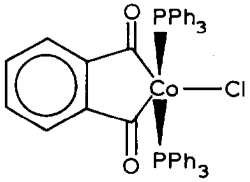
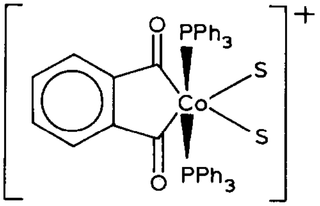


[7]

in acetonitrile (S) to give [9] which reacts further with triphenylphosphine,

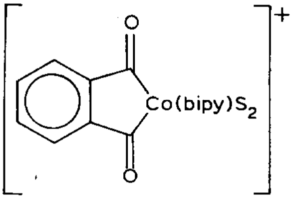


[8]

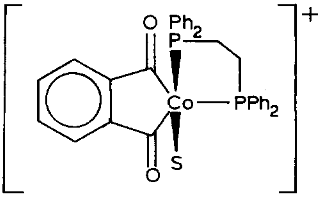


[9]

diphos and bipy to yield [10], [11] and [12] respectively. Complexes [11] and [12]



[10]



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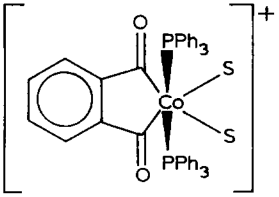
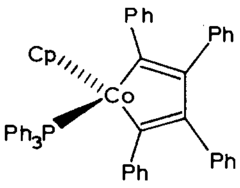
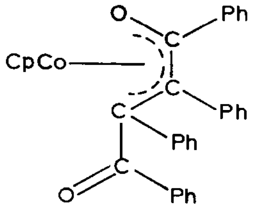


[12]

react with a variety of alkynes to produce substituted naphthoquinones (ref. 87). Photolysis of [13] under nitrogen produces [cpCo(η^4-C_4Ph_4)] while in the presence of oxygen the (Z)-dibenzoylstilbene complex [14] results. As the former reaction



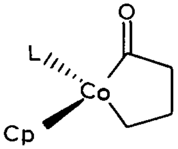
[13]



[14]

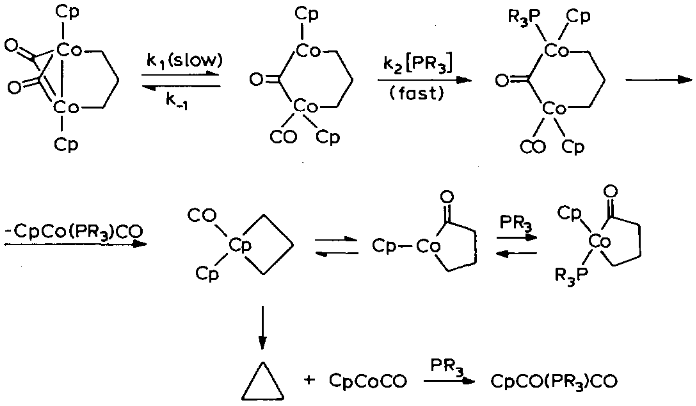
is inhibited by the addition of triphenylphosphine or trimethylphosphite while the latter is not indicates that different paths are followed. In the reaction with oxygen, intermediates resulting from insertion of O_2 into a cobalt-carbon bond or from addition of O_2 to the two α-carbon atoms are suggested (ref. 88).

Full reports on the synthesis and chemistry of the bimetallacycloalkanes $[cp_2Co_2(\mu\text{-}CO)_2(\mu\text{-}(CH_2)_n)]$ (n = 3,4) have now appeared. Both are obtained from the radical anion $[cp_2Co_2(\mu\text{-}CO)_2]^{\dot{-}}$ and $I(CH_2)_nI$ and while no analog with n = 2 could be formed, the reaction with gem-diiodoalkanes gives the corresponding methylene-bridged dimers. Thermal decomposition of the bimetallacycle with n = 3 yields propene (73%) and cyclopropane (18%) by processes established by labelling and crossover experiments to be intramolecular. Reaction of $[cp_2Co_2(\mu\text{-}CO)_2(\mu\text{-}(CH_2)_3)]$ with an excess of Lewis bases (L = CO, PMe_3, PPh_3) yields [cpCo(L)(CO)] and [15]



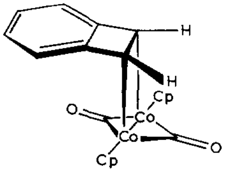
[15]

while with decreasing phosphine concentration the reaction rate decreases and in addition to [cpCo(L)(CO)] significant amounts of cyclopropane together with some propene are produced. On the basis of kinetic studies and trapping experiments the mechanism of Scheme I is proposed. To determine if a four-membered bimetallacycle

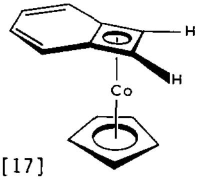


Scheme I

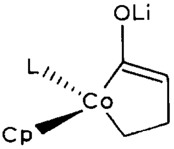
could be formed, $[cp_2Co_2(\mu\text{-}CO)_2]^{\dot{-}}$ was reacted with the diiodide of benzocyclobutadiene. The expected bimetallacycle [16] was produced in low yield and found to readily rearrange to [17] at room temperature (refs. 89, 90). The chemistry of [15] (L = PPh_3) has been further explored. Treatment with lithium diisopropylamide generates the enolate [18] which shows a high diastereoface selectivity on reaction with acetone, alkyl iodides, CH_3OD and Bu^tCHO. The predominant product (90%) is [19] (R = CMe_2OH, Me or Et, D and $CHBu^tOH$ respectively). Reaction of [19] (L = (+)-$CHMePhNMePPh_2$; R = $CHBu^tOH$) with iron(III) chloride at 0° C provided a high yield of optically active 2-(1-hydroxy-2,2-dimethyl)cyclobutanone (ref. 91).



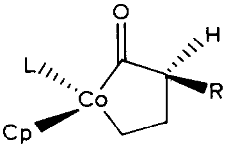
[16]



[17]



[18]



[19]

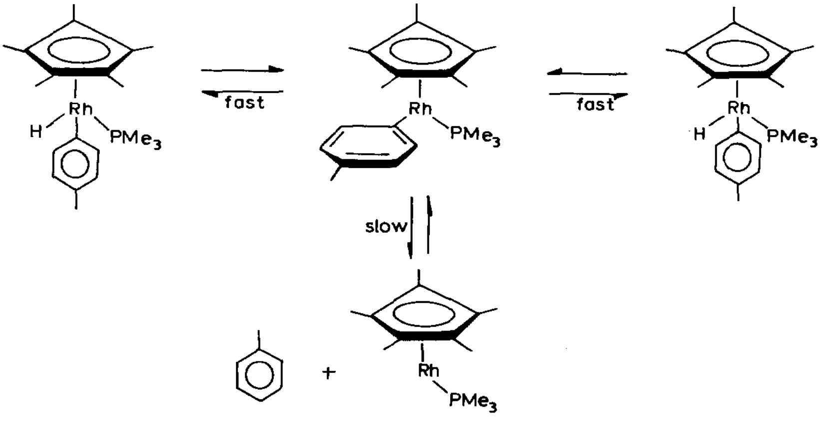
Methylfluorosulfonate converts [$cpCo(CO)_2$] to [$cpCoMe(CO)(SO_3F)$] presumably <u>via</u> initial electrophilic attack at the metal (ref. 92). The $[Co(CN)_4]^{3-}$ ion is proposed to be a catalyst for the cyanation of vinyl halides to produce 2-alkene nitriles in aqueous base under hydrogen. The reaction proceeds stereoselectively except with (Z)-2-bromobut-2-ene where inversion and reduction to the saturated nitrile occur to a significant extent. The formation of σ-vinyl intermediates has been detected by NMR and the rate-determining step appears to be reductive elimination of the product unsaturated nitrile (ref. 93). The hydrogenolysis of oct-1-ene over cobalt supported on alumina gives linear products (α-and β-olefins plus alkanes) in the C_2-C_{11} range. The results are consistent with the degradation of surface alkyl groups to give surface methylene and smaller surface alkyl groups which can be hydrogenolyzed, undergo β-elimination or polymerize on the surface. By contrast, <u>n</u>-octane yields only <u>n</u>-alkanes which was interpreted to indicate random C-H cleavage to give surface alkyls with the branched species undergoing further cleavage (ref. 94).

Studies on the oxidative addition of methyl iodide to [$RhCl(CO)(PR_3)_2$] (R = <u>p</u>-$Bu^nC_6H_4$, Bu^n, <u>n</u>-C_8H_{17}, <u>n</u>-$C_{18}H_{37}$) have been interpreted according to Scheme II (ref. 95).

$$\begin{tikzcd}
{[RhCl(CO)L_2]} \arrow[r, shift left, "MeI"] \arrow[d, shift left, "I^-"] & {[RhClI(Me)(CO)L_2]} \arrow[l, shift left] \arrow[d] \\
{[RhClI(CO)L]^-} \arrow[u, shift left] \arrow[d, "MeI"] & {[RhCl(COMe)IL_2]} \\
{[RhClI_2Me(CO)L]^-} \arrow[r] & {[RhCl(COMe)I_2L_2]^-} \arrow[u]
\end{tikzcd}$$

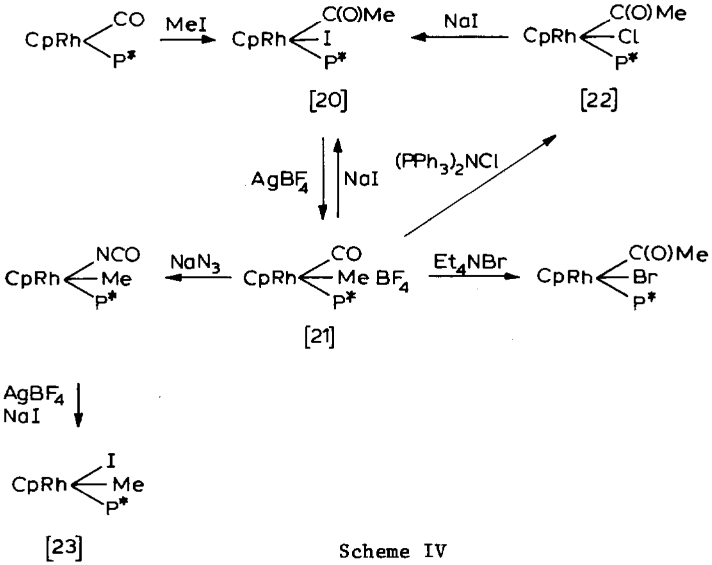
Scheme II

Some aspects of the mechanism of arene carbon-hydrogen bond activation have been studied using $[cp'Rh(R)Br(PMe_3)]$ (R = Ph, *p*-tolyl) which can be prepared from $[cp'RhCl_2(PMe_3)]$ and the appropriate Grignard reagent at -40° C. Reduction of the phenyl complex with lithium tri-*sec*-butylborohydride yields the hydride $[cp'RhH(Ph)(PMe_3)]$ which on refluxing in C_6D_6 produces both C_6H_6 and C_6H_5D. Evaporation of the volatiles followed by refluxing the residue in C_6H_6 yields a product identical with the original $[cp'RhH(Ph)(PMe_3)]$. Reduction of the *p*-tolyl derivative with lithium tri-*sec*-butylborohydride yields initially [cp'RhH(*p*-tolyl)-$(PMe_3)]$ which partially isomerizes to the *m*-tolyl derivative. The same mixture of isomeric tolyl hydride complexes results when $[cp'RhH(Ph)(PMe_3)]$ is refluxed in toluene. The data thus indicate that [cp'RhH(*p*-tolyl)$(PMe_3)]$ isomerizes to the *m*-tolyl complex more readily than exchange with external toluene occurs thereby providing evidence for arene coordination prior to the carbon-hydrogen bond activation as indicated in Scheme III (ref. 96). Retention of configuration during



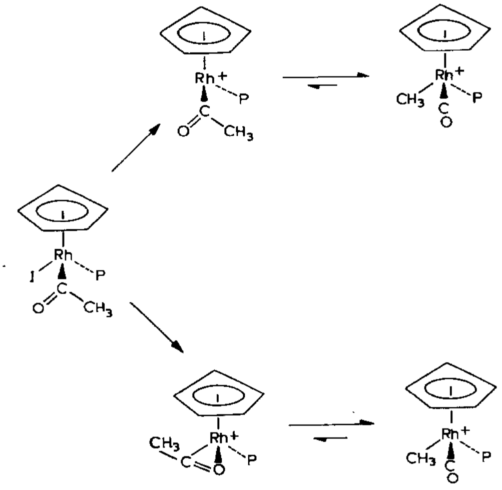
Scheme III

substitution in some chiral rhodium complexes is depicted in Scheme IV (P* = (S)-$PPh_2NHCHMePh$). The mixture of diastereomers [20] initially produced from [cpRh(CO)(P*)] was separated by fractional crystallization and using a single diastereomer of [20] successive conversion to [21], [22] and back to [20] was accomplished with essentially complete retention of configuration. Similarly [21]



Scheme IV

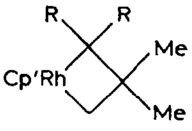
reacts stereospecifically with bromide and azide ions however removal of the isocyanate ligand before reaction with iodide to give [23] resulted in complete epimerization. Resolution of the diasteromeric mixture of complex [23] and treatment of one diastereomer with silver tetrafluoroborate and sodium iodide again resulted in epimerization. The results indicate that the presence of an acyl group provides a "chiral memory" through a sequence of substitution reactions. Scheme V



Scheme V

provides two possible paths by which this may occur with the upper path requiring that the intermediate be trapped before it can racemize (ref. 97).

Grignard and organolithium reagents convert $[MCl(CO)(PPh_3)_2]$ to $[M(R)(CO)(PPh_3)_2]$ (M = Rh; R = Ph, o-tolyl, p-tolyl, mesityl. M = Ir; R = $PhCH_2$. M = Rh, Ir; R = Me, CH_2SiMe_3, CH_2Bu^t). Those complexes with R = mesityl, CH_2SiMe_3 and CH_2Bu^t exist in both cis and trans isomers (ref. 98). A mixture of the complexes [24] - [26] results when $[cp'RhCl_2(PPh_3)]$ reacts with MCR_2Bu^t (M = Li, MgBr; R = H, D) in diethyl ether but in pentane only [24] and [25] are formed suggesting that



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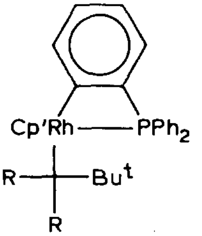
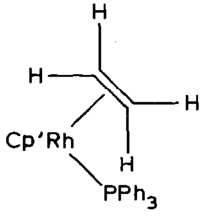
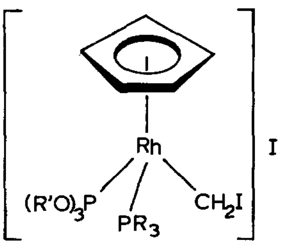


[25]

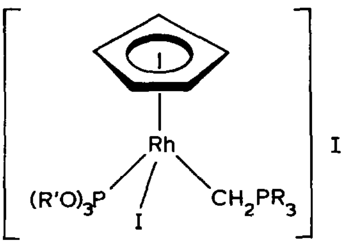


[26]

the ether solvent undergoes cleavage by the alkylating agent. As [24] and [25] do not interconvert they must be formed by independent paths (ref. 99). Triethylaluminum reacts with [Rh(ttp)Cl](ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$) to yield $[(ttp)Rh(AlEt_3)_2]$ which decomposes to $[(Rh(ttp)Et(AlEt_3)]$. With diethylaluminum chloride [RhEt(ttp)] forms initially and reversibly reacts to give [RhH(ttp)] and ethylene. Reaction of the hydride with other olefins generates alkyl complexes which slowly react with hydrogen to produce alkane and regenerate the hydride complex (ref. 99a). Oxidative addition of diiodomethane to $[cpRh(P(OR')_3)(PR_3)]$ (R' = Me; PR_3 = PMe_3, PMe_2Ph, $PMePh_2$. R' = Et; PR_3 = PMe_3) yields [27] which on treatment with base rearranges to [28]. Treatment of $[RhCl(C_2H_4)_2]_2$ with L_2 (= diphos or 1,2-bis(dimethylphosphino)ethane(dmpe)) followed by sodium cyclopentadienide yields

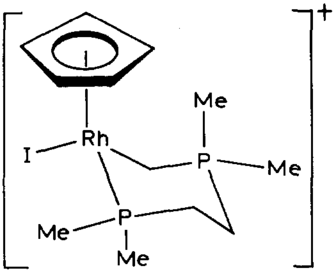


[27]

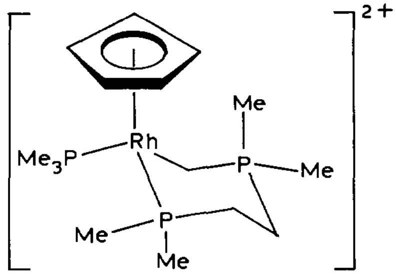


[28]

$[cpRh(L_2)]$ which reacts with diiodomethane to give $[cpRh(L_2)CH_2I]PF_6$ after metathesis with hexafluorophosphate ion. When L_2 = dmpe, treatment with base yields [29] which is converted to [30] by trimethylphosphine. Complex [30] undergoes chelate ring inversion (ref. 100). In related work, [cpRh(PMe_3)(C_2H_4)] reacts with polyhalomethanes to give [cpRh(PMe_3)(CHRX)X'] (R = H; X = X' = Br; X = Cl, X' = I. R = X = X' = Br, I) while [cp'Rh(CO)L] yields [cp'Rh(L)(X)(CHRX)] (L = CO, R = H, X = I; R = X = Br. L = PMe_3, R = X = Br) (ref. 101).

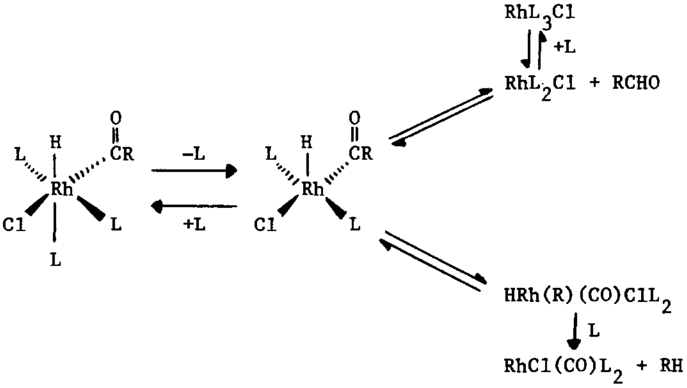


[29]



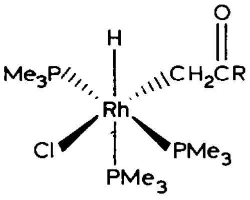
[30]

Aldehydes undergo oxidative addition to [RhCl(PMe_3)$_3$] to yield mer-[RhH(Cl)-(COR)(PMe_3)$_3$] (R = Me, Ph, p-FC_6H_4, OMe). The same reaction occurs with [Rh(PMe_3)$_4$]Cl but at a reduced rate while [RhCl(CO)(PMe_3)$_2$] fails to react. Thermal decomposition in benzene yields mainly RH and [RhCl(CO)(PMe_3)$_2$] via migratory deinsertion followed by reductive elimination. Chloride abstraction by silver hexafluorophosphate considerably accelerates the reaction. On the other hand thermal decomposition of the acetyl complex in vacuo proceeds almost exclusively via direct reductive elimination of acetaldehyde which from crossover experiments appears to be intramolecular as depicted in Scheme VI.



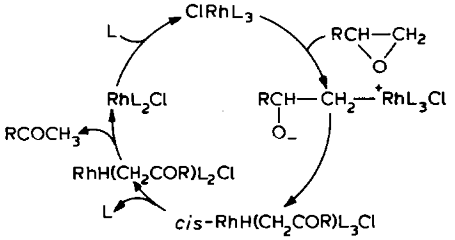
Scheme VI

This path is also supported by the observed acceleration upon addition of [Rh(acac)$(C_2H_4)_2$] which reacts with the dissociated phosphine and by the fact that the *p*-fluorophenyl derivative is the most resistant to thermal decomposition (ref. 102). When pent-4-en-1-al is the aldehyde, the acyl hydride complex is also isolable and the dissociation of the phosphine *trans* to the hydride has been demonstrated by equilibration with $P(CD_3)_3$. Decomposition occurs at 50° C to give cyclopentanone thus providing evidence for previously proposed mechanisms for the rhodium-catalyzed hydroacylation of olefins by aldehydes (ref. 103). In a related study, [RhCl$(PMe_3)_3$] reacts with propylene oxide or styrene oxide to yield [31] (R = Me, Ph) and large quantities of acetone or acetophenone. The isolated complexes

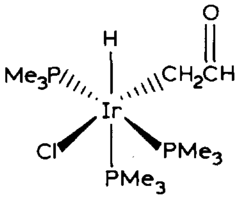


[31]

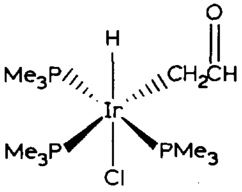
[31] undergo intramolecular reductive elimination of ketone on heating and initial dissociation of a phosphine ligand appears to be rate-limiting. Thus [RhCl$(PMe_3)_3$] catalyzes the isomerization of epoxides to the corresponding ketones as depicted in Scheme VII (L = PMe_3). With ethylene oxide is obtained the acetyl hydride complex rather than the expected formyl methyl species presumably because the latter rapidly eliminates acetaldehyde which can then oxidatively add as described above (ref. 104). On the other hand, the related iridium systems are thermally more stable and thus [32] can be isolated from [Ir$(PMe_3)_4$]Cl. A small amount of [33] also forms while from [Ir(CO)$(PMe_3)_4$]Cl and ethylene oxide [34] is produced. Iridium analogs of [31] are also formed starting with [Ir(*cyclo*-C_8H_{14})Cl$(PMe_3)_3$] and as with the rhodium systems, *mer*-[IrHCl(COMe)$(PMe_3)_3$] results on reaction with acetaldehyde . Reaction of [32] with [RhCl$(PMe_3)_3$] causes decarbonylation and the formation of *mer*-[IrHCl(Me)$(PMe_3)_3$] plus [RhCl(CO)$(PMe_3)_2$]. Scheme VIII portrays



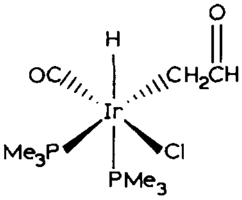
Scheme VII



[32]

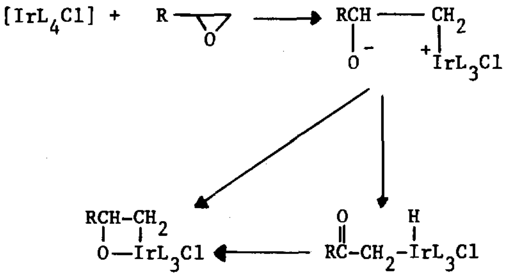


[33]

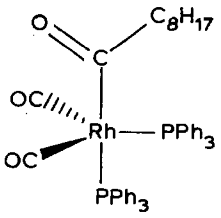


[34]

possible mechanisms for the formation of [32] and its analogs (ref. 105). In a study of the mechanism of olefin hydroformylation catalyzed by $[RhH(CO)(PPh_3)_3]$, this complex was labelled with ^{13}CO and reacted with oct-1-ene to give an acyl complex which was shown to be [35] by low temperature ^{13}C NMR spectroscopy. On warming, evidence for phosphine interchange is seen followed at higher temperatures by intermolecular phosphine and carbonyl exchange processes. Corresponding NMR studies on [36] show that phosphine dissociation and rapid alkyl-acyl

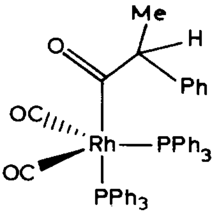


Scheme VIII



[35]

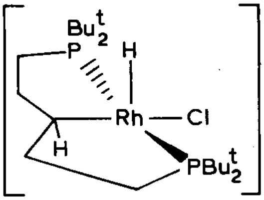
interconversion occur in solution. Since these acyl species accumulate in hydroformylation systems, it is suggested that the catalytic cycle involves their



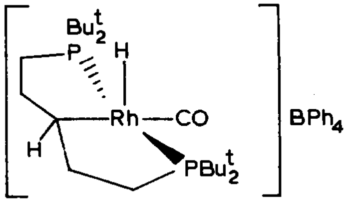
[36]

formation and subsequent trapping by hydrogen following loss of a phosphine ligand. It is further suggested that the linear/branched isomer ratio in the product aldehydes may be due to differing kinetic labilities of the acyls corresponding to [35] and [36] rather than to the existence of a dual pathway as previously proposed (ref. 106).

A new preparation of the cyclometallated phosphine complex [37] involves the reaction of $Bu^t{}_2P(CH_2)_5PBu^t{}_2$ with $[RhCl(\underline{cyclo}\text{-}C_8H_{14})_2]_2$ in toluene or with $RhCl_3{\cdot}3H_2O$ in THF. Carbonylation of [37] in ethanol in the presence of sodium tetraphenylborate gives [38]. By contrast reaction of $L_2 = Bu^t{}_2P(CH_2)_5PBu^t{}_2$ or $Bu^t{}_2PCH_2CH{=}CHCH_2PBu^t{}_2$ with $[Rh(CO)_2Cl]_2$ yields the dimers $[Rh_2(CO)_2Cl_2(L_2)_2]$ in

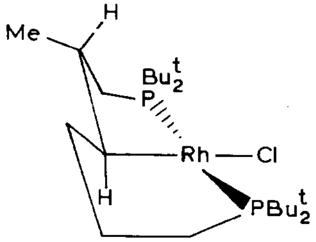


[37]

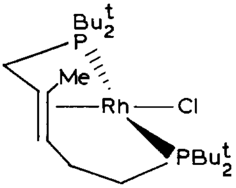


[38]

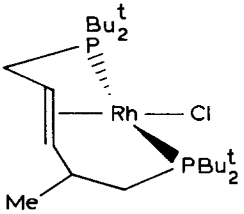
which two trans-Rh(CO)Cl moieties are bridged by the diphosphine ligands. Isocyanide analogs $[Rh_2Cl_2(CNR)_2(L_2)_2]$ (R = Me, Bu^t) can be got from $[RhCl(\underline{cyclo}\text{-}C_8H_{14})_2]_2$ and the two diphosphine ligands in the presence of stoichiometric amounts of isocyanide. The cationic dimer $[Rh_2(CNR)_4(Bu^t{}_2P(CH_2)_5PBu^t{}_2)_2]^{2+}$ (R = Me, Bu^t) can be prepared from the ligand and $[Rh(CNR)_4]^+$ in refluxing acetone or from [37] and the isocyanide in ethanol in the presence of a large counterion. The latter reaction in isopropanol containing sodium isopropoxide without the addition of a large counterion gave an inseparable mixture of complexes. Refluxing hydrated rhodium(III) chloride with $Bu^t{}_2PCH_2CHMe(CH_2)_3PBu^t{}_2$ in isopropanol gives a mixture of [39] and dehydrogenated species such as [40] or [41]. A pure sample of [39] can be prepared starting with $[RhCl(\underline{cyclo}\text{-}C_8H_{14})_2]_2$ and dehydrohalogenation with sodium isopropoxide under carbon monoxide gives a neutral monocarbonyl derivative. The iridium analog of [39] has also been prepared from $[IrCl(\textit{cyclo}\text{-}C_8H_{14})_2]_2$ and if the workup is rapid, a small quantity of the isomer with the methyl group in an axial



[39]

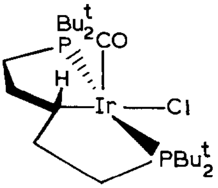


[40]

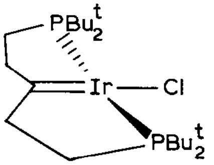


[41]

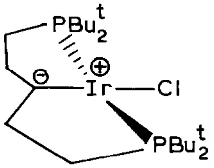
position is observed. This rapidly converts the equatorial isomer *via* a reductive elimination/oxidative addition sequence. The same route has been used to prepare the iridium analog of [37] and is preferred to the reaction of $Bu^t{}_2P(CH_2)_5PBu^t{}_2$ with hydrated iridium(III) chloride in refluxing isopropanol since the latter route also gives a species formulated as $[Ir_2H_2Cl_4(L_2)_2]$ and other uncharacterized material. The first complex reacts with carbon monoxide to give [42] and on vacuum pyrolysis loses hydrogen with the formation of a species formulated as either the carbene [43a] or the ylide [43b]. It also reacts with hydrogen in the presence of



[42]

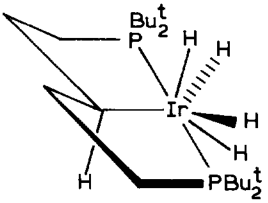


[43a]

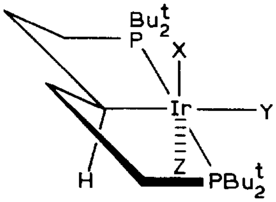


[43b]

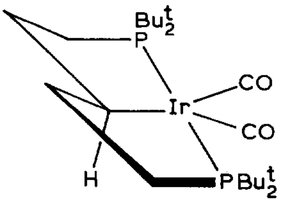
sodium isopropoxide in benzene to give the tetrahydride [44] which was identified in solution but not isolated because of its high solubility and air-sensitivity. It is fluxional down to at least -99° C. Complex [44] reacts with carbon monoxide to give a mixture of isomers of [45] (X = Z = H, Y = CO. Y = Z = H, X = CO. X = Y = H, Z = CO) and [46]. Isocyanide analogs of [45] and [46] were also prepared (refs. 107-111).



[44]

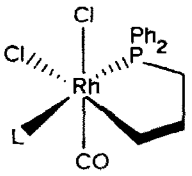


[45]

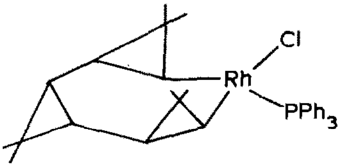


[46]

Under mild conditions 3-chloropropyldiphenylphosphine (L) forms $[RhCl(CO)L_2]$ from $[RhCl(CO)_2]_2$ but on heating, oxidative addition of the carbon-chlorine bond occurs yielding [47] (ref. 112). Condensation of 3,3-dimethylcyclopropene occurs in the presence of $[RhCl(PPh_3)_3]$ at 35° C in toluene to give the metallacycle [48].

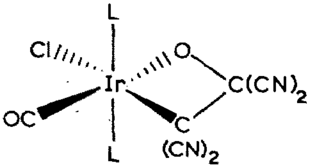


[47]

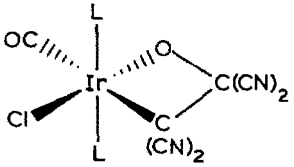


[48]

Carbonylation of [48] yields a mixture of hexamethyl-tris-σ-homobenzene and hexamethyl-tris-σ-homotropone with the rhodium being recovered as $[RhCl(CO)(PPh_3)]_2$. Reaction of the cyclopropene with $[RhCl(CO)(PPh_3)_2]$ produces [48] and tetramethyl-bis-σ-homocyclopentadienone (ref. 113). Tetracyanoethylene oxide reacts with $[RhCl(CO)(PPh_3)_2]$ in refluxing benzene to yield $[Rh(CN)Cl(CO)(OC(CN)=C(CN)_2)(PPh_3)_2]$ while with $[IrCl(CO)(PMe_3)_2]$ at room temperature the isomeric mixture [49a] and [49b] (L = PMe_3) results. On the other hand the reaction of

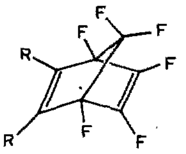


[49a]



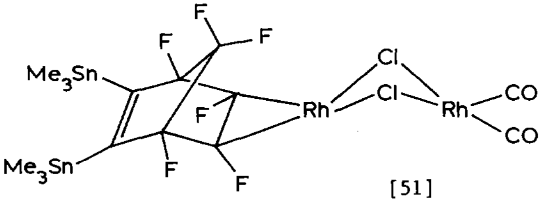
[49b]

"$MCl(PPh_3)_2$" (M = Rh, Ir) with neat styrene oxide gave only $[MCl(CO)(PPh_3)_2]$ and a complex organic mixture (ref. 114). The fluorinated norbornadiene [50] (R = Cl)



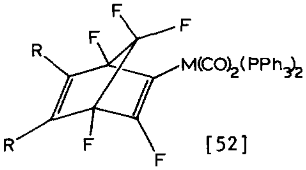
[50]

does not react with $[Rh(acac)(C_2H_4)_2]$ however when R = $SnMe_3$ either one or two ethylene ligands can be replaced by the diene which functions as a mono-olefin ligand. With R = H, both ethylene ligands are replaced by the diene which now acts as a bidentate ligand. Diene [50] (R = Cl) does not react with $[RhCl(CO)_2]_2$ while with R = H reaction occurs but no product was isolated. When R = $SnMe_3$ the product is [51] which can be cleaved to a monomeric species with triphenylphosphine.

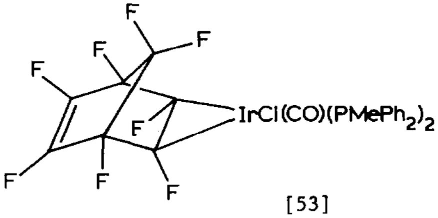


[51]

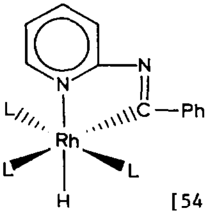
Reaction of [50] with $[M(CO)_2(PPh_3)_2]^-$ yields [52] (R = Cl, $SnMe_3$; M = Co, Rh. R = F; M = Rh, Ir). Finally [50] (R = F) adds to $[Ir(CO)Cl(PMePh_2)_2]$ to yield [53] but is unreactive towards $[RhCl(CO)_2]_2$, $[Rh(acac)(C_2H_4)_2]$ and [cp'Rh(COD)] (refs. 115, 116). The iminoacyl hydride complex [54] (L = PPh_3) can be reduced with dimethylcadmium to the Rh(I) complex [55] which displays a reactivity like that of



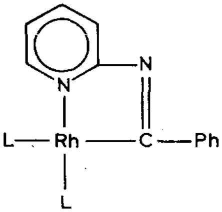
[52]



[53]



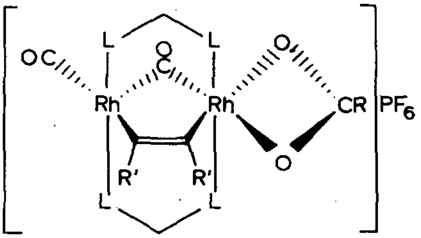
[54]



[55]

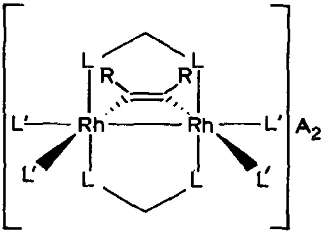
an acyl anion. Thus it reacts with methyl iodide, benzyl bromide and benzoyl chloride to give respectively the 2-aminopyridine imines of acetophenone, benzylphenylketone and benzophenone (ref. 117). A highly regioselective reduction of α,β-unsaturated carbonyl compounds to the corresponding saturated species or to allylic alcohols can be effected by hydrosilylation using $[RhCl(PPh_3)_3]$ as a catalyst followed by methanolysis (ref. 118).

Considerable interest continues to be shown in the A-frame type binuclear complexes typified by $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]PF_6$ (L_2 = bis(diphenylphosphino)methane (DPM), bis(diphenylarsino)methane (DAM)). Reaction with silver carboxylates yields $[Rh_2(CO)_2(\mu\text{-}O_2CR)(L_2)_2]PF_6$ (L_2 = DPM, DAM; R = Me. L_2 = DAM; R = Et) which react further with electrophilic acetylenes to give the dimetallated olefin complexes [56] (L_2 = DPM, DAM; R = Me; R' = CO_2Me, CF_3. L_2 = DAM; R = Et; R' = CO_2Me, CF_3).



[56]

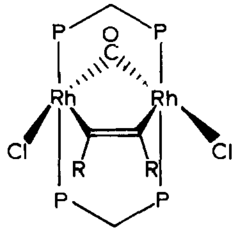
The terminal carbonyl group is readily replaced by trimethylphosphite and <u>tert</u>-butylisocyanide <u>via</u> an associative process. Complex [56] (L_2 = DPM, R = Me; R' = CO_2Me) reacts readily with hydrogen (2 atm, 25° C) to produce dimethylmaleate with the resulting rhodium complex catalyzing the further reduction of the dimethylmaleate to dimethylsuccinate. Electrophilic acetylenes also add to $[Rh_2(CNBu^t)_4(L_2)_2]A_2$ (L_2 = DPM, DAM; A = BPh_4^-, PF_6^-) to yield [57] (L' = $CNBu^t$; R = CO_2Me,



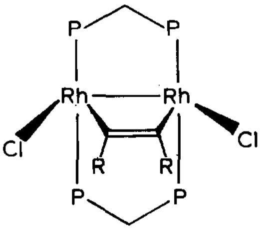
[57]

CF_3) (ref. 119). In related work, $[Rh_2(CO)_2Cl_2(DPM)_2]$ and $[Rh_2(CO)Cl_2(DPM)_2]$ add electrophilic acetylenes in dichloromethane solution to give [58] (R = CO_2Me, CF_3). When R = CF_3, thermal decarbonylation yields [59]. In methanol, $[Rh_2(CO)_2Cl_2(DPM)_2]$ catalyzes the cyclotrimerization of dimethylacetylene dicarboxylate.

However this reaction does not occur in dichloromethane and [58] (R = CO_2Me) is not a catalyst. Complex [59] (R = CF_3) reacts with diazomethane at -78° C to yield a



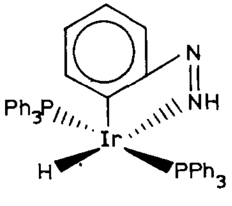
[58]



[59]

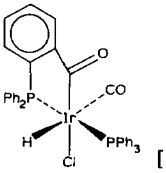
methylene-bridged species with a structure analogous to [58] and not containing a metal-metal bond (refs. 120, 121). Extended Hückel molecular orbital calculations on models for [58] indicate that the proposed dimetallated olefin description is most appropriate (ref. 122).

The iridium trihydride, $[IrH_3(PPh_3)_2]$ reacts with aryldiazonium tetrafluoroborates at -10° C to produce $[IrH_2(NH{=}NR)(PPh_3)_2]BF_4$ (R = p-C_6H_4X(X = F, OMe)) which reacts with carbon monoxide to yield $[IrH_2(CO)_2(PPh_3)_2]BF_4$ and ultimately $[Ir(CO)_3(PPh_3)_2]BF_4$. At room temperature, ortho-metallation occurs to give [60] in which the vacant coordination site can be filled by iodide, triphenylphosphine or

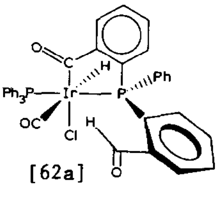


[60]

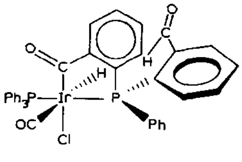
carbonyl ligands (ref. 123). Although $[IrCl(N_2)(PPh_3)_2]$, $[Ir(R)(CO)(PPh_3)_2]$ (R = Me, Ph), $[(RhH(Pcy_3)_2)_2(\mu\text{-}N_2)]$ and $[(Co(PPh_3)_3)_2(\mu\text{-}N_2)]$ fail to react with dry, liquid carbon dioxide, reaction is observed with $[Ir(O_2)R(CO)(PPh_3)_2]$ (R = Me, Ph), $[(Co(PEt_2Ph)_3)_2(\mu\text{-}N_2)]$ and $Na[Co(N_2)(PEt_2Ph)_3]$. The iridium product is thought to be the peroxycarbonate complex $[Ir(R)(OCO_3)(CO)(PPh_3)_2]$ while the cobalt-containing products appear to contain both carbonyl and carbonate ligands indicating that reductive disproportionation of the carbon dioxide has occurred. It is concluded that steric factors are important for the stabilization of reactive carbon dioxide adducts (ref. 124). A comparison has been made between the ease of oxidative addition of hydroxyl, carboxyl and aldehyde functionalities attached to coordinated phosphine ligands in Ir(I) complexes and uncoordinated molecules containing the same groups. The resulting chelate assistance increases the tendency towards oxidative addition by three to four orders of magnitude. Thus benzaldehyde shows no tendency to react with $[IrCl(CO)(PPh_3)_2]$ but with _o_-diphenylphosphinobenzaldehyde substitution of one triphenylphosphine occurs followed by facile oxidative addition to yield [61]. Similarly phenylphosphinodibenzaldehyde gives a mixture of the non-interconverting diastereoisomers [62a,b] (ref. 125). Acid chlorides oxidatively add to $[IrCl(PMePh_2)_3]$ to yield the six-coordinate alkyl carbonyl species $[IrCl(R)(CO)(PMePh_2)_3]$ (R = Me, Et, Pr^n). When R = Et or Pr^n these



[61]



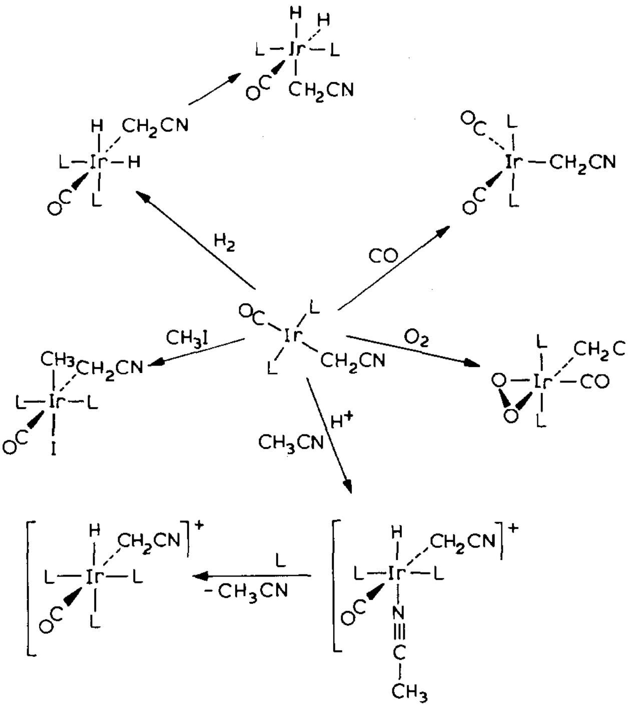
[62a]



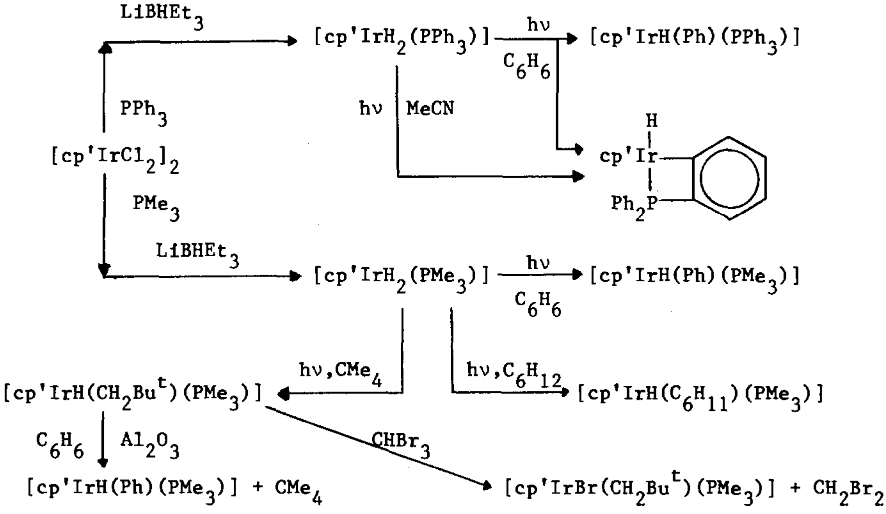
[62b]

products are in equilibrium with the corresponding five-coordinate acyl species. The initial six-coordinate complexes are facial isomers and the subsequent isomerization to meridional isomers is facilitated by polar solvents indicating that chloride loss is required for the process to occur. Reaction of $[MCl(ol)_2]_2$ (M = Rh; ol = C_2H_4. M = Ir; ol = _cyclo_-C_8H_{14}) with six equivalents of methyldiphenylphosphine followed by addition of the same acid chlorides provides the acyl complexes $[MCl_2(COR)(PMePh_2)_3]$. Alkyl migration occurs only when one chloride is replaced by hexafluorophosphate ion indicating a vacant site is required. The complexes $[IrClI(Pr^i)(CO)L_2]$ (L = PMe_3, PMe_2Ph) isomerize to $[IrClI(Pr^n)(CO)L_2]$ in solution. Halide scrambling and decomposition also occur. In mixtures of dichloromethane and polar solvents, the ease of isomerization increases in the order of the ability of the polar solvent to solvate ionic species indicating that loss of iodide ion is probably the initial step. This was confirmed by the observation of immediate isomerization on removal of iodide with silver hexafluorophosphate. The subsequent steps probably involve β-elimination and readdition of propene to the iridium hydride (ref. 126). Iodoacetonitrile oxidatively adds to $[IrCl(CO)(PPh_3)_2]$ and the product can be electrolytically reduced to $[Ir(CH_2CN)(CO)(PPh_3)_2]$. Further chemistry of the latter complex is detailed in Scheme IX (L = PPh_3) (ref. 127).

Two important papers reporting approaches to facile activation of unactivated carbon-hydrogen bonds have appeared. Scheme X details one of these studies. Control experiments appear to exclude the participation of radical processes and the results suggest that activation of a primary carbon-hydrogen bond is preferred over a secondary one (ref. 128). A simpler system starts with $[cp'Ir(CO)_2]$ which has the advantage that internal ligand metallation does not occur. Photolysis in neopentane and cyclohexane solutions produces the unstable alkyl hydride complexes $[cp'IrH(R)(CO)]$ (R = CH_2Bu^t, _cyclo_-C_6H_{11}) which can be converted into the more stable $[cp'IrCl(R)(CO)]$ species with carbon tetrachloride. Photolysis in hexane



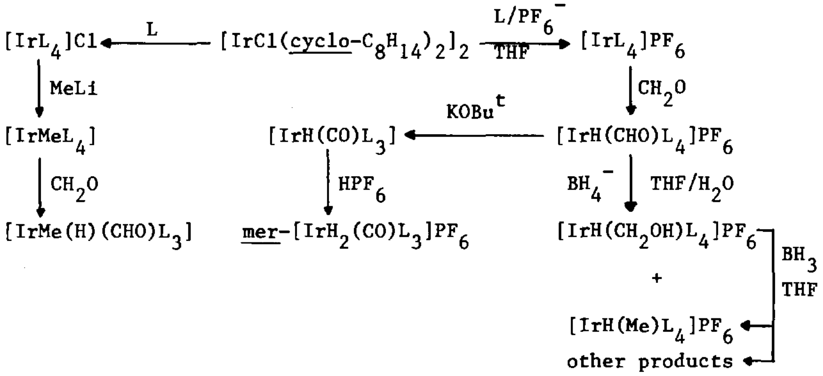
Scheme IX



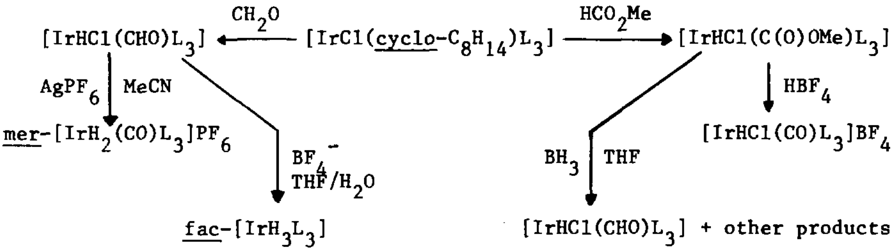
Scheme X

and benzene solutions appeared to give analogous hexyl and phenyl derivatives. In competition reactions, activation of the carbon-hydrogen bond in benzene was preferred to that in cyclohexane or neopentane by a factor of two which may indicate formation of a π-complex by benzene prior to carbon-hydrogen bond activation (see also ref. 96) (ref. 129).

A full report has now appeared on the chemistry of some formyl hydride and related complexes of iridium. This is depicted in Schemes XI and XII (L = PMe_3). In addition, $[Ir(CO)L_4]Cl$ reacts with methanol and hexafluorophosphate ion to

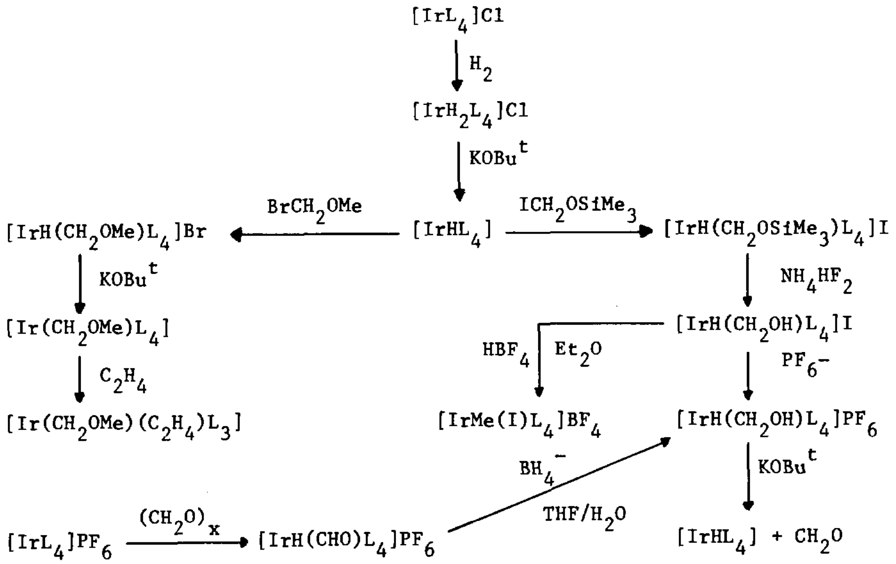


Scheme XI



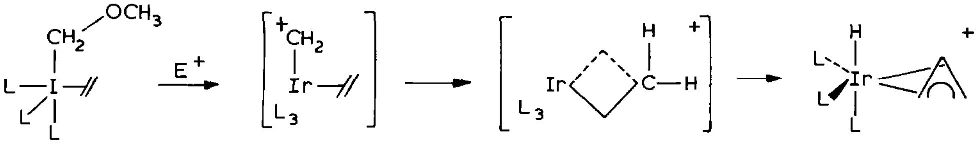
Scheme XII

yield $[IrH(C(O)OMe)L_4]PF_6$ which is converted into $[IrHCl(CHO)L_3]$ and other unidentified products by $BH_3{\cdot}THF$. The results indicate feasible routes for the reduction of carbon monoxide to a methyl group in the coordination sphere of iridium but unfortunately some of the steps afford only very low yields (ref. 130). Scheme XIII (L = PMe_3) details further chemistry related to the possible existence of species proposed as intermediates in the reduction of coordinated carbon monoxide. The preparation of $[IrH(CH_2OH)L_4]PF_6$ from $[IrL_4]PF_6$ and paraformaldehyde although shorter than that given on the right of Scheme XIII gives a significantly poorer yield. This hydroxymethyl complex can be decomposed by other strong bases in



Scheme XIII

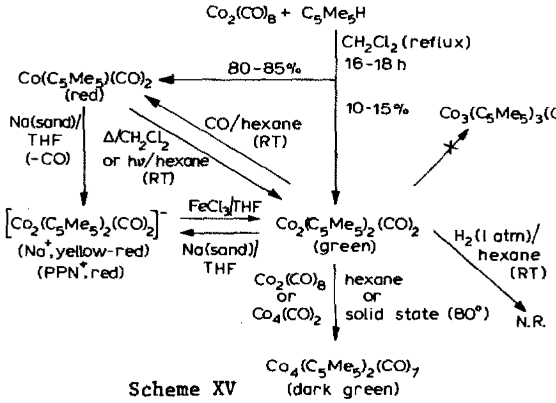
addition of KOBu^t and in particular [IrHL$_4$] itself is sufficiently strong so that the decomposition soon becomes a chain process. Reaction of [Ir(CH$_2$OMe)(C$_2$H$_4$)L$_3$] (left side of Scheme XIII) with trimethylsilyltrifluoromethanesulfonate in hexamethyldisiloxane provides [(η^3-C$_3$H$_5$)IrHL$_3$]OSO$_2$CF$_3$ with the mechanism of Scheme XIV depicting the preferred route. Other electrophiles will also effect the conversion but the reaction is not a general one for other olefins nor could the rhodium analogs be synthesized. It is proposed as a homogeneous model for the carbene/metallacycle mechanism for the olefin metathesis reactions (refs. 131, 132). As part of a study of unstable formyl complexes, [Ir(CO)$_3$(PPh$_3$)$_2$]PF$_6$ was reduced to [Ir(CO)$_2$(CHO)(PPh$_3$)$_2$] at -78° C with lithium triethylborohydride in good yield. Although identified spectroscopically at this temperature, it decomposes at -40° C to [IrH(CO)$_2$(PPh$_3$)$_2$] (ref. 133).



Scheme XIV

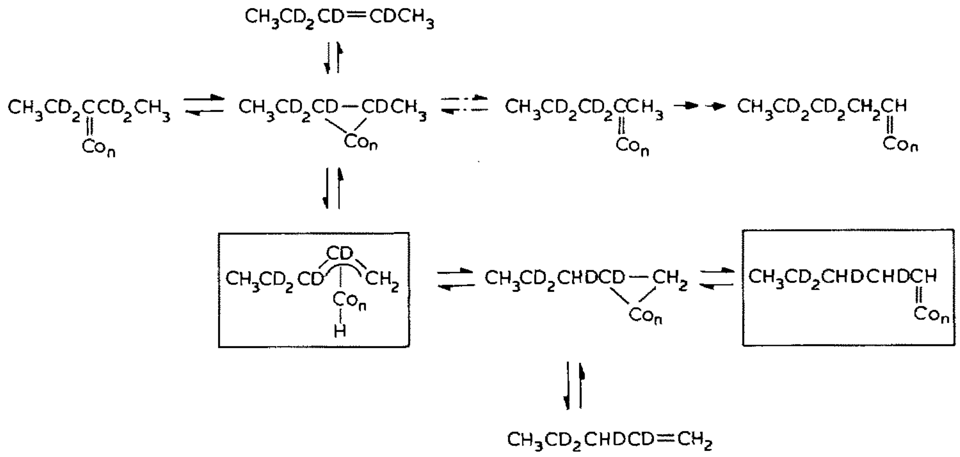
Intense interest continues in the chemistry of [cp$_2$M$_2$(μ-CO)$_2$] (M = Co, Rh), their pentamethylcyclopentadienyl analogs and related species. The structures of the radical anion [cp$_2$Co$_2$(μ-CO)$_2$]$^{\dot{-}}$, its pentamethylcyclopentadienyl analog and

$[cp'_2Co_2(\mu\text{-}CO)_2]$ have been determined to explore the effects of oxidation to the neutral dimer on the metal-metal distance. A decrease of 0.034 Å in this parameter accompanied by an increase in the Co–CO distances occurs on oxidation. The decrease in the Co–Co distance is about one half of that predicted theoretically and the discrepancy is explained by the fact that since Co–CO bonds are stronger than the Co–Co bond their lengthening tends to dominate the structural changes. Some chemistry of the system is detailed in Scheme XV (ref. 134). As described



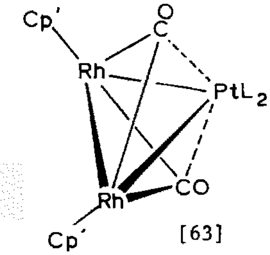
Scheme XV

earlier in this section, $[cp_2Co_2(\mu\text{-}CO)_2]^{\cdot-}$ reacts with *gem*-diiodides to yield $[cp_2Co_2(\mu\text{-}CO)_2]$ and the methylene-bridged dimers *trans*-$[cp_2Co_2(CO)_2(\mu\text{-}CRR')]$ (R = R' = H, Et, CD_3, CD_2CH_3. R = H; R' = Et, Bu^n. R = Me, R' = Pr^n). These are in equilibrium with the *cis* isomers as well as the triply-bridged isomers $[cp_2Co_2(\mu\text{-}CO)_2(\mu\text{-}CRR')]$ and reversibly lose carbon monoxide to give $[cp_2Co_2(\mu\text{-}CO)(\mu\text{-}CRR')]$. At 80° C in deuterobenzene $[cp_2Co_2(CO)_2(\mu\text{-}CMe_2)]$ reacts to give $[cp_2Co_2(CO)_2(\mu\text{-}CHEt)]$ and propene. Similarly $[cp_2Co_2(CO)_2(\mu\text{-}CEt_2)]$ at 60° C in deuterotoluene gives a mixture of $[cp_2Co_2(CO)_2(\mu\text{-}CMePr^n)]$, $[cp_2Co_2(CO)_2(\mu\text{-}CHBu^n)]$, $[cp_2Co_2(\mu\text{-}CO)(\mu\text{-}CMePr^n)]$ and pentenes. Isolated $[cp_2Co_2(CO)_2(\mu\text{-}CMePr^n)]$ also converts to $[cp_2Co_2(CO)_2(\mu\text{-}CHBu^n)]$ demonstrating the stepwise nature of the isomerization. The observation that $[cp_2Co_2(CO)_2(\mu\text{-}C(CD_2CH_3)_2)]$ isomerizes to $[cp_2Co_2(CO)_2(\mu\text{-}C(H)CHDCHDCD_2CH_3)]$ under these conditions leads to the proposed mechanism of Scheme XVI. In this scheme it is not certain whether the binuclear complex remains intact (ref. 135). Reaction of $[cp'_2Co_2(\mu\text{-}CO)_2]$ with diazomethane gives $[cp'_2Co_2(CO)_2(\mu\text{-}CH_2)]$ while with diazoethane the product is $[cp'_2Co_2(\mu\text{-}CO)_2(\mu\text{-}CHMe)]$. These can be reversibly decarbonylated to $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}CHR)]$ (R = H, Me) which react further with the appropriate diazoalkane to give $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}CHMe)]$. Sulfur dioxide adds to $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ to yield $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}SO_2)]$ (ref. 136). A complete report on the rhodium analog of the above system has now been published. It is presumed that all reactions proceed *via* initial formation of $[cp'_2Rh_2(\mu\text{-}CO)_2(\mu\text{-}CRR')]$ but the nature of the isolated products



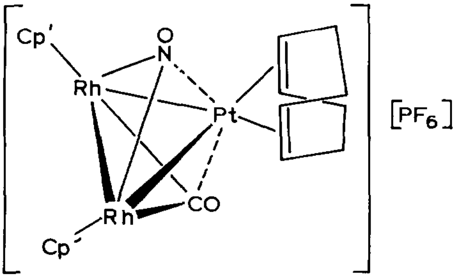
Scheme XVI

depends on the substituents on the methylene carbon. Thus for R = H; R' = H, Me, CF_3, Et, CO_2Et and R = R' = CO_2Me, Ph, *o*-phthaloyl, CH=CH-CH=CH the product is $[cp'_2Rh_2(CO)_2(\mu\text{-}CRR')]$ while for R = R' = 2,2'-biphenylyl or CX=CX-CX=CX (X = Cl, Br) it is $[cp'_2Rh_2(\mu\text{-}CO)(\mu\text{-}CRR')]$. Thermal decarbonylation of $[cp'_2Rh_2(CO)_2(\mu\text{-}CPh_2)]$ yields $[cp'_2Rh_2(\mu\text{-}CO)(\mu\text{-}CPh_2)]$ which reacts further with diazomethane to give $[cp'_2Rh_2(\mu\text{-}CO)(\mu\text{-}CPh_2)(\mu\text{-}CH_2)]$ (ref. 137). Pursuing the analog between low-valent platinum complexes and carbenes $[Pt(COD)_2]$ has been reacted with $[cp'_2Rh_2(\mu\text{-}CO)_2]$ to yield [63] (L_2 = COD). The same reaction with $[Pt(C_2H_4)_n(PPh_3)_{3-n}]$



[63]

(n = 1,2) yielded a mixture of species of which the major component was [63] (L_2 = $(CO)(PPh_3)$). This complex could be oxidized by ferricinium hexafluorophosphate to a monocation. A much higher yield of $[cp'_2Rh_2Pt(\mu\text{-}CO)_2(CO)(PPh_3)]$ could be realized from the reaction of $[cp'Rh(CO)_2]$ and $[Pt(C_2H_4)_2(PPh_3)]$ but on carbonylation $[cp'Rh(CO)_2]$ was reformed together with the platinum clusters $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ and $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$. Complex [63] ($L_2$ = $(CO)_2$) could however be prepared from stoichiometric quantities of $[cp'Rh(CO)_2]$ and $[Pt(COD)_2]$ or from $[cp'_2Rh_2(\mu\text{-}CO)_2]$ and $[cp_2Pt_2(CO)_2]$. The nickel-rhodium cluster $[cp'_2Rh_2Ni\text{-}(\mu\text{-}CO)_2(COD)]$, presumably having the same structure as [63], has been prepared by the same route as the platinum analog and characterized by field-desorption mass spectrometry because of its considerable air-sensitivity and thermal instability. A related complex is [64] which was prepared from $[cp'_2Rh_2(\mu\text{-}CO)(\mu\text{-}NO)]PF_6$ and $[Pt(COD)_2]$ (ref. 138). Reaction of $[cp'_2M_2(\mu\text{-}CO)_2]$ (M = Co, Rh) with cyclohexanone hydrazone in the presence of activated manganese dioxide yields $[cp'_2M_2(CO)_2\text{-}(\mu\text{-}cyclo\text{-}C_6H_{10})]$ as the first example of a saturated carbocyclic alkylidene bridge. On thermal decomposition, cyclohexane is the major organic product (ref. 139). The chemistry of these metal-metal doubly bonded dimers has been expanded with investigations of the reactions of $[cp'_2Rh_2(\mu\text{-}CO)_2]$ with α-diazoketones and 3,3-dimethylcyclopropene. In the first study the product is [66] (R = R' = Ph, Me, *p*-anisyl. R = Me; R' = Ph) proposed to be formed as shown from the intermediate methylene complex [65]. For successful production of [66], the keto carbene moiety must be able to twist about the central carbon-carbon bond and the keto group must have a strongly nucleophilic oxygen (ref. 140). In the second, the product is [68] which is thought to form *via* the intermediate [67]. Protonation with trifluoroacetic acid yields [69]. This is reported as the first example of carbon-carbon double bond cleavage in a cyclopropene and therefore presumably formally generates a



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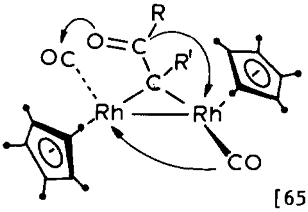
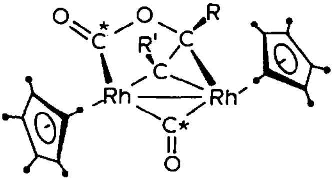
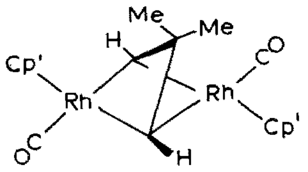


[65]



[66]

dicarbene making this reaction formally the reverse of the reaction of carbenes to form olefins as is proposed to occur in Fischer-Tropsch chemistry (ref. 141). An example of ring expansion in μ-methylene complexes is the formation of [70] from $[cp'_2Rh_2(CO)_2(\mu\text{-}CH_2)]$ and sulfur dioxide (ref. 142). Bis[diazo(ethoxycarbonyl)-methyl] mercury reacts with $[cp'_2Rh_2(\mu\text{-}CO)_2]$ to give [71] which is very air sensitive in solution (ref. 143). Methylene-bridged species can also be prepared from $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}F_3CC{=}CCF_3)]$ and diazo compounds. These have the structure [72] ($R^1 = R^2 = H$, CO_2Et. $R^1 = H$, $R^2 = CF_3$, CO_2Et) and certain ones rearrange in chloroform to give [73] ($R^1 = H$, $R^2 = H$, CO_2Et) or [74] ($R = H^1$; $R^2 = CO_2Et$) (ref. 144). Finally, the x-ray photoelectron spectra (XPES) of $[cp_2M_2(CO)_2(\mu\text{-}CH_2)]$ (M = Co, Rh) indicate that the methylene group bears considerable negative charge which is consistent with its ability to be protonated (ref. 145).



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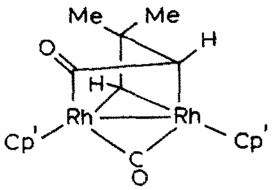

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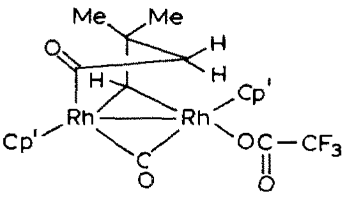

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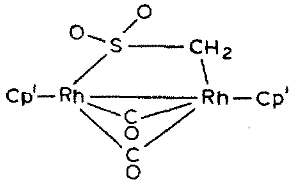

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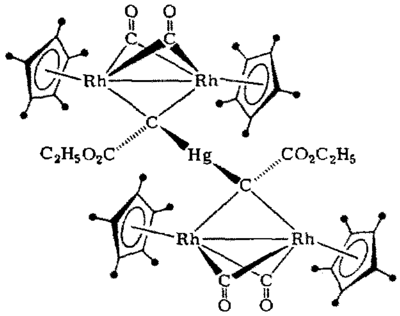
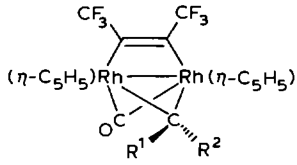


[71]

A different series of μ-methylene complexes is derived from $[cp'_2Rh_2Cl_4]$ which reacts with trimethylaluminum below -30° C to yield a species thought to be [75]

L = $AlMe_2Cl$, etc.). Treatment with acetone furnishes a high yield of



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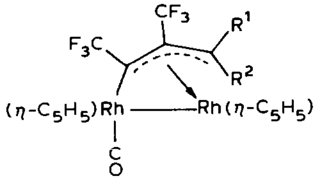

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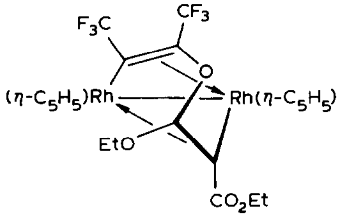
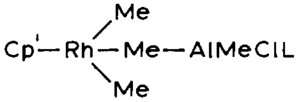


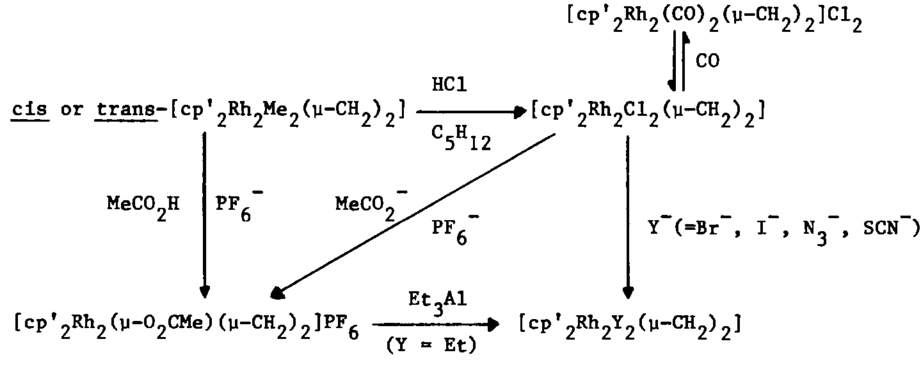
[74]

<u>cis</u>-[$cp'_2Rh_2Me_2(\mu-CH_2)_2$] which can be converted to the corresponding <u>trans</u> isomer. No radicals were detected in the last two steps and as no H/D scrambling is



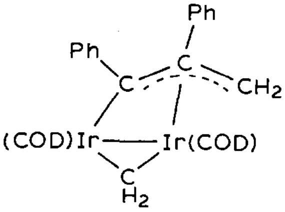
[75]

observed when fully deuterated [$cp'_2Rh_2Cl_4$] is reacted with [$Al_2(CH_3)_6$] and then with deuteroacetone it is considered that species such as [$cp'Rh(=CH_2)(Me)$] are not formed. Some further chemistry of [$cp'_2Rh_2Me_2(\mu-CH_2)_2$] is outlined in Scheme XVII (refs. 146, 147). Diphenyl acetylene readily adds to [$Ir_2(COD)_2(\mu-CH_2)_2$] to



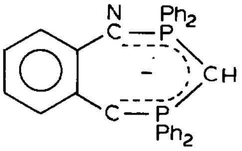
Scheme XVII

produce [76] (ref. 148). Addition of methyllithium to a mixture of $[IrCl(COD)]_2$ and cyclooctadiene at -78° C affords the methyl-bridged dimer $[Ir_2(COD)_2(\mu\text{-}CH_3)_2]$ (ref. 149) (see also 1981 Survey). The analogous ethyl-bridged rhodium dimer, $[Rh_2(COD)_2(\mu\text{-}CH_2CH_3)_2]$ is prepared in like fashion and on warming to 20° C decomposes to the tetrameric hydride complex $[Rh_4(COD)_4(\mu\text{-}H)_4]$. This species is fluxional and reacts with hydrogen to produce cyclooctane and rhodium metal. No metal forms on reaction of the hydride with hydrogen in the presence of ethylene, but the rate of production of ethane is slow (ref. 150).



[76]

The double ylide tetraphenyl-1H,2λ^5,4λ^5-benzodiphosphepin is converted into the anion [77] on treatment with butyllithium. This in turn forms a 2:1 complex with cobalt(II) ions which appears to contain high-spin tetrahedral cobalt. From the structure of the manganese analog it is considered that the cobalt is coordinated to the carbon atoms adjacent to the aromatic ring (ref. 151). Dirhodium tetraacetate and [RhI(TPP)] are catalysts for the conversion of aryldiazomethanes to cis-1,2-diarylethylenes. It is proposed that an initially formed ylide, $\{\bar{R}h\text{-}\overset{+}{C}HAr\}$, couples with a second molecule of the diazo-compound followed by elimination of dinitrogen and rhodium complex. Presumably the bulk of the rhodium moiety in the coupling product is sufficient to force the aryl groups to be cis (ref. 152). Alkenyl, alkynyl and aryl mercuric halides are stoichiometrically methylated by $[RhMeI_2(PPh_3)_2]$ in hexamethylphosphoramide (HMPA) containing lithium chloride or methyl iodide. The system can be made catalytic when methyl iodide is present but dimerization of the mercurials is a serious problem (ref. 153). Organocobalt complexes are proposed as intermediates in the $[CoCl_2(PPh_3)_2]$-catalyzed coupling of alkenyl and aryl tellurides with Grignard reagents (ref. 154). Finally, ion

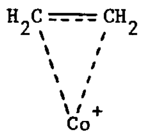


[77]

cyclotron resonance measurements have been used to get bond energies for the gas phase complexes $[CoLL']^+$ (L = EtOH, Me_2O; L' = but-1-ene. L = Pr^nOH; L' = $Me_2C=CH_2$. L = $Me_2C=CH_2$; L' = EtCHO). The observation of a synergistic stability of a σ-base/π-base complex provided a direct measure of the thermodynamic trans influence (ref. 155).

Studies of the chemistry of cobaloximes and particularly their alkyl derivatives continue to be numerous. Two reports on the cleavage of alkyl(pyridine)cobaloximes by acids in deuterochloroform conclude that the process occurs by an S_E2 mechanism but they differ in the sequence of steps preceeding alkyl cleavage. Thus addition of hydrochloric acid to $[RCo(dmgH)_2py]$ (R = Me, Et, Pr^i, CH_2Bu^t, *cyclo*-C_6H_{11}; dmgH = dimethylglyoximate; py = pyridine) is thought to involve initial removal of pyridine by protonation followed by stepwise protonation of both dimethylglyoximate ligands to give $[RCo(dmgH_2)_2Cl]Cl$ which then slowly eliminates alkane to finally yield $[Co(dmgH_2)Cl_2]$. However when R = benzyl the organic product is 1,2-diphenylethane rather than toluene indicating that in this case homolysis of the cobalt-carbon bond occurs (ref. 156). If the protonation is effected by trifluoroacetic acid (R = Me, CH_2Cl, $CHCl_2$, Et, Pr^i, Bu^n, $CH_2CH_2CH=CH_2$, $CH_2CHMeCH=CH_2$) it is proposed that the dimethylglyoximate ligands protonate first followed by removal of pyridine and then loss of alkane to finally form *cis*-$[Co(dmgH)(O_2CCF_3)_2]$ (ref. 157). While the difference in the final cobalt-containing product may reflect the ability of trifluoroacetate to act as a bidentate ligand, it is not clear whether the different order of protonation is real because of the different acids used. Protonation of $[RO(CH_2)_2Co(dmgH)_2(OH_2)]$ (R = H, Et, Ph) takes a different course in that ethylene is produced with the final cobalt product being $[Co(dmgH)_2(OH_2)_2]^+$. Kinetic evidence was obtained for the existence of a cationic intermediate which is proposed to be either [78] or [79] with the latter being preferred. For R = Et or Ph the kinetics show an induction period followed by a rate of decomposition identical to that for R = H. This is interpreted to indicate that these complexes are initially hydrolyzed to $[HO(CH_2)_2Co(dmgH)_2(OH_2)]$ prior to loss of the alkyl group (ref. 158). The decomposition of $[PhCHMeCo(dmgH)_2(OH_2)]$ in aqueous methanol has been studied under acidic and neutral conditions. The organic products were

[78]



[79]

identified as 1,3-diphenylbutane, meso- and rac-2,3-diphenylbutane, styrene and ethylidene-4-(α-phenylethyl)cyclohexa-2,5-diene indicating that decomposition occurs by both homolysis of the cobalt-carbon bond (72%) and by β-elimination (27%). The intermediacy of $[Co(dmgH)_2]$ was demonstrated (Co^{2+}_{aq} is the final cobalt product) and it is concluded that previous reports of exclusive β-elimination was due to the special nature of the conditions used there (ref. 159). The base induced decomposition of alkylcobaloximes, -cobalamins and -cobinamides generates both alkenes and alkanes by β-elimination and homolysis respectively. These paths are competitive with the former tending to predominate at higher pH. The proportion of alkene is increased in the presence of oxygen presumably because the alkyl radicals produced by homolysis are intercepted by O_2 to form alkylperoxy radicals which can decompose to alkenes (ref. 160). Oxygen-17 NMR has been used to follow the course of hydrolysis of $[(MeC(^{17}O)OC_2H_4)Co(dmgH)_2py]$ to $[(HOC_2H_4)Co(dmgH)_2py]$ and $[(HO)Co(dmgH)_2py]$. While this reaction appears to follow a $B_{AL}1$ mechanism, $[HC(^{17}O)CH_2Co(dmgH)_2py]$ undergoes a hydration-dehydration sequence to yield the unlabelled formylmethyl complex (ref. 161).

The reaction of vitamin B_{12s} with alkyl bromides (RBr, R = $CH_2CMe_2CO_2Et$, $CH_2CMe(CO_2Et)_2$, $CH_2CMe(COSEt)CO_2Et$, $CH_2CMe(COSEt)CO_2Et$, $CH_2CH(CO_2Et)_2$) produces alkylcobalamins the first three of which exist predominantly in the base-on form in neutral solution. Photolysis under anaerobic conditions leads to very slow decomposition but in the presence of oxygen this process is greatly accelerated. Aerobic decomposition in neutral solution is also fast and occurs by sterically induced cobalt-carbon bond homolysis except in the last case where β-elimination occurs. Rearrangement of the alkyl groups on cleavage occurs only upon borohydride reduction, a process which is faster than homolysis. The results thus indicate that the radicals produced in homolytic decomposition do not rearrange so that if rearrangement occurs in the organic product, decomposition must involve carbanion formation. This is taken to support the proposal of a carbanionic mechanism for the rearrangements seen in the methylmalonyl-CoA mutase reaction (ref. 162). Similar results have been observed for the photodealkylation of [RCo(chel)X] (R = Me, Et; chel = N,N'-bis(salicylidene)ethylenediamino(salen), N,N'-bis(salicylidene)-o-phenanthrolino(salophen); X = H_2O, py, PPh_3). Thus under anaerobic decomposition the quantum yield is low due to rapid recombination of the radicals but in the presence of oxygen or other radical scavengers it increases since recombination is now prevented (ref. 163). Photolysis of hex-5-en-1-yl(pyridine)cobaloxime and substituted derivatives thereof in carbon tetrachloride provides a synthetic route to trichloroethylcyclopentanes. If carried out in the presence of sulfur dioxide, trichloroethylsulfolanes are produced (ref. 164). In related work, photolysis of mixtures of $[RCo(dmgH)_2py]$ (R = alkyl or substituted alkyl) and trichloromethanesulfonyl chloride in dichloromethane yields the corresponding alkane sulfonyl chlorides and in most cases significant amounts of hexachloroethane. The absence of $RCCl_3$ implies that the trichloromethyl radical is incapable of displacing alkyl radicals from cobalt. Initial homolysis of the cobalt-carbon bond is proposed with the alkyl radical thus formed attacking sulfur (ref. 165). Finally the use of spin traps such as nitrosodurene to study the course of the photolysis of alkylcobaloximes and related compounds has been reported. These results indicate that in addition to the expected alkyl radicals hydrogen radicals originating from the chelated hydroxyl hydrogens of the dimethylglyoximate ligand are produced (ref. 166).

The cobalt(II) species $[Co(dmgH)_2L]$ (L = py, PPh_3) reacts with tetrahalomethanes to yield $[XCo(dmgH)_2L]$ and $[RCo(dmgH)_2L]$ (R = CCl_3; X = Cl, Br. R = CBr_3; X = H, Br). Trapping experiments with 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy indicate that halogen atom abstraction from RX occurs in the initial slow step with the alkyl radical thus produced rapidly reacting with a second molecule of $[Co(dmgH)_2L]$ (ref. 167). The anion $[Co(dmgH)_2]^-$ reacts with 2-(allyloxy)ethyl halides and tosylates to produce $[(tetrahydro\text{-}3\text{-}furanyl)methylCo(dmgH)_2]$. The cyclization of the organic moiety in the course of the reaction is taken to indicate that the initial step is electron transfer to the alkyl halide to give a radical anion which can then lose halide ion followed by cyclization of the resulting organic radical before recombination with the $[Co(dmgH)_2]$ moiety (ref. 168). On the other hand, $[Co(salen)]^-$ causes dimerization of methyl pyruvate to dimethyl 2,3-dimethyltartrate. Initial formation of a cobalt-carbon bond to the pyruvate moiety followed by homolysis and coupling of the organic radicals is proposed (ref. 169). While low yields were generally observed on the attempted synthesis of arylcobaloximes from aryl bromides and $[Co(dmgH)_2py]^-$ (ref. 170), this cobaloxime when generated from $[NCCH_2CH_2Co(dmgH)_2py]$ by treatment with potassium *tert*-butoxide in dimethylsulfoxide (DMSO) reacts with a variety of alkyl halides (RX: X = I; R = Me, CH_2I, $CH_2CMeR'R''$ (R' = R'' = CO_2Et, CO_2Bu^t, CO_2CH_2Ph. R' = CO_2Et; R'' = $COSBu^n$). X = Br; R = $PhCH_2$, $PhC(O)CH_2$, *cyclo*-C_6H_{11}. X = tosylate, mesylate; R = $CH_2CMe(CO_2CH_2Ph)_2$) to give alkyl(pyridine)cobaloximes. It is proposed as a facile route to base-sensitive complexes of this type (ref. 171). A second route to very similar alkyl cobaloximes involves reaction of $[Co(dmgH)_2py_2]$ generated *in situ* with alkyl bromides and iodides in benzene in the presence of powdered zinc. The reaction is considered to occur *via* Scheme XVIII (ref. (172).

$$[Co(dmgH)_2(py)_2] \xrightarrow{RX} [XCo(dmgH)_2py] + R$$

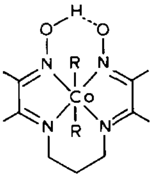
$$[XCo(dmgH)_2(py)] \xrightarrow{Zn} [Co(dmgH)_2(py)_2]$$

$$[Co(dmgH)_2(py)_2] + R\cdot \longrightarrow [RCo(dmgH)_2py]$$

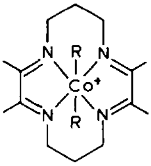
Scheme XVIII

Thermodynamic parameters for the binding of a sixth ligand to $[RCo(L_4)]$ (R = CF_3, Me; L_4 = dianion of N,N'-ethylenebis(acetylacetonimine)(BAE) or its trifluoromethyl analog (F_3BAE). R = Ph; L_4 = BAE. R = Me, $CHCl_2$; L_4 = salen) have been measured where the added ligand is py, THF, N,N'-dimethylacetamide (DMA) or tetrahydrothiophene (THT). The binding is enhanced by electronegative R groups and is decreased if R is bulky since in this case, steric pressure displaces the equatorial ligand towards the vacant site. A cis effect on the binding is also seen with enhancement by increased electronegativity of L_4 (ref. 173). The pK_a's of the carbonyl ligand in $[(HO_2CCHR)Co(dmgH)_2(B)]$ (R = H, Me; B = axial base) correlate well with those of substituted acetic and propionic acids implying a substantial β-effect which appears as an apparent extreme donation of electron density to the carbonyl carbon. This is considered to arise from hyperconjugation rather than from neighboring group participation (ref. 174). The structures of $[MeCo(dmgH)_2L]$ (L = PMe_3, Pcy_3) have been determined and the cobalt-methyl bond lengths are found to be essentially equal. The equatorial ligands are nearly planar but are bent somewhat away from the phosphine ligand. This is more pronounced for the tricyclohexylphosphine complex which also shows a very long cobalt-phosphorus bond. The rate of replacement of tricyclohexylphosphine by pyridine is rapid due to the considerable steric interaction of the bulky phosphine with the equatorial ligands (ref. 175). Kinetic and equilibrium measurements have been made on the decomposition of $[(PhCHMe)Co(dmgH)_2L]$ (L = py, imidazole, p-RC_5H_4N(R = Me, NH_2, CN)) to styrene, $[Co(dmgH)_2L]$ and hydrogen in order to obtain cobalt-carbon bond strength data. The bond dissociation energies increase with increased basicity of L which is consistent with initial homolysis of the bond. The observation of styrene as a product is explained by a β-hydride abstraction from the α-styryl radical within the solvent cage (ref. 176). A companion study on the thermal decomposition of [RCo(saloph)py] (saloph = N,N'-bis(salicylidene)-o-phenylenediamine. R = Pr^n, Pr^i, CH_2Bu^t, CH_2Ph) in pyridine led to the same conclusion concerning the mechanism. In addition the cobalt-carbon bond dissociation energy was low for bulky alkyl groups indicating a steric effect on the strength of this bond (ref. 177).

The first example of a charge-transfer complex between an electrophile (here tetracyanoethylene (TCNE)) and methylcobalamin prior to cleavage of the methyl group has been reported. Methyl transfer to TCNE occurs in the presence of a proton donor but it was not confirmed that the initial charge-transfer complex lay on the reaction coordinate for demethylation (ref. 178). Demethylation can also be effected by $[AuCl_4]^-$, a process which involves reversible association of $[AuCl_4]^-$ and methylcobalamin followed by electron transfer from cobalt to gold, within the encounter complex. Subsequent aquation of cobalt occurs with release of gold and a methyl radical which then abstracts chlorine from $[AuCl_4]^-$ (ref. 179). Complexes [80] and [81] (R = Me) rapidly methylate Cd^{2+} and Zn^{2+} in acetonitrile and Pb^{2+}, $PbMe_2^{2+}$ and $PbMe_3^+$ in isopropanol. In the former system $MeCd^+$ and $MeZn^+$ are detected (refs. 180, 181). The reaction of vitamin B_{12r} with the radicals $\cdot CH_2CMe_2OH$, $\cdot CMe_2OH$, $\cdot CH_2CHO$ and $\cdot CH(OH)CH_2OH$ produced by pulse radiolysis initially



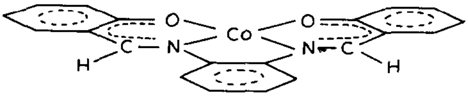
[80]



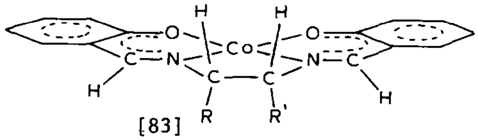
[81]

produce cobalt(III) alkyl complexes. That with R = CH_2CHO hydrolyzes to vitamin B_{12a} and acetaldehyde while those with R = CMe_2OH and $CH(OH)CH_2OH$ decompose heterolytically to vitamin B_{12s} (ref. 182).

Complexes [82] and [83] (R = R' = H, Me, Ph. R = H; R' = Me, Ph. RR' = $-(CH_2)_4-$) prepared in optically active, racemic or meso forms have been reduced



[82]



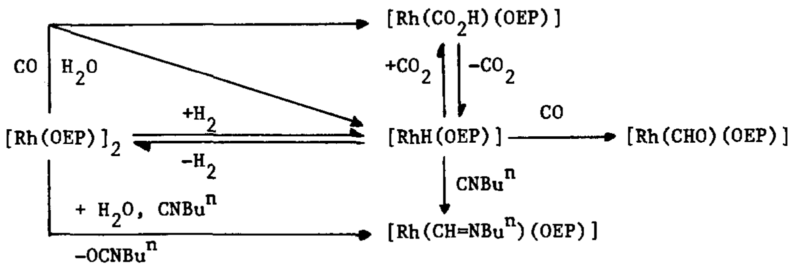
[83]

electrolytically and reacted with alkyl bromides (RBr: R = Pr^n, Bu^n, Bu^t). The corresponding alkyl cobalt complexes are formed from the first two but with the last decomposition occurred rapidly giving isobutene and hydrogen. Observed differences in the second order rate constants for the alkylation reactions are attributed to distortions of the reduced Co(I) species. The formation of the cobalt-carbon bond is thought to occur via an inner-sphere, alkyl-bridged electron transfer process (ref. 183).

A number of electrochemical studies of alkylcobalt macrocycles have appeared. Cyclic voltammograms of $[MeCo(dmgH)_2py]$ and related compounds in N,N'-dimethylformamide (DMF) show a reversible one-electron oxidation process under fast-scan conditions at -20° C. At higher temperatures or with slower scan rates the oxidized species decompose rapidly via solvent-assisted processes (ref. 184). In [MeCo(salen)] and related complexes of tri-and tetradentate Schiff-base ligands, variation in ligand substituents have small but noticeable effects on the electron density at cobalt. All but the salen complex react with methyltin trichloride with homolytic cleavage of the cobalt-carbon bond (ref 185). By contrast, methylcobalamin and $CoEB_{12}$ show two-electron oxidation processes giving CH_3^+ and cobalt-(III) species and a one-electron reduction which generates ethane. The data are interpreted to indicate that the reduction step involves addition of one electron to the $Co-CH_3$ σ^* orbital with the remaining chemistry occurring away from the electrode interface (ref. 186). Complexes [80], [81] and $[cpCoMe_2(PPh_3)]$ have been oxidized electrochemically in the presence of nucleophiles in an attempt to find a system for efficiently coupling alkyl groups with nucleophiles but no success was noted. Only low yields of ethane and methane were noted (ref. 187). Electron-capture (electrons generated by ^{60}Co γ-rays) by methylcobalamin at 77 K in D_2O/MeOD occurs in a π* orbital of the corrin ligand. On warming this electron migrates to a cobalt $d_{x^2-y^2}$ orbital presumably because of the considerable covalent character in the cobalt-carbon bond. Photolysis of the same system at 77 K gives the [Co^{II}, Me•] radical pair. A ligand-to-metal electron transfer is proposed to occur on photolysis with the electron now entering the d_{z^2} orbital to generate the alkyl radical (ref. 188).

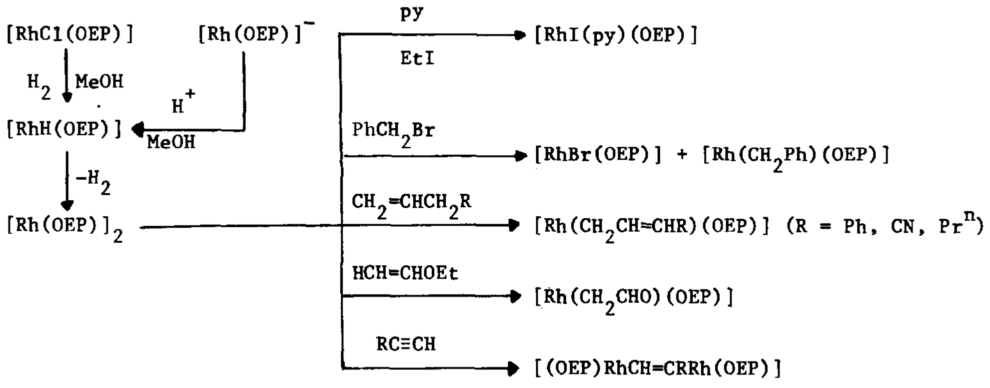
Carbon-13 NMR studies on [MeCo(salen)L] (L = H_2O, py, DMSO, CN^-, NH_3) show a downfield shift of the resonance for the methyl carbon with increased donor strength of L. The chemical shift is in the range found for carbanions which indicates the cobalt is formally Co(III) (ref 189). Further results have been reported for the solid state racemization of cobaloximes using [((S)-1-cyanoethyl)-Co(dmgH)$_2$py]. This undergoes a first order racemization on exposure to x-rays with one of the two independent molecules in the original unit cell converting to the (R) configuration. The driving force probably derives from the fact that the methyl group which moves is initially subjected to very severe intermolecular contacts (ref. 190).

What appears to be the first example of a thermodynamically favorable reaction of a metal hydride with an aldehyde is the reaction of [RhH(OEP)] with hydrogen and various aldehydes to give [Rh(CH(OH)R)(OEP)] (R = H, Me, Et, Ph). When R = Me this slowly converts in benzene solution to [(OEP)RhCHMeOCHMeRh(OEP)] with elimination of water followed by fragmentation to [Rh(C(O)Me)(OEP)] and [RhEt(OEP)] (ref. 191). Some chemistry of the dimer [Rh(OEP)]$_2$ is detailed in Scheme XIX (ref. 192).



Scheme XIX

Related chemistry is shown in Scheme XX (ref. 193). The complexes [EtRh(dmgH)$_2$py]

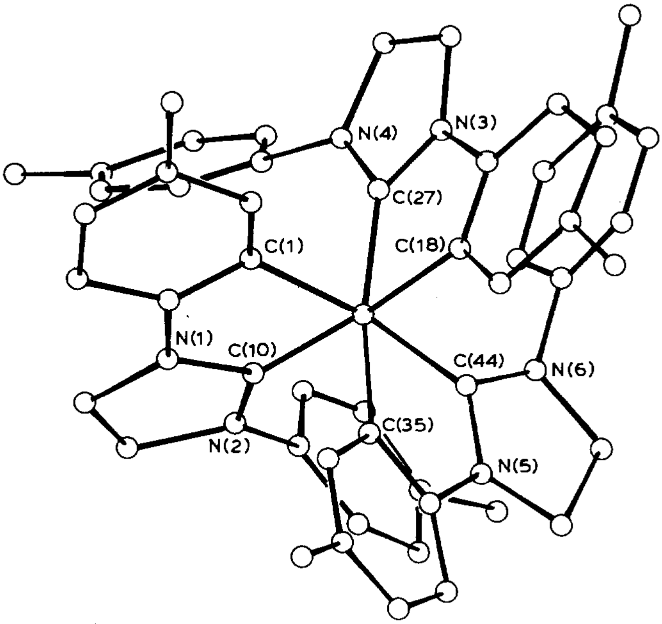


Scheme XX

and [RRh(salen)py] (R = Et, Bu^n) have been oxidized by bromine or cerium(IV) and the ESR spectra of the products measured. The results indicate the unpaired electron is largely localized on the metal in the 4d$_{x^2-y^2}$ orbital (ref. 194). Finally, [IrCl(CO)(OEP)] reacts with silver perchlorate in boiling benzene to give [Ir(OClO$_3$)(CO)(OEP)] which reacts with MX (M = H; X = BF$_4$. M = K; X = Br, CN) yielding [IrX(CO)(OEP)]. Also [IrMe(OEP)] adds axial ligands to give [IrMe(L)-(OEP)] (L = CO, CN$^-$, py, NH$_3$, N-methylimidazole (MeIm)). The chemical shift of the meso protons of the OEP ligand in these complexes correlates with the Ir(I)-Ir(III) redox potential (ref. 195).

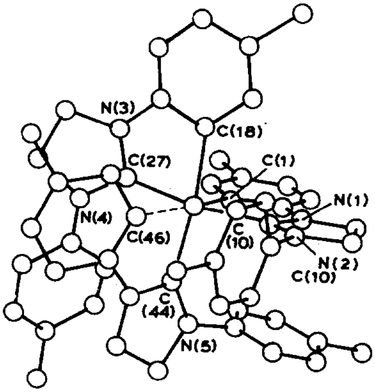
Metal Carbene Complexes

Reduction of [Co(acac)$_3$] with trimethylaluminum in o-terphenyl produces a slurry of finely-divided cobalt metal which on treatment with methanol or a mixture of carbon monoxide and hydrogen gives methane, ethane and propene as the major products indicating that surface carbene species may be generated (ref. 196). Carbene intermediates are also proposed to be formed in the conversion of methyl-benzoyloxy-α-diazopropionate to α-benzoyloxymethyl acrylate catalyzed by [Rh$_2$(O$_2$CMe)$_4$]. This is proposed as a general method for the preparation of cis-disubstituted enoates (ref. 197). Reaction of anhydrous rhodium(III) chloride with benzylmagnesium chloride yields toluene, 1,2-diphenylethane and stilbenes. Hydrolysis of the residue produces more toluene suggesting that this material contains carbene species which may have resulted from the α-disproportionation of benzylrhodium species formed in the initial reaction (ref. 198). An excess of the electron-rich olefin [=$\overline{\text{CN(p-tolyl)(CH}_2\text{)}_2\text{N}}$(p-tolyl)]$_2$ reacts with [IrCl(COD)]$_2$ in refluxing toluene to give [84] containing o-metallated carbene ligands. Reaction with hydrogen chloride cleaves one metallated tolyl group giving [85] (ref. 199).



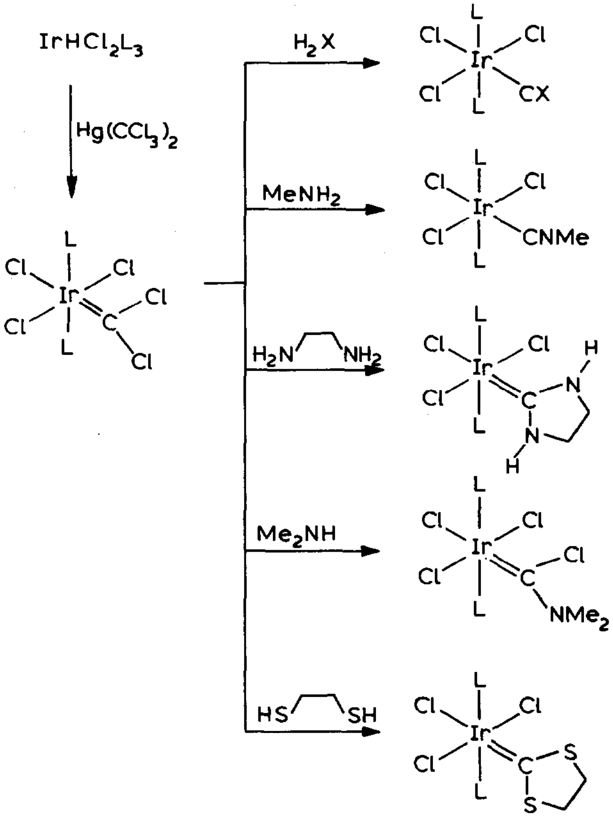
[84]

The dichlorocarbene complex $[Ir(=CCl_2)Cl_3L_2]$ (L = PPh_3) is formed when $[IrHCl_2L_2]$ is briefly refluxed with $[Hg(CCl_3)_2]$ in toluene. Further chemistry is outlined in



[85]

Scheme XXI ($L = PPh_3$; X = 0, S) (ref. 200).



Scheme XXI

Metal Isocyanide Complexes

A full paper describing the $[Co(H_2O)_6]Cl_2$-catalyzed substitution of isocyanide for carbonyl ligands in $[Fe(CO)_5]$ indicates that the system behaves somewhat differently from what was originally reported. In particular the existence of species such as $[(OC)_4Fe(\mu\text{-}CO)(\mu\text{-}RNC)CoCl_2(CNR)_{n-1}]$ (see J. Organometal. Chem., 230(1982) 99, Scheme XI) has been ruled out (ref. 201).

The complexes $[Rh_2(L_2)_4]X_2$ (L_2 = (1R, 2R)- or (1S, 2S)-diisocyanocyclohexane; X = BPh_4^-, PF_6^-, ClO_4^-, Cl^-) and $[Rh(CNR)_4]Cl$ (R = (R)- or (S)-CHMePh) have been synthesized from $[RhCl(COD)]_2$ by standard routes and their electronic and circular dichroism (CD) spectra measured. The dimers show evidence of metal-metal interaction which is thought to be inter- rather than intramolecular while the monomers show considerable oligomerization in aqueous acetonitrile (ref. 202). The chemical and electrochemical oxidation of a variety of mono- and binuclear rhodium isocyanide complexes is reported in a series of four papers. Photolysis (λ>550 nm) of $[Rh_2(br)_4]^{2+}$ (br = 1,3-diisocyanopropane) in the presence of *n*-butyl iodide yields $[Bu^nRh(br)_4RhI]^{2+}$ with the high quantum yield indicating a radical chain process. A mechanism is proposed wherein the photoexcited complex undergoes an electron-transfer with *n*-butyl iodide to form the radical anion of the alkyl iodide which subsequently fragments to butyl radical and iodide ion followed by combination with the oxidized complex (ref. 203). The kinetics of the oxidative addition of iodine to $[Rh(CNR)_4]^+$ and $[Rh(CNR)_2(PPh_3)_2]^+$ (R = Ph, mesityl) indicate that a two-step process is followed. Initial formation of 1:1, 2:1 or 1:2 adducts of iodine with the complexes depending on the ratio of reactants used is seen prior to the formation of the first oxidative adducts which may be the *cis*-diiodo species. The second step then produces the final *trans*-diiodo complexes. The observation of a linear free energy relationship between the rate constant for the first step and those for the oxidation of the Rh(I) complexes by $[Co(bipy)_3]^{3+}$ and $[Fe(ophen)_3]^{3+}$ suggests this step may involve electron transfer to iodine. Analogous results were found for the dimers $[Rh_2(br)_4]^{2+}$ and $[Rh_2(CNR)_4(DPM)_2]^{2+}$ (refs. 204, 205). Cyclic voltammetric measurements on $[Rh(CNR)_4]^+$ (R = Bu^t, *cyclo*-C_6H_{11}, mesityl, *p*-anisyl) and $[Rh_2(CNPh)_4(DPM)_2]^{2+}$ show evidence for irreversible oxidation. In the monomers the *p*-anisyl compound shows three oxidation waves implying the presence of oligomers in solution. The other three show only one. Since the anodic peak potentials correlate with the logarithm of the rate constants for the oxidation by $[Fe(ophen)_3]^{3+}$, these values provide a relative scale of single electrode potentials for the complexes (ref. 206).

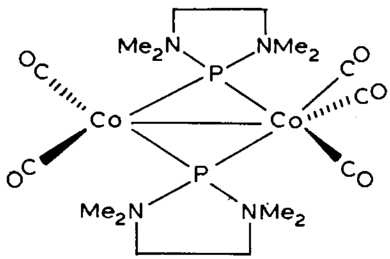
The polymeric complex $[RhCl(CO)(L_2)]_n$ (L_2 = 1,4-diisocyanobenzene), prepared from $[RhCl(CO)_2]_2$ shows evidence for weak metal-metal interaction between neighboring polymer chains and is a modest catalyst for the hydrogenation of hex-1-ene under mild conditions. Isomerization of substrate to *cis*- and *trans*-hex-2-ene also occurs. The catalysis is enhanced by brief irradiation but under continuous irradiation ($\lambda \geq 350$ nm) isomerization is enhanced at the expense of hydrogenation possibly because this labilizes the presumed intermediate olefin complex. No isomerization occurs in the absence of hydrogen (ref. 207). Related polymers $[M(L_2)_2Cl]_n$ (M = Rh, Ir; L_2 = *p*,*p*'-diisocyanobiphenyl, *m*-diisocyanobenzene, 2,4-diisocyanotoluene, bis(*p*-isocyanophenyl)methane, 1,5-diisocyanonaphthalene) are prepared from $[RhCl(CO)_2]_2$ and $[IrCl(COD)]_2$. Weak metal-metal interaction between polymer units exists in the rhodium complexes but not in the iridium analogs (ref. 208). The same synthetic routes have been employed to prepare $[ML_4]Cl$ (M = Rh, Ir; L = bromotetracarbonyl(*p*,*p*'-diisocyanobiphenyl)manganese) (ref. 209). Pendant isocyanomethyl groups attached to phenyl groups of polystyrene have been used to anchor $\{Rh(CO)_2Cl\}$ moieties to provide a supported catalyst for cyclohexene hydrogenation (ref. 210).

Fluorescence and phosphorescence spectra have been measured for $[Rh_2L_4(DPM)_2](PF_6)_2$ (L = CNPh, $CNBu^t$) and $[Rh_2(CNBu^n)_4(DPM)_2](BPh_4)_2$. The phosphorescence originates in a manifold split by spin-orbit coupling but is only 20% of that observed for the corresponding monomers. The insensitivity of the spectra to changing the ligand from DPM to DAM indicates the LUMO is primarily metal-centered in contrast to the monomers where it has considerable ligand character (ref. 211). The XPES spectrum of $[Rh(CNBu^t)_4]PF_6$ shows N_{1s} shake-up satellites while that of $[Rh(CNBu^t)_2(PPh_3)_2]PF_6$ does not. The satellites are thought to arise from $d \rightarrow \pi^*$ transitions (ref. 212). The formation of highly substituted derivatives of $[Ir_4(CO)_{12}]$, e.g. $[Ir_4(CO)_7(CNBu^t)_5]$ and $[Ir_4(CO)_6(CNBu^t)_6]$ is catalyzed by palladium-on-carbon in refluxing toluene (ref. 213).

Metal Carbonyl Complexes and Related Compounds

a) Homonuclear Carbonyl Compounds

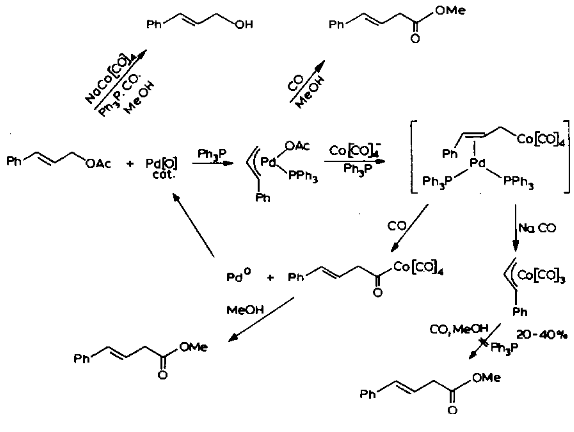
Displacement of fluoride in $F\overline{PNMe_2(CH_2)_2N}Me_2$ by $[Co(CO)_4]^-$ in THF affords [86]



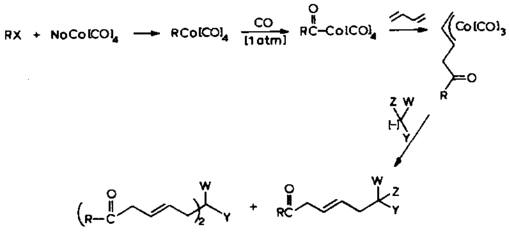
[86]

containing bridging phosphenium ions. Since the cobalt-phosphorus distances involving the $\{Co(CO)_2\}$ unit are significantly shorter than the other two, the complex is considered to be formally a combination of $\{(OC)_2\overset{+}{C}oP_2\}$ and $\{\bar{C}o(CO)_3\}$ units with the unfavorable polarity of the Co-Co bond offset by the asymmetric bridging of the phosphenium ions. This proposal has been supported by molecular orbital calculations (ref. 214).

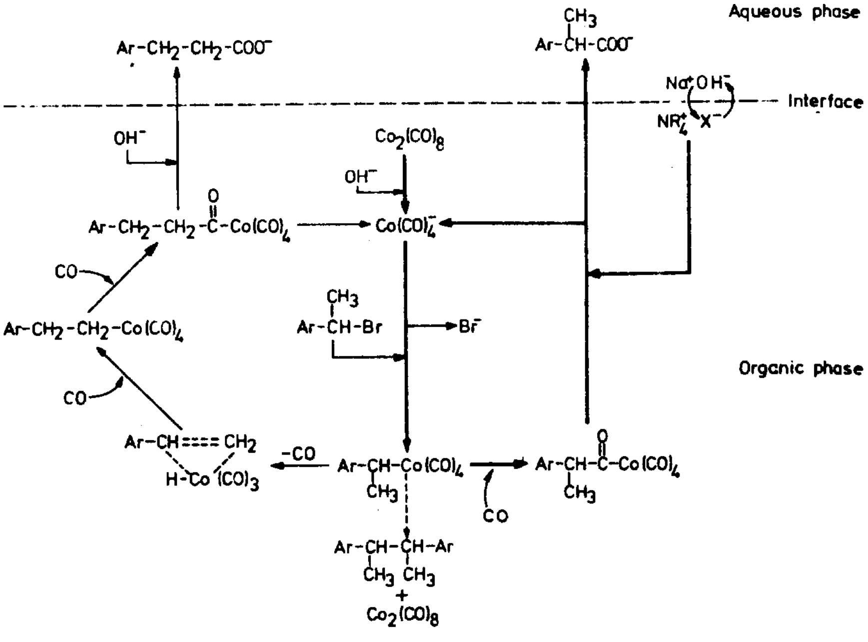
Carboxymethylation of cinnamyl acetate is catalyzed by a mixture of $Na[Co(CO)_4]$, $[(\eta^3\text{-}1\text{-}PhC_3H_4)PdCl]_2$ and triphenylphosphine under carbon monoxide. The process is thought to involve a Pd(0) species as outlined in Scheme XXII (ref. 215). A one-pot, cobalt-mediated, 1,4-acylation/alkylation of 1,3-dienes is shown in Scheme XXIII (ref. 216). The carbonylation of secondary benzyl halides is catalyzed by $[Co(CO)_4]^-$ under phase-transfer conditions. Monocarbonylation is favored in the system $NaOH(40\text{-}50\%)/H_2O/ROH(R = Bu^n, Am^t)/R'_4N^+/CO(1\ atm)$ where the tetraalkylammonium ion facilitates attack of hydroxide on the acyl complex making this step faster than isomerization (Scheme XXIV). The same system with a lower hydroxide concentration and higher carbon monoxide pressure results in double carbonylation. In this case, enolization is now favored since hydroxide attack is now not as fast



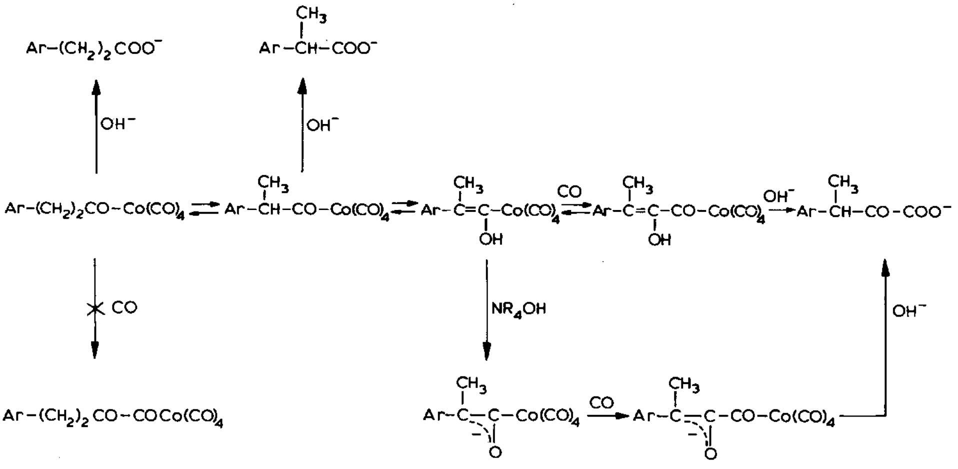
Scheme XXII



Scheme XXIII

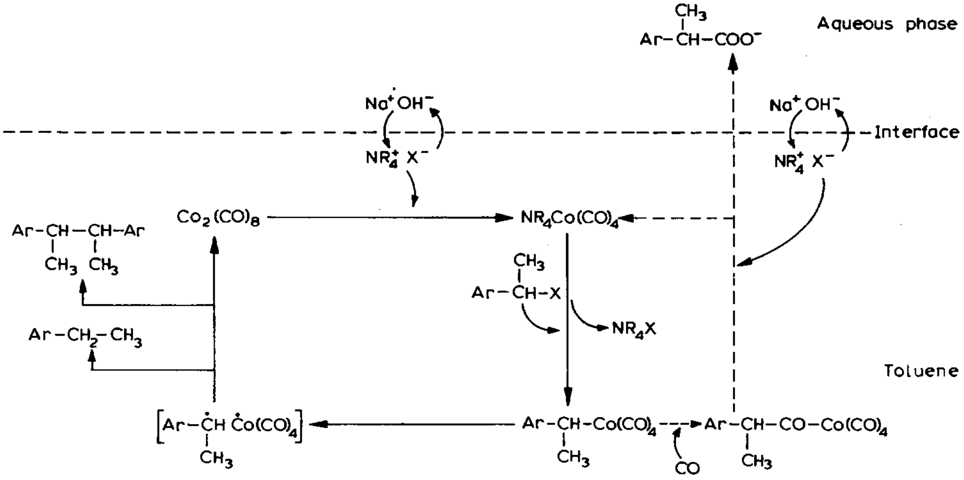


Scheme XXIV



Scheme XXV

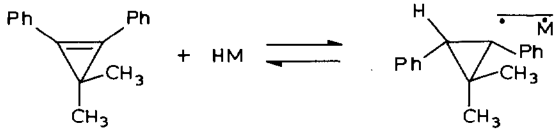
(Scheme XXV). With low hydroxide concentration and an aromatic solvent, coupling is favored since the hydroxide concentration in the organic phase is now quite low (Scheme XXVI) (ref. 217). Another phase-transfer system, $PhCH_2Et_3NCl/NaOH/H_2O$/-$C_6H_6/Na[Co(CO)_4]$, effects the conversion α-chloromethylnaphthalene to α-naphthylacetic acid (ref. 218). Reaction of $[PPN][Co(CO)_4]$ (PPN = bis(triphenylphosphine)iminium cation) with trihetero carbenium ions such as 2-dimethylamino-1,3-dithioanylium ion results in simple cation metathesis (ref. 219). The infrared and electronic spectra of $[C_5H_5NH][Co(CO)_4]$ in butanone and pyridine solutions are consistent with the existence of contact ion-pairs. Addition of water produces



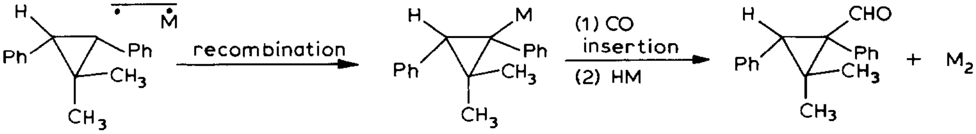
Scheme XXVI

solvent-separated ion pairs. The stability constant for the former ion-pair was determined (ref. 220). A new version of the CNDO method using a separation of the metal s, p and d orbitals has been applied to $[Co(CO)_4]^-$ and $[Co(N_2)_4]^-$ (ref. 221).

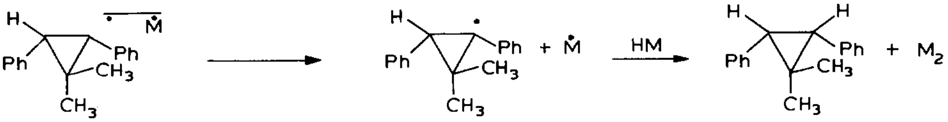
The possibility of Lewis acid-promoted migration of hydride to coordinated carbon monoxide in $[HCo(CO)_4]$ has been explored but no formyl species were detected. Both boron trichloride and aluminum tribromide simply scavenge the $[Co_2(CO)_8]$ formed in the decomposition of $[HCo(CO)_4]$ and no adducts with $[HCo(CO)_4]$ were detected. A similar lack of success with $[Ir(CO)_2H_2(PPh_3)_2]BPh_4$ was noted (ref. 222). Several studies on the reaction of $[HCo(CO)_4]$ with olefins have been described. In most instances radical intermediates have been detected or implicated. The rate of reaction of $[HCo(CO)_4]$ and the corresponding deuteride with aromatic olefins such as ethylidene fluorene and bifluorenylidene show significant differences in the kinetic isotope effects implying that the extent of hydrogen transfer in the transition state leading to the radical intermediates is markedly dependent on the nature of the olefin (ref. 223). In the reaction with the cyclopropenes PhC=CPhCRR' (R = R' = H, Me, CO_2Me. R = H; R' = CO_2Me) and $Pr^nC{=}CPr^nCHCO_2Me$, the observed partitioning between hydroformylation and hydrogenation was explained by differences in the rates of reaction within the radical pair



(a) Hydroformylation



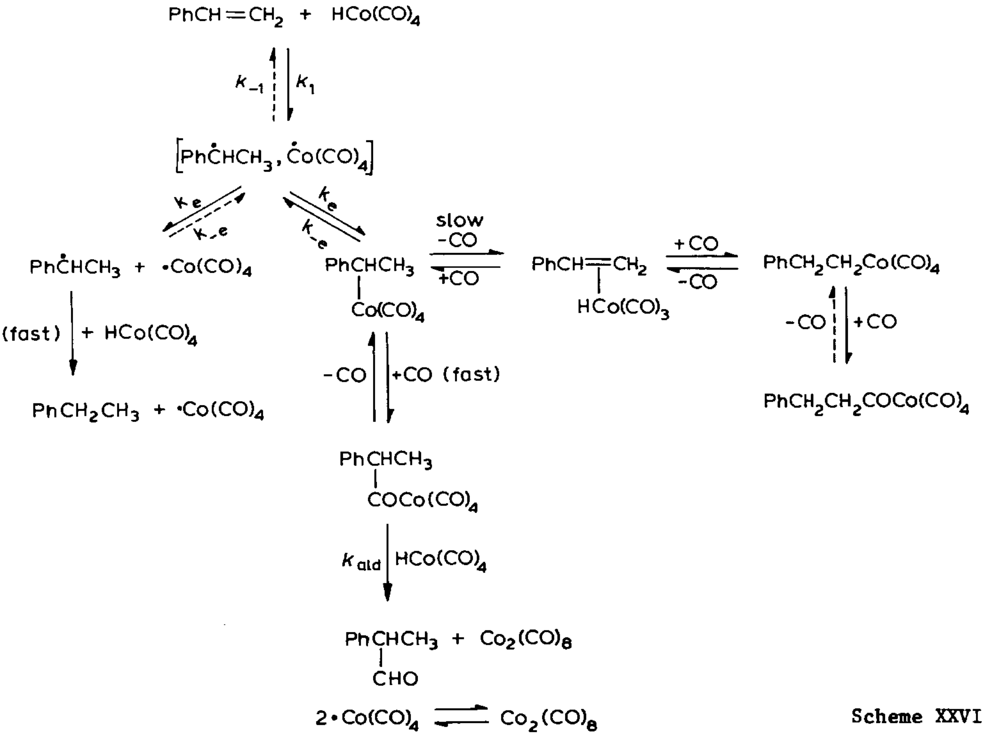
(b) Hydrogenation



(M = $Co(CO)_4$, $Mn(CO)_5$)

Scheme XXVII

and the rates of escape from it as shown in Scheme XXVII. With α-methylstyrene the observation of some hydroformylation rather than exclusive hydrogenation was attributed to a more pyramidal carbon at the radical center which would favor recombination and carbonyl insertion within the radical pair (ref. 224). With 1,1-diphenylethylene at -78° C, the radical pair $[Ph_2\dot{C}Me][\cdot Co(CO)_4]$ has been detected by CIDNP. Reaction with more $[HCo(CO)_4]$ leads to hydrogen abstraction giving 1,1-diphenylethane with $[Co_2(CO)_8]$ forming by coupling of the $[\cdot Co(CO)_4]$ radicals. Since a mixture of bromodiphenylmethane and $[Co_2(CO)_8]$ reacts with $[HCo(CO)_4]$ to give only diphenylmethane it appears that the diphenylmethyl radical abstracts hydrogen from $[HCo(CO)_4]$ faster than it can dimerize (ref. 225). The kinetics of the hydrogenation of styrene by $[HCo(CO)_4]$ have been rationalized in terms of electronic and steric effects in the radical pair mechanism (ref. 226). When this reaction is run under carbon monoxide it is proposed to occur as shown in Scheme XXVIII. The initial products are ethylbenzene and $[PhCHMeC(O)Co(CO)_4]$. The

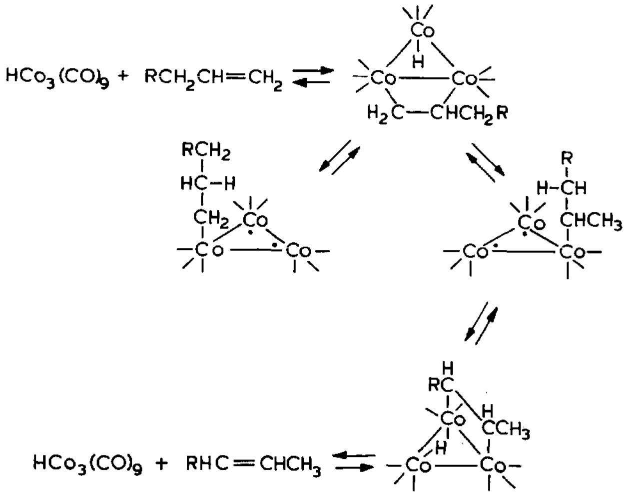


Scheme XXVIII

acyl more slowly decomposes as shown on the right side of the Scheme and if styrene is not present in large excess, the secondary process to produce PhCHMeCHO also is seen. A large inverse H/D isotope effect is seen for the steps leading to both ethylbenzene and the acyl complex (ref. 227).

Triphenylmethanol is reduced to triphenylmethane by [HCo(CO)$_4$] in a reaction showing second order kinetics. The increase in rate with increased solvent polarity implicates the participation of the triphenylmethyl carbonium ion. With triphenylmethyl tetrafluoroborate, the intermediate formation of [Ph$_3$CCo(CO)$_4$] indicates that direct abstraction of hydrogen from [HCo(CO)$_4$] does not occur (ref. 228).

It has previously been shown that the cluster [HCo$_3$(CO)$_9$] is present in solutions containing mixtures of [HCo(CO)$_4$] and [Co$_2$(CO)$_8$], and now studies at -35° C show that this cluster effects the isomerization of neat n-hexenes as shown in Scheme XXIX. The production of significant amounts of (Z)-hex-2-ene from hex-1-ene in the early stages of the reaction is indicative of kinetic control of the course of the isomerization. The results are interpreted to suggest that [HCo$_3$(CO)$_9$] is the active species in olefin isomerizations promoted by [HCo(CO)$_4$] and [Co$_2$(CO)$_8$] (ref. 229).



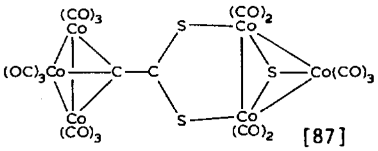
Scheme XXIX

A number of catalyst systems based on [HCo(CO)$_4$] has been reported including ones for the conversion of alcohols and vinyl ethers to acetals (ref. 230) and those modified by trialkylphosphines for olefin hydroformylation (refs. 231, 232).

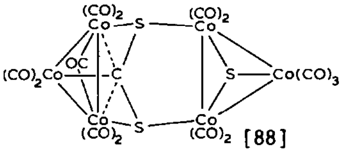
Photolysis of [HCo(CO)$_4$] at 254 nm in ^{13}CO matrices shows that the frequency of loss of a carbonyl ligand is approximately eight times that for cobalt-hydrogen bond homolysis. It was further determined that the 227 nm band in the electronic spectrum is a ligand-to-metal charge transfer band involving hydride as the ligand (ref. 233). In a companion study, photolysis in an Ar/H$_2$ matrix yielded [H$_3$Co(CO)$_3$] presumably via a thermal oxidative addition of dihydrogen to the photolytically produced [HCo(CO)$_3$] moiety. Apparently the [·Co(CO)$_4$] also formed is unreactive towards dihydrogen (ref. 234).

Molecular orbital calculations on the hydroxycarbyne $[(OC)_3Co{\equiv}COH]$ suggest it to be slightly more stable than the corresponding formyl complex but ca 15 kcal/mol less stable than $[HCo(CO)_4]$. Thus hydroxycarbynes appear to be viable intermediates to be considered in carbon monoxide hydrogenation mechanisms (ref. 235). Two other computational studies on $[HCo(CO)_4]$ have been reported (refs. 236, 237).

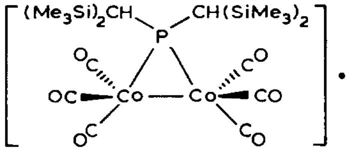
A full report of the structures of two products formed from carbon disulfide and $[Co_2(CO)_8]$ ([87] and [88]) also includes a partial analysis of the infrared spectrum of [88]. Comparison with the spectrum of the analog prepared from $^{13}CS_2$ permitted identification of bands due to the Co_3CS_2 subcluster. The observation of only one half of the expected carbonyl bands was attributed to the approximate cancellation of the overall dipole moment change for the cluster for several of the stretching modes (ref. 238). Reaction of $[(\eta^5\text{-}C_5R_5)_2V]$ (R_5 = H_4Bu^t, H_4CO_2Me) with $[Co_2(CO)_8]$ initially yields $[(\eta^5\text{-}C_5R_5)_2VCo(CO)_4]$ which reacts further to give $[(\eta^5\text{-}C_5R_5)_2V(CO)_2][Co(CO)_4]$ and $[(\eta^5\text{-}C_5R_5)_2VOCCo_3(CO)_9]$. When R_5 = Me_5 or Me_4Et the products are $[(\eta^5\text{-}C_5R_5)_2V(CO)_2][Co(CO)_4]$ and $[Co_4(CO)_{12}]$ (ref. 239). The unusual radical [89] is prepared from the phosphinyl radical $\{[(Me_3Si)_2CH]_2P\}^{\bullet}$ and $[Co_2(CO)_8]$. The ESR spectrum indicates delocalization of the unpaired electron onto the Co_2 unit (refs. 240, 241). Two binuclear cobalt complexes related to the rhodium A-frame species mentioned earlier are [90] and [91]. The first is formed from $[Co_2(CO)_8]$ and $MeN(P(OMe)_2)_2$ and is unusual in that one cobalt atom adopts a trigonal bipyrimidal coordination while the other is square pyramidal (ref. 242).



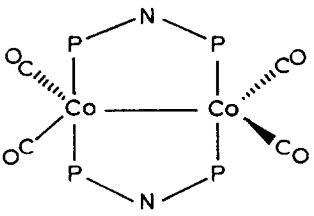
[87]

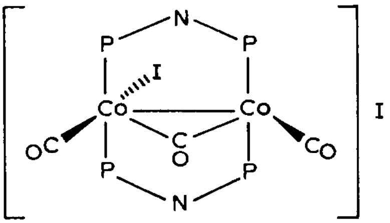


[88]



[89]





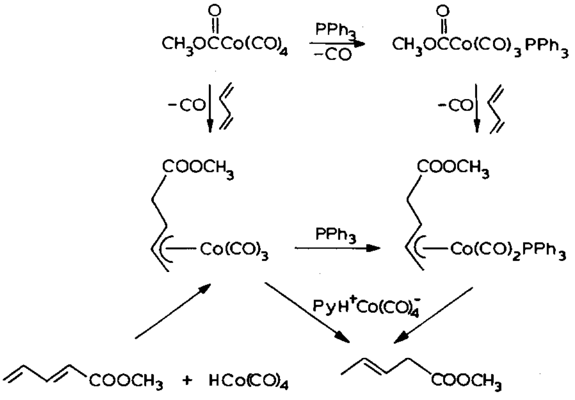
[90]

[91]

The second results when $[Co_2(CO)_6(DPM)]$ reacts with iodine in the presence of DPM. Refluxing $[Co_2(CO)_6(DPM)]$ in benzene converts it to $[Co_4(CO)_8(DPM)_2]$ while at 100° C under hydrogen pressure $[Co_2(CO)_4(\mu\text{-}DPM)(\mu\text{-}H)(\mu\text{-}PPh_2)]$ is formed. Both could be reconverted to $[Co_2(CO)_6(DPM)]$ at 100° C under carbon monoxide pressure. The hydride complex reacts with diphenylacetylene to give $[Co_2(CO)_4(C_2Ph_2)(DPM)]$ (ref. 243). The phospha-alkyne $:P{\equiv}CBu^t$ behaves as an acetylene on reaction with $[Co_2(CO)_8]$. The product is $[Co_2(CO)_6(\mu\text{-}PCBu^t)]$ in which the lone pair on phosphorus can coordinate to another metal atom. Thus reaction with $[W(CO)_5(THF)]$ yields $[Co_2(CO)_6(\mu\text{-}Bu^tCPW(CO)_5)]$ (ref. 244). Photolysis of $[(\eta^5\text{-}C_5H_4R)Co(CO)_2]$ (R = H, Me) at 0° C under a nitrogen purge yields a trimer having the structure $[(\eta^5\text{-}C_5H_4R)_3Co_3(\mu\text{-}CO)_2(\mu_3\text{-}CO)]$ in the solid. In solution the infrared spectrum shows two doubly-bridging and one terminal carbonyl group (ref. 245). Detailed studies of the reaction of $[Co_2(CO)_8]$ with sodium amalgam under various conditions suggest that this method of generating $[Co(CO)_4]^-$ in anhydrous solution has considerable drawbacks. Thus reaction in ether under carbon monoxide initially yields mainly $[Co_3(CO)_{10}]^-$ and some $[Hg(Co(CO)_4)_3]^-$. As the reaction proceeds the concentrations of these two species grow and small amounts of $[Co(CO)_4]^-$ appear. The final solution contains $[Co(CO)_4]^-$ but also significant quantities of $[Hg(Co(CO)_4)_3]^-$. If halide is present the mercury-containing species appears to be $[Hg(Co(CO)_4)_2X]^-$ (X = Cl, Br) (ref. 246). Further attempts to discover systems in which coordinated carbonyl groups can be reduced to hydrocarbons have focused on a number of polynuclear, cobalt-containing carbonyl complexes. Protonation of $[Co_2(CO)_8]$ with trifluoromethanesulfonic acid gave only hydrogen and carbon monoxide however with the clusters $[Co_4(CO)_{12}]$, $[FeCo_3(CO)_{12}]^-$, $[M_3Co(CO)_{13}]^-$ (M = Ru, Fe) methane was generated with the yield increasing in the order listed. This is attributed to the greater stability of the Fe_3 and Ru_3 clusters in acid. Small yields of methane were also seen on protonation of $[Co_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{16}]$. Thus it appears that at least four metal atoms must be present in the cluster in order to generate methane from coordinated carbon monoxide (ref. 247). Oxidation of $[Co_2(CO)_8]$ by dioxygen in hydrocarbon solvents gives cobalt(II) carbonate and carbon monoxide while in alcohols Co^{2+} and $[Co(CO)_4]^-$ form (ref. 248).

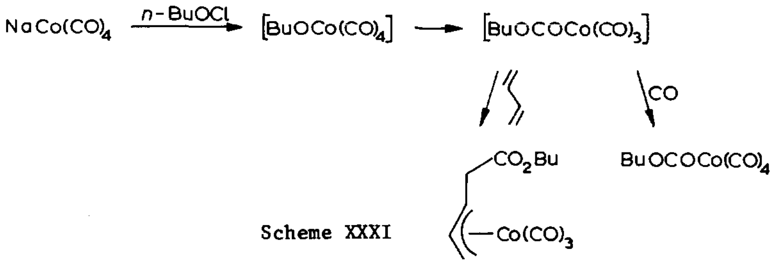
The use of $[Co_2(CO)_6(PPh_3)_2]$ and related complexes as catalysts for the hydrogenation of polynuclear aromatics has been reported. Under water-gas-shift conditions a 3% conversion of anthracene to 9,10-dihydroanthracene was seen. Using a carbon monoxide/hydrogen (syngas) mixture the heterocyclic rings of 7,8 benzoquinoline, phenanthridine, acridine and quinoline were hydrogenated in 8, 21, 100 and 70% yields respectively (ref. 249). The addition of diphosphines such as diphos, cis-1,2-bis(diphenylphosphino)ethylene (vdiphos) or 1,4-bis(diphenylphosphino)-butane (dppb) to $[Co_2(CO)_8]$ gives olefin hydroformylation catalysts significantly less active than those with monophosphines, but the isomerization usually observed is almost completely suppressed (ref. 250). Under water-gas-shift conditions the same systems convert methylacrylate to dimethyl-4-oxopimelate at low temperatures while at elevated temperature catalytic dimerization to 1,3-bis(methoxycarbonyl)-1-butene and dimethyl-2-methylglutarate is observed (ref. 251). Hydroformylation of 3,3,3-trifluoropropene catalyzed by $[Co_2(CO)_8]$ and $[Rh_6(CO)_{16}]$ occurs in 95% yield with the former giving predominantly $CF_3CH_2CH_2CHO$ while the latter gives $CF_3CHMeCHO$ almost exclusively. Addition of triphenylphosphine to the cobalt system repressed hydroformylation almost completely while no effect was seen in the rhodium system. Other rhodium complexes, in particular $[HRh(CO)(PPh_3)_3]$, gave catalysts yielding up to 95% aldehyde which was primarily the branched-chain isomer. With $C_6F_5CH{=}CH_2$ as the substrate, $[Co_2(CO)_8]$ gave a 54% yield of aldehyde with the straight chain isomer predominating by a factor of about four. Catalysts derived from $[Rh_6(CO)_{16}]$, $[RhCl(PPh_3)_3]$ and $[HRh(CO)(PPh_3)_3]$ provided quantitative conversion to aldehyde, almost completely the branched-chain isomer. The observed differences in regioselectivity is attributed to the relative stabilities of the secondary versus primary metal alkyl intermediates. The former is stabilized if the metal induces a negative charge on the α-carbon while the latter is preferred if the metal induces a positive charge on this atom (ref. 252). Other related studies include the hydroformylation of polypropylene oil, primarily at branch points, using $[Co_2(CO)_8]$ and $[RhCl(CO)(PPh_3)_2]$ as catalyst precursors (ref. 253), a one-step hydroformylation/aldol condensation of propylene to give 2-ethylhexanol catalyzed by $[Co_2(CO)_6(PBu^n_3)L]$ and $[Co_2(CO)_5(PBu^n_3)_2L]$ (L = 2-aminopyridine) (ref. 254) and olefin hydroformylation using $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ as catalyst precursors (ref. 255).

Carbalkoxylation of olefins can be carried out at high pressure of carbon monoxide in pyridine containing $[Co_2(CO)_8]$. In particular, butadiene and methanol are converted to methyl-3-pentenoate by this system. Evidence for the addition of a carboalkoxy cobalt complex (in preference to $[HCo(CO)_4]$) to the olefin was obtained from the chemistry of $[MeOC(O)Co(CO)_4]$ (prepared from $Na[Co(CO)_4]$ and methyloxalyl chloride) (Scheme XXX). All the indicated reactions were carried out

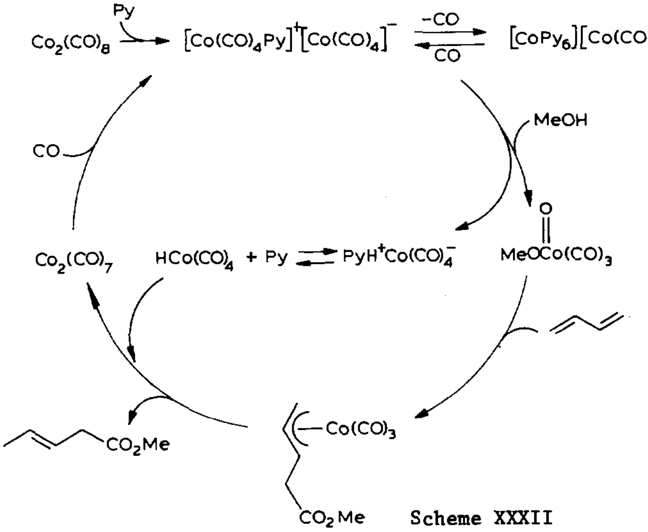


Scheme XXX

stepwise and the intermediate cobalt complexes isolated. At -40° C the reactions in Scheme XXXI were observed with the allyl complex forming instantaneously in the absence of carbon monoxide. However under the same conditions, reaction of $[pyH][Co(CO)_4]$ with butadiene to form $[(\eta^3\text{-crotyl})Co(CO)_3]$ was incomplete after 2 h. These results are proposed to support the mechanism of carboalkoxylation shown in Scheme XXXII (ref. 256). The amidocarbonylation of allylic alcohols to N-acyl-α-amidoacids is catalyzed by a mixture of $[Co_2(CO)_8]$ and $[RhH(CO)(PPh_3)_3]$ in dioxane. It is proposed that the aldehyde formed by isomerization of the alcohol is rapidly involved in the subsequent amidocarbonylation (ref. 257).

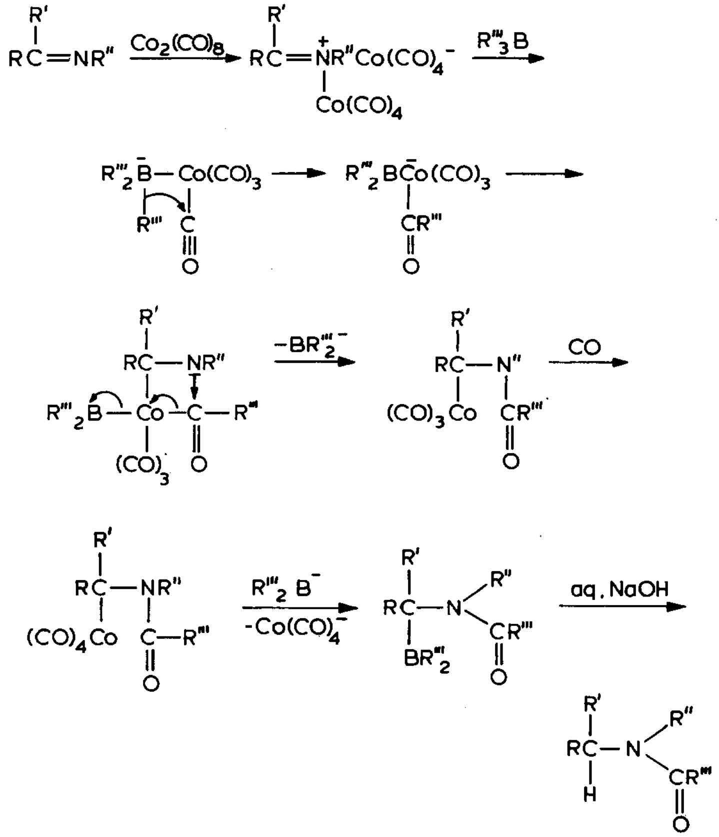


Scheme XXXI



Scheme XXXII

The major product of the reaction of carbon monoxide with diethyl magnesium and particularly ethylmagnesium bromide in THF containing $[Co_2(CO)_8]$ is 2-propanoyltetrahydrofuran indicating that radical intermediates are formed. Other products include pentan-3-one, pentan-3-ol and other ketoalcohols and diols (ref. 258). Treatment of $[Co_2(CO)_8]$ with tetrabutylammonium fluoride in aqueous THF yields $[Co(CO)_4]^-$ but the resulting solution does not effect the reduction of nitrosoalkanes to the corresponding amines as do solutions similarly generated from [Fe$_3$(CO)$_{12}$] or [Mn$_2$(CO)$_{10}$]. However the cobalt carbonyl-containing solution generated in like manner from [Co(CO)$_3$NO] under carbon monoxide effects the conversion of 2-bromomethylnaphthalene to β-naphthylacetic acid. Tetrabutylammonium fluoride does not react with [cpCo(CO)$_2$] however (ref. 259). Schiff bases can be carbonylated to the corresponding amides in THF solution in the presence of organoboranes and [Co$_2$(CO)$_8$] as shown in Scheme XXXIII (R = PhCO; R' = R'' = Ph; R''' = Et, Bu^n, *n*-C$_7$H$_{15}$, PhCH$_2$CH$_2$, Ph, PhCHMeCH$_2$) (ref. 260). Mixtures of [Co$_2$(CO)$_8$] and tri-*n*-butyl-phosphine in the presence of potassium acetate, formate or carbonate catalyze the conversion of butyraldehyde to 2-ethylhexanol (ref. 261) while benzyl alcohols are carbonylated to phenylacetic esters or amides in the presence of [Co$_2$(CO)$_8$] and alcohols or amines in ethylpolyphosphate as the solvent (ref. 262). Moderate yields of compounds containing {-OCH$_2$CH$_2$O-} and methoxy groups can be obtained by the hydrogenation of carbon monoxide at high pressure and



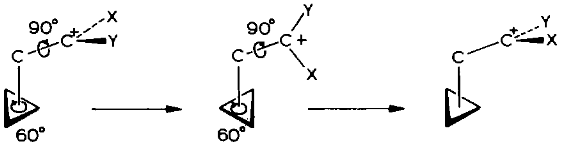
Scheme XXXIII

270° C catalyzed by $[Co_2(CO)_8]$ or $[Rh(acac)(CO)_2]$ promoted by tri-n-hexylsilane however $[RhCl(CO)(PPh_3)_2]$ was inactive (ref. 263). In tetraglyme, cobalt carbonyls can be generated from syngas and cobalt(II) acetate and small amounts of ethanol and n-propanol are formed. Approximately 90% of the syngas consumed appears in the alcohol products and addition of phosphines to the system increases the selectivity to ethanol synthesis (ref. 264). While a mixture of $[Co_2(CO)_8]$ and $[Ru_3(CO)_{12}]$ is an effective catalyst precursor for the reductive carbonylation of methyl acetate to ethyl acetate (ref. 265), $[Co_2(CO)_8]$ is a poor catalyst for the formation of cyclohexylchloride from cyclohexane and carbon tetrachloride. Here the metal complex is thought to initiate a radical chain reaction (ref. 266).

Three papers report studies on catalysis by cobalt carbonyl complexes anchored to silica surfaces by pendant phosphine groups. Using diphenylphosphino groups, both Co(0) and Co(I) surface species were identified. The identity and relative proportions of which depended on the length of the anchoring chain, the extent of surface coverage and the amount of dehydration of the silica. In situ Raman spectroscopic measurements support the conventional hydroformylation mechanism for this system (ref. 267). Using $L = -CH_2CH_2CH_2Pcy_2$ as the anchoring group, $[Co_2(CO)_6L_2]$ species are seen. These can be treated with [bis(benzylideneacetone)Pd] to give what is thought to be a supported Pd-Co cluster possibly analogous to $[(diphos)_2PdCo_2(CO)_7]$. In the catalysis of the gas-phase hydroformylation of propylene the mixed catalyst is more active than the cobalt one but the selectivity to straight-chain aldehyde is lower (refs. 268, 269). Deposition of $[Co_2(CO)_8]$ on oxide supports followed by pyrolysis gives catalysts for olefin hydroformylation and the carbon monoxide hydrogenation. The species produced on La_2O_3 have only about half the activity of those on silica but are more selective. In propylene hydroformylation they produce mainly butanols (ref. 270). On NaY zeolite, thermolysis leads to stepwise loss of carbonyl groups and disproportionation of cobalt to cationic and anionic species. The final product has the metal in both low and high oxidation states and as a carbon monoxide hydrogenation catalyst favors the formation of short-chain hydrocarbons (ref. 271). A fast pyrolysis of $[Co_2(CO)_8]$ on titanium dioxide surfaces produces ferromagnetic cobalt particles which are said to be superior to other systems for carbon monoxide hydrogenation (ref. 272). An infrared study of $[Co_2(CO)_8]$ supported on partially dehydroxylated silica and alumina showed the presence of adsorbed $[Co_4(CO)_{12}]$, $[Co_2(CO)_6B_2]$ and $[Co(CO)_3B]_2$ (B = surface O_2^- or OH^-) species (ref. 273).

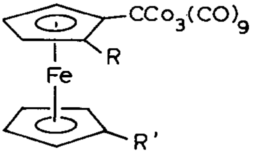
Irradiating 2-methyltetrahydrofuran glasses containing $[Co_2(CO)_6L_2]$ ($L = PBu^n_3$, $P(OMe)_3$, $AsBu^1_3$) with ^{60}Co γ-rays produces radical anions in which the odd electron occupies a metal-metal σ* orbital (ref. 274). The solid state ^{13}C NMR spectrum of $[Co_2(CO)_8]$ has been determined by the magic-angle spinning (MAS) technique. The observation of fewer resonances than expected suggests the possibility of dynamic processes occurring (ref. 275). Electronic effects which may be pertinent to the catalytic carbonylation of acetylenes in the presence of cobalt carbonyls have been probed by molecular orbital calculations on $[Co_2(CO)_6L]$ ($L = C_2H_2$, HC_2Me, Me_2C_2) using the CNDO/2 method (ref. 276) while other calculations on the hypothetical species $[Co_2(CO)_6(\eta_2-\mu^2-N_2)]$ indicate that it should be stable enough to exist (ref. 277). Finally a molecular orbital calculation has been performed on the phosphoranium ion $[(OC)_3Co(C(PH_3)_3)]^+$ to see how similar the $\{C(PH_3)_3\}$ moiety might be to trimethylenemethane. The most stable orientation is that with the $\{Co(CO)_3\}$ moiety staggered with respect to the PH_3 substitutients and inclusion of phosphorus d orbitals increases the stability slightly. Overall, the preferred geometry is similar to that for $[(OC)_3Co(C(CH_2)_3)]^+$(ref 278).

Alkylidynenonacarbonyltricobalt complexes continue to be the subject of considerable study. Carbonyl substitution in $[ClCCo_3(CO)_9]$ by phosphines, phosphites and isocyanides is facilitated by sodium benzophenone ketyl which presumably generates a cluster radical anion in which carbonyl lability is enhanced. In this manner, $[ClCCo_3(CO)_6(CNBu^t)_3]$, $[ClCCo_3(CO)_7(diphos)]$, $[ClCCo_3(CO)_8(P(O\text{-}\underline{p}\text{-}tolyl)_3)]$ and $[ClCCo_3(CO)_7(P(O\text{-}\underline{p}\text{-}tolyl)_3)(PPh(OMe)_2)]$ were prepared. The same procedure was used to prepare $[Rh_6(CO)_{12}(CNBu^t)_4]$. For the method to be successful, the cluster radical anion must not readily fragment and the ligands used must be poorer π-acids than the carbonyl ligand and must not react with the ketyl (refs. 279, 280). Reaction of 1,1,1-trichloro-3-methylbut-2-ene with $[Co_2(CO)_8]$ in THF yields $[Me_2C{=}CHCCo_3(CO)_9]$ which can be protonated by fluorosulfonic acid to give $[Me_2CH\overset{+}{C}HCCo_3(CO)_9]$. Variable temperature ^{13}C NMR studies on the ion show two signals for the isopropyl methyl groups at low temperature but only one at high temperature. This is interpreted to indicate that the apical substituent is canted in the ground state and undergoes the rearrangement depicted schematically in Scheme XXXIV. It



Scheme XXXIV

is also suggested that the protonated species is not a simple three-coordinate carbenium ion as proposed by Hoffman but involves stabilization by direct interaction of the cationic carbon atom with the cobalt triangle (ref. 281). Refluxing $[HCCo_3(CO)_9]$ with $[(\eta^5-C_5H_4R')Fe(\eta^5-C_5H_3RHgCl)]$ ($R = R' = H$. $R = Me$, O_2CMe; $R' = H$. $R = H$; $R' = O_2CMe$) yields [92]. Cyclic voltammetric measurements show reversible formation of radical cations and anions with the cation centered on iron and the anion on cobalt. Only slight perturbation of one center by the other is noted. The structure of the complex with $R = R' = H$ has been determined and it is noted that the alkylidyne carbon is displaced towards the edge of the cobalt triangle while the carbon-carbon distances in the attached cyclopentadienyl ring are significantly unequal. These features are attributed to steric and electronic effects resulting from efficient transmission of charge between iron and cobalt.



[92]

The carbonyl groups on cobalt in [92] can be substituted by phosphines and phosphites. The related complex $[cpFe(\eta^5\text{-}C_5H_4CCo_3(CO)_6(P(OPh)_3)_3)]$ is oxidized to $[cpFe(\eta^5\text{-}C_5H_4CCo_3(CO)_6(P(OPh)_3)_3)](PF_6)_2$ by excess silver hexafluorophosphate but with one equivalent the monocation $[cpFe(\eta^5\text{-}C_5H_4CCo_3(CO)_6(P(OPh)_3)_3)]PF_6$ is formed which shows a strong intervalence transfer absorption in its electronic spectrum (ref. 282).

Alkylidynenonacarbonyltricobalt moieties can be immobilized on supports in a variety of ways. If the substituent on the alkylidyne carbon contains a vinyl group, this can be copolymerized with other vinyl monomers (ref. 283) while if it is $-(CH_2)_nSiR_3$ (n = 2; R = OEt. n = 0; R = Cl) the clusters can be attached to silica, alumina TiO_2, SnO_2, ZnO_2 or MgO. On silica the clusters catalyze olefin hydroformylation but significant cobalt leaching from the surface occurs (refs. 284, 285). Sublimation of $[MeCCo_3(CO)_9]$ onto silica, alumina or NaY zeolites results in the reaction of the cluster with the support to generate formic acid (ref. 286).

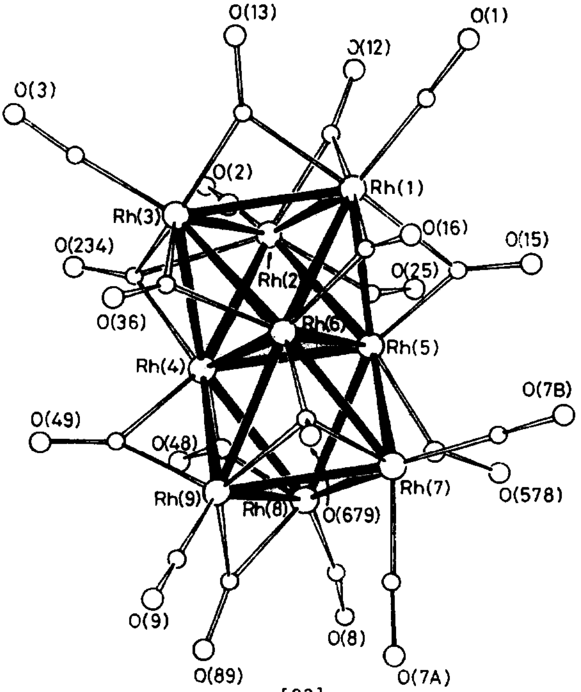
The photoelectron spectra (He(I) and He(II)) of $[RCCo_3(CO)_9]$ (R = H, F, Cl, Br, I, Me, CF_3, CO_2Me, Me_2N, MeO) have been measured and used to develop qualitative molecular orbital schemes which indicate that the bonding to the apical substituent is much more important than metal-metal bonding to the stability of the cluster. The orbitals localized on the metal triangle appear to constitute an electron reservoir which is only slightly perturbed by the apical group. However when R is capable of functioning as a π-donor or π-acceptor there is substantial delocalization of π-electrons on R over the entire cluster (refs. 287-289). Since extensive mixing of the orbitals of the CH fragment in $[HCCo_3(CO)_9]$ into the cobalt d manifold occurs whether or not the apical substituent is tilted with respect to the Co_3 plane according to a series of Fenske-Hall calculations, it is concluded that photoelectron spectroscopy will be of little use in analyzing the orientation of CH fragments on cobalt surfaces (ref. 290).

The kinetics of carbon monoxide exchange in $[Co_4(CO)_{11}L]$ (L = CO, PMe_3, $P(OMe)_3$, PEt_3, $P(OEt)_3$) have been determined by following the incorporation of ^{13}CO. The rate appears to be primarily affected by steric factors which implies that the actual carbon monoxide exchange occurs in the vicinity of the ligand L. From structural studies the carbonyl ligand on the metal bearing the L substituent appears to be more strongly bound than the axial carbonyl groups on adjacent metal atoms. Thus it is suggested that it is one of these axial carbonyls that initially dissociates but subsequent rapid intramolecular rearrangements preclude a determintion which one actually does. Facile loss of larger L groups limited the scope of the study. The results are proposed to indicate that the rate enhancements seen in the reactions of triphenylphosphine with $[Ir_4(CO)_{12}]$ are steric rather than electronic in origin (ref. 291). Steric effects also appear to be important in the substitution reactions of $[Co_4(CO)_{12}]$ with triphenylphosphine. In heptane or 1,2-dichloroethane only $[Co_4(CO)_{11}(PPh_3)]$ and $[Co_4(CO)_8(PPh_3)_4]$ are seen implying that the bis- and tris(phosphine) derivatives are quite labile. $[Co_4(CO)_8(PPh_3)_4]$ appears to be an equilibrium mixture of species with symmetrically bridging and semi-bridging carbonyl groups. The latter predominate. In dichloroethane solution fragmentation to $[Co_2(CO)_6(PPh_3)_2]$ occurs by three paths: rate-determining phosphine dissociation, carbonyl dissociation and spontaneous activation without ligand loss. The greater resistance of $[Co_4(CO)_8L_4]$ (L = $P(OMe)_3$, $PBu^n{}_3$, ½ diphos) to fragmentation reinforces the importance of steric factors in the process (ref. 292).

An improved synthesis of $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu\text{-}PPh)_2]$ involves reaction of $[Co_2(CO)_8]$ with phenylphosphine in toluene at room temperature followed by a period of reflux. It catalyzes the hydroformylation of olefins and only under quite extreme conditions (200° C, 2500 psi) is significant decomposition observed. At 180° C and 2600 psi it catalyzes the hydrogenation of carbon monoxide giving primarily methyl formate (refs. 293, 294).

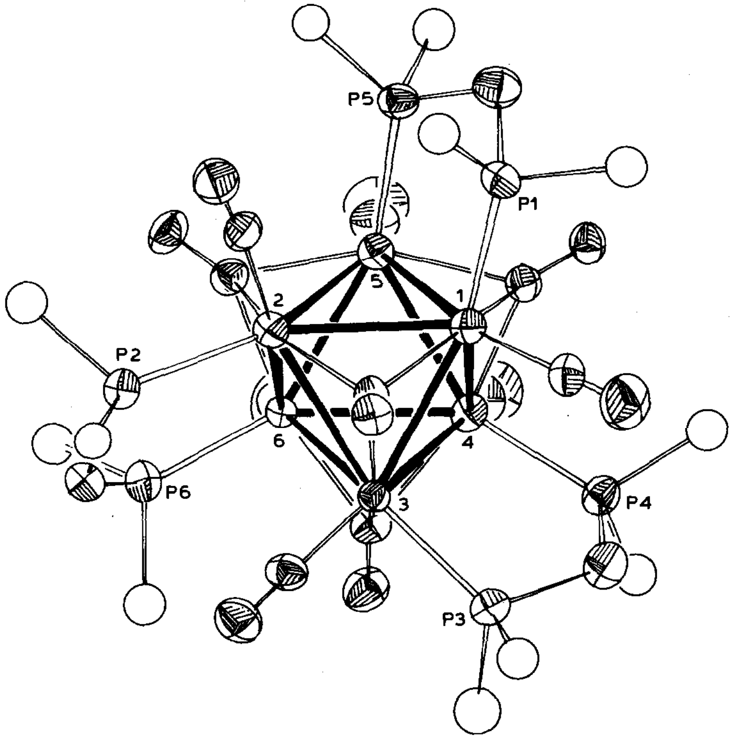
A relatively simple synthesis of $[Co_6(CO)_{14}C]^-$ is provided by the reaction of $[Co_6(CO)_{15}]^{2-}$ with acetyl chloride in THF. It is suggested that the reaction proceeds <u>via</u> cleavage of a carbonyl group possibly through the formation of an intermediate {-COC(O)Me} species (ref. 295). Heating $[ClCCo_3(CO)_9]$ with $Na[Co(CO)_4]$ in diisopropyl ether gives $Na_2[Co_6(CO)_{15}C]$ which on refluxing under nitrogen in diglyme yields $[Co_{13}(CO)_{24}C_2]^{4-}$ which was isolated as the benzyltrimethylammonium salt. It is paramagnetic with the odd electron proposed to reside in an antibonding cluster orbital (ref. 296). A preliminary report of this work was cited (as ref. 243) in the 1981 Annual Survey. A high-yield synthesis of $[Rh_{15}(CO)_{27}]^{3-}$ involves reaction of a mixture of $[Rh(acac)(CO)_2]$, cesium benzoate and N-methylmorpholine in tetraglyme under 10 atm of hydrogen and carbon monoxide. The reactivity of the cluster is quite solvent-dependent indicating that the extent of ion-pairing is important. In polar solvents where ion-pairing is low, release of an $\{Rh(CO)_2\}$ fragment is facilitated leading to formation of $[Rh_{14}(CO)_{25}]^{4-}$ (ref. 297). Condensation of $(PPN)[Rh_5(CO)_{15}]$ and $(PPN)_2[Rh_4(CO)_{11}]$ in acetonitrile produces $(PPN)_3[Rh_9(CO)_{19}]$ ([93]) however carbonylation of [93] gives only

$(PPN)[Rh_5(CO)_{15}]$ (ref. 298). The room temperature reaction of $[Rh_4(CO)_{12}]$ with bis(triphenylphosphine)iminium thiocyanate in isopropanol under nitrogen yields



[93]

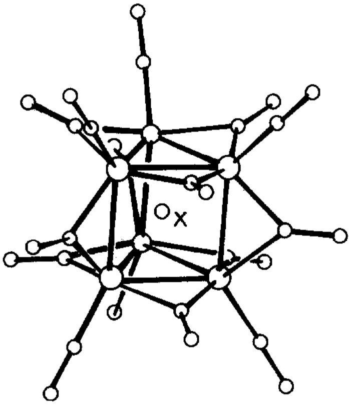
$(PPN)_2[Rh_{10}S(CO)_{10}(\mu\text{-}CO)_{12}]$ together with a small amount of $(PPN)[Rh_3S_2(CO)_6]$. The structure of the major product consists of a bicapped square antiprism of rhodium atoms with the sulfur at the center. At 60° C complete fluxionality of all carbonyl ligands and the rhodium atoms occurs as determined by ^{103}Rh, ^{13}C and $^{13}C\{^{103}Rh\}$ NMR spectroscopy. The reaction of $[Rh_4(CO)_{12}]$ with potassium thiocyanate in THF is much slower and after the initial formation of unstable species, $[Rh_5(CO)_{15}]^-$ and $[Rh_5(CO)_{14}(SCN)]^{2-}$ are obtained. Independent syntheses of these last two complexes followed by their reaction in equimolar quantities in THF also yields $[Rh_{10}S(CO)_{22}]^{2-}$ indicating the probable intermediacy of the thiocyanate complex in the original reaction. The cleavage of the thiocyanate ion is thought to occur at this stage of the process since in $[Rh_5(CO)_{14}(SCN)]^{2-}$ the thiocyanate ligand is S-bonded to an apical rhodium atom (ref. 299). Six carbonyl groups in $[Rh_6(CO)_{16}]$ are replaced by DPM on heating in toluene to give $[Rh_6(CO)_{10}(DPM)_3]$ ([94]). The crystal is racemic and the compound is stereochemically rigid at and below room temperature (ref. 300). The same complex together with $[Rh_6(CO)_{14}(DPM)]$ and $[Rh_6(CO)_{12}(DPM)_2]$ all containing bridging DPM ligands, which were obtained under milder conditions have been reported by a second research group. Reaction of



[94]

$[Rh_4(CO)_{12}]$ with one equivalent of DPM in a hexane/toluene mixture yields $[Rh_4(CO)_{10}(DPM)]$ which precipitates from solution. On dissolution further reaction occurs to give $[Rh_4(CO)_8(DPM)_2]$, $[Rh_6(CO)_{14}(DPM)]$ and $[Rh_6(CO)_{12}(DPM)_2]$. Reduction of $[Ir(CO)_2$(p-toluidine)Cl] with zinc in the presence of DPM and carbon monoxide yields a mixture of $[Ir_4(CO)_{10}(DPM)]$ and $[Ir_4(CO)_8(DPM)_2]$. The latter cluster can also be prepared directly from $[Ir_4(CO)_{12}]$ (ref. 301).

Two extensive papers presenting NMR spectra of rhodium carbonyl clusters have appeared. The ^{13}C and $^{13}C\{^{103}Rh\}$ spectra of $[Rh_5(CO)_{15}]^-$ at 201 K are simpler than would be expected if the static solid-state structure were maintained in solution suggesting the existence of either fluxional processes or of semi-bridging carbonyl groups on all the axial-equatorial edges of the trigonal bypyramidal cluster. Under nitrogen some conversion to $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_6(CO)_{15}]^{2-}$ is detected but pressurization with carbon monoxide converts these back to $[Rh_5(CO)_{15}]^-$. Variable temperature spectra of $[Rh_{12}(CO)_{30}]^{2-}$ under 1 atm of nitrogen shows evidence of exchange of carbonyl ligands between face-bridging and terminal sites but no fragmentation as previously reported by Vidal. Incomplete cleavage to $[Rh_5(CO)_{15}]^-$ occurs at 221 K under 575 atm of carbon monoxide and no further change occurs on addition of hydrogen. The complete conversion can be accomplished however if the solution is warmed to room temperature and then recooled. Even under the high pressures used, the exchange between free and bound carbon monoxide is slow on the NMR time scale (ref. 302). Protonation of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}C]^{2-}$ at low temperature yields $[Rh_6H(CO)_{15}]^-$ and $[Rh_6H(CO)_{15}C]^-$ respectively. These have been studied by ^1H, $^1H\{^{103}Rh\}$, ^{13}C, $^{13}C\{^{103}Rh\}$ and ^{103}Rh NMR from which it was determined that the hydride ligand in the first complex is terminal while in the second it is face-bridging (ref. 303). The ESR spectra of $[Rh_{12}(CO)_{13}(\mu\text{-}CO)_{10}(C)_2]^{3-}$, $[Co_{13}(CO)_{12}(\mu\text{-}CO)_{12}(C)_2]^{4-}$ and $[Co_6(CO)_8(\mu\text{-}CO)_6C]^-$ have been measured to determine the location of the odd electron. The rhodium complex is considered to be a d^7 Rh(II) system with the HOMO consisting mainly of the d orbitals of the rhodium atoms in the central plane. For the Co_{13} cluster the HOMO appears to be mainly Co-d_{z^2} in composition and derived largely from three of the five cobalt atoms in the central plane while in the Co_6 cluster there appears to be significant ligand contribution to the HOMO (ref. 304). Infrared spectra of ^{13}C- and ^{15}N-labelled $[M_6(CO)_{15}X]^-$ (M = Co, Rh; X = C, N) ([95]) have been used to identify ν_{M-X} of which there are two in each complex. The analysis of the spectra assumes no coupling



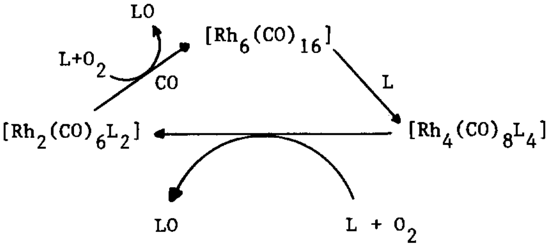
[95]

of these vibrations with either the M-M vibrations or those associated with the carbonyl ligands and leads to their assignment as vibrations along and perpendicular to the three-fold axis of the cluster. From the derived force constants the M-X bonding is proposed to involve interaction of a p orbital with multicenter orbitals in the triangular face and of an sp^2 hybrid with analogous orbitals in the square face. Equivalent bonding of X to all six metals is not as good a model (ref. 305). The splitting of degenerate vibrations of tetrahedral M_4 and octahedral M_6 clusters due to asymmetry in the distribution of force constants or atomic masses has been investigated. To a first order approximation, perturbations which retain C_3 symmetry do not split the three-fold degenerate vibrations, thus accounting for the very small splitting observed for the t_2 cluster mode of $[Rh_4(CO)_{12}]$ (ref. 306).

Cyclic voltammetric measurements on $(Bu^n{}_4N)_2[Rh_{12}(CO)_{30}]$ in THF show the existence of a two-electron reduction wave yielding $[Rh_{12}(CO)_{30}]^{4-}$ which fragments to $[Rh_6(CO)_{15}]^{2-}$ followed by further reduction. If the scan is reversed before cleavage occurs, the reduction wave is reversible. A two-electron oxidation to $[Rh_{12}(CO)_{30}]$ is also observed. The products of further reaction of the oxidized species have not been identified but they do not include $[Rh_6(CO)_{16}]$ (ref. 307). A cluster cone angle, defined as the angle subtended by a ligand at the center of a cluster rather than at the attached metal atom has been proposed as a better measure of steric effects related to the synthesis of high nuclearity clusters than is the original Tolman ligand cone angle. On this basis, steric effects on the stereochemistry of binary carbonyl clusters should be observed for sterically saturated species (cluster cone angles fill all space about center). Otherwise the shape will be that which maximizes metal-metal and metal-carbon bonding (ref. 308).

A variety of systems using $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ as catalyst precursors have been reported but in most cases there is no direct evidence for cluster catalysis. Both species give systems for the carbonylation of mixtures of acetylenes and ethylene to substituted furanones (ref. 309) while $[Rh_4(CO)_{12}]$ provides catalysts for the hydrocarbonylation of acrylic acid derivatives to γ-ketopimelic acid (ref. 310) and the cross-hydrocarbonylation of ethylene plus various acetylenes to give α,β-unsaturated esters (ref. 311). Both clusters mediate the reduction of nitric oxide by carbon monoxide to nitrous oxide, dinitrogen and ammonia in aqueous potassium hydroxide. In the absence of nitric oxide the system catalyzes the water-gas-shift reaction but no mechanistic details were provided (ref. 312). Under water-gas-shift conditions $[Rh_6(CO)_{16}]$ plus TMEDA (TMEDA = $Me_2NCH_2CH_2NMe_2$) provides a high-yield conversion of aldehydes to alcohols. Non-cluster precursors such as $[RhCl(CO)_2]_2$ are less active. Ketones can be reduced but with greater difficulty however the system appears to selectively reduce the carbonyl group of α,β-unsaturated aldehydes. It is thought that the reaction conditions favor the formation of hydrido carbonyl metallates which can attack the carbonyl group (ref. 313). The hexanuclear cluster in methanol in the presence of sodium bicarbonate effects the hydrogenation of benzeldehyde. The kinetics of the reaction were interpreted to indicate catalysis by cluster species such as $[Rh_5(CO)_{15}]^-$ and/or $[Rh_{12}(CO)_{30}]^{2-}$ (ref. 314). When the CO: C_2H_4: H_2 ratio is 0.2:1:1, ethylene can be hydroformylated in the presence of $[Rh_4(CO)_{12}]$ but extensive inhibition occurs at higher carbon monoxide pressures. In situ monitoring by infrared spectroscopy indicated the presence of a species proposed to be $[HRh(CO)_3(C_2H_4)]$, an oft-proposed intermediate, which decomposes on attempted isolation. Pressurization of the solution with more carbon monoxide converted the rhodium species to $[Rh_4(CO)_{12}]$. Under 274 atm of carbon monoxide, solutions of $[(\eta^3\text{-}C_3H_5)Rh(CO)_2]$ showed the presence of $[Rh_4(CO)_{12}]$ and possibly $[(\eta^1\text{-}C_3H_5)\text{-}Rh(CO)_4]$ and its acyl derivative. Addition of hydrogen produced a species thought to be $[RhH(CO)_3(CH_2{=}CHMe)]$ (ref. 315). Radiocarbon tracer studies on the conversion of syngas in N-methylpyrroliden-2-one and tetraglyme in the presence of $[Rh_4\text{-}(CO)_{12}]$ indicated that the primary products, methanol and ethylene glycol, are not solvent-derived. These products do not undergo further transformation under the reaction conditions. When labelled paraformaldehyde was added to the system typical syngas products were formed and their labelling pattern suggested that paraformaldehyde was a precursor to methanol and glycolaldehyde. Thus coordinated aldehydes were thought to be important intermediates with the paraformaldehyde being converted into a common intermediate for all subsequent products (ref. 316).

The oxidation of triphenylphosphine and triphenylarsine to their oxides by molecular oxygen is catalyzed by $[Rh_6(CO)_{16}]$ possibly according to Scheme XXXV.



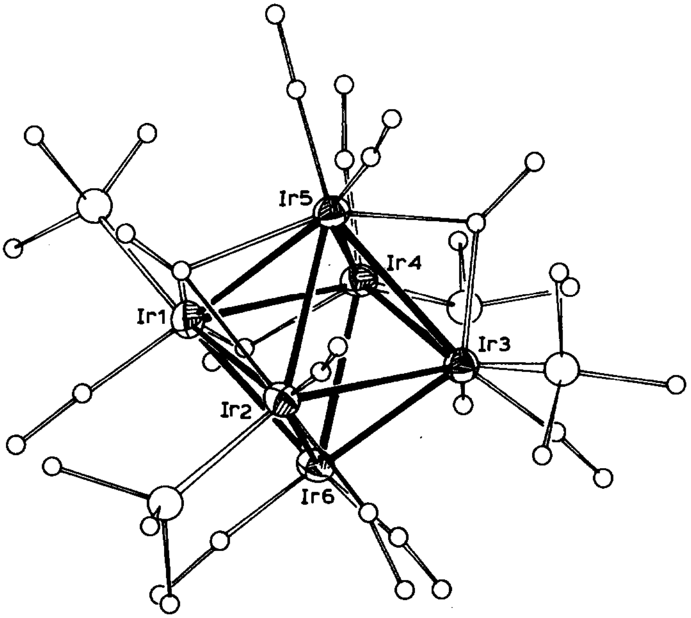
Scheme XXXV

The cluster also catalyzes the autoxidation of ketones and cyclic alcohols to dicarboxylic acids presumably by catalytic decomposition of intermediate hydroperoxides (ref. 317). Homogeneous systems based on $[Rh_6(CO)_{16}]$ are proposed to be models for hydrodenitrogenation systems normally catalyzed by cobalt molybdate. That it can convert triethylamine into diethylamine indicates that carbon-nitrogen bond fission occurs (ref. 318).

Supporting $[Rh_4(CO)_{12}]$ on γ-alumina improves its stability and ability to be recycled when used to catalyze the hydrogenation of 1,3-pentadiene although the activity is lower than when used homogeneously. Little effect is noted on its selectivity towards hydrogenation of the terminal double bond. Inhibition by added carbon monoxide and phosphines suggests formation of the active site occurs by dissociation of a carbonyl ligand (ref. 319).

Controversy continues over the origins of the differences seen in rates of substitution in phosphine derivatives of $[Ir_4(CO)_{12}]$. In $[Ir_4(CO)_9L_3]$ (L = PR_3 R =

Me, Et, Pr^i, Bu^n, Ph)), the rate of carbon monoxide exchange, which presumably reflects the rate of dissociation of a carbonyl group in the initial complex, was found to depend on L in the order PMe_3<$PBu^n{}_3$<PEt_3<$PPr^i{}_3$<PPh_3 and although a small electronic effect was seen, the major factor was attributed to steric effects. A similar correlation of rate with steric bulk was seen in the conversion of $[Ir_4(CO)_8L_4]$ to $[Ir_4(CO)_9L_3]$ (L = PR_3 (R = Me, Et, Bu^n, OMe, OPh)) (ref. 320). On the other hand, in the reaction of $[Ir_4(CO)_{11}L]$ (L = $PBu^n{}_3$, PPh_3, $P(OPh)_3$, $AsPh_3$) with ligands from this list to substitute up to three carbonyl groups or in the formation of $[Ir_4(CO)_{10-n}L_2L'_n]$ from $[Ir_4(CO)_{10}L_2]$ (L = L' = PPh_3; n = 1. L = L' = $PBu^n{}_3$, $P(OPh)_3$; n = 1, 2. L = $P(OPh)_3$; L' = PPh_3, $PBu^n{}_3$; n = 2. L = $AsPh_3$; L' = PPh_3; n = 1. L = L' = $AsPh_3$; n = 2) where in both cases the kinetics indicate loss of carbon monoxide to be the primary step the variation in rate with L is attributed to electronic effects. The mechanism is proposed to involve loss of carbon monoxide from a phosphine-substituted vertex followed by transfer of coordination unsaturated to an unsubstituted vertex via a carbonyl-bridged transition state with the ligand effect on the rate depending on the ability of L to stabilize this transition state (refs. 321, 322). An excess of triphenylphosphite (L) reacts with $[Ir_6(CO)_{16}]$ in hot toluene to give $[Ir_6(CO)_{12}L_4]$ ([96]) (ref. 323).

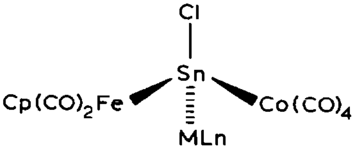


[96]

Low temperature infrared and room temperature Raman spectra of [$Ir_4(CO)_{12}$] have been measured. The low frequency modes could be adequately assigned on the basis of tetrahedral symmetry (ref. 324). When this cluster is deposited on alumina it appears to chemisorb by reaction with surface hydroxyl groups but on silica it exists as crystallites dispersed throughout the pores. Thermal decomposition of the silica-supported material produces iridium metal on the surface but partial oxidation occurs with the alumina-supported material. Hydrogenation of both species produces highly dispersed iridium metal possibly existing as "rafts" of $\geqslant$20 atoms (ref. 325).

b) Heteronuclear Metal-Metal Bonded Compounds

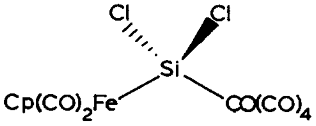
Reaction of [$Co_2(CO)_6(PBu^n{}_3)_2$] with PbX_2 (X = O_2CMe, NO_3, Cl, cp, I), $PbEt_4$, Ph_2PbCl_2, Ph_6Pb_2 or even elemental lead in refluxing benzene yields [$Pb(Co(CO)_3$-$PBu^n{}_3)_4$]. Lead(II) acetate and [$Co(CO)_3PBu^n{}_3$]$^-$ also give the same product (ref. 326). The same cobalt complex reacts with tri-n-butyltin hydride to give [$Bu^n{}_3Sn$-$Co(CO)_3(PBu^n{}_3)$] and hydrogen under either photolytic or thermal conditions. From a kinetic study the reaction is proposed to proceed via homolysis of the Co-Co bond, loss of carbon monoxide, oxidative addition of the Sn-H bond, hydrogen abstraction and reductive elimination of hydrogen. With [$HMn(CO)_5$] the products are [Mn_2-$(CO)_{10}$] and [$(OC)_5MnCo(CO)_3PBu^n{}_3$] (ref. 327). At -20° C in THF, Na[$Co(CO)_4$] reacts with a variety of lanthanide trichlorides to give [$Cl_2MCo(CO)_4(THF)_n$] (M = Ho, Dy, Yb, Sm, La. n = 2-4) or [$M(THF)_4(Co(CO)_4)_3$] (M = Yb, Er). The first series reacts with triphenylphosphine to give [$Cl_2MCo(CO)_3PPh_3$]·THF which also can be prepared from MCl_3 and [$Co(CO)_3PPh_3$]$^-$ (refs. 328, 329). Using thulium amalgam and [Co_2-$(CO)_8$] provides the analogous [$Tm(THF)_4(Co(CO)_4)_3$] (ref. 330). While [$Co_2(CO)_8$] or Tl[$Co(CO)_4$] reacts with [$Cl_2Sn(Fecp(CO)_2)ML_n$] (ML_n = $cpMo(CO)_3$, $cpNi(CO)$) to yield [97], [$Cl_2Sn(Fecp(CO)_2)(Co(CO)_4)$] and [$cpNi(CO)$]$_2$ give only [$Cl_2Sn(Fecp(CO)_2)$-$(Nicp(CO))$]. From [$Cl_3SnFecp(CO)_2$] and [$Co_2(CO)_8$] can be obtained [$Cl_{3-n}Sn$-$(Fecp(CO)_2)(Co(CO)_4)_n$] (n = 1,2) depending on the ratio of reactants used (ref. 331).



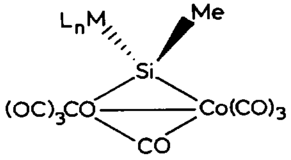
[97]

The formation of [$(OC)_4CoSiMe_2Fecp(CO)_2$] is implicated as an unstable intermediate in the reaction of [$cpFe(CO)_2SiMe_2H$] and [$Co_2(CO)_8$] which produces [$HCo(CO)_4$] and [$cpFeH(CO)_2$]. The stable analog [98] can be isolated in the reaction with [$cpFe(CO)_2SiCl_2H$] and undergoes substitution at cobalt with trimethylphosphine. With [$L_nMSiMeH_2$] (L_nM = $cpFe(CO)_2$, $cpW(CO)_2(PMe_3)$), [$Co_2(CO)_8$] yields

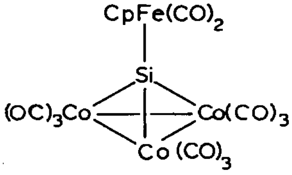
[99] while $[cpFe(CO)_2SiH_3]$ gives [100]. Hydrolysis of [99] produces $[cpFe(CO)_2$-$SiMe(OH)_2]$ and $[Co_2(CO)_8]$ while reaction of [100] with acetic acid yields $[cpFe$-$(CO)_2Si(O_2CMe)_3]$ and $[Co_4(CO)_{12}]$ (ref. 332). Attack of $[cpFe(CO)_2]^-$ on $[S(+)$-$(OC)_4CoGeMePh(1\text{-naphthyl})]$ gives only racemic $[cpFe(CO)_2GeMePh(1\text{-naphthyl})]$ while



[98]



[99]

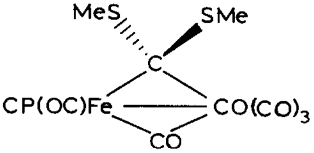


[100]

triphenylgermyllithium reacts with $[Co_2(CO)_8]$ to give $[(Ph_3Ge)_2Co(CO)_3]^-$ possibly via initial formation of $[Ph_3GeCo(CO)_3Co(CO)_4]^-$ (ref. 333). The racemization observed in the first reaction probably indicates the presence of radical intermediates since it has been shown that in the cleavage of tin-cobalt bonds in related complexes by $[cpFe(CO)_2]^-$, $BHEt_3^-$ and Ph_3Sn^- electron transfer occurs with the formation of triorganostannyl radicals (ref. 334). Displacement of chloride in $[InCl(OEP)]$ by $[Co(CO)_4]^-$ yields $[(OEP)InCo(CO)_4]$ (ref. 335).

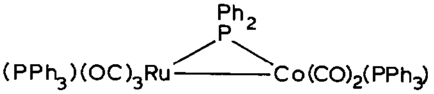
Several studies have been reported on tetracarbonylcobalt derivatives of zinc and mercury and related compounds. In anhydrous methanol $[Zn(Co(CO)_4)_2]$ partially dissociates into $[Co(CO)_4]^-$ and $[ZnCo(CO)_4]^+$ however in a mixed hexane-methanol solvent, methanolysis occurs to yield the cubane-type tetramer $[MeOZnCo(CO)_4]_4$ and (presumably) $[HCo(CO)_4]$. Hydrolysis in wet toluene yields $[HCo(CO)_4]$ and a polymeric material of empirical formula $[(HO)ZnCo(CO)_4]$ which may also be tetrameric (ref. 336). Reaction of $[HCo(P(OPh)_3)_3L]$ with HgX_2 in acetone yields $[HgX(Co(P$-$(OPh)_3)_3L)]$ (X = Cl, Br, I; $L = P(OPh)_3$, CO. X = Br, $L = P(OMe)_3$). The solid complexes are air-stable but decompose in solution. No evidence was found for disubstitution at mercury (ref. 337). A complete vibrational analysis has been made of $[Hg(Co(CO)_3L)_2]$ (L = phosphine) and the dipole moment induced along the Co-Hg-Co axis during the equatorial A_{2u} vibration of the carbonyl groups was estimated. Comparison of the spectra with those of the corresponding $[Co_2(CO)_6L_2]$ complexes indicated that the mercury atom withdraws electron density from the cobalt moieties and acts as a buffer to attenuate the effects on the carbonyl stretching frequencies of changes in the σ-donor or π-acceptor properties of the phosphine ligands (ref. 338, 339). The He(I) and He(II) photoelectron spectra of $[M(Co(CO)_4)_2]$ (M = Zn, Cd, Hg) indicate that there is considerable ionic character to the M-Co bond (ref. 340).

Tetracarbonylcobaltate ion adds to the iron carbene complex $[cp(CO)(MeCN)-Fe{=}C(SMe)_2]PF_6$ to give [101] which on oxidation by bromine, iodine, Ph_3C^+, cp_2Fe^+



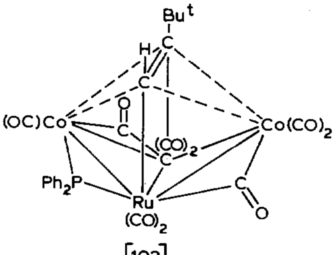
[101]

or $C_7H_7^+$ generates $[cp(CO)_2Fe{=}C(SMe)_2]^+$ (ref. 341). With $[RuHCl(CO)(PPh_3)_3]$, $Na[Co(CO)_4]$ produces [102] which reacts stepwise with carbon monoxide to first



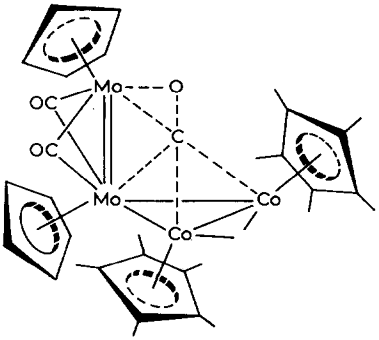
[102]

replace the phosphine on cobalt and then that on ruthenium. Heating the final product with triphenylphosphine reverses the process. Complex [102] reacts with hydrogen chloride to generate a mixture of two species of composition $[CoRu(CO)_4-(PPh_3)_2(\mu\text{-}PPh_2)HCl]$ one containing a terminal hydride and another with a bridging hydride (ref. 342). In THF solution $[Co_2(CO)_8]$ reacts with $[(\eta^6\text{-}p\text{-cymene})RuCl_2L]$ (L = PPh_2Cl, PPh_2H) to yield $[(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3]$. When L = PPh_2H a small amount of $[(\eta^6\text{-}p\text{-cymene})(OC)Ru(\mu\text{-}PPh_2)Co(CO)_3]$ is also formed. When L = $Ph_2PC{\equiv}CBu^t$ the product is [103]. The reaction is proposed to occur <u>via</u> dehalogenation of the ruthenium complex by $[Co(CO)_4]^-$ to give $[RuCo_3(Ph_2PC{\equiv}CBu^t)(CO)_{11}]^-$ which loses

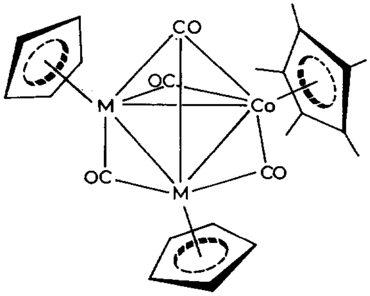


[103]

carbon monoxide, rearranges to $[RuCo_3(PPh_2)(C{\equiv}CBu^t)(CO)_9]^-$ and is protonated during chromatographic workup. The protonation step is confirmed by the observation of extensive deuterium incorporation in the acetylenic ligand when D_2O is added to the reaction mixture just prior to the chromatographic step. Also reported is the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2(P(OMe)_3)]$ with $[Co_2(CO)_8]$ which produces $[HRuCo_3(CO)_{11}\text{-}(P(OMe)_3)]$ (refs. 343, 344). Either $[RuCl_3L_3]$ (L = *o*-tolylCN, PhSMe) or hydrated ruthenium(III) chloride reacts with $Na[Co(CO)_4]$ to produce a mixture of clusters one of which was identified as $Na[RuCo_3(CO)_{12}]$. The former route provides the better yield of this cluster which reacts further with $[(PPh_3)AuCl]$ to yield $[(PPh_3)AuCo_3Ru(CO)_{12}]$ in which the $\{Au(PPh_3)\}$ moiety caps the Co_3 face of the original tetrahedral cluster (ref. 345). Photochemical reaction of $[cp'Co\text{-}(C_2H_4)_2]$ with $[cp_2M_2(CO)_4]$ (M = Mo or Fe, Ru) produces [104] and [105] (M = Fe, Ru)

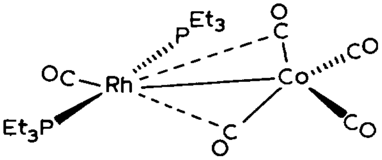


[104]



[105]

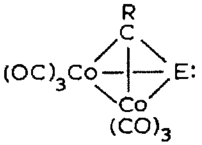
respectively. Since [104] is a 62-electron cluster, it is coordinatively unsaturated at molybdenum even if the central carbonyl group is considered to be a 6-electron donor and is thought to be a model for coordinatively unsaturated sites on stepped metal surfaces (ref. 346). Complex [106] is formed when $K[Co(CO)_4]$ reacts with $[RhCl(CO)(PEt_3)_2]$ in warm THF. The original rhodium complex is regenerated on



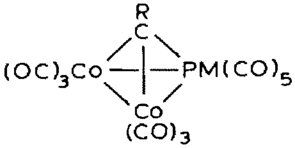
[106]

treatment with hydrogen chloride while reaction with methyl iodide generates $[RhI\text{-}(CO)(PEt_3)_2]$ and $[MeCo(CO)_4]$. In acetonitrile solution reversible dissociation to $[Co(CO)_4]^-$ and $[Rh(CO)(MeCN)(PEt_3)_2]^+$ occurs suggesting that the metal-metal bond is polarized Rh→Co. Surprisingly the complex is unreactive towards hydrogen (ref. 347). The dimetallated phosphines and arsines, [107] (R = Me, Ph, Me_3Si; E = P, As. R = H; E = As), are formed as oils on reaction of $RCCl_2ECl_2$ with $[Co_2(CO)_8]$ at

-78° C in THF followed by warming to 0° C. Two of the phosphines react with

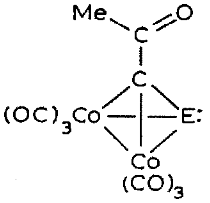


[107]



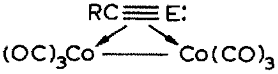
[108]

[M(THF)$(CO)_5$] to give [108] (R = Me; M = Cr, W. R = Ph; M = Cr, Mo, W); however the arsines are unreactive. When R = Me, addition of triphenylphosphine yields [$Co_2(CO)_5$ECMe(PPh_3)] (E = P, As). In the presence of aluminum trichloride, acetyl chloride reacts with [107] (R = Ph) to give [109] (E = P, As) while [107] (R = Me;



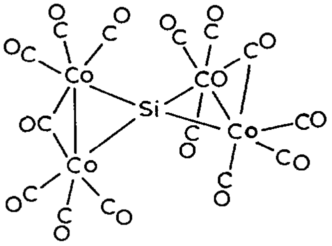
[109]

E = P) on standing at room temperature for a week condenses to [$MeCPCo_2(CO)_5]_3$. The ^{13}C NMR spectra of [$RCECo_2(CO)_6$] are interpreted to indicate that the representations [107] and [110] contribute equally to the overall bonding description (ref. 348).

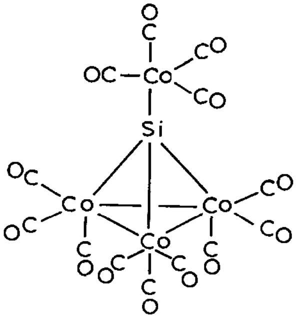


[110]

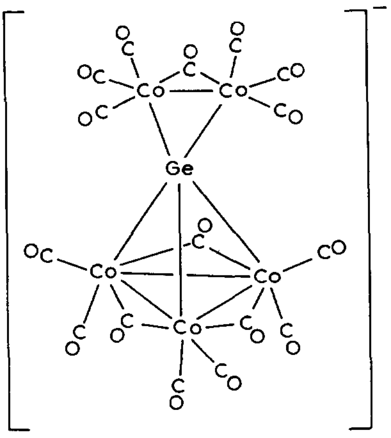
The room temperature reaction of silane with [$Co_2(CO)_8$] yields [111] which rearranges at 40° C to [112] (ref. 349). Refluxing the germanium analog of [111] with (Et_4N)[$Co(CO)_4$] in dichloromethane yields the tetraethylammonium salt of [113] which reacts further with [$Co_2(CO)_8$] in refluxing THF to give a mixture of species one of which was shown to be [114]. Complex [113] is also obtained from [Ge(Co-$(CO)_4)_4$] or from the germanium analog of [112] with the latter thought to be the immediate precursor. Recrystallization of an aged sample of [113] which appeared



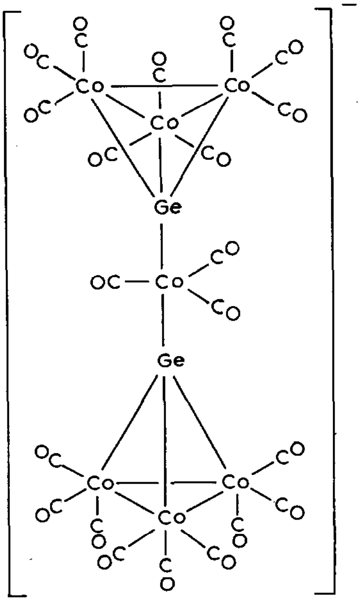
[111]



[112]



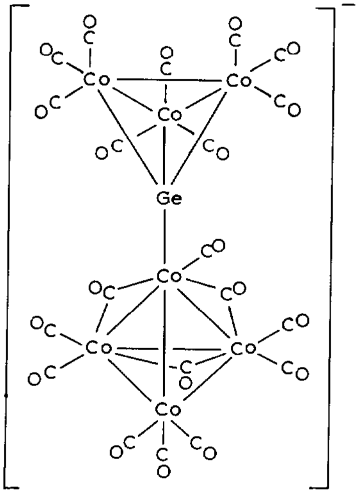
[113]



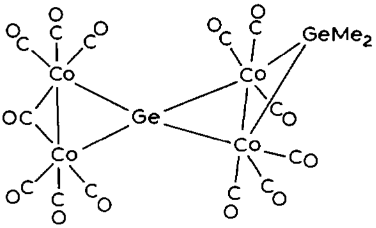
[114]

to contain some $[Co_4(CO)_{12}]$ and $(Et_4N)[Co(CO)_4]$ yielded a small amount of [115]. Other reactions of the germanium analog of [111] include those with H_2GeMe_2, GeH_4 and $MeGeH_3$ which produce [116a], [116b] and [117] respectively. Also formed in the last reaction is [116b] and $[H_2MeGeCo(CO)_4]$. A better route to [116b] is the reaction of digermane with $[Co_2(CO)_8]$ in which [116a] is also formed (refs. 350-353). Reaction of $[Co_2(CO)_8]$ with $[H_3GeMn(CO)_5]$ or $[H_2MeGeMn(CO)_5]$ produces $[(OC)_5MnGeCo_3(CO)_9]$ (structure analogous to [112]) plus $[Co_4(CO)_{12}]$ and $[(OC)_5MnGe(Me)Co_2(CO)_7]$ respectively. The tricobalt complex is formed together with

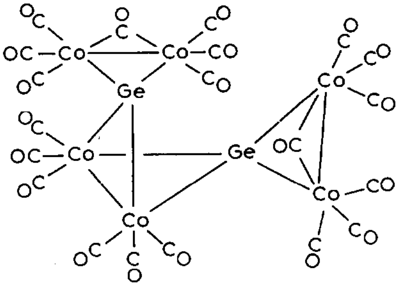
$[Co(CO)_4]^-$ and [113] on refluxing $[Mn(CO)_5]^-$ with the germanium analog of [111] in dichloromethane (ref. 354).



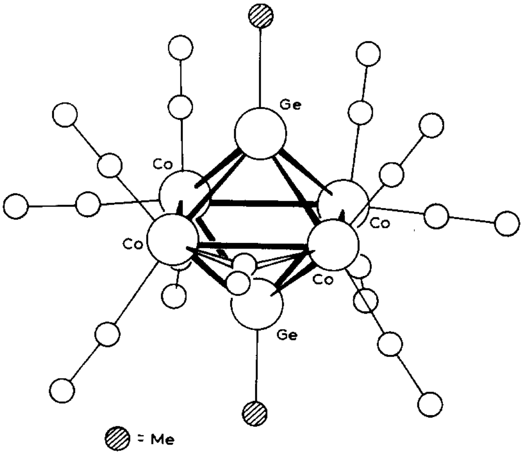
[115]



[116a]

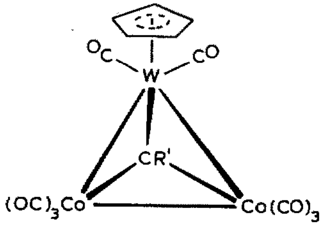


[116b]

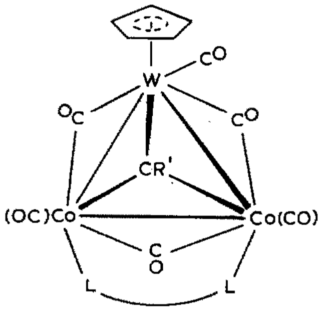


[117]

That the tungsten carbyne complex [cpW≡C-p-tolyl$(CO)_2$] is isolobal with acetylenes is indicated by its reaction with $[Co_2(CO)_8]$ where [118] (R' = p-tolyl) is formed. Substitution of one or two carbonyl groups on cobalt occurs on reaction with dimethylphenylphosphine or trimethylphosphite while with bidentate ligands (L-L = DPM, 1,2-bis(dimethylarsino)benzene(diars)) [119] (R' = p-tolyl) is formed.

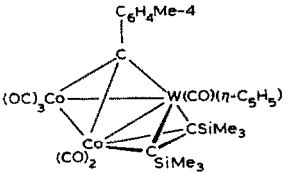


[118]



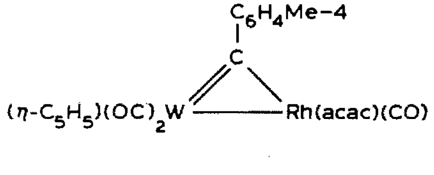
[119]

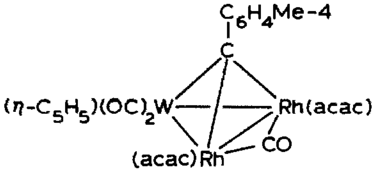
Complex [118] reacts with bis(trimethylsilyl)acetylene (BTMSA) to give [120]. Addition of $[Rh(acac)(CO)_2]$ to the carbyne complex occurs stepwise to yield [121]



[120]

and [122] while with $[cp'_2Rh_2(CO)_2]$ in warm toluene the products are [123] and

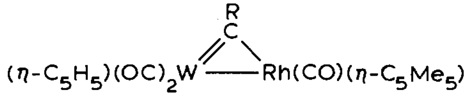




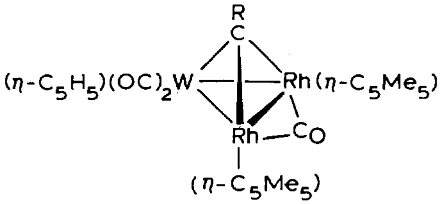
[121]

[122]

[124] (R = p-tolyl). The formation of [123] in this latter reaction indicates that fragmentation of the dimer rather than simple addition to the rhodium-rhodium double bond occurs. The ketenyl tungsten complex $[cpW(CO)(PMe_3)(\eta^2$-p-tolylCCO)] although expected to react differently than the carbyne complex with $[Co_2(CO)_8]$ in fact gives an analog of [118] where one of the carbonyl groups on tungsten is replaced by trimethylphosphine. In solution this complex slowly isomerized by

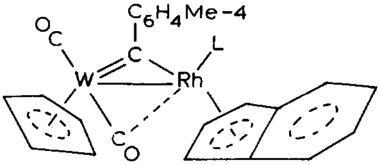


[123]



[124]

interchanging the phosphine with a carbonyl ligand on cobalt. The ketenyl complex also reacts with [(η^5-C_9H_7)Rh(C_2H_4)$_2$] in refluxing THF to yield [125] (L = PMe_3) which can be protonated to [126] by tetrafluoroboric acid in ether. The formation of [125] is taken to indicate that the initial step involves formation of [cpW≡C-p-tolyl$(CO)_2$] and [(η^5-C_9H_7)Rh(PMe_3)(C_2H_4)] followed by their combination. Complex [125] (L = CO) reacts with [$Fe_2(CO)_9$] at room temperature in THF or with [(η^5-C_9H_7)Rh$(CO)_2$] in warm toluene to give [127] and [128] (R = p-tolyl) respectively (refs. 355-357). In THF, [RhCl$(PPh_3)_3$] reacts with Na[cpM$(CO)_3$] (M = Mo, W) or Na[Mn$(CO)_5$] to give [cp(CO)M(μ-CO)$_2$Rh$(PPh_3)_2$] and [(PPh_3)$(CO)_2$Mn(μ-CO)$_2$-Rh$(PPh_3)_2$] respectively. In all three, the metal-metal bond is considered to be best represented as $\mathrm{Rh}\overset{\blacktriangle}{=}\mathrm{M}$. The molybdenum-rhodium complex is an olefin hydrogenation catalyst but cleavage of the metal-metal bond also occurs (ref. 358).



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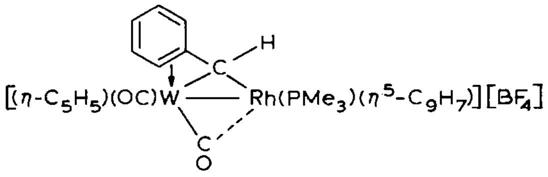
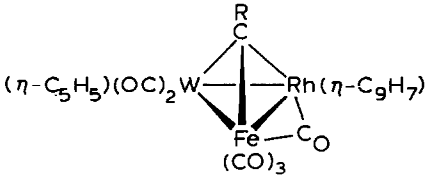
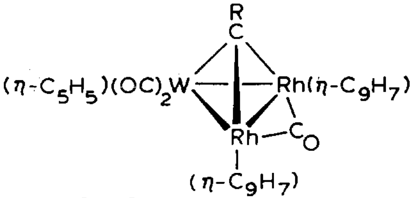


[126]

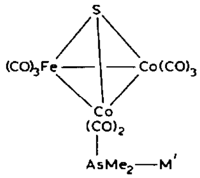


[127]



[128]

Several papers continuing the study of mixed metal clusters containing three different metal atoms have appeared. From stoichiometric quantities of [$FeCo_2$-$(CO)_9(\mu_3$-S)] and [$AsMe_2M'$] (M' = cpM$(CO)_3$ (M = Cr, Mo, W), cpFe$(CO)_2$) [129] is obtained while an excess of [$AsMe_2M'$] (M' = cpFe$(CO)_2$) affords [130]. Complex [129] with M' = $Mn(CO)_5$ can be prepared from [$FeCo_2(CO)_8(AsMe_2Cl)(\mu_3$-S)] and



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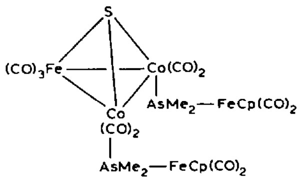
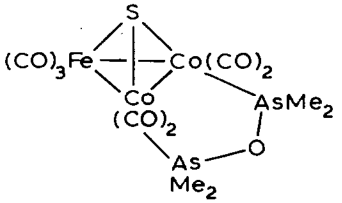


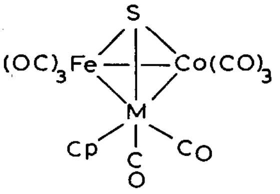
[130]

Na[Mn(CO)$_5$]. Reaction of [FeCo$_2$(CO)$_9$(μ_3-S)] with dimethylaminodimethylarsine gives a mixture of products including [131] which can also be got directly by reaction



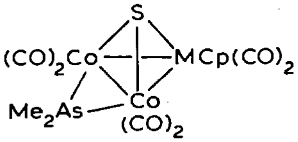
[131]

with (Me$_2$As)$_2$O. Thermolysis of [129] (M' = cpM(CO)$_3$ (M = Cr, Mo, W)) under nitrogen yields the chiral clusters [132] (M = Cr, Me, W) but when M' = cpFe(CO)$_2$ either disproportionation to [FeCo$_2$(CO)$_9$(μ_3-S)] and [130] or decomposition

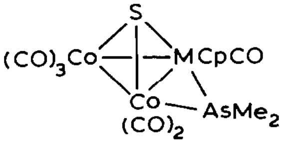


[132]

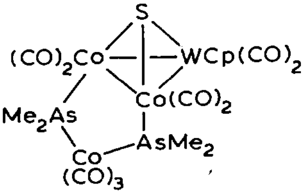
occurred. Additional products of the first reaction are [133], [134] and [135] (ref. 359). On the other hand, heating [129] (M' = cpM(CO)$_3$ (M = Mo, W) in cyclohexane at 80° C under vacuum yields [136] which reversibly unfolds on carbonylation



[133]

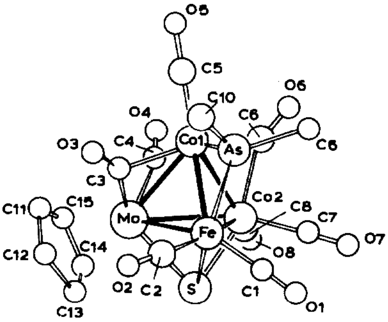


[134]

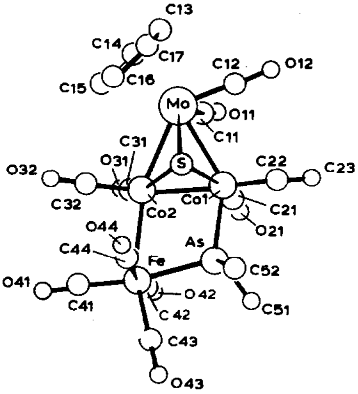


[135]

at room temperature to give [137]. Further treatment with carbon monoxide at 50° C

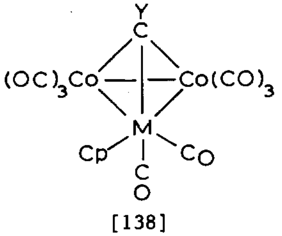


[136]

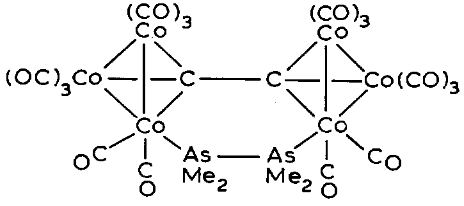


[137]

gives [132] (M = Mo, W) (ref. 360). The racemic mixture of complexes [132] (M = Cr, Mo, W) undergoes monosubstitution at cobalt by (-)-(R)-methylphenylpropylphosphine and the diastereomeric products could be separated by fractional crystallization. Reconversion to pure, optically active carbonyl clusters was accomplished by carbonylation in the presence of methyl iodide as a phosphine trap. Crystal structure studies of the molybdenum and tungsten clusters showed them to be the (+)-(S,S) and (-)-(R,S) forms respectively. Although resistant to thermal racemization they could be readily racemized on photolysis (ref. 361). At room temperature [$YCCo_3(CO)_9$] (Y = H, Me, Ph, p-tolyl, F) reacts with [$cpM(CO)_3(AsMe_2)$] (M = Cr, Mo, W) to give [$YCCo_3(CO)_8(AsMe_2Mcp(CO)_3)$] which reacts further on heating to yield [138], [$YCo_3(CO)_9$], [$(OC)_3CoAsMe_2]_x$ and [$cpM(CO)_3]_2$. For Y = Cl, the reaction provides [139] when carried out at elevated temperature while with

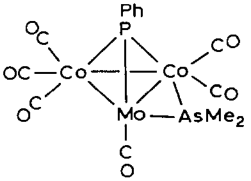


[138]



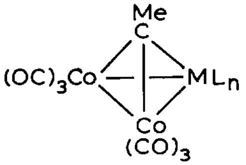
[139]

$[Co_3(CO)_9(\mu_3\text{-}PPh)]$, a mixture of $[Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh)]$ and [140] is formed. Reaction of $[XCo_3(CO)_9]$ (X = $Co(CO)_3$, cpNi, $HFe(CO)_3$) with $[cpMo(CO)_3AsMe_2]$ yields

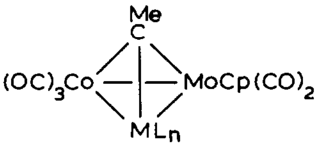


[140]

$[XCo_3(CO)_8(AsMe_2Mo(CO)_3cp)]$ (refs. 362-363). The complex $[FeCo(CO)_7(\mu\text{-}AsMe_2)]$ and related species have been investigated as hydrogenation catalysts for olefins and carbon monoxide. Although no observable metal-hydrides were formed on heating under hydrogen, isomerization and hydrogenation of oct-1-ene occurred indicating unstable hydrides evidently were generated. No hydrogenation of carbon monoxide was observed and all studies were hampered by decomposition of the starting complexes (ref. 364). The clusters [141] (ML_n = $cpMo(CO)_2$, cpNi), [142] (ML_n = $Co(CO)_2(P(OMe)_3)$, cpNi) and [143] (X = CH; ML_n = $cpW(CO)_2$; M' = Co. X = S; ML_n = $cpW(CO)_2$; M' = Fe. X = PhP; ML_n = $Fe(CO)_3$; M' = Co) have been studied as catalysts in the photoinitiated hydrosilylation of acetophenone. All appear to resist degradation under reaction conditions but the rapid racemization of [143] (X = S; ML_n = $cpW(CO)_2$; M' = Fe) foiled attempts at asymmetric hydrosilylation (ref. 365).



[141]



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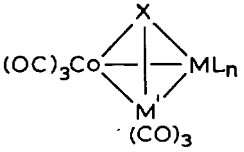
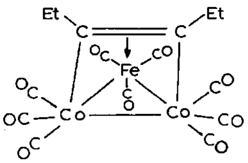
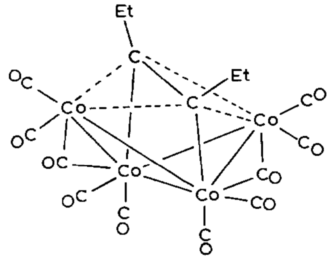


[143]

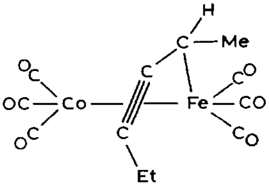
A full report has appeared on the use of $[HFeCo_3(CO)_{12}]$ and $[HCo(CO)_4]$ as acids for the protonation of cis-$[W(N_2)_2(PMe_2Ph)_4]$ in methanol. Very low yields of ammonia and hydrazine were observed despite the fact that the two complexes are strong acids in methanol since side reactions liberate carbon monoxide from the carbonyl hydrides which displaces dinitrogen and phosphine from tungsten. Reaction under hydrogen gave somewhat increased yields of nitrogen reduction products. Although no ammonia was formed using $[W(N_2)_2(diphos)_2]$, the complex $[W(OR)(NNH_2)(diphos)_2]X$ (R = Me; X = $[FeCo_3(CO)_{12}]^-$, $[Co(CO)_4]^-$) could be isolated. Analogs with R = Et, Pr^n, Pr^i, Bu^n, Bu^s, cyclo-C_6H_{11}, $PhCH_2$ could also be prepared using the corresponding alcohols as solvent. The formation of these complexes is thought to involve stepwise protonation of coordinated dinitrogen by two molecules of carbonyl hydride to give the coordinated $\{NNH_2\}$ moiety followed by coordination of the alkoxide ligand (ref. 366). The reaction of hex-3-yne with a mixture of $[Co_2(CO)_8]$ and $[Fe(CO)_5]$ in refluxing acetone gives mainly $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C_2Et_2)]$ together with small amounts of [144], [145], [146], $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}EtC_2CHOHMe)]$



[144]



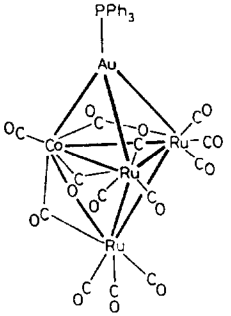
[145]



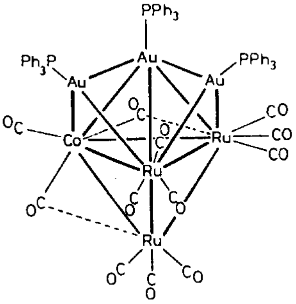
[146]

and $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}EtC_2COMe)]$. The last two products require the presence of iron and water for their formation but the mechanism is unknown. The same reaction with $[HFeCo_3(CO)_{12}]$ yields the same set of complexes except for [146] but now the major product is [144] and $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C_2Et_2)]$ forms in relatively low yield (ref. 367).

The gold oxonium ion $[(Au(PPh_3))_3O]^+$ reacts with $[HCoRu_3(CO)_{13}]$ in THF to give a mixture of [147], [148] and $[HAu_2CoRu_3(CO)_{12}(PPh_3)_2]$. Complex [147] can also be

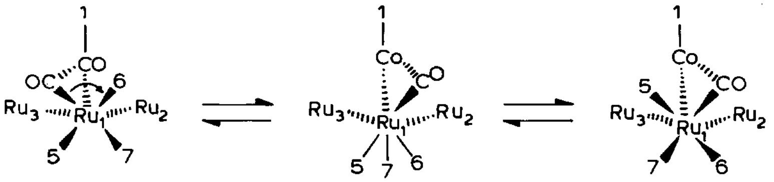


[147]



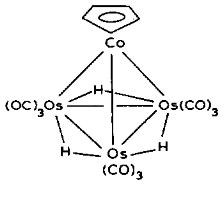
[148]

prepared from $Na[CoRu_3(CO)_{13}]$ and $[Au(PPh_3)Cl]$ while action of $[(Au(PPh_3))_3O]^+$ on $(PPN)[CoRu_3(CO)_{13}]$ gives [148]. The formation of the species containing two and three gold atoms evidently does not occur in a stepwise fashion since [147] is unreactive towards $[(Au(PPh_3))_3O]^+$. In [148] a delocalized bonding model is considered superior to viewing the $\{Au(PPh_3)\}$ moieties as hydride equivalents and bonding <u>via</u> localized two-electron bonds (ref. 368). A variable temperature ^{13}C NMR study of the chiral cluster $[CoRu_3(CO)_{13}]^-$ shows that while all carbonyl ligands are equivalent at room temperature, at −112° C one of these no longer equilibrates. The apparently concerted process which interconverts the other twelve is suggested to be that of Scheme XXXVI (ref. 369). Extended reaction of

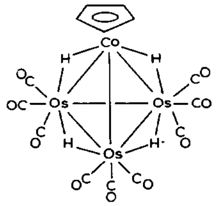


Scheme XXXVI

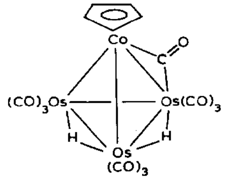
$[cpCo(CO)_2]$ with $[H_2Os_3(CO)_{10}]$ in refluxing toluene under hydrogen produces moderate yields of [149] and [150] plus a small amount of [151]. In the absence of



[149]



[150]

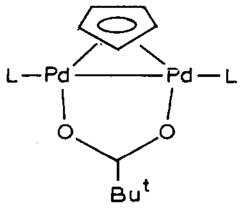


[151]

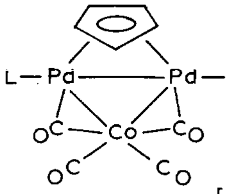
hydrogen, [151], which shows fluxionality for both carbonyl and hydride ligands at ambient temperature, is the major product (refs. 370, 371). What is probably the ethyltetramethylcyclopentadienyl analog of [151] is prepared by reaction of $[(\eta^5\text{-}C_5Me_4Et)CoMe_2(C_2H_4)]$ with $[H_2Os_3(CO)_{10}]$ although the hydride ligands were not located in the crystal structure determination. On treatment with hydrogen at 80° C the analog of [150] is formed which is cleaved on reaction with carbon monoxide to $[Os_3(CO)_{12}]$ and $[(\eta^5\text{-}C_5Me_4Et)Co(CO)_2]$ (ref. 372).

The tripod phosphine tris(diphenylphosphino)methane (L_3) replaces three carbonyl groups in the clusters $[M_4(CO)_{12}]$ (M_4 = Co_4, Rh_4, Ir_4, Co_2Rh_2, $HFeCo_3$) to give the capped clusters $[M_4(CO)_9(L_3)]$. In the last two complexes, the Rh_2Co and Co_3 faces respectively contain the ligand. The Co_4 and Rh_4 complexes are unaffected by heating to 100° C under 30 atm of carbon monoxide while refluxing the Co_4 complex in toluene gives $[(\eta^6\text{-}PhMe)Co_4(CO)_6(L_3)]$ (ref. 373). On reaction with stoichiometric quantities of trimethylphosphite $[Co_2Ir_2(CO)_{12}]$ yields $[Co_2Ir_2(CO)_{12-n}\text{-}(P(OMe)_3)_n]$ (n = 1 or 2 respectively). With an excess of ligand $[Co_2Ir_2(CO)_8\text{-}(P(OMe)_3)_4]$ is the major product at elevated temperatures. A small quantity of the tris(phosphite) derivative is also formed. In all cases, the basal plane contains three bridging carbonyl ligands and although it is assumed that the phosphite ligands substitute one per metal, this was not confirmed (ref. 374). Reduction of $[cp'CoNi_2cp_2(\mu_3\text{-}CO)_2]$ with potassium naphthalenide in the presence of the cryptand 2,2,2-crypt yields $[K(2,2,2\text{-}crypt)][cp'CoNi_2cp_2(\mu_3\text{-}CO)_2]$ in which the three metal-metal bond distances are increased to a significant extent over what is observed in the neutral cluster with the increase in the Ni-Ni bond distance being largest. This indicates that the extra electron occupies a metal-metal antibonding orbital which is preponderantly nickel in character (ref. 375).

Complex [152] is converted into [153] (L = PPr^i_3) on reaction with $Na[Co(CO)_4]$ in toluene. The 2-methylallyl-bridged dimer reacts in the same fashion (ref. 376).

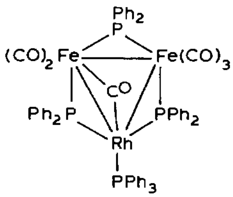


[152]

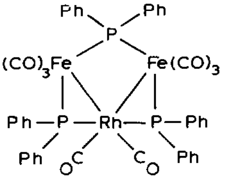


[153]

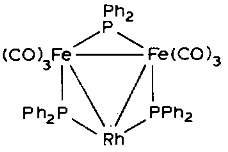
Addition of $[RhCl(CO)L_2]$ (L = PPh_3, PEt_3) to $Li[Fe_2(\mu\text{-}PPh_2)_2(CO)_5(PPh_2)]$ yields [154] which decomposes in solution but is reversibly carbonylated to [155]. Under reduced pressure [155] converts to [156] from which [155] can be regenerated on addition of carbon monoxide (ref. 377). Under nitrogen $[RhCl(CO)_2]_2$ reacts with either $(PhCH_2Me_3N)[Fe_3(CO)_{11}]$ or $(Et_4N)[HFe(CO)_4]$ to give $[Fe_2Rh(CO)_x]^-$ (x = 10 or 11) whose subsequent reactions are shown in Scheme XXXVII. The structure of



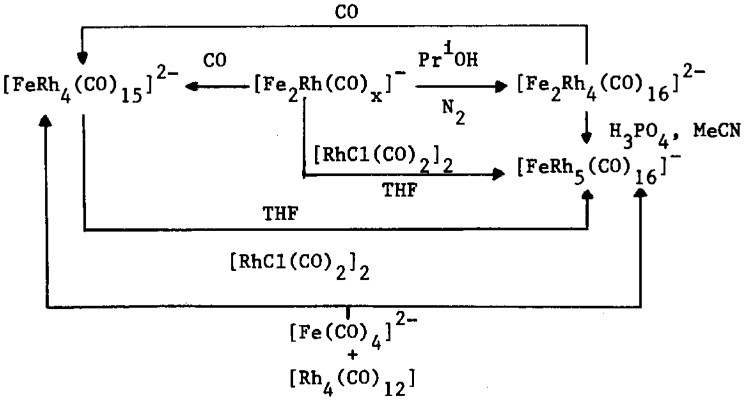
[154]



[155]

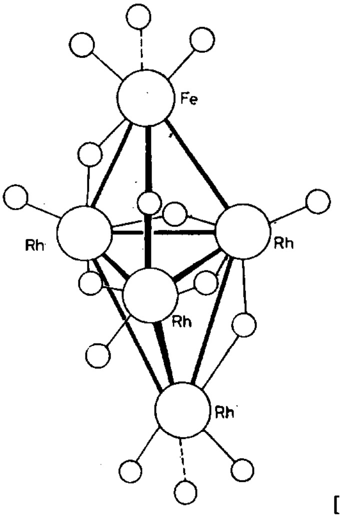


[156]

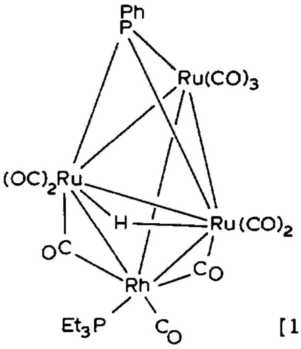


Scheme XXXVII

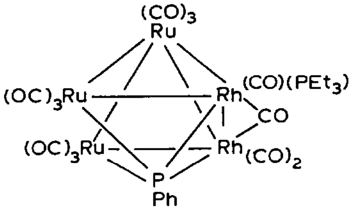
$[FeRh_4(CO)_{15}]^{2-}$ was found to be [157] (small circles = CO). At -70° C the anion has this structure in solution however at 65° C all but the equatorial bridging carbonyl groups migrate over the Rh_4Fe skeleton. The metal skeleton appears non-fluxional. The two six-atom complexes are disordered in the solid state so all that could be determined is that they are isostructural with $[Rh_6(CO)_{16}]$ although NMR measurements suggest that $[Fe_2Rh_4(CO)_{16}]$ exists as a 3:1 mixture of trans-Fe_2 and cis-Fe_2 isomers. Both complexes show fluxionality for the carbonyl ligands but not the metal core (ref. 378). Treatment of $[Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}PPh)]$ with methanolic potassium hydroxide followed by addition of $[Rh(CO)_3(PEt_3)_2]BF_4$ yields a mixture of [158] and [159] (ref. 379).



[157]

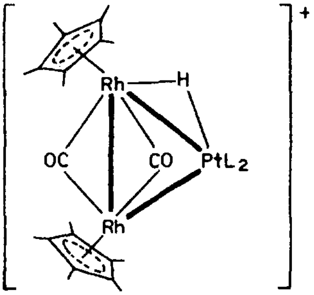


[158]



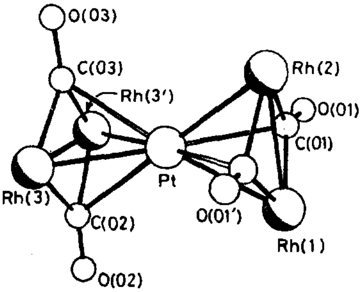
[159]

Protonation of [63] (L_2 = $(CO)_2$, $(CO)(PPh_3)$, COD) with tetrafluoroboric acid in ether yields [160] which is fluxional via a process thought to involve rotation



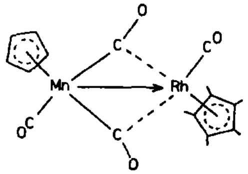
[160]

of the {$PtHL_2$} moiety. From the structure of the triphenylphosphine derivative it appears that carbonyl groups bridging the rhodium-rhodium bond interact less with the platinum atom than they do in [63] (ref. 380). Reaction of [$cp'_2Rh_2(\mu\text{-}CO)_2$] with [$Pt(C_2H_4)_3$] forms [161] (cp' groups on rhodium omitted for clarity), which exists in two crystalline modifications. The difference between the two involves



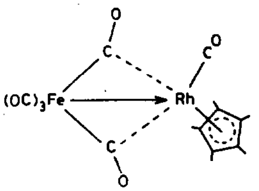
[161]

primarily a small difference in the dihedral angles between the two $PtRh_2$ planes ref. 381). Complex [162] is formed from [$cp'Rh(CO)_2$] or [$cp'_2Rh_2(\mu\text{-}CO)_2$] (but in lower yield) and [$cpMn(CO)_2THF$]. The related iron complex [163] together with [164] are formed on reaction of [$cp'Rh(CO)_2$] with [$Fe_2(CO)_9$] while with [cp'_2Rh_2-

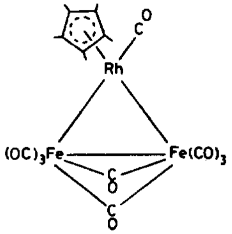


[162]

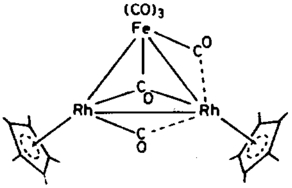
$(\mu\text{-}CO)_2$] *this reaction yields* [164] *and* [165]. *Conversion of* [$cp'Rh(CO)_2$] *to* [$cp'_2Rh_2(\mu\text{-}CO)_2$] *occurs in refluxing acetone in the presence of anhydrous*



[163]

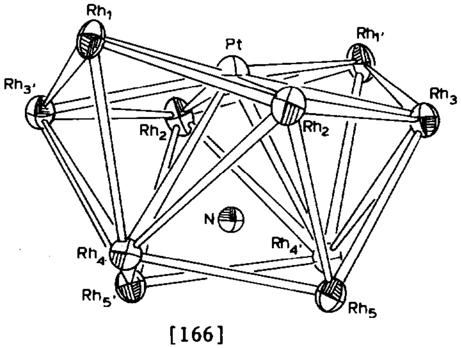


[164]

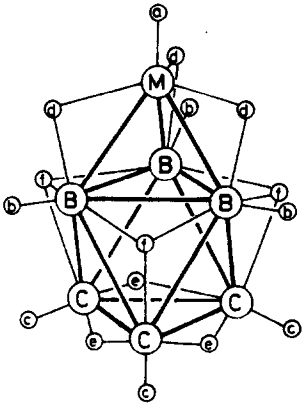


[165]

trimethylamine oxide. However attempts to effect the same reaction with $[(\eta^5-C_9H_7)Rh(CO)_2]$ at -50° C produced $[(\eta^5-C_9H_7)_3Rh_3(\mu-CO)_3]$ instead. Heating $[cp'Rh(CO)_2]$ in vacuo converts it to $[cp'_3Rh_3(\mu-CO)_2(\mu_3-CO)]$ which unlike its cobalt analog appears to have the same structure in solution as in the solid state. The complex is fluxional even at -156° C presumably via interconversion of the carbonyl groups between terminal and μ_2- and μ_3-bridging modes. It can be reversibly protonated on the unbridged edge of the metal triangle (ref. 382). The clusters $[Rh_6N(CO)_{15}]^-$ and $[PtRh_4(CO)_{14}]^{2-}$ react in refluxing acetone under nitrogen to give a variety of products one of which has been identified as $K_3[PtRh_{10}N(CO)_{11}(\mu-CO)_{10}]$. The structure of the core is shown as [166] and demonstrates the tendency for interstitial nitrogen atoms to occur in irregular cavities with a low coordination number (here 5) (ref. 383). Variable temperature $^{13}C\{^{103}Rh\}$ NMR spectra of $[NiRh_6(CO)_{16}]^{2-}$ ([167] (M = Ni, B = C = Rh; small circles = CO)) provide additional information contradicting Johnson's proposal that fluxionality in carbonyl clusters arises from movement of the metal skeleton within the polyhedron of carbonyl groups. The process indicated here differs from that observed for the isostructural species $[Rh_7(CO)_{16}]^{3-}$ and involves equilibration of carbonyl groups b, d and f at -40° C, additional equilibration of groups c and e at 25° C and all carbonyl groups at 90° C (ref. 384).

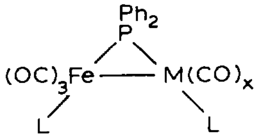


[166]



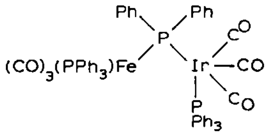
[167]

A palladium-iridium complex formulated as $[(PPh_3)_2Ir(CO)_2PdCl_2]$ but of unknown structure is formed from $[PdCl_2(NCPh)_2]$ and $[Ir(C(O)OMe)(CO)_2(PPh_3)_2]$. It reacts with carbon monoxide and hydrogen to give metallic palladium and a carbonyl phosphine iridium complex (ref. 385). Reaction of $Li[Fe(CO)_4PPh_2]$ with $[MCl(CO)L_2]$ yields [168] (M = Rh; L = PEt_3; x = 1. M = Ir; L = PPh_3; x =2). The iridium complex reversibly adds or loses carbon monoxide to give [169] and [170] respectively

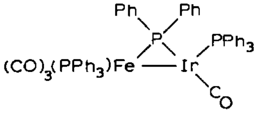


[168]

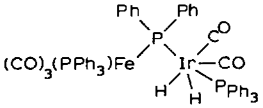
and reversibly adds hydrogen to produce [171]. Complex [170] reversibly adds hydrogen to give [172]. The rhodium complex reversibly adds carbon monoxide but is



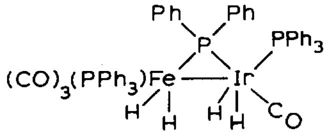
[169]



[170]

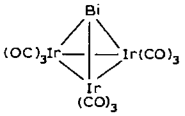


[171]



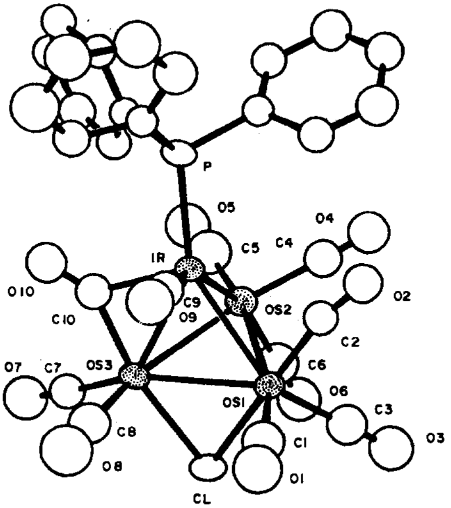
[172]

unreactive towards hydrogen (ref. 386). Bismuth trichloride reacts with Na[Ir(CO)$_4$] to give [173] (ref. 387) while [$H_2Os_3(CO)_{10}$] adds [Ir(N_2)Cl(PPh_3)$_2$] in



[173]

refluxing benzene to give [174]. The hydride positions indicated are consistent with the bond length data but these atoms were not located crystallographically (ref. 388).



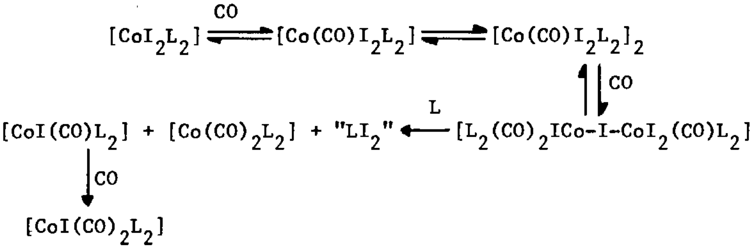
[174]

Methanol can be homologated by syngas using a catalyst prepared from [$Co_2(CO)_8$] and a small amount of hydrated ruthenium(III) chloride in THF or dioxane in 60% yield with an 80% selectivity to ethanol (ref. 389). On the other hand, methanol homologation in the presence of [$FeCo_3(CO)_{12}$]$^-$ and methyl iodide gives acetaldehyde and a small quantity of methyl acetate. Infrared spectral measurements indicate that cluster fragmentation occurs so that the active catalyst species is unknown (ref. 390).

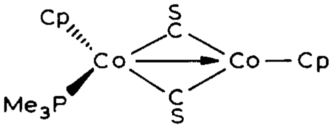
The photoelectron and electronic spectra of [$MeCCo_3(CO)_9$] have been compared with those of the isoelectronic [$MeCFe_3(\mu\text{-}H)_3(CO)_9$] cluster and interpreted using Fenske-Hall molecular orbital calculations. Although the population analysis indicates that the cobalt cluster contains little direct cobalt-cobalt bonding, orbital contour plots show that cobalt-cobalt orbital overlap does occur. In the iron complex the bridging hydrogens are found to be hydridic and to function as localized ligands. The calculations also indicate that the cluster bonding capabilities of the $\{Co(CO)_3\}$ and $\{Fe(CO)_3\}$ fragments can be satisfactorily modeled by $\{CH\}$ and $\{BH\}$ fragments respectively (ref. 391).

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

The kinetics of the reduction of $[CoI_2L_2]$ ($L = PEt_3$) to $[CoI(CO)_2L_2]$ by carbon monoxide in the presence of triethylphosphine are interpreted in terms of Scheme XXXVIII (ref. 392). The dimeric thiocarbonyl complex [175] is one of several species reported to be formed from the reaction of $[cpCo(PMe_3)(CS)]$ with diiodomethane (ref. 393). The tridentate phosphine bis(diphenylphosphinoethyl)-cyclohexylphosphine behaves as a bidentate ligand in $[cpMn(CO)(Ph_2P(CH_2)_2P(cy)(CH_2)_2PPh_2)]$ so that the free diphenylphosphino group is able to coordinate a second metal. Reaction with $[cpCo(CO)_2]$ thus affords $[cpMn(CO)(Ph_2P(CH_2)_2P(cy)(CH_2)_2PPh_2)Co(CO)cp]$ (ref. 394).

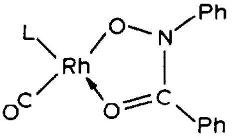


Scheme XXXVIII



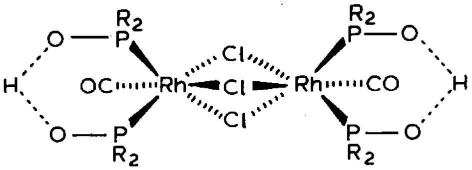
[175]

A sizeable number of papers report chemistry of rhodium(I) carbonyl complexes most of which are derived from $[RhCl(CO)_2]_2$ and to a lesser extent $[Rh(acac)(CO)_2]$. While many are relatively routine, several novel results have appeared. Triphenylphosphite replaces both carbonyl ligands in $[Rh(acac)(CO)_2]$ but then the product adds carbon monoxide to finally yield $[Rh(acac)(CO)(P(OPh)_3)_2]$ (ref. 395). Among the reactions of $[RhCl(CO)_2]_2$ is that with N-hydroxybenzanilide from which [176] (L = CO) is formed. This reacts further with triphenylphosphine to give the

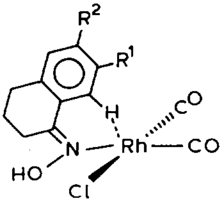


[176]

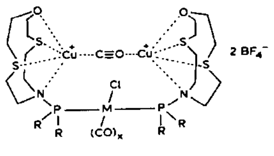
analog with L = $\mathrm{PPh_3}$ (ref. 396). The diaryltriazenido complex $[\mathrm{Rh(ArN_3Ar)(CO)_2}]$ (Ar = Ph, *p*-tolyl, *p*-anisyl) are formed on refluxing ArN=N-NHAr with $[\mathrm{RhCl(CO)_2}]_2$ in ethanol in the presence of triethylamine. The related complexes $[\mathrm{Rh(ArN_3Ar)L_2(PPh_3)}]$ ($\mathrm{L_2}$ = COD or $\mathrm{(CO)(PPh_3)}$) are formed from $[\mathrm{RhCl(COD)(PPh_3)}]$ in benzene and $[\mathrm{RhCl(CO)(PPh_3)_2}]$ in 2-methoxyethanol respectively under similar conditions (ref. 397). Other reactions of $[\mathrm{RhCl(CO)_2}]_2$ are those with triisopropylphosphite in the presence of oxygen which forms [177] (R = $\mathrm{OPr^i}$) (ref. 398), with a variety of


[177]

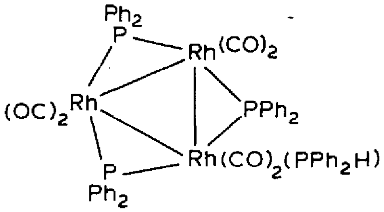
N-substituted 2-amino-1,3,2-dioxaphosphorinanes (L) which give *cis*- and *trans*-$[\mathrm{RhCl(CO)L_2}]$ (refs. 399, 400), with 1-tetralone oximes to give [178] ($\mathrm{R_1 = R_2 = H}$.


[178]

$\mathrm{R_1 = H}$; $\mathrm{R_2 = OMe}$. $\mathrm{R_2 = H}$; $\mathrm{R_1 = OMe, NO_2}$) in which the indicated interaction of the aromatic proton with the metal is proposed from its significant downfield shift in the NMR spectrum (ref. 401) and with substituted quinoline ligands to give $[\mathrm{RhCl(CO)(L_2)}]$ ($\mathrm{L_2}$ = 8-quinolinyldiphenylphosphine or -arsine) or $[\mathrm{Rh(CO)_2(L_2)}]\mathrm{Cl}$ ($\mathrm{L_2}$ = 8-aminoquinoline). With $[\mathrm{Ir(CO)_2Cl_2}]^-$ the products are $[\mathrm{IrCl(CO)(L_2)}]$ ($\mathrm{L_2}$ = 8-quinolinyldiphenylphosphine, 8-aminoquinoline) or $[\mathrm{IrH(CO)Cl_2(L_2)}]$ ($\mathrm{L_2}$ = 8-quinolinyldiphenylarsine) (ref. 402). The ligands N-diphenylphosphino-1-aza-4,10-dithia-7-oxocyclododecane and its dimethylphosphino analog (L) form complexes $[\mathrm{MCl(CO)L_2}]$ (M = Rh, Ir) on reaction with $[\mathrm{RhCl(CO)_2}]$ and $[\mathrm{IrCl(CO)(}$*cyclo*-$\mathrm{C_8H_{14})_2}]_2$ respectively which further react with $[\mathrm{Cu(MeCN)_4}]\mathrm{BF_4}$ to yield $[\mathrm{MCl(CO)(LCu)_2}](\mathrm{BF_4})_2$ in which the copper ions are bound to the $\mathrm{NS_2O}$ donor set of the macrocyclic ligand. The iridium complex oxidatively adds hydrogen and all react with carbon monoxide to

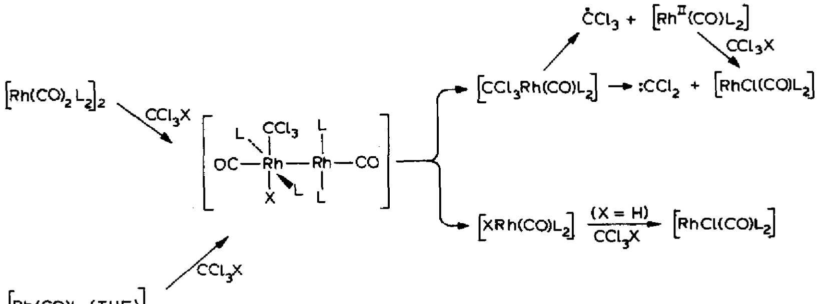

[179]

give [179] (R = Ph, Me; M = Rh; x = 1. R = Ph; M = Ir, x = 2) (ref. 403). The phosphine ligand $[cp_2Zr(Cl)CH_2PPh_2]$ (L) reacts with $[RhCl(CO)_2]_2$ to give trans-$[RhCl(CO)L_2]$ which exists in solution at room temperature as a mixture of slowly interconverting rotamers. Both zirconium atoms coordinate a carbonyl ligand but presumably because of steric hindrance, no acyl formation is seen as was observed for L itself (ref. 404). The related ligands $[Cl_2M(\eta^5-C_5H_4(CH_2)_2PPh_2)_2]$ (M = Ti, Zr) (L_2) react with $[RhCl(CO)(C_2H_4)]_2$ to form complexes of empirical formula $[RhCl(CO)(L_2)]$ which are thought to possibly be face-to-face dimers (ref. 405). Diphenylphosphine reacts with $[RhCl(CO)_2]_2$ in ethanol under carbon monoxide to yield [180] which is stable only in a carbon monoxide atmosphere. Under reduced pressure it converts to $[Rh_3(\mu-PPh_2)_3(CO)_5]$ which can be reconverted to [180] on reaction with diphenylphosphine and carbon monoxide in methanol (ref. 406).

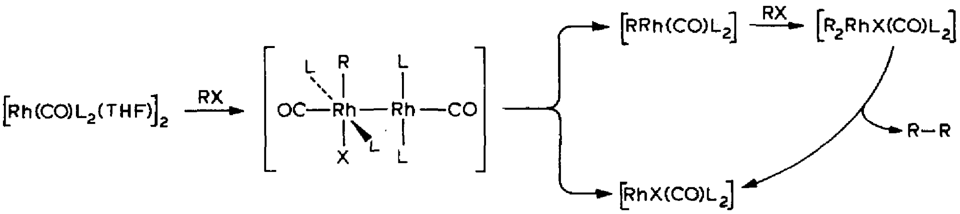


[180]

The course of the reactions of $[Rh(CO)_2(L)_2]_2$ and/or its THF solvate (L = PPh_3) with various organic halogen compounds is detailed in Schemes XXXIX (X = H, Cl), XL (R = allyl, 3-methylallyl; X = Br) and XLI (R_2CX_2 = Ph_2CCl_2, $Br_2C(CO_2Me)_2$, 9,9-dichlorofluorene. R_2CXCXR_2 = $Ph_2CClCClPh_2$, 9,9'-dichlorobisfluorenyl). In the

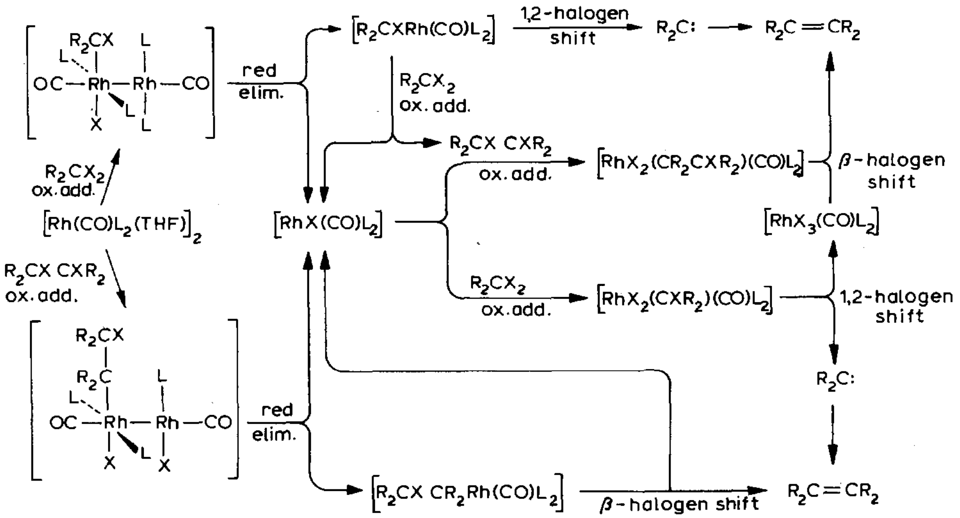


Scheme XXXIX



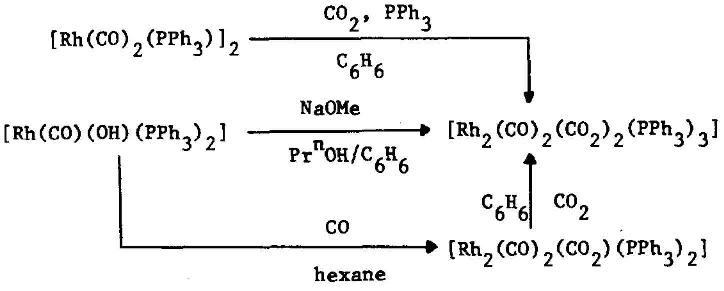
Scheme XL

reaction with carbon tetrachloride addition of cyclohexene does not affect the yield of [RhCl(CO)(PPh$_3$)$_2$] but some 7,7-dichlorobicycloheptane is formed implying

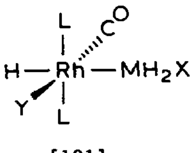


Scheme XLI

the generation of dichlorocarbene. This system also catalyzes the copolymerization of styrene with methylmethacrylate, a process which is quenched by addition of diphenylpicrylhydrazyl thereby suggesting the formation of trichloromethyl radicals (ref. 407). Some routes to carbon dioxide complexes are shown in Scheme XLII (ref. 408). The complexes [181] (L = PEt$_3$. M = Si, Ge; X = Y = Cl, I. M = Si; X = I; Y



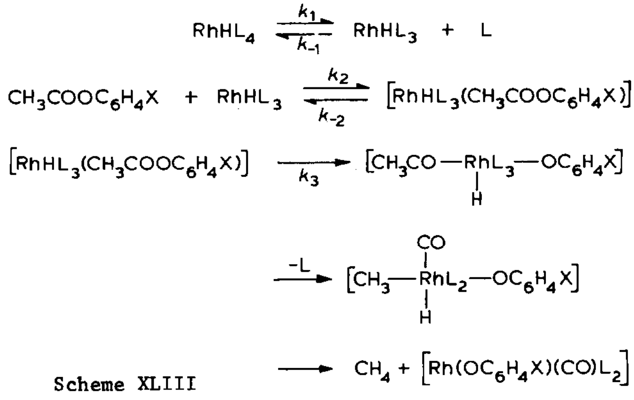
Scheme XLII



[181]

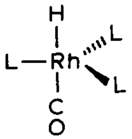
= Cl) are formed at low temperature from MH_3Y and $[Rh(CO)XL_2]$. Halogen scrambling also is observed in the reaction of $[RhCl(CO)L_2]$ with iodosilane where a mixture of $[RhH(CO)ClL_2(SiH_2Cl)]$, $[RhH(CO)IL_2(SiH_2Cl)]$ and $[RhH(CO)IL_2(SiH_2I)]$ is formed. Oxidative addition of silane, methylsilane and methylgermane to $[RhX(CO)L_2]$ (X = Cl, I) also occurs at low temperature but the adducts dissociate on warming with the tendency being greater for the chloride complexes (ref. 409).

Reaction of hydrated rhodium(III) or iridium(III) chloride with tri-tert-butylphosphine in refluxing DMF yields isobutene and $[MCl(CO)(PHBu^t{}_2)_2]$ (M = Rh, Ir). At room temperature only intractable products resulted but the presence of the tri-tert-butylphosphonium ion was detected as were species containing metal-hydrogen bonds suggesting the possible initial formation of $[MH_2Cl(PBu^t{}_3)_3]$ complexes. The subsequent course of the reaction at elevated temperature is uncertain but it was established that no formation of stable cyclometallated species or thermal decomposition of the ligand occurred (ref. 410). The possibility of oxidative addition of formyl fluoride as a route to formyl complexes has been explored and found to be unsuitable. Thus from $[RhCl(PPh_3)_3]$ only $[RhCl(CO)(PPh_3)_3]$ was formed while with $[IrCl(CO)L_2]$ (L = PPh_3, PMe_3) the product was $[IrH(CO)ClFL_2]$ (ref. 411). At 80–110° C $[RhH(PPh_3)_4]$ reacts with $MeCO_2C_6H_4X$ (X = H, p-OMe) to give trans-$[Rh(OC_6H_4X)(CO)(PPh_3)_2]$ and methane with the mechanism of Scheme XLIII (L = PPh_3) as the preferred process (ref. 412). The same rhodium

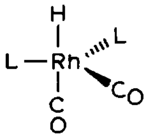


Scheme XLIII

hydride reacts with carbonyl sulfide to yield trans-$[Rh(SH)(CO)(PPh_3)_2]$ presumably via initial formation of $[RhH(PPh_3)_3(\eta^2\text{-SCO})]$ although the mechanism was not studied (ref. 413). The related complex $[RhHL_4]$ (L = 9-phenyl-9-phosphafluorene) was studied by proton NMR spectroscopy in the presence of carbon monoxide. Formation of [182] and [183] occurred with the former predominating. Slow precipitation of $[Rh_2L_4(\mu\text{-CO})_2]$ occurred and [183] could be selectively trapped with methylene cyclopropane. A comparison study of $[RhH(CO)(PPh_3)_3]$ showed that slow reversible dissociation of one phosphine occurred in the absence of carbon monoxide at 273 K while at the same temperature in the presence of carbon monoxide the processes of

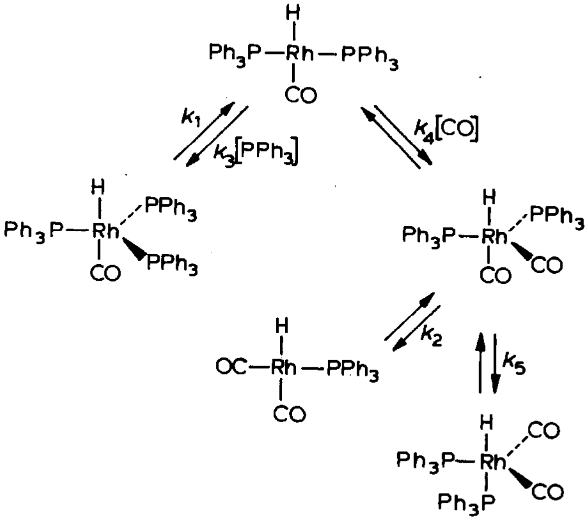


[182]



[183]

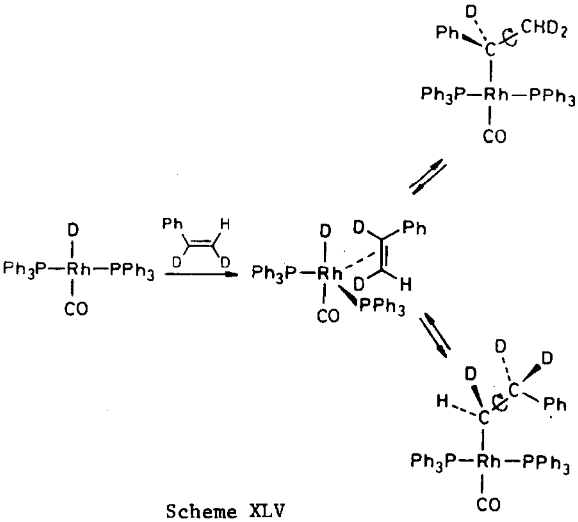
Scheme XLIV were detected. A ratio of k_3/k_4 of 0.2 was determined while k_2 and k_5 were found to be 0.5 and 10^7 sec^{-1} and all equilibrations were fast compared to



Scheme XLIV

the rate of olefin hydroformylation catalyzed by the system. At 148 K both isomers of $[RhH(CO)_2L_2]$ were seen with the one having two equatorial carbonyl groups accounting for 15% of the complex. In the presence of catalytic quantities of $[RhH(CO)(PPh_3)_3]$ (Z)-[1,2-$^2H_2$]styrene isomerized much more rapidly than hydrogen was scrambled between the 1 and 2 positions suggesting Scheme XLV for the process. Addition of phosphine or carbon monoxide markedly suppressed the isomerization. Under identical conditions the hydroformylation of the deuterated styrene is significantly slower than its isomerization but on the addition of a five-fold excess of triphenylphosphine the reverse is true suggesting that $[RhH(CO)L_2]$ is not on the hydroformylation path as it is too efficiently trapped by phosphine or carbon monoxide. However $[RhH(CO)_2L]$ may be an important intermediate (ref. 414). In contradiction to this conclusion a second study of this system proposed that the rate determining step in the hydroformylation reaction is addition of olefin to

$[RhH(CO)L_2]$. However there is no indication that these authors had information on the conclusions reached in the previous paper or vice versa (ref. 415).

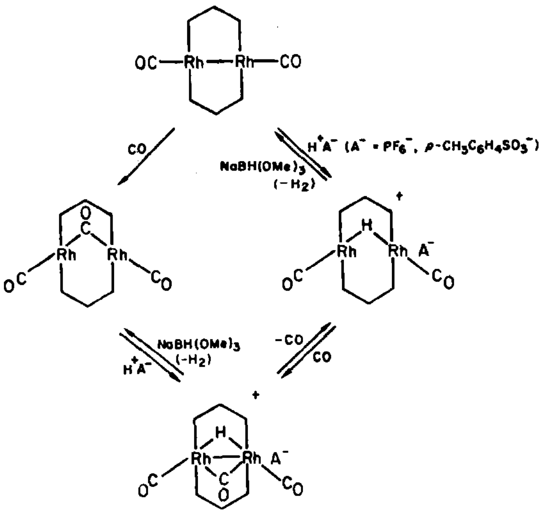


Scheme XLV

A reinvestigation of the formation of $[MH(CO)(SO_2)(PPh_3)_2]$ (M = Rh, Ir) from $[MH(CO)(PPh_3)_3]$ and sulfur dioxide has led to the location of the metal hydride resonance which had originally not been observed. Thus the original proposal of the equilibrium: $M(H)(SO_2) \rightleftharpoons M(SO_2H)$ to account for the absence of this resonance seems to be incorrect. In the formation of the iridium complex the intermediate <u>mer</u>-$[IrH(CO)(SO_2)(PPh_3)_3]$ was detected at low temperature (ref. 415).

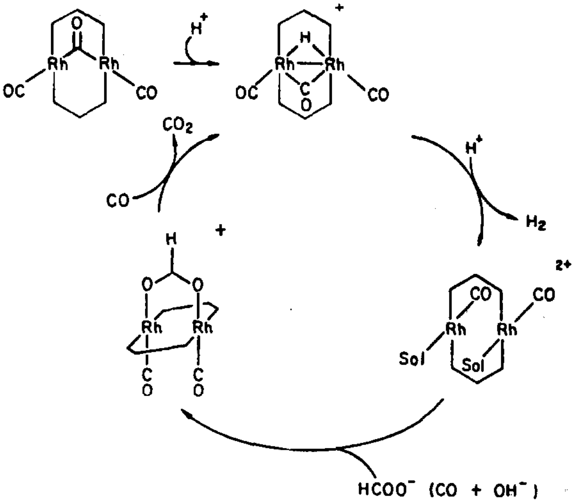
The hyponitrite complexes $[(RhCl(X)(PPh_3)_2)_2N_2O_2]$ (X = Cl, Br) are reported to be formed from $[RhCl(CS)(PPh_3)_2]$ and the corresponding nitrosyl halide (ref. 417) while the thiazate complex $[Rh(NSO)_2Cl(PPh_3)(H_2O)]_2$ is claimed to form when NSOH reacts with $[RhCl(PPh_3)_3]$ or $[RhCl(CO)(PPh_3)_2]$. Cleavage of the dimer to $[Rh(NSO)_2Cl(PPh_3)_2H_2O]$ occurs on reaction with triphenylphosphine (ref. 418).

A full paper has now appeared on the chemistry of $[Rh_2(CO)_2(DPM)_2]$ which can be synthesized by borohydride reduction of $[Rh_2(CO)_2Cl_2(DPM)_2]$ in ethanol. Some reactions are shown in Scheme XLVI. It also adds acetylene to give a 1:1 adduct of unknown structure which reacts with hydrogen to produce ethane and with carbon dioxide to give $[Rh_2(CO)_2(CO_2)(DPM)_2]$. In this last complex displacement of carbon dioxide by carbon monoxide gives $[Rh_2(CO)_2(\mu\text{-}CO)(DPM)_2]$ while protonation yields $[Rh_2(CO)_2(\mu\text{-}H)(DPM)_2]^+$ which reversibly inserts carbon dioxide to give the formate complex $[Rh_2(CO)_2(\mu\text{-}O_2CH)(DPM)_2]$ a species which also can be got from $[Rh_2(CO)_2Cl_2\text{-}(DPM)_2]$ and sodium formate. The complex $[Rh_2(CO)_2(DPM)_2]$ in the presence of <u>p</u>-toluenesulfonic acid and two equivalents of a lithium halide in isopropanol is a catalyst for the water-gas-shift reaction according to Scheme XLVII but its



Scheme XLVI

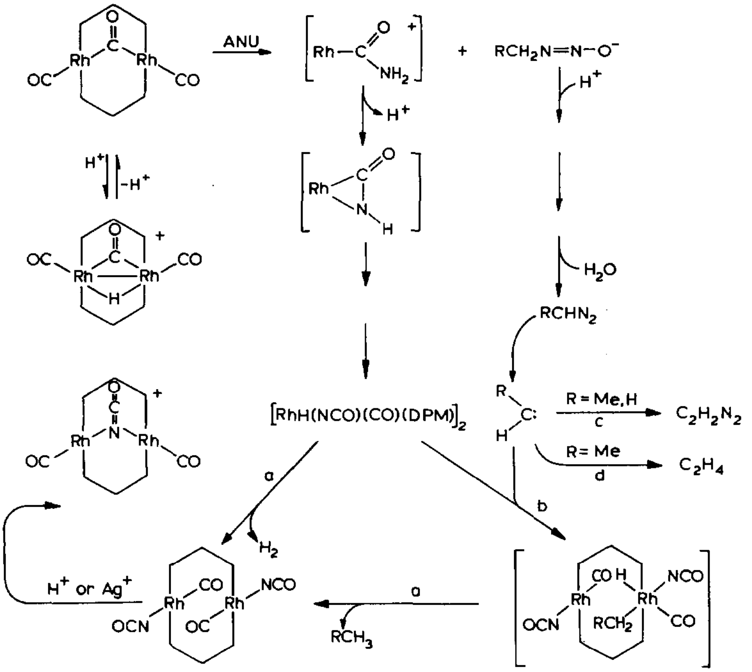
activity is short-lived (ref. 419). Methyl- or ethylnitrosourea also react with [Rh$_2$(CO)$_2$(μ-CO)(DPM)$_2$] to give the face-to-face dimer [Rh$_2$(CO)$_2$(NCO)$_2$(DPM)$_2$] plus



Scheme XLVII

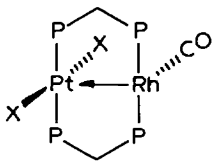
carbon monoxide, carbon dioxide, hydrogen, methane and ethylene. With methylnitrosourea partially deuterated at nitrogen, D_2, HD, H_2, CH_2D_2, CH_3D and CH_4 are formed indicating that the $-NH_2$ group is responsible for the dihydrogen and half of the hydrogen atoms of the methane; the rest of the methane is proposed to come from a carbene (Scheme XLVIII). These ureas also form [Rh$_2$(CO)$_2$(μ-NCO)(DPM)$_2$]$^+$ from

$[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2]^+$ (ref. 420). The A-frame complexes $[Rh_2(CO)_2(\mu\text{-}X)(L_2)_2]^+$ (X = Cl, Br; L_2 = DPM, DAM) catalyze the hydrogenation of hex-1-ene in methanol and these plus $[Rh_2X_2(CO)_4(L_2)_2]$ (X = CN, NCS) catalyze the stepwise hydrogenation of phenylacetylene. That none of the styrene produced is hydrogenated until all of the acetylene is consumed suggests the latter coordinates more strongly to the complex. An apparent correlation of catalyst activity with the ability to form a carbonyl-bridged species is suggested to imply coordination of substrate to only one metal but this is a very tentative proposal (ref. 421). Heterobinuclear, DPM-bridged species have been generated in a stepwise manner from trans-$[PtX_2(DPM)_2]$ (X = CN, C≡CR (R = Me, Ph, p-tolyl) and cis-$[R_2Pt_2(DPM)_2]$ (R = o-tolyl, 1-naphthyl). The products obtained on reaction with $[RhCl(CO)_2]_2$ are [184] (X = C≡CR), [185] (X = CN) and [186]. A palladium analog of [185] was also prepared and on refluxing [184] in toluene, the carbonyl group is replaced by chloride. Complex [186] appears to exist as a mixture of syn and anti isomers. An iridium analog of [185] (X = p-tolylC≡C) is prepared from $[IrCl(CO)(PPh_3)_2]$ in refluxing benzene while from $[IrCl(\text{cyclo-}C_8H_{14})_2]_2$ is obtained [187] (X = p-tolylC≡C) which reacts with hydrogen to form [188] (refs. 422-424).



a) reductive elimination, b) carbene insertion, c) dimerization, d) internal rearrangement

Scheme XLVIII



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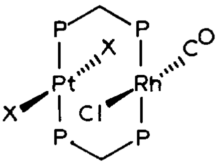

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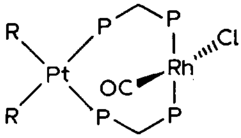

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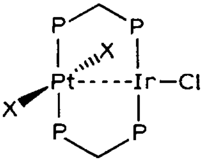

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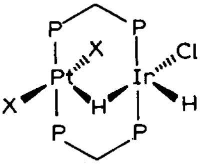


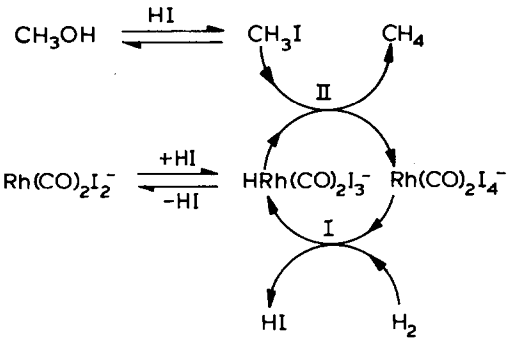
[188]

The presence of free phosphine increases the lability of the coordinated ligand in [Rh(acac)(CO)(PH$_3$)]; presumably a five-coordinate intermediate is formed (ref. 425). A two-bond carbon-carbon coupling constant of 9.2 Hz has been observed in [Rh(OXQ)(^{13}CO)$_2$] (OXQ = 8-oxyquinolinate) (ref. 426). The enthalpy of oxidative addition of iodine to [RhCl(CO)(diphos)], [Rh(L$_2$)$_2$]$^+$ (L$_2$ = diphos, vdiphos) and [RhCl(CO)(DPM)]$_2$ has been measured. In all cases a 1:1 stoichiometry was found and the rhodium-iodine bonds are stronger in the first compound than in the second possibly due to lower steric pressure (ref. 427). Photolysis of [RhL(CO)$_2$] (L = acac, trifluoroacetylacetonate (tfac), hexafluoroacetylacetonate (hfac)) in argon and methane matrices generates some [RhL(CO)] while in nitrogen matrices both this and [RhL(CO)(N$_2$)] are seen. The removal of the carbonyl group is reversible while upon prolonged photolysis, a species containing monodentate L is also detected. Similar behavior was observed for the iridium analogs. In ^{13}CO-doped methane matrices rapid ^{13}CO enrichment in all complexes occurs on photolysis with all the data being consistent with the initial process being dissociation of a carbonyl group (ref. 428).

Only one phosphorus ligand can be added to [cp'$_2$Rh$_2$(μ-CO)$_2$] giving [cp'Rh(L)-(μ-CO)$_2$Rhcp'] (L = PMe$_2$H, PMe$_3$, P(OMe)$_3$) while with [cp'Rh(CO)$_2$] one obtains [cp'Rh(CO)L] (L = PMe$_2$H, P(OMe)$_3$, PEt$_3$, P(OEt)$_3$, PMe$_2$Ph) (ref. 429). Reaction of [RhCl(CS)(PPh$_3$)$_2$] with silver perchlorate in acetone followed by addition of pyrazole or its 3-methyl or 3,5-dimethyl analogs (HL) yields [Rh(CS)(HL)(PPh$_3$)$_2$]ClO$_4$ in which the pyrazole ligands can be deprotonated with potassium hydroxide to yield the pyrazolate-bridged dimers [Rh(μ-L)(CS)(PPh$_3$)]$_2$. The same dimers are formed directly from [RhCl(CS)(PPh$_3$)$_2$] and the pyrazoles in the presence of sodium hydroxide, a reaction which can be reversed on refluxing in dichloromethane in the presence of triphenylphosphine. Attempts to prepare the dimer from [RhCl(CS)(Pcy$_3$)$_2$]

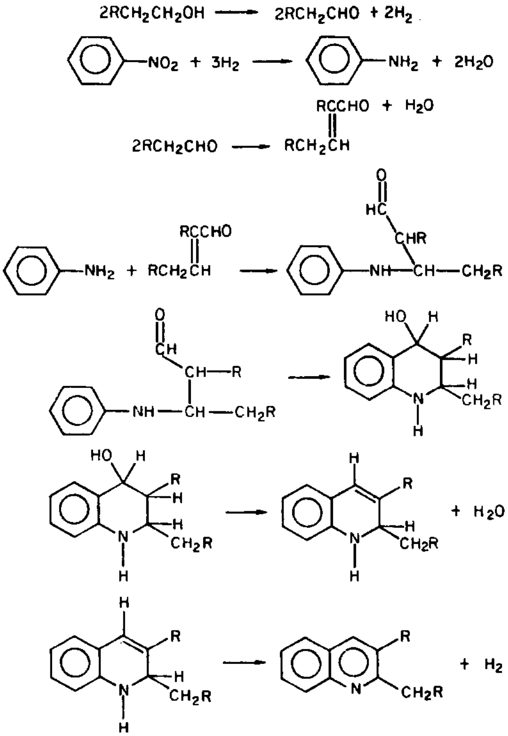
failed and only $[Rh(L)(CS)(Pcy_3)_2]$ was formed (ref. 430). The related complexes $[M(CO)L'(\mu\text{-}L)]_2$ (M = Rh, Ir; L = 3,5-dimethylpyrazolate, 3,5-diphenylpyrazolate; L' = phosphine or phosphite) are readily prepared from $[M(CO)_2(\mu\text{-}L)]_2$ and oxidatively add iodine or react with 1,2-diiodoethane to give $[M(CO)(L')I(\mu\text{-}L)]_2$ when L' = PMe_2Ph, $PMePh_2$, $P(OPh)_3$ or $AsMe_2Ph$. However the rhodium complexes with L = 3,5-dimethylpyrazolate and L' = PPh_3 or L = 3,5-diphenylpyrazolate and L' = $PMePh_2$ or $AsMe_2Ph$, give $[Rh_2(L')_2I_2(\mu\text{-}L)_2(\mu\text{-}CO)]$ in which no metal-metal bond is present (ref. 431). A variety of mono- and bidentate nitrogen-donor ligands (L or L_2) including pyridine and its derivatives react with $[RhCl(CO)(PPh_3)]_2$ in the presence of large anions to give $[Rh(CO)L_2(PPh_3)]A$ (A = ClO_4^-, BPh_4^-) (ref. 432).

The pyrazolate bridged dimers $[Rh(CO)(\mu\text{-}L)(P(OPh)_3)]_2$ and $[Rh(\mu\text{-}L')(COD)]_2$ (L = pyrazolate. L' = pyrazolate, 3-methylpyrazolate, 3,5-dimethylpyrazolate) are hydroformylation catalysts for hept-1-ene in acetone. The selectivity of the latter group of complexes is increased on addition of triphenylphosphine (ref. 433). Modification of the $[RhH(CO)(PPh_3)_3]$ system for hydroformylation of terminal olefins by addition of various bidentate phosphines increases its thermal stability and its selectivity to the straight-chain aldehyde. The best results seem to be provided by ligands which are relatively inflexible such as <u>trans</u>-1,2-bis(diphenylphosphinomethyl)cyclobutane or 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (DIOP) (refs. 434-436). Methyl crotonate can be hydrogenated under water—gas-shift conditions in the presence of $[RhH_2(O_2COH)(PPr^i_3)_2]$ or a mixture of $[RhCl(NBD)]_2$, butyllithium and triisopropylphosphine. The active species is thought to be <u>trans</u>-$[Rh(OH)(CO)(PPr^i_3)_2]$ (ref. 437). High yields and selectivity can be realized in the $[RhCl(CO)(PPh_3)_2]$-catalyzed hydroformylation of formaldehyde. A mechanism involving successive formation of $[RhCl(CO)(PPh_3)]$, $[RhH_2Cl(CO)(PPh_3)]$, $[RhHCl(CH_2OH)(CO)(PPh_3)]$ and $[RhHCl(COCH_2OH)(CO)(PPh_3)]$ is proposed (ref. 438). The hydrogenolysis of methanol to methane is catalyzed homogeneously by the system $[Rh_2(O_2CMe)_4]/CO/H_2/HI/H_2O/EtCO_2H$. The catalytically active rhodium species are thought to be iodo carbonyl complexes as indicated in Scheme XLIX (ref. 439). The same active species are proposed to be involved in the carbonylation of benzyl alcohol to phenylacetic acid when catalyzed by hydrated rhodium(III) chloride in the presence of benzyl iodide. The rate determining step is thought to be the oxidative addition of benzyl iodide to $[Rh(CO)_2I_2]^-$. In the early stages of the reaction dibenzyl ether and benzyl phenylacetate are detected but appear to be eventually converted to phenylacetic acid as well (ref. 440). The synthesis of esters from mixtures of aldehydes and simple primary alcohols is catalyzed by $[RhH(CO)(PPh_3)_3]$ or a mixture of hydrated rhodium(III) chloride, triphenylphosphine and sodium carbonate. The second product is the alcohol resulting from reduction of the aldehyde. A mechanism involving formation of a rhodium alkoxide complex from the primary alcohol followed by oxidative addition of aldehyde and transfer of the alkoxy group to the coordinated acyl group is proposed (ref. 441). The isomerization of 1,3-dehydroadamantane to 3-methylenebicyclo[3.3.1]non-6-ene is catalyzed by $[RhCl(CO)_2]_2$ in benzene (ref. 442).



Scheme XLIX

Equimolar mixtures of $[RhCl(CO)_2]_2$ and molybdenum pentachloride catalyze the conversion of nitrobenzene plus ethanol to 3-methylquinoline. With higher alcohols, 2,3-dialkylquinolines are formed. The mechanism of Scheme L is proposed with

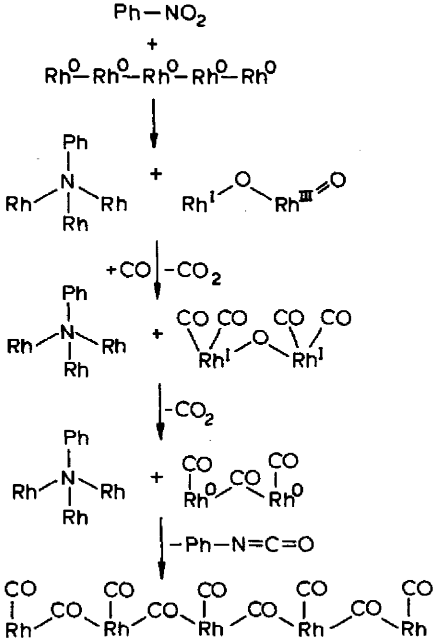


Scheme L

the molybdenum possibly serving to deoxygenate the nitrobenzene (ref. 443). In a related study, conversion of nitrobenzene plus aldehydes bearing two α-hydrogens to quinolines is catalyzed by $[RhCl(PPh_3)_3]$, $[RhH(CO)(PPh_3)_3]$ and $[RhCl(CO)(PPh_3)_2]$ while with $[RhCl(L_2)]_2$ (L_2 = NBD, COD), $[Rh_4(CO)_{12}]$, $[Rh_6(CO)_{16}]$ and $[RhCl(CO)_2]_2$ the major product is the corresponding dialkylaniline. Addition of palladium(II) chloride to the $[RhCl(PPh_3)_3]$-catalyzed system increases the yield of quinoline but the mechanism is uncertain (ref. 444). Three other catalyst systems briefly mentioned include the mixture hydrated rhodium(III) chloride/MeI/PPh_3/$[Cr(CO)_6]$ which converts dimethyl ether to acetic anhydride in the presence of carbon monoxide (ref. 445), a combination of $[RhCl(CO)_2]_2$ and tetra-n-butylammonium iodide in HMPA which produces diarylketones from diarylmercurials and carbon monoxide (ref. 446) and $[RhCl(CO)_2]_2$ itself which catalyzes the formation of biaryls from diarylmercurials or arylmercuric halides (ref. 447).

On the subject of supported rhodium catalysts is found first a report of the synthesis of the silanolato complexes $[Rh(OSiR'_3)(CO)(PR_3)_2]$ (R = Bu^n, Ph; R' = Me, Ph), $[Rh(OSiR'_3)(CO)_2]_2$, $[Rh_2(CO)_3(OSiR'_3)_2(PBu^n_3)]$ and $[Rh_4(CO)_8(OSiPh_2)_2]$ to be used as models for silica-supported rhodium compounds (ref. 448). Pendant $-(CH_2)_8-PPh_2$ groups on silica react with $[Rh(acac)(CO)_2]$ to give a variety of species determined by ^{31}P NMR to have resulted from displacement of carbonyl and/or acetylacetonate ligands (ref. 449). In a different approach, a divinylbenzene/polystyrene copolymer functionalized with acetylacetone has been used to support $\{Rh(CO)_2\}$ moieties. Irreversible loss of carbon monoxide and carbon dioxide occurs on heating to form species proposed to involve acetylacetonate-bridged {Rh-CO} units. On attempted olefin hydrogenation reduction to rhodium metal was detected (ref. 450). On the other hand, $[Rh(acac)(CO)_2]$ supported on phosphinated polypropylene is a good catalyst for the hydroformylation of hex-1-ene and gives a significantly higher selectivity to the straight-chain aldehyde than does its homogeneous counterpart (ref. 451). Hydroformylation catalysis by $[RhCl(CO)(PPh_3)_2]$ supported on silica or alumina (ref. 452) and by Rh(III)-Y zeolites (ref. 453) has been reported. The selectivity of the former system is enhanced by the presence of added phosphine while in the latter $\{Rh(CO)_2\}$ moieties were detected by infrared spectroscopy. Another rhodium-zeolite catalyst system was prepared from $[RhH(CO)(PPh_3)_3]$ and used for the carbonylation of an ethanol-ethyl iodide mixture to ethyl propionate. Only a small fraction of the total supported rhodium appeared to be catalytically active (ref. 454). Nitrobenzene can be catalytically carbonylated to phenylisocyanate by rhodium on alumina. Infrared studies suggest the conversion occurs according to Scheme LI (ref. 455).

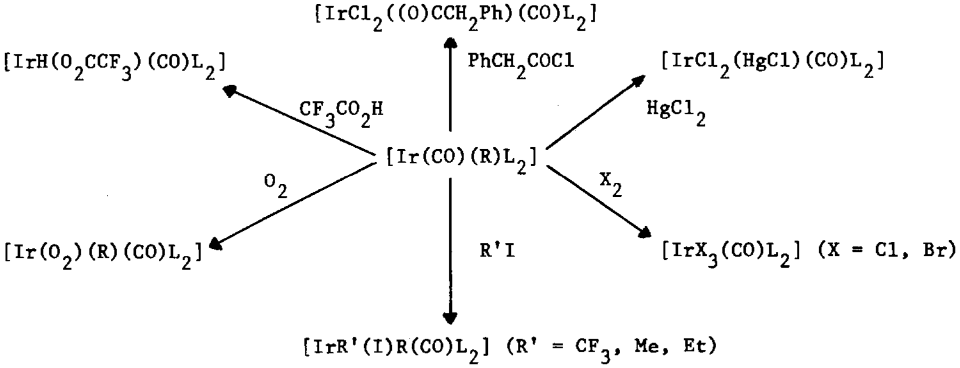
From $^{31}P\{^{103}Rh\}$ and related NMR measurements on $[RhX(CO)(PPh_3)_2]$ (X = F, Cl, Br, I, OH, O_2CMe, O_2CCF_3, NCS, NO_2) the first determination that $^1J_{Rh-P}$ is negative has been made. Also for ligands X not involving a ligating oxygen atom the ^{103}Rh chemical shifts correlate with the ligand electronegativity (ref. 456). The



Scheme LI

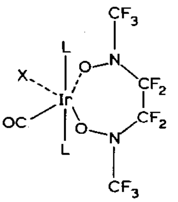
ultraviolet photoelectron spectrum of $[cp_2Rh_2(CO)_2(\mu\text{-}CO)]$ has been measured and discussed in the context of CNDO molecular orbital calculations. The HOMO's appear to mainly involve Rh-Rh and Rh(μ-CO)Rh bonding and to be relatively close in energy. This contrasts with what is observed for the corresponding methylene-bridged complex where the Rh-Rh bonding orbital is significantly below the $Rh(\mu\text{-}CH_2)Rh$ orbital implying that in this system the $\mu\text{-}CH_2$ ligand is a better π-acceptor than is the μ-CO ligand (ref. 457).

The peroxy complexes, $[IrX(O_2R)(CO)L_2]$ ($R = Bu^t$; X = Cl, Br; $L = PPh_3$, $AsPh_3$. X = Cl; $L = PMePh_2$. R = cumyl; X = Cl, Br; $L = PPh_3$. X = Cl; $L = AsPh_3$) and $[IrI_2(O_2R)(CO)(PPh_3)_2]$ are formed in low yield from organic hydroperoxides and $[IrX(CO)L_2]$. They are proposed to form via initial coordination of the hydroperoxide to the metal and although are not themselves catalysts for decomposition of hydroperoxides this process can be initiated upon photolysis. Acids with pKa's above four react with $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$ to yield $[IrCl(O_2Bu^t)(O_2CR)(CO)(PPh_3)_2]$ ($R = CF_3$, CCl_3, $CHCl_2$, CO_2H, cis-$CH{=}CHCO_2H$, C_6F_5, H) while at low temperature, mineral acids (HY = HCl, HBr, HNO_3) give $[IrClY(O_2Bu^t)(CO)(PPh_3)_2]$. Heating $[IrClX(O_2Bu^t)(CO)(PPh_3)_2]$ (X = Cl, O_2CCl_3) to 60° C decomposes it to $[IrCl_3(CO)(PPh_3)_2]$ (refs. 458, 459). Attempts to prepare peroxy carboxylate complexes were generally unsuccessful. Thus on reaction of $[M(CO)(MeCN)(PPh_3)_2]ClO_4$ with peroxy carboxylic acids only trans-$[M(O_2CR)(CO)(PPh_3)_2]$ (M = Rh, Ir; R = Me, Ph, m-ClC_6H_4) was obtained. Certain of these underwent oxidative addition with methyl iodide to give [IrMe(I)(O_2C-m-ClC_6H_4)(CO)$(PPh_3)_2$] and [RhI((O)CMe)(O_2CR)$(PPh_3)_2$]. With [Rh(CO)(MeCN)$(PPh_3)_2]^+$ and sodium m-chloroperbenzoate the products were [Rh(O_2C-m-ClC_6H_4)(CO)$(PPh_3)_2$] and its dioxygen adduct. The same reaction with the iridium analog did produce some [Ir(O_3C-m-ClC_6H_4)(CO)$(PPh_3)_2$] but the dioxygen adduct of this species plus [Ir(O_2C-m-ClC_6H_4)(CO)$(PPh_3)_2$] and its dioxygen adduct also formed. Reaction of [Ir(CO)(MeCN)$(PPh_3)_2]^+$ with the tert-butyl peroxide ion even in dry dichloromethane yielded only [Ir(OH)(CO)$(PPh_3)_2$] (ref. 460). The same group has also reported the reactions of nitroxyl radicals with square planar rhodium(I) and iridium(I) complexes. With [IrCl(CO)L_2] (L = PPh_3, $AsPh_3$, $PMePh_2$), bis(trifluoromethyl)amino-oxyl gives trans-[IrCl(CO)$(ON(CF_3)_2)_2L_2$] while the bromo and iodo analogs give [Ir$(ON(CF_3)_2)_2$($CO_2N(CF_3)_2$)$(PPh_3)_2$] plus [IrX_3(CO)$(PPh_3)_2$] (X = Cl, Br). With the sodium salt of bis(trifluoromethyl)hydroxylamine, [M(CO)(MeCN)-$(PPh_3)_2]^+$ (M = Rh, Ir) also yields [M(CO)($ON(CF_3)_2$)$(PPh_3)_2$] the iridium version of which reacts further according to Scheme LII (R = $ON(CF_3)_2$; L = PPh_3) (ref. 461).



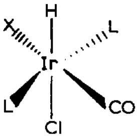
Scheme LII

With [IrX(CO)L_2] (X = Cl; L = PPh_3, $AsPh_3$, $PMePh_2$. X = $ON(CF_3)_2$; L = PPh_3) the stable diradical $F_3CN(O)(CF_2)_2N(O)CF_3$ yields [189] as a mixture of two conformational isomers which interconvert at room temperature (ref. 462).



[189]

A number of iridium(III) catecholate complexes have been prepared from functionalized o-catechols in order to provide means of anchoring them to biological molecules. The success of the latter effort has been limited to date (ref. 463). In pentane, acids of weakly coordinating anions add to $[IrCl(CO)(PPh_3)_2]$ to give [190] ($X = OSO_2CF_3$, FBF_3) or [191] ($X = OSO_2C_4F_9$) both of which isomerize to [192] in dichloromethane. The original reaction in this latter solvent gives [192] for



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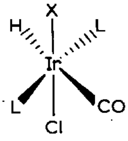

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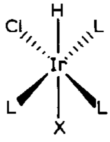
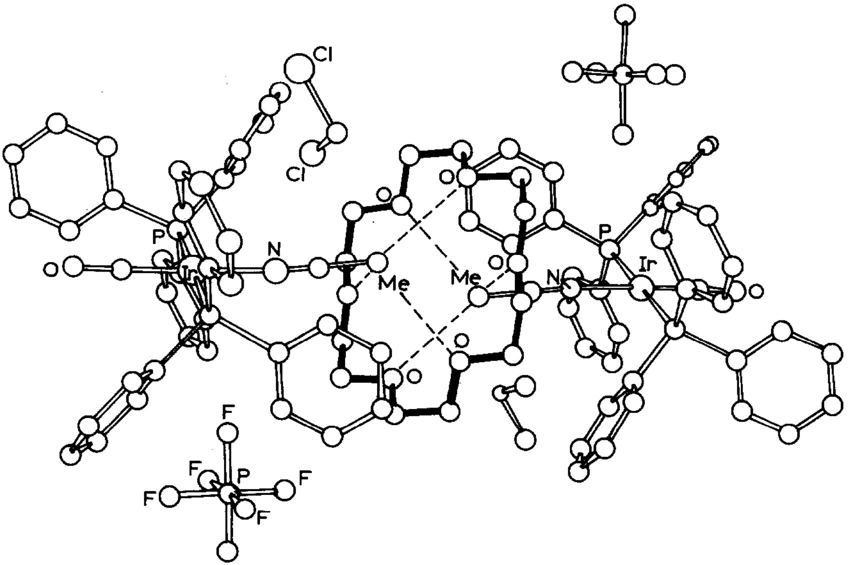


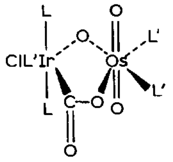
[192]

all three acids. The weakly coordinated anion is readily displaced by Lewis bases to yield $[IrHCl(CO)(B)(PPh_3)_2]X$ ($B = PPh_3$, MeCN, H_2O, acetone, THF). Trimethyloxonium tetrafluoroborate also reacts with $[IrCl(CO)(PPh_3)_2]$ to give $[Ir(Me)Cl(FBF_3)(CO)(PPh_3)_2]$ having the same stereochemistry as [190] (ref. 164). The crown ether 18-crown-6 coordinates via C-H----O hydrogen bonds to the acetonitrile ligands of two molecules of $[Ir(CO)(MeCN)(PPh_3)_2]PF_6$ to give the dication [193] (ref. 465). Carbon disulfide and carbonyl sulfide form the adducts $[IrCl(CO)(\eta^2\text{-SCY})L_2]$ ($Y = S$; $L = PMePh_2$, PMe_2Ph, PMe_3. $Y = O$; $L = PMe_2Ph$, PMe_3) with $[Ir(Cl)(CO)L_2]$ which show increased stability as the basicity of L increases (ref. 466). The unusual carbon dioxide-bridged complex [194] (L' = 4-tert butylpyridine) is formed when $[IrCl(CO)(PPh_3)_2]$ reacts with osmium tetroxide at -78° C followed by warming and addition of 4-tert-butylpyridine. It is converted to [195] (R =



[193]

Bu^t) on reaction with tert-butylisocyanide with further conversion to [196] occurring with methyl trifluoromethanesulfonate (ref. 467).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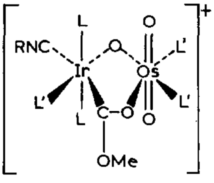
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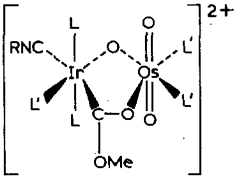
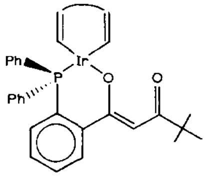

[196]

Deprotonation of [o-(diphenylphosphino)benzoyl]pinacolone (HacacP) with potassium tert-butoxide followed by reaction with $[IrCl(COD)]_2$ yields [197] which can be converted to [198] on reaction with carbon monoxide. Reaction of HacacP with $[IrCl(CO)_2(p\text{-toluidine})]$ yields $[IrCl(CO)(HacacP)_2]$ which reacts further with copper carboxylates to give [199]. No strong Ir–Cu interaction appears to occur however (ref. 468).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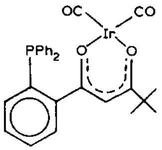
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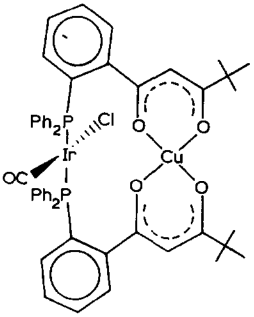
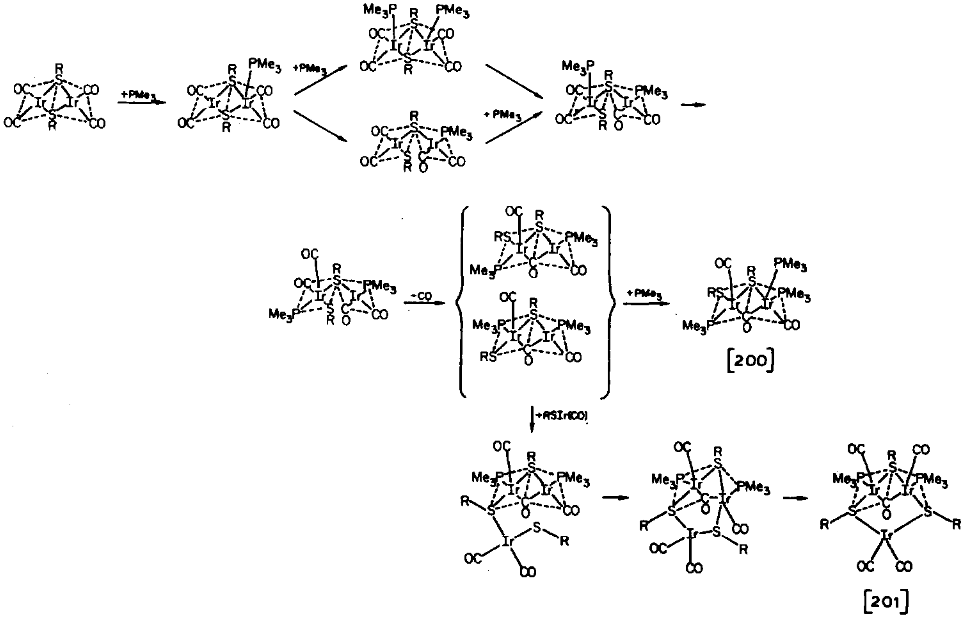
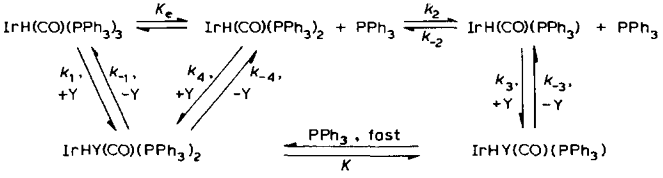

[199]

The course of the reaction of $[IrCl(CO)(PPh_3)_2]$ with pyrazolide ions (pz) appears to be dependent on the extent of substitution on the ring. With the 3,4-dimethyl (or bis(trifluoromethyl)) and the 3,4-dimethyl-5-nitro derivatives the mononuclear trans-$[Ir(pz)(CO)(PPh_3)_2]$ complexes form (ref. 469) while the unsubstituted pyrazolide yields the dimer $[Ir(CO)(PPh_3)(\mu\text{-pz})_2Ir(CO)(PPh_3)]$. The latter complex adds methyl iodide to give $[IrMe(CO)(PPh_3)_2(\mu\text{-pz})_2IrI(CO)(PPh_3)]$ and reacts with chlorine to not only add a chloride to each metal but to also chlorinate the pyrazolide ring at the 4-position (ref. 470). It can also be prepared in a stepwise fashion by the reaction of $[IrCl(COD)]_2$ with pyrazole in the presence of triethylamine to first give $[(COD)Ir(\mu\text{-}pz)_2Ir(COD)]$ which is then reacted successively with carbon monoxide and triphenylphosphine. The cyclooctadiene dimer also reacts with methyl iodide to give $[(COD)IrMe(\mu\text{-}pz)_2IrI(COD)]$, with a stoichiometric quantity of halogen to yield $[Ir_2X_2(COD)_2(\mu\text{-}pz)_2]$ (X = Cl, Br) and with electrophilic acetylenes to give the dimetallated olefin derivatives $[Ir_2(COD)_2(\mu\text{-}pz)_2\text{-}(\mu\text{-}RC{=}CR)]$ (R = CF_3, CO_2Me) (ref. 471). The thiolate-bridged dimers $[Ir_2(CO)_2(L)_2\text{-}(\mu\text{-}SBu^t)_2]$ oxidatively add iodine in a stepwise fashion giving first $[Ir(CO)(L)I\text{-}(\mu\text{-}SBu^t)_2Ir(CO)(L)I]$ and then $[Ir_2I_4(CO)_2(L)_2(\mu\text{-}SBu^t)_2]$ (L = CO, $P(OMe)_3$, PMe_2Ph, PMe_3). With bromine the intermediate iridium(II) dimer could be detected spectroscopically while with chlorine only the final iridium(III) dimer was seen. In some instances mixture of isomers were formed and a radical process is preferred for the first step of the reaction (ref 472). Reaction of $[Ir_2(CO)_4(\mu\text{-}SBu^t)_2]$ with two equivalents of trimethylphosphine provides [200] and [201] as suggested in Scheme LIII (R = Bu^t) (ref. 473).



Scheme LIII

The standard method of refluxing hydrated iridium(III) chloride in DMF in the presence of a phosphine provides $[IrCl(CO)(PEtPh_2)_2]$ whose dioxygen adduct was prepared and structurally characterized. The relatively long oxygen-oxygen bond of 1.469(10)Å was interpreted to indicate that the coordinated dioxygen moiety should be considered as a peroxide (ref. 474). The kinetics of the addition of hydrogen and phenylacetylene to $[IrH(CO)(PPh_3)_3]$ to give $[IrH(Y)(CO)(PPh_3)_2]$ (Y = H_2, PhC_2H) have been interpreted according to Scheme LIV. With hydrogen the rate



Scheme LIV

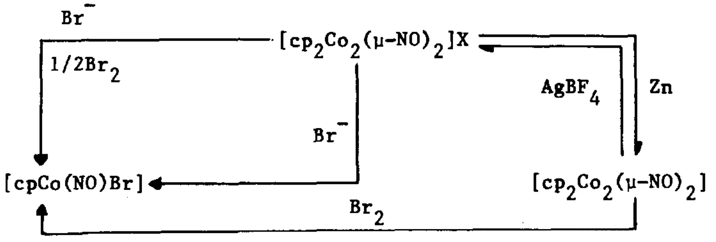
constants k_{-1}, k_{-3} and k_4 appear to be negligibly small while for phenylacetylene both these and k_1 are insignificant. The results are interpreted to indicate that molecular hydrogen adds directly to the five-coordinate starting complex and the absence of the k_4 path implies the existence of a reactive 14-electron species ($[IrH(CO)PPh_3]$). Oxidative addition of hydrogen to this species followed by addition of triphenylphosphine can give a product having trans hydride ligands so that postulation of a direct trans oxidative addition of hydrogen is not necessary (ref. 475).

The cyclo-triarsenic species 4-methyl-1,2,6-triarsatricyclo$[2.2.1.0^{2.6}]$heptane (L) appears not to be able to function as a tridentate capping ligand. Fragmentation occurs on reaction with $[Co_4(CO)_{12}]$ while with $[IrCl(CO)_2$(p-toluidine)$]$ in THF a product formulated as $[(IrCl(CO)(THF))_3(L)_2]$ with the As_3 ring opened up is formed. With $[Co_2(CO)_8]$ a polymeric product of empirical formula $[Co_2(CO)_6L]$ forms in which $\{Co_2(CO)_6\}$ moieties are bridged by the ligand but it is uncertain whether the As_3 ring remains intact (ref. 476). Cocondensation of iridium atoms with oxalyl chloride yields a species containing only terminal carbonyl groups which reacts with triphenylphosphine to yield $[IrCl_3(CO)_2PPh_3]$ (ref. 477).

The rearrangement of the exo and endo isomers of tricyclo$[3.2.1.0^{2.4}]$oct-6-ene and the corresponding tricyclooctane is catalyzed by $[IrCl(CO)(PPh_3)_2]$ in benzene. The presence of oxygen is required and triphenylphosphine oxide is detected as a product indicating that generation of a highly coordinatively unsaturated iridium species by irreversible removal of phosphine is involved. The major organic products are exo-methylenenorbornene and exo-methylenenorbornane. The results contrast with previous work which reported that the endo-tricyclohydrocarbons were unreactive. Also the reactivity of the tricyclooctane indicates that bidentate coordination of substrate is not required. The intermediacy of iridacyclobutane and iridium carbene species is postulated (ref. 478). Catalytic hydrogenation of acrylonitrile is catalyzed by $[IrCl(CO)(PPh_3)_2]$ under pressure (ref. 479). Support of $[IrCl(CO)(Ph_2P(CH_2)_2Si(OEt)_3)_2]$ on silica provides a catalyst for the production of alkoxysilanes from $HSiR_3$ (R = Et, OEt) or polysiloxanes and primary alcohols. The catalyst rapidly deactivates and a better system was prepared by functionalizing the silica surface with the silylphosphine ligand followed by reaction with $[IrCl(\textit{cyclo}\text{-}C_8H_{14})_2]_2$. A kinetic analysis showed the presence of two pathways one proposed to involve a phosphine-supported iridium species while the other was thought to involve an iridium species directly attached to the surface (ref. 480). Two related studies report on the redistribution reactions of siloxanes catalyzed by $[IrCl(CO)(PPh_3)_2]$, $[RhCl(PPh_3)_3]$, $[Rh(acac)(C_2H_4)_2]$ and $[RhCl(CO)_2]_2$. The products involve the scrambling of all groups attached to silicon atoms bearing a hydrogen substituent indicating that oxidative addition of silicon-hydrogen bonds is involved. With the iridium complex in benzene solutions evidence for aromatic carbon-hydrogen bond activation was detected (refs. 481, 482).

Metal Nitrosyl and Aryldiazo Complexes

The dimer $[Co(NO)_2Br]_2$ acts as a nitrosyl-transfer agent in reaction with $(Et_4N)[V(CO)_{6-n}L_n]$ to yield $[V(CO)_{5-n}(NO)L_n]$ (n = 2; L_n = dmpe, diphos, 1,2-bis(diphenylarsino)ethane (dpae), dppp, diars, *o*-diphenylarsinophenyldiphenylphosphine. n = 3; L_n = 1.5 diars, *tris*(diphenylphosphinomethyl)ethane) (ref. 483). Reaction of $[cpCo(CO)_2]$ with NOX (X = PF_6, BF_4) yields $[cp_2Co_2(\mu\text{-}NO)_2]X$ whose further reactions are depicted in Scheme LV (ref. 484). The kinetics of the transfer



Scheme LV

of a nitrosyl group from $[Co(NO)(dmgH)_2]$ to hemoglobin have been studied and the process is described by the mechanism of Scheme LVI (L = β-93 cysteine residue on hemoglobin (Hb), B = cysteine, histidine and lysine residues) (ref. 485). Attempts to prepare nitrosyl cobalt complexes by reaction of sodium nitrite and $[Co_2(CO)_8]$ in the presence of bis(triphenylphosphine)iminium chloride were unsuccessful (ref. 486). The kinetics of the thermal decomposition of $[Co(CO)_3(NO)]$ have been studied but the presence of side reactions prevented definition of a reasonable mechanism (ref. 487).

$$[Co(NO)(dmgH)_2] + L \xrightleftharpoons[k_{-5}]{k_5} [LCo(NO)(dmgH)_2]$$

$$[Co(NO)(dmgH)_2] \xrightleftharpoons[k_{-6}]{k_6} [Co(dmgH)_2] + NO$$

$$B + [Co(dmgH)_2] \xrightleftharpoons[k_{-7}]{k_7} [BCo(dmgH)_2]$$

$$Hb + NO \xrightarrow{k_8} Hb(NO)$$

Scheme LVI

Coordination of [Co(TPP)] to imidazole supported on silica generates a system which absorbs nitric oxide to give a species proposed to contain a bent nitrosyl ligand due to the π-donor ability of imidazole. The supported complex catalyzes the reduction of nitric oxide by hydrogen to give nitrogen, nitrous oxide and ammonia (ref. 488). In a companion study [Co(TPP)] supported on titanium dioxide catalyzes the reduction of nitric oxide by carbon monoxide to yield nitrous oxide and ultimately nitrogen. Coordination of both reactants to cobalt is proposed (ref. 489).

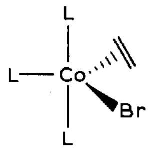
Electrochemical studies on $[Co(NO)_2(P(OEt)_3)_2]BPh_4$ show the presence of two one-electron reduction steps, the first of which is reversible, and a single one-electron oxidation process. The first reduction step gives neutral $[Co(NO)_2\text{-}(P(OEt)_3)_2]$ which is moderately stable when oxygen is rigorously excluded. The second reduction is thought to be reversible but is accompanied by rapid chemical reactions. Electrolysis at this potential generates a small amount of $[Co(NO)\text{-}(P(OEt)_3)_3]$ plus cobalt species containing no nitrosyl ligands (ref. 490). The Auger spectrum of $[Co(NO)(CO)_3]$ has been measured and it appears that the core and valence electrons of the carbonyl and nitrosyl ligands are involved. The relative intensities of the transitions observed vary according to the polarization of electron density in the various orbitals and it appears that the electron density is more equally distributed across the nitrosyl ligand than it is in the carbonyl ligands (ref. 491). Metal and ligand core binding energies have been determined by XPES for cobalt nitrosyl phosphine complexes, rhodium carbonyl, nitrosyl and/or phosphine complexes and iridium carbonyl and/or phosphine complexes. The metal binding energies can be fit by a single set of group shifts for σ-donor ligands which shows a linear correlation with ligand electronegativity. A poorer fit is found when π-acceptor ligands are present (ref. 492).

Nitrosyl tetrafluoroborate reacts with $[\mathrm{cp'Rh(CO)_2}]$ to give $[\mathrm{cp'_2Rh_2(\mu\text{-}CO)(\mu\text{-}NO)}]\mathrm{BF_4}$ which forms methylene-bridged derivatives $[\mathrm{cp'_2Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\mu\text{-}CRR')}]\mathrm{BF_4}$ (R = R' = H, Ph. R = H; R' = Me, Ph) on reaction with the corresponding diazomethanes at -78° C. Only those with phenyl substituents are thermally stable and on heating they lose carbon monoxide to give $[\mathrm{cp'_2Rh_2(\mu\text{-}NO)(\mu\text{-}CRR')}]$ (ref. 493). Carbon disulfide reacts with $[\mathrm{Rh(NO)X_2L_2}]$ (X = Cl, Br; L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$) to give $[\mathrm{(RhX_2L)_2CS_2}]$ (ref. 494) while $[\mathrm{RhH(PPh_3)_4}]$ reacts with trithiazyltrichloride to give the thionitrosyl complex $[\mathrm{Rh(NS)Cl_2(PPh_3)}]_2$. The dimer can be cleaved to give $[\mathrm{Rh(NS)Cl_2(PPh_3)L}]$ (L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$) (ref. 495).

Molecular orbital calculations on $[\mathrm{Ir_2(NO)_2(PH_3)_2(\mu\text{-}O)}]$ as a model for the known triphenylphosphine complex using the SCF-Xα-SW method have been carried out to assess the nature of the metal-metal interaction. As the HOMO has more nitrosyl than iridium character the molecule is considered to be closer to an iridium(I) complex of neutral nitric oxide than to an iridium(-1) complex with $\mathrm{NO^+}$ ligands. Nevertheless, the HOMO is still considered to involve a substantial amount of iridium-iridium bonding (bent bond) (ref. 496).

Metal Alkene Complexes

Ethylene adds to $[\mathrm{CoBr(PMe_3)_3}]$ in methanol, acetone or toluene to give [202] (L = $\mathrm{PMe_3}$) in which the bromine is replaced by acetonitrile to give a mixture of [203] and [204] (Y = $\mathrm{C_2H_4}$ or MeCN). At -80° C $[\mathrm{CoBr(PMe_3)_3}]$ in acetonitrile gives $[\mathrm{Co(NCMe)_2(PMe_3)_3}]\mathrm{Br}$ while at room temperature $[\mathrm{Co(PMe_3)_4}]\mathrm{BPh_4}$ gives $[\mathrm{Co(NCMe)(PMe_3)_4}]\mathrm{BPh_4}$ (ref. 497). Olefins substitute one phosphine ligand in $[\mathrm{cpCo(PPh_3)_2}]$ giving $[\mathrm{cpCo(L)(PPh_3)}]$ (L = dimethylfumaronitrile, dimethylmaleonitrile, maleic anhydride). With fumarontrile itself a mixture of the analogous products with L = fumaronitrile or maleonitrile forms suggesting reaction <u>via</u> an ionic transition state. The remaining phosphine ligand is replaced by cyclohexylisocyanide (L') to give [cpCoLL']. Reaction of fumaronitrile with $[\mathrm{cpCoL_2}]$ (L = CO, $\mathrm{PPh_3}$, *o*-xylylisocyanide) at elevated temperature gives only [cpCo(NCCH=CHCN)L] (ref. 498). Replacement of one ethylfumarate ligand (L) in $[\mathrm{Co(MeCN)_2L_2}]$ by phosphites yields $[\mathrm{CoL(P(OR)_3)_3}]$ (R = Me, Et, $\mathrm{Pr^1}$) which reacts further with maleic anhydride (MA) to give $[\mathrm{Co(MA)(P(OR)_3)_3}]$ (R = Me) (ref. 499).



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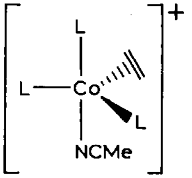

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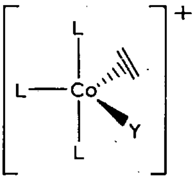
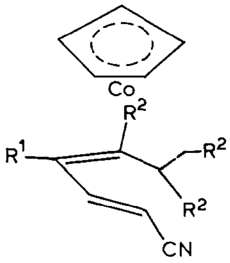


[204]

The crystal structures of $[\mathrm{cp'Co(\eta^4\text{-}C_4Ph_4HSiEt_3)}]$, [205], [206] and [207] ($\mathrm{R^1}$ = Ph; $\mathrm{R^2}$ = $\mathrm{CO_2Me}$) have been correlated with molecular orbital calculations to suggest



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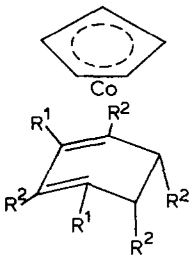

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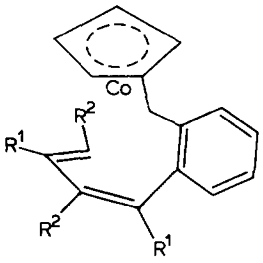


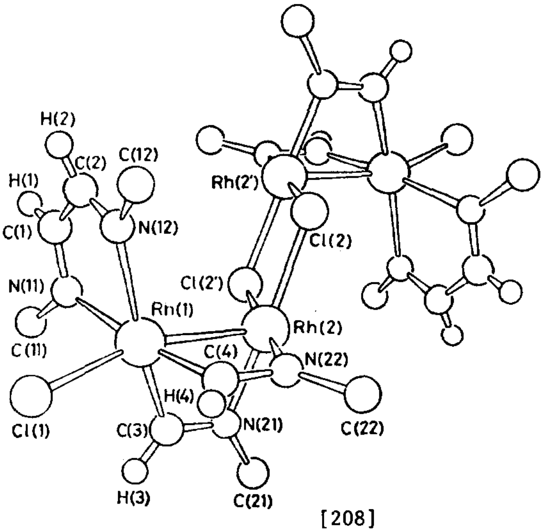
[207]

that the observed displacements of the substituents at the 1- and 4-positions of the diene moieties out of the plane of the diene is the result of twists of the C=C units to maximize overlap with cobalt d orbitals rather than indications of rehybridization of the 1- and 4-carbon atoms (ref. 500). Under photolysis, $[cpCo(CO)_2]$ reacts with di-tert-butoxyacetylene to yield $[cpCo(\eta^5-C_4(OBu^t)_4CO)]$. The tert-butoxy groups can be hydrolyzed and the complex chemically degraded and converted to dimethoxycyclopentenetrione, a precursor to croconic acid. Alternatively the substituted cyclopentadienone ligand can be removed directly in high yield by electrochemical oxidation (refs. 501, 502). Addition of tetrafluoroboric acid to $[(\eta^5-C_5Me_4Et)Co(C_2H_4)_2]$ in dichloromethane/diethyl ether at -78° C gives $[(\eta^5-C_5Me_4Et)CoH(C_2H_4)_2]$ which shows two different fluxional processes at low temperature. The same reaction at room temperature gives ethylene, ethane and a blue material which reacts with acetonitrile to give $[(\eta^5-C_5Me_4Et)Co(MeCN)_3]^{2+}$ and with toluene to give $[(\eta^5-C_5Me_4Et)Co(\eta^6-C_6H_5Me)]^{2+}$ (ref. 503).

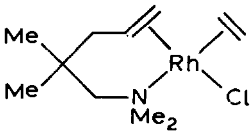
A cobalt-based catalyst for the hydrodimerization of methylacrylate to dimethyladipate is proposed to be a cobalt(I) complex containing chloride, acetonitrile and dimethylfumarate ligands (ref. 504). A zerovalent cobalt complex is thought to be the active catalyst in the cobalt-promoted coupling of acrylonitrile to adiponitrile (ref. 505). Attempts to catalyze the asymmetric hydrogenation of 2-phenylbutenes with a system prepared from $[Co(acac)_3]$, triethylaluminum and neomenthyldiphenylphosphine were only slightly successful. A catalyst derived in the same fashion from $[Co((L)\text{-leucine})_2]$ gave a better optical yield but the chemical yield was quite poor (ref. 506).

Electrochemical oxidation of $[(\eta^5-C_5R_5)Co(L)]$ (R = H, Me; L = COD, cyclooctatetraene (COT)) in acetonitrile yields $[(\eta^5-C_5R_5)_2Co]^+$ and cobalt(II) species while in dichloromethane a reversible one-electron oxidation is seen for the COD complex. No isomerization to the 1,3-COD complex occurs. The COT complex is irreversibly oxidized but no COT cleavage is seen (ref. 507). From the proton NMR spectrum of $[cpCo(\eta^4-C_4H_6)]$ it appears that any "$\sigma+\pi$" contribution to the bonding of the butadiene is very small (ref. 508). Details of cobalt-olefin bonding in the related molecules [cpCo(L)] (L = COD, duroquinone, substituted cyclopentadienones) together with $[cp_2Co]^+$ and $[cpCo(\eta^4-C_4Ph_4)]$ have been probed by ^{59}Co NQR spectroscopy. In the last two the electron density is symmetrical as expected. For the others, the bond strength decreases in the order given which is interpreted to be due to the decreasing ability of the diene to distort so as to maximize overlap of the π-system with the d_{xz} orbital on cobalt. In the cyclopentadienones, the electron density is partially localized and the bond strength is largely unaffected by the nature of the substituents (ref. 509).

Rhodium(I) olefin complexes continue to be employed as starting materials in a variety of synthetic studies. Ready cleavage of the diazabutadienes RN=CHCH=NR (R = Bu^t, Pr^i) occurs on reaction with $[\mathrm{RhCl(C_2H_4)_2}]$ to give [208] which contains μ-azomethine groups (ref. 510). The same rhodium complex also reacts with 2,2,N,-N-tetramethylbut-3-en-1-amine to yield [209] in which the ethylene ligand can be replaced by acetonitrile and a variety of pyridine ligands. Unlike related olefinic phosphine ligands, a bis(ligand) complex is not formed. The ^{1}H, ^{13}C and ^{103}Rh NMR spectra were obtained (ref. 511). Monodentate 1,3-pentadiene (L') complexes of formula trans-[MCL'L$_2$] are prepared from $[\mathrm{MCl(ol)_2}]_2$ (M = Rh; ol = C_2H_4; L = $\mathrm{SbPh_3}$. M = Ir; ol = cyclooctene; L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{SbPh_3}$), a stoichiometric quantity of a group VA ligand and an excess of the diene. In the iridium

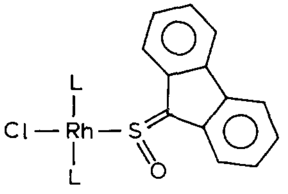


[208]

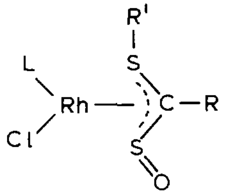


[209]

triphenylstibine complex the diene appears to be coordinated *via* the terminal double bond but in the others the mode of coordination is uncertain. Analogous complexes of cyclobutene can be obtained when M = Ir and L = $AsPh_3$, $SbPh_3$ (ref. 512). Sulfines react with $[RhCl(\underline{cyclo}\text{-}C_8H_{14})_2]_2$ in the presence of phosphine ligands to give either [210] or [211] (L = Pcy_3, PPr^i_3. R = R' = *p*-tolylS, PhS;

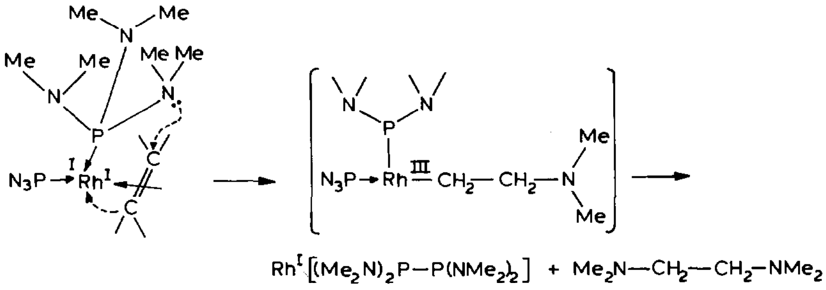


[210]

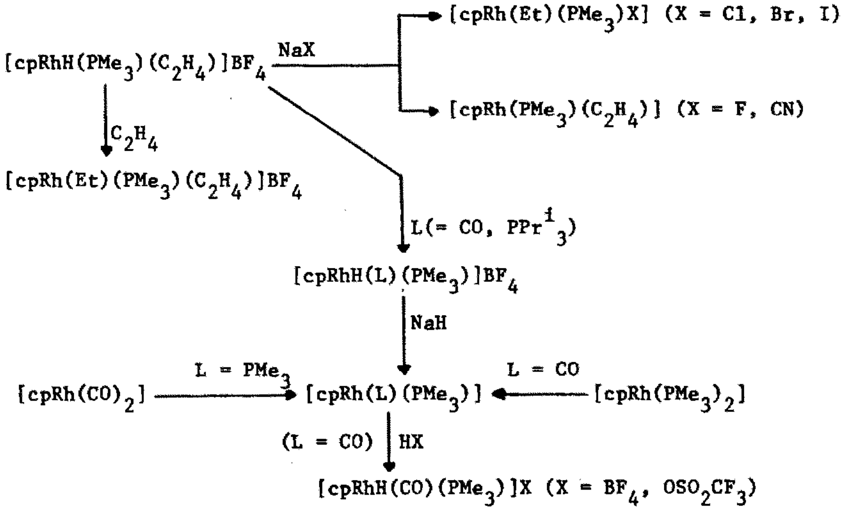


[211]

R = *p*-tolyl, R' = Me). In complexes [211] when the original ligand is the (E) isomer fluxionality *via* (E)$\rightleftharpoons$(Z) isomerization in the ligand is observed (ref. 513). At room temperature in toluene, tris(dimethylamino)phosphine reacts with $[RhCl(C_2H_4)_2]_2$ to give $[RhCl(C_2H_4)(P(NMe_2)_3)_2]$ which appears to be *cis*. However in refluxing benzene ligand decomposition also occurs to give the biphosphine complex $[Rh_4Cl_4(P_2(NMe_2)_4)_6]$ and $[RhCl(P(NMe_2)_3)(P_2(NMe_2)_4)_2]$. The biphosphine ligand is thought to form according to Scheme LVII. Carbon dioxide inserts into a P-N bond of the ligand when the original reaction is carried out under carbon dioxide to yield $[RhCl(P(O_2CNMe_2)(NMe_2)_2)_2]\cdot CO_2$ (ref. 514). Scheme LVIII outlines some chemistry of $[cpRhH(PMe_3)(C_2H_4)]BF_4$. The triisopropylphosphine analog reacts similarly (ref. 515). In related work, $[RhCl(PMe_3)(C_2H_3R)]_2$ (R = H, Me, Ph) and $[RhCl(L)(C_2H_4)]_2$ (L = PMe_2Ph, PPr^i_3) react with thallium cyclopentadienide to give $[cpRh(PMe_3)(C_2H_3R)]$ and $[cpRh(L)(C_2H_4)]$ respectively. These can be reversibly protonated by tetrafluoroboric acid in ether to yield $[cpRhH(L)(C_2H_3R)]BF_4$ (L = PMe_3; R = H, Me. L = PPr^i_3; R = H) however when $[cpRh(PMe_3)(C_2H_3Ph)]$ is protonated with trifluoroacetic acid in the presence of ammonium hexafluorophosphate the allyl complex $[cpRh(PMe_3)(\eta^3\text{-MeCHPh})]PF_6$ forms (ref. 516).

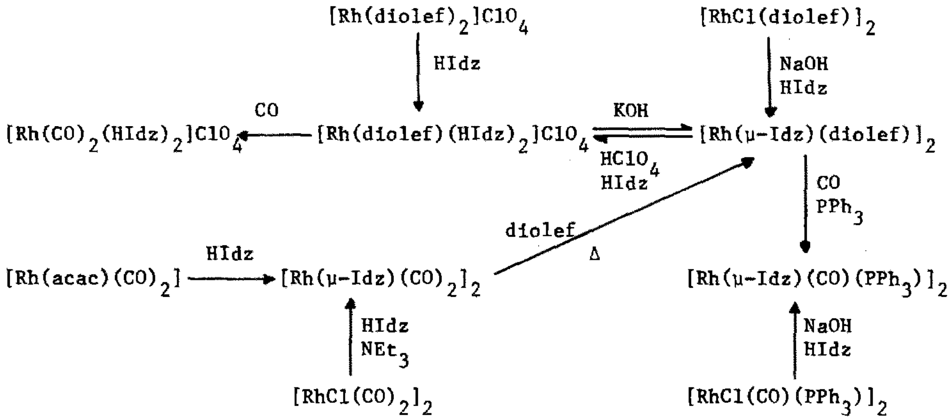


Scheme LVII



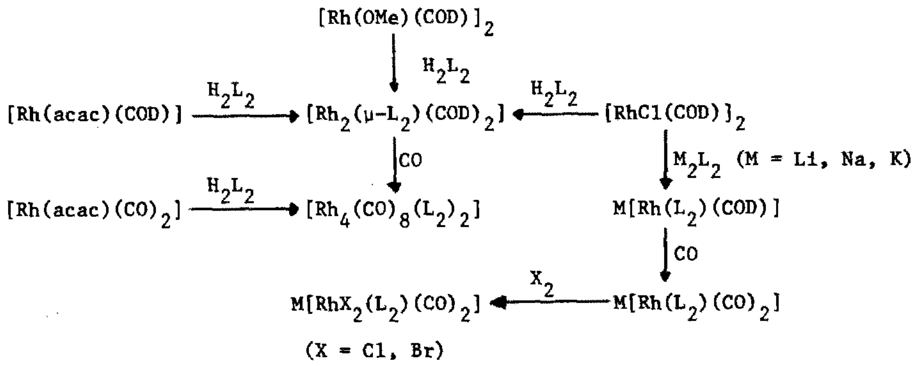
Scheme LVIII

A large number of rhodium complexes of nitrogen-containing ligands have been prepared from rhodium diolefin complexes. For example addition of a stoichiometric quantity of a phosphine, excess nitrogen-containing ligand and sodium tetraphenylborate to $[\mathrm{RhCl(diolef)}]_2$ in methanol yields $[\mathrm{Rh(diolef)LL'}]\mathrm{BPh}_4$ (diolef = NBD; L = py, 2-ethylpyridine; L' = PPh_3. L = quinoline; L' = *m*-tolyl$_3$P. diolef = NBD; L = py, 2-ethylpyridine, quinoline; L' = PPh_3. L = 2-ethylpyridine, quinoline; L' = AsPh_3), $[\mathrm{Rh(diolef)L_2L'}]\mathrm{BPh}_4$ (diolef = NBD; L = quinoline; L' = PPh_3, *p*-tolyl$_3$P, $(p\text{-}\mathrm{FC_6H_4})_3\mathrm{P}$) and $[\mathrm{Rh(diolef)}(\eta^6\text{-}\mathrm{C_6H_5BPh_3})]$ (diolef = NBD; L = quinoline; L' = *o*-tolyl$_3$P. L = py, 2-ethylpyridine, quinoline; L' = AsPh_3)(ref. 517). Reaction of $[\mathrm{RhCl(diolef)}]_2$ with silver perchlorate followed by other ligands yields $[\mathrm{Rh(diolef)L_2}]\mathrm{ClO}_4$ (diolef = NBD; L = substituted quinolines) or $[\mathrm{Rh(diolef)(L_2)}]\mathrm{ClO}_4$ (diolef = COD; L_2 = substituted *o*-phenanthrolines). The diolefin ligands can be replaced by triphenylphosphine and/or carbon monoxide (refs. 518, 519). The same reaction using indole gives $[(\eta^6\text{-indole})\mathrm{Rh(diolef)}]\mathrm{ClO}_4$ (diolef = COD, tetrafluorobenzobarrelene (TFB)) which on attempted deprotonation with potassium hydroxide in methanol or aqueous acetone gave $[\mathrm{Rh(OMe)(diolef)}]_2$ and $[\mathrm{Rh(OH)(diolef)}]_2$ respectively. No η^5-coordination of indole was observed (ref. 520). With indazole (HIdz) only N-coordination was observed as detailed in Scheme LXIX (diolef = COD, NBD, TFB) while $[\mathrm{Rh(diolef)(HIdz)_2}]\mathrm{ClO}_4$ reacts with $[\mathrm{Rh(acac)(CO)(PPh_3)}]$ in the presence of triethylamine to yield $[\mathrm{Rh(diolef)(\mu\text{-}Idz)_2Rh(CO)(PPh_3)}]$ (ref. 521).



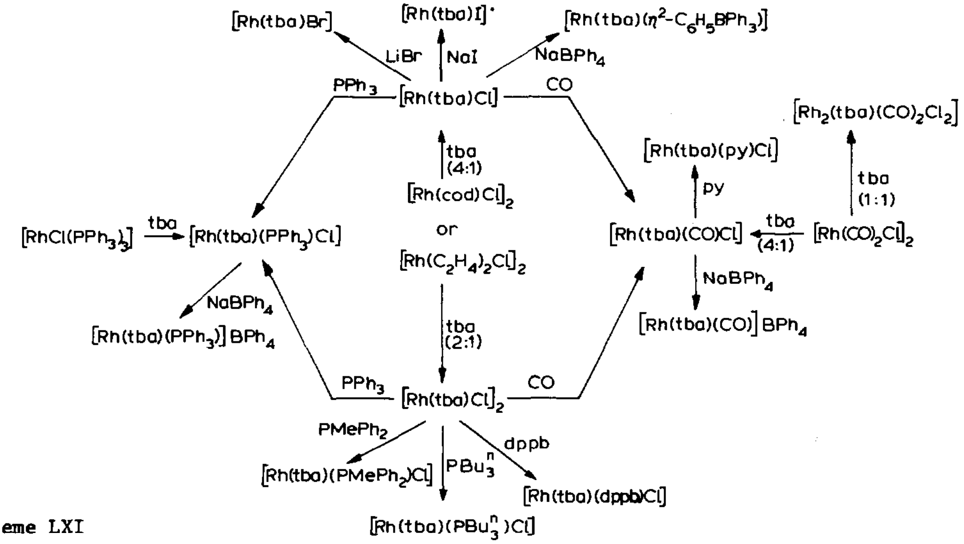
Scheme LIX

Imidazolate complexes of empirical formula [Rh(diolef)(Im)] (diolef = COD, TFB; Im = imidazolate, 2-methylimidazolate) are formed from the imidazole and [Rh(acac)-(diolef)] and are thought to be trimeric. The diolefin ligand can be replaced by two carbonyl ligands and one of the latter is further replaced by triphenylphosphine (ref. 522). Several complexes derived from 4,4',5,5'-tetracyano-2,2'-biimidazole (H_2L_2) can be prepared as indicated in Scheme LX. Iridium analogs of many of these complexes were also synthesized (ref. 523). On the other hand, with H_2L_2 as 3,3',5,5'-tetramethyl-4,4'-bipyrazole, $[RhCl(L'_2)]_2$ (L'_2 = COD, NBD, TFB, $(CO)_2$) reacts to give $[(RhCl(L'_2))_2H_2L_2]$ which on deprotonation with triethylamine yields an apparently polymeric material of empirical formula $[(RhCl(L'_2))_2L_2]$ (ref. 524). A variety of pyridine-N-oxide and phosphine oxide complexes of formula $[Rh(COD)L_2]ClO_4$ (L = $OPPh_3$, $OAsPh_3$, ONC_5H_5 for example) have been similarly prepared from $[Rh(COD)(acetone)_x]ClO_4$ (refs. 525, 526).



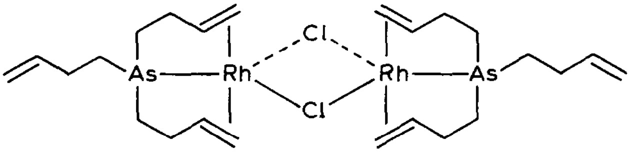
Scheme LX

Substituted thallium cyclopentadienides react with $[RhCl(diolef)]_2$ to give $[(\eta^5-C_5H_4R)Rh(diolef)]$ (diolef = NBD, COD, cyclohexa-1,3-diene; R = $\underline{m}$-FC_6H_4, $\underline{p}$-FC_6H_4) (ref. 527). Tri(3-butenyl)arsine (tba) reacts with a variety of rhodium-(I) complexes according to Scheme LXI. The structure of $[RhCl(tba)]_2$ is thought



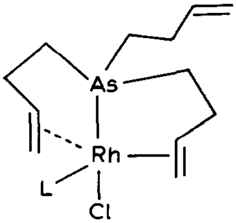
Scheme LXI

to be [212] in which exchange of the free and uncoordinated arms occurs in solution.



[212]

The products [RhCl(tba)(L)] (L = PPh_3, $PMePh_2$, $PBu^n{}_3$) and $[Rh(tba)(L)]BPh_4$ (L = PPh_3, CO) have structures [213] and [214] respectively while [RhCl(tba)] and



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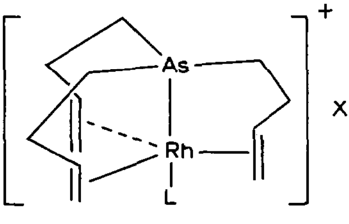
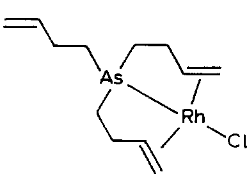


[214]

$[Rh(tba)(\eta^2\text{-}C_6H_5BPh_3)]$ have structures [215] and [216]. Finally $[Rh_2(tba)Cl_2(CO)_2]$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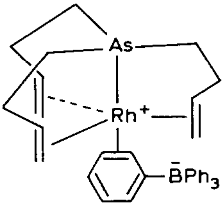
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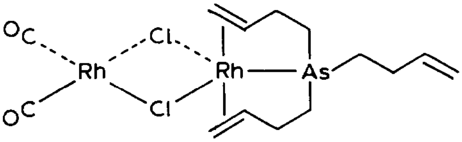
is thought to be [217] while $[RhCl(CO)(tba)]_2$ is considered to be a mixture of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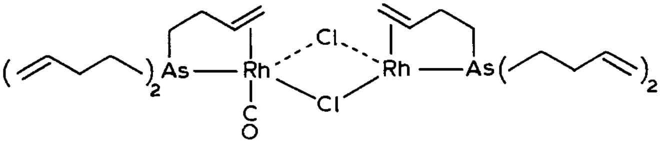
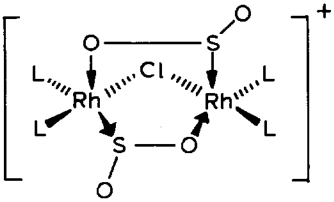
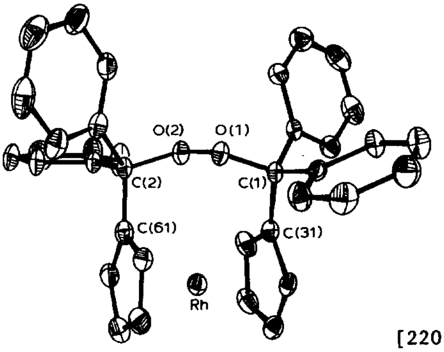
[218] and its trans isomer (ref. 528). In methanol $[RhCl(COD)]_2$ with four


[218]

equivalents of triphenylphosphine forms $[Rh(COD)(PPh_3)_2]^+$ which on successive treatment with sulfur dioxide and sodium perchlorate forms [219] (L = PPh_3) as a mixture of its perchlorate and sulfate salts (ref. 529). Reaction of potassium

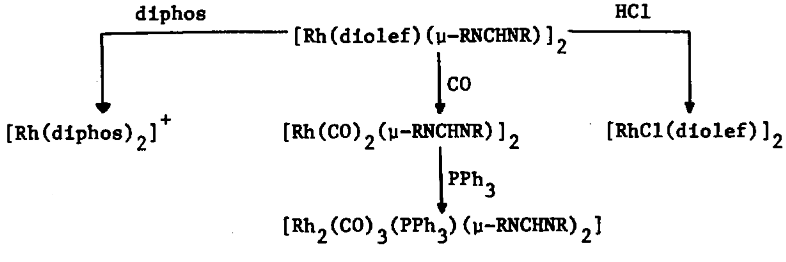

[219]

superoxide with $[Rh(COD)_2]BF_4$ yields $[Rh(COD)(O_2)]_2$ which can transfer oxygen to the coordinated COD ligand. At 150° C in benzene the products are cyclooctanone and cyclooct-1-en-5-one. The same reaction in the presence of cyclohexene and using deuterobenzene again gives cyclooctanone plus protiobenzene, cyclohexane and water. The absence of oxygenated products derived from cyclohexene indicates that coordination of the olefin is required for oxygenation to occur (ref. 530). Addition of diphenylfulvene to $[RhL_2]^+$ (L = $P(OPh)_3$, L_2 = COD) generated in situ from $[RhCl(COD)]_2$ in THF yields $[(\eta^4\text{-}C_5H_4CPh_2)RhL_2]^+$. However starting with similarly-generated $[Rh(CO)_2]^+$, a blue solution is formed which reacts with oxygen to give [220] (ref. 531). The ligand 2,2'-bis(dimethylphosphino)biphenyl (L_2) has been



[220]

synthesized and forms $[RhCl(L_2)]_2$ on reaction with $[RhCl(COD)]_2$. Further reaction with the ylide $MeBu^t{}_2P{=}CH_2$ produces the metallacycle $[(L_2)\overline{RhCH_2P(C}H_2)Bu^t{}_2]$ (ref. 532). Only one cyclooctadiene ligand in $[Rh(\mu\text{-}PPh_2)(COD)]_2$ can be replaced on reaction with phosphines to give $[L_2Rh(\mu\text{-}PPh_2)_2Rh(COD)]$ (L = PPh_3, $PMePh_2$, PEt_3). From a crystal structure study the rhodium-phosphorus bridge bonds to the substituted center are significantly shorter than the other two and this metal is considered to form a donor bond to the second metal (ref. 533). Formamidine-bridged dimers, $[Rh(diolef)(\mu\text{-}RNCHNR)]_2$ (R = p-tolyl; diolef = COD, NBD), are formed from $[RhCl(diolef)]_2$ and K[RNCHNR]. These react with triphenylphosphine in boiling toluene to give $[Rh(PPh_3)_2(O_2)(RNCHNR)]$ which can also be got from $[RhCl(PPh_3)_3]$ and K[RNCHNR]. With rigorous exclusion of oxygen no pure product of any kind could be isolated. Further reactions of $[Rh(diolef)(\mu\text{-}RNCHNR)]_2$ are detailed in Scheme LXII while the COD complex reacts with carbon disulfide to give species of



Scheme LXII

empirical formula $[Rh(CS_2)_2(RNCHNR)]$ that can be alkylated with trimethyloxonium hexafluorophosphate to give $[Rh(CS_2)(CSMe)(RNCHNR)]PF_6$ (ref. 534).

Some pyrazolylborate complexes $[(H_nBpz_{4-n})Rh(LL)]$ (n = 1; LL = $(C_2H_4)_2$, COD. n = 0; LL = COD, NBD, duroquinone. n = 2, LL = COD) have been prepared from KH_nBpz_{4-n} and $[RhCl(LL)]_2$. The complexes with n = 0 are fluxional and show an averaging of all four pyrazolate groups. The first two react with carbon monoxide to give species proposed to be $[(HBpz_3)_2Rh_2(\mu\text{-}CO)_3]$ but these and the others form mixture of substitution products with phosphines and isocyanides (ref. 535). Reaction of $[Rh(NBD)(NCMe)_2]PF_6$ with $(Bu^n{}_4N)_4$[*cis*-$Nb_2W_4O_{19}$] gives $(Bu^n{}_4N)_3[((NBD)Rh)_5(Nb_2W_4O_{19})_2]$ in which the two $\{Nb_2W_4O_{19}\}$ units are bridged by the five rhodium atoms *via* coordination of the terminal oxygen atoms attached to niobium (ref. 536). The heteroallyls $[XC(S)Y]^-$ (X = Ph_2P; Y = NPh, NMe. X = NMe_2, NEt_2; Y = S, NPh) react with hydrated rhodium(III) chloride to give $[Rh(XC(S)Y)_3]$ as a mixture of *fac*- and *mer*-isomers. Attempts to prepare mixed derivatives from $[RhCl(XC(S)Y)]_2$ were generally unsuccessful but by reaction of one equivalent of $[Me_2NC(S)S]^-$ with [RhCl(*cyclo*-$C_8H_{14})_2]_2$ to give [Rh(S(S)CNMe$_2$)(*cyclo*-C_8H_{14})] followed by reaction with $[Et_2NC(S)S]^-$ gave the desired $[Rh(Me_2NC(S)S)(Et_2NC(S)S)_2]$ (ref. 537).

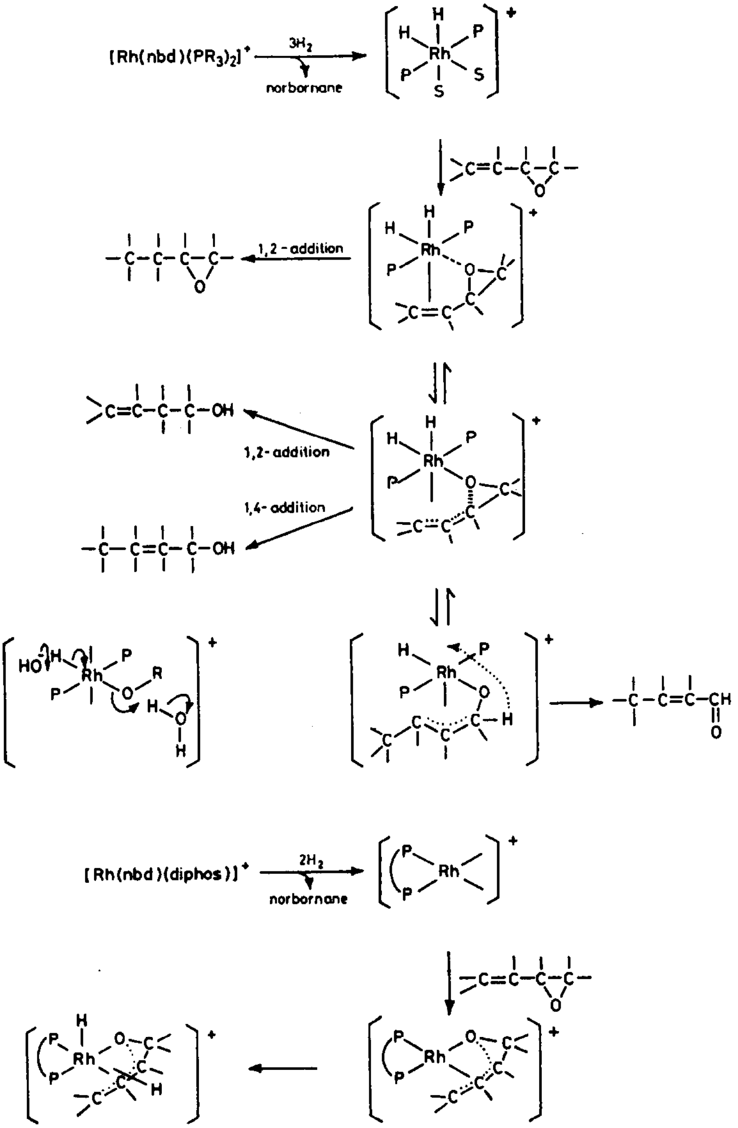
The dimeric hydride complex $[Rh_2(\mu\text{-}H)_2(P(NMe_2)_3)_4]$ reversibly adds hydrogen to give the mixed Rh(III)-Rh(I) dimer $[RhH_2(P(NMe_2)_3)_2(\mu\text{-}H)_2Rh(P(NMe_2)_3)_2]$ which reacts with ethylene to form ethane and regenerate the original dihydride. It is proposed to be analogous to the species to which the olefin adds in hydrogenations catalyzed by $[Rh_2(\mu\text{-}H)_2(P(OPr^i)_3)_4]$ (ref. 538). Tetracyanoethylene adds to $[Rh(C{\equiv}CPh)(CO)(PPh_3)_2]$ to give a five-coordinate species with the carbonyl and acetylide ligands in axial positions. In an attempt to promote migration of the acetylide ligand to TCNE the complex was refluxed in acetonitrile but only carbonyl replacement by solvent occurred (ref. 539). The kinetics of the reaction of COD with $[Rh(dike)(CO)_2]$ (dike = RC(O)CHC(O)R' (R = Ph; R' = Me, CF_3. R = Me; R' = CF_3. R = R' = Ph, CF_3)) in methanol have been studied. Both solvent-assisted and direct paths have been observed and the reaction appears to exhibit considerable associative character (ref. 540). Reaction of $[Rh(OMe)(COD)]_2$ with salophen gives $[(Rh(COD))_2salophen]$ in which the COD ligand undergoes an intramolecular fluxional process as determined from a variable temperature ^{13}C NMR study (ref. 541).

The ^{103}Rh NMR spectra of $[cp_2Rh]Cl$ and a large number of rhodium complexes containing cyclic and acylic diene ligands together with cyclopentadienyl or acetylacetonate ligands have been measured. The shielding of the ^{103}Rh nucleus decreases with increasing oxidation state and is less for 16-electron species than with 18-electron ones (ref. 542). The proton and ^{103}Rh NMR spectra of $[Rh(Bpz_4)(diolef)]$ (diolef = COD, NBD, duroquinone) have also been measured and an intramolecular exchange of free and bound pyrazolate groups is found to occur (ref. 543). Carbon-13 NMR spectra of $[Rh(acac)(C_2H_3R)_2]$ (R = cy, Ph, CO_2H, CO_2Me, O_2CMe, p-anisyl, p-$NO_2C_6H_4$, o-anisyl) have been measured to probe their dynamic behavior and to determine the orientation of the olefin ligands. For R = cy, the substituents are exclusively exo and slow exchange with free olefin occurs. For the styrene ligands a significant population of the endo-rotamers is seen which is attributed to a weak interaction of the phenyl groups with the metal (ref. 544). Monitoring of the thermal rearrangement of $[Rh(acac)(\eta^4\text{-}C_7H_8)]$, labelled with ^{13}C in the 3- and 7-positions, by ^{13}C NMR led to the conclusion that the scrambling of the label occurs in a random fashion (ref. 545). In order to determine the solution structures of rhodium complexes of chiral phosphines which are frequently used as catalyst precursors for asymmetric hydrogenations, the ^{31}P NMR spectra of $[Rh(COD)(L_2)]^+$ (L_2 = diphos, R,R-1,2-bis(o-anisylphenylphosphino)ethane (DIPAMP), (2S, 4S-N-tert-butoxycarbonyl)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine (BPPM), (2S, 3S)-bis(diphenylphosphino)butane (CHIRAPHOS)) and $[Rh(NBD)(L_2)]^+$ (L_2 = DIOP, CHIRAPHOS, (R)-1,2-bis(diphenylphosphino)propane (PROPHOS)) in solution were compared to those of the solid complexes determined by the MAS technique. Most showed some differences but no definite conclusions could be reached (ref. 546).

Absorption, emission and excitation spectra of $[M(L_2)_2]^+$ (M = Rh, Ir; L_2 = vdiphos, cis-1,2-bis(diphenylarsino)ethylene (vdiars), 1-diphenylarsino-2-diphenylphosphinoethane (ARPHOS), (o-diphenylphosphinophenyl)diphenylphosphine. M = Rh; L_2 = dppp, 1,2-bis(dicyclohexylphosphino)ethane) and $[M(diolef)(L_2)]^+$ (M = Rh, Ir; diolef = COD; L_2 = vdiphos, diphos. diolef = COD, NBD, 1,5-hexadiene; L_2 = ethylenediamine, bipy, ophen, bipyrazine) have been obtained. In all cases the emission spectra indicated splitting of the emitting manifold by spin-orbit coupling. Cyclic voltammetric studies of the last group of complexes showed two reversible one-electron reduction waves. In contrast to $[Rh(diphos)_2]$ the neutral species produced on one-electron reduction of these complexes appear to be relatively stable and their ESR spectra indicate the odd electron resides in a π^* orbital of the L_2 ligand (refs. 547-549). Confirmation of the presence of synergic bonding of the ethylene to rhodium in $[RhCl(C_2H_4)_2]_2$ has been obtained from an analysis of the photoelectron spectrum of this complex (ref. 550).

The complex $[RhCl(\textit{cyclo}\text{-}C_8H_{14})_2]_2$ has also been used as a phosphine scavenger for the conversion of $[Au_8L_8](NO_3)_2$ (L = PPh_3) to $[Au_8L_7](NO_3)_2$ (ref. 551) and as a source of rhodium for the formation of silica-supported catalysts (via pendant phosphine groups) for olefin hydrogenation (ref. 552). Reduction of [RhCl(ttp)] with triethylaluminum (see also section on σ-bonded complexes) gives a catalyst system more active than $[RhCl(PPh_3)_3]$ for olefin and acetylene hydrogenation (ref. 553). Several complexes containing imidazole or phosphine ligands prepared in situ from $[Rh(NBD)_2]ClO_4$, $[Rh(OMe)(COD)]_2$ or $[MCl(COD)]_2$ (M = Rh, Ir) catalyze the transfer of hydrogen from isopropanol to olefins and ketones (refs. 554-556). Hept-1-ene and variously substituted styrenes are hydroformylated in the presence of complexes prepared in situ from $[RhCl(NBD)]_2$ and triarylphosphines (refs.

557-559). Ketones and aldehydes are hydrogenated in methanol solution in the presence of $[Rh(NBD)(Pr^i_2P(CH_2)_nPPr^i_2)]ClO_4$ (n = 3,4). The 4-tert-butylcyclohexan-1-ol formed from the corresponding cyclohexanone is predominantly (90%) the trans-isomer indicating kinetic control. Unlike systems employing monodentate phosphines relatively little dehydrogenation of the product alcohols is seen (ref. 560). The complexes $[Rh(NBD)L_n]ClO_4$ (n = 2; L = PEt_3, PPh_3, ½ diphos. n = 3; L = PMe_3) are catalyst precursors for the hydrogenation of 3,4-epoxybut-1-ene to predominantly but-2-enal. A minor product is the unsaturated alcohol. Scheme LXIII (S =

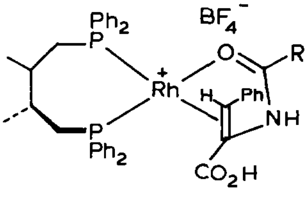


Scheme LXIII

solvent) is proposed (ref. 561). Complexes of the type $[M(diolef)L_2]X$ (M = Rh, Ir; diolef = NBD, COD, TFB; X = ClO_4^-. M = Rh; diolef = COD; X = PF_6^-) show high selectivity for the catalytic hydrogenation of hex-3-yne and a variety of dienes to mono-olefins (ref. 562) and catalyze the condensation of butadiene with but-3-enoic acid to give primarily octa-3,6-dienoic acid. The regioselectivity is attributed to chelation of the butenoic acid to the catalyst (ref. 563). Catalytic oligomerization of α- and β-hydroxy acetylenes occurs in the presence of $[RhCl(PPh_3)_3]$ or mixtures of $[RhCl(\underline{cyclo}\text{-}C_8H_{14})_2]_2$ with varying amounts of triphenylphosphine or triphenylarsine. Generally dimers and trimers were formed and only with the arsine at ligand/metal ratios less than three was selective cyclotrimerization observed (ref. 564) while polymerization of phenylacetylene could be effected by $[Rh(COD)(bipy)]ClO_4$ (ref. 565). Reaction of $[RhCl(NBD)]_2$ with phosphinated polydiacetylene, phosphinated silica or phosphinated styrene/divinylbenzene copolymer gave supported catalysts, the first two of which were effective for hydrogenation of arenes to cyclohexanes. It was proposed that no metallic rhodium was present (ref. 566).

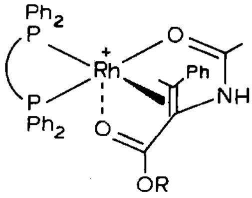
The reactions of gaseous Rh^+ with hydrocarbons has been examined by Fourier transform mass spectrometry. In contrast to what was reported for Co^+ in the 1981 Annual Survey the major reaction appears to be dehydrogenation. Thus with propylene, allyl complexes are detected while with butane a butadiene complex forms. Hexanes and higher hydrocarbons form triene complexes and while considerable ring-cleavage is seen with cyclopropane and cyclobutane, with larger rings again dehydrogenation predominates (ref. 567).

Interest in the use of chiral rhodium catalysts for the asymmetric hydrogenation of prochiral substrates continues to be high with the publications on the subject divided between those reporting mechanistic studies and those which simply report applications. The substrates employed are primarily α-acetamido unsaturated acids, their esters and related compounds. In the first category is a study comparing the binding of substrate to rhodium complexes of chiral and achiral diphosphines. In all cases the initial $[Rh(NBD)(L_2)]^+$ (L_2 = DIOP, dppp, dppb) is hydrogenated to $[Rh(L_2)(MeOH)_2]^+$ in methanol which subsequently adds substrate to give $[Rh(L_2)(substrate)]^+$. With (Z)-benzamido- or (Z)-acetamidocinnamic acids and their esters as substrates NMR studies show that both $[Rh(L_2)(MeOH)_2]^+$ and $[Rh(L_2)(substrate)]^+$ ([221] (R = Me, Ph)) are present. Only one diastereoisomer of the latter is seen



[221]

and exchange between the two occurs. The equilibrium constant for the formation of [221] is significantly smaller than for related complexes where the diphosphine forms a five-membered chelate ring and the exchange with the solvento species is least noticeable with the dppb complex. A variable temperature ^{13}C NMR study of complexes [221] in which the substrate is labelled at the carboxyl carbon atom shows that the chemical shift of this carbon is significantly temperature dependent suggesting the formation of either [222] or [223]. When (E)-benzamidocinnamic acid



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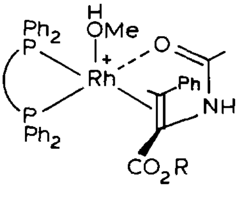
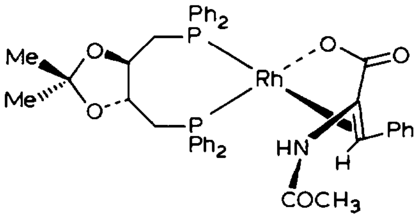


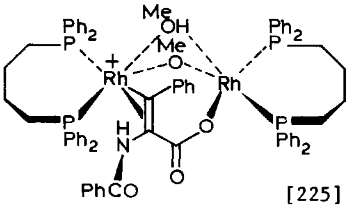
[223]

is used as the substrate, no $[Rh(L_2)(MeOH)_2]^+$ is observed and with L_2 = DIOP, two diastereoisomeric adducts are seen. If the methyl ester of this substrate is used, no complex is seen initially but isomerization to the (Z)-substrate then occurs with the formation of an adduct proposed to be [224]. The ^{31}P NMR spectrum of the



[224]

adduct of (E)-benzamidocinnamic acid with the dppb complex differs considerably from those of the other species and the structures [225] or [226] are proposed



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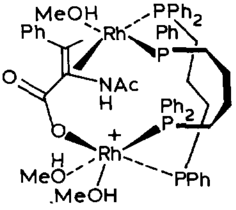
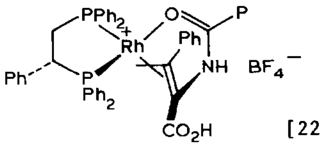
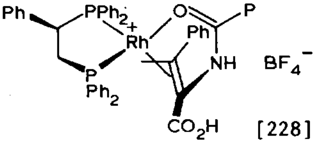


[226]

(ref. 568). Hydrogenation of $[Rh(NBD)(L_2)]^+$ (L_2 = (R)-1,2-bis(diphenylphosphino)-phenylethane) in methanol yields a mixture of monomeric and dimeric solvate complexes which add (Z)-benzamidocinnamic acid to give a mixture of the regio-isomers [227] and [228]. When L_2 = (R,R)-1,2-bis(diphenylphosphino)-1,2-diphenylethane, hydrogenation of the original diene complex gives an insoluble, presumably oligomeric compound. Various cinnamic acid derivatives give mixtures of diastereoisomeric adducts when added to the species generated by hydrogenation of $[Rh(NBD)(L_2)]^+$ (L_2 = rac-1,3-bis(diphenylphosphino)-1,3-diphenylpropane) but with



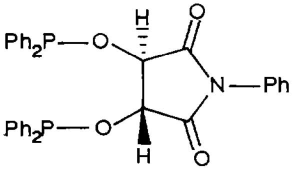
[227]



[228]

α-acetamidoacrylic acid a different adduct possibly involving tridentate coordination of substrate was observed. Similar behavior was observed with the complex containing rac-1,4-bis(diphenylphosphino)-1,4-diphenylbutane. As in the previous paper, increasing the size of the phosphine chelate ring increases the extent of exchange between solution species (ref. 569). Adduct formation of α,β-unsaturated acids, their amides and β,γ-unsaturated amides with rhodium complexes of DIOP and DIPAMP generated in situ as described above has been further studied. Substrates such as cis-cinnamic acid, atropic acid and N,N-dimethylatropamide form mixtures of diastereoisomeric adducts while the weak complexation of trans-cinnamic acid suggests that steric interactions between the substrate and the phenyl groups of the phosphine ligand is important. Hydrogenation of the adducts gave reduced products in varying optical yields but as has been mentioned in previous Annual Surveys, there is little resemblance between the structure of the initial adducts, the ratio of diastereoisomers seen prior to hydrogenation and the optical yield. The highest reactivity is seen when the phosphine forms a five-membered chelate ring and the substrate can also chelate. With amide substrates the optical yield is increased on addition of triethylamine but as this does not affect the formation of the initial substrate adduct, its effect must operate at a later stage of reaction. When the hydrogenation is run in CH_3OD H/D exchange at the α-position of the product is observed. This appears to occur in the catalytic cycle, possibly at the point that the hydrido alkyl metal complex forms (ref. 570). Related studies by the same group appear in two other papers (refs. 571, 572).

In considering the second category of papers it will be assumed that the catalysts described are generated by hydrogenation of $[Rh(diolef)L_2]^+$ (diolef = NBD, COD; L_2 = (monodentate phosphine)$_2$, diphosphine) in an alcoholic solvent unless otherwise stated. Use of the ligands phenyl(o- or p-tolyl)(1-naphthyl)phosphine (NPTP), 1,2-bis(o- or p-tolylphenylphosphino)ethane (BTPE), 1,2-bis(1-naphthylphenylphosphino)ethane (BNPE) or 1,2-bis(diphenylphosphino)phenylethane ((R)-PDPE) and α-acetamidoacrylic acid provided 20-76% optical yields with the last two being the best. However with 2,2'-bis(diphenylphosphino)biphenyl (bpbp) optical yields were minimal although the hydrogenation rate was rapid under ambient conditions. Investigation of the recycle characteristics of these and related catalyst precursors indicated that chloride was the best counterion since $[RhCl(L_2)]_2$ which is easy to recover forms in the absence of substrate following hydrogenation. This does have its disadvantages however as other workers have reported that optical yields can be higher when non-coordinating counterions are used (refs. 573-575). With (S)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl a catalyst superior to that with bpbp is formed (ref. 576). Analogs of DIPAMP generally do not provide as selective catalysts as DIPAMP itself except when the phenyl substituent is replaced by a 2-naphthyl or an *m*-chlorophenyl group. The analog of BPPM with a methylsulfonyl group replacing the *tert*-butylcarbonyl substituent gave optical yields comparable to BPPM itself with the only advantage being its ability to be used in aqueous media. Alteration of the substituents on phosphorus in DIOP also produced no improvement in selectivity (ref. 577). Complexes of CHIRAPHOS, PROPHOS and SKEWPHOS ((S,S)-$Ph_2PCHMeCH_2CHMePPh_2$) gave selective catalysts but CHAIRPHOS((S)-$Ph_2PCH_2CH_2CHMePPh_2$) did not presumably because it cannot maintain a chiral array of phenyl groups in its complex (ref. 578). Two additional systems giving high optical yields use the ligands (R)-3-benzyloxy-1,2-bis(diphenylphosphino)propane, its (S)-3-trityloxy analog (ref. 579) and 5-methylbicyclo-[2.2.1]hept-5-ene-2,3-diylbis(diphenylphosphine) (MeNORPHOS) (ref. 580). Moderate optical yields can be realized using (3S)-[N,N-bis(diphenylphosphino)-3-aminopiperidine] and its methylamino analog (ref. 581) and (S)-N-(diphenylphosphino)-2-diphenylphosphinoxymethylpyrrolidine (S-PROLOPHOS) or (S)-1-diphenylphosphinoxy-2-N-ethyl-N-diphenylphosphinoaminobutane (S-BUTAPHOS). The observation of higher optical yields in the hydrogenation of itaconic acid using the S-PROLOPHOS catalyst than with the S-BUTAPHOS system suggests that a rigid ligand backbone is important as this can better establish a chiral array of phenyl groups in the catalyst (ref. 582). Sulfur-containing molecules evidently do not poison chiral rhodium catalysts formed from DIOP ligands as quantitative hydrogenation of 2-benzamido-3-(2-thienyl)-2-propenoic acid could be achieved. However very low optical yields were obtained (ref. 583). Complexes of the chiral phosphinites [229] and [230] give moderate optical yields with standard substrates and are better with the first ligand than the second possibly because the phosphorus atoms are closer to the chiral centers. Monitoring the optical rotation of the product with time showed it to reach a maximum well before the complete consumption of substrate suggesting degradation of



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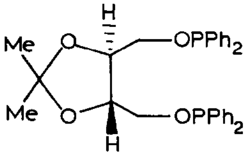
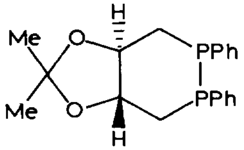


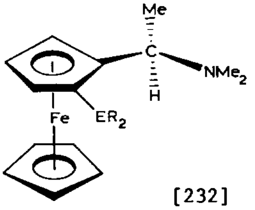
[230]

the catalyst to unselective species (ref. 584). The phosphine [231] ((-)-cyclodiop) when added to $[RhCl(C_2H_4)_2]_2$ and hydrogenated provides a catalyst with good selectivity however with $[RhCl(COD)]_2$ under the same conditions the optical yield dropped to zero. The ^{31}P NMR spectrum of the latter system indicated the presence of a mixture of chelated and possibly monodentate phosphine complexes (ref. 585). Phosphine ligands derived from sugars, particularly 6-0-(diphenylphosphino)-1,2:3,4-d-0-isopropylidene-α-D-galactopyranose, provide moderately selective catalysts (ref. 586) as does ethylene-d-N,N'-2-amino-1-hydroxy-di-N,N'-diphenylphosphinobutane (ref. 587), the lactone of (1S, 3R)-1-hydroxy-1-diphenylphosphinomethyl-2,2,3-trimethylcyclopentane-3-carboxylic acid and (1R, 3R)-bis(diphenylphosphinoxymethyl)-2,2,3-trimethylcyclopentane (ref. 588).



[231]

A number of optically active ferrocenyl phosphines have also been used to generate chiral rhodium catalysts. With [232] (ER_2 = PPh_2, $AsPh_2$, $AsMe_2$, PBu^t_2) the best yields in the reduction of acetamidocinnamic acid derivatives are 84% (S)-product when ER_2 = PBu^t_2 and 76% (R)-product when ER_2 = PPh_2 (ref. 589). The asymmetric hydrogenation of the prochiral phosphinates $H_2C{=}C(R)OP(O)Ph_2$ (R = Ph, Pr^i, Bu^t, n-C_6H_{13}) is catalyzed by rhodium complexes of (R)-1-[(S)-1',2-bis-(diphenylphosphino)ferrocenyl]ethanol. The resulting saturated phosphinates are precursors to optically active alcohols. Poorer yields are obtained with DIOP and BPPM (ref. 590). Rhodium complexes of the ligands [233] (R = NR_1R_2 (R_1 and R_2 = various combinations of H, Me, Et, allyl, $Me_2NCH_2CH_2$, $MeNHCH_2CH_2$, $HOCH_2CH_2$, pyrrolidino, piperidino)), have been studied as catalysts for the asymmetric hydrogenation of prochiral carbonyl compounds. When R = OH high optical yields of (R)-epinepherine hydrochloride can be obtained from 3,4-dihydroxyphenylmethylamino methyl ketone hydrochloride (ref. 591). Hydroformylation of olefins is catalyzed



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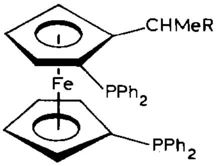
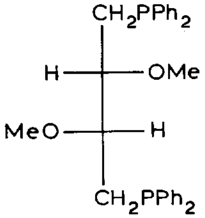


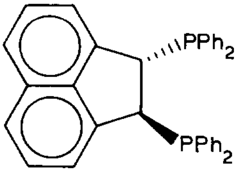
[233]

by rhodium complexes of 1,1'-bis(diphenylphosphino)ferrocene with the most active system proposed to involve a binuclear complex with three phosphorus atoms coordinated to each metal. Analogs with electron-withdrawing substituents on the phenyl groups give higher rates and greater selectivity to the straight-chain aldehyde (ref. 592).

The ligands $Ph_2PCH_2C(O)NHCHRR'$ ($R = CO_2Bu^t$; $R' = Pr^i$ (VAT), CH_2Ph (FAT). $R = CO_2Et$; $R' = CH_2Ph$(FAE). $R = Ph$; $R' = Me$(FEA)) and $Ph_2PCH_2C(O)\overline{NCH(CO_2Bu^t)(CH_2})_3$ (PT) coordinated to rhodium have been studied as catalysts for the asymmetric hydrogenation of acetophenone. Only the PT and FEA complexes were active and the optical yields and rates were low. A significant rate increase was observed when a two-phase benzene-water system was used in the presence of triethylamine which was attributed to this system favoring the reaction of $[RhClH_2L_3]$ with the base to give $[RhClHL_3]$ because the triethylammonium ion so produced is extracted into the aqueous layer (ref. 593). Complexes derived from $[RhH(CO)(PPh_3)_3]$, $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ and the ligands trans-1,2-bis(diphenylphosphinomethyl)cyclobutane, DIOP, [234] and [235] are efficient catalysts for the asymmetric hydrogenation of



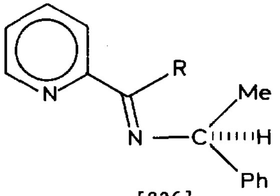
[234]



[235]

α,β-unsaturated aldehydes. For example (+)-citronellal is obtained in 70–79% optical yield from neral (ref. 594). Other catalyst systems are those using dppb to give good optical yields of N-(N-acetyl-α-aminoacyl)-β-amino alcohols from the appropriate prochiral olefins (ref. 595) and those with DIOP which are highly selective for the hydrogenation of (N,N-dialkylamino)alkyl aryl ketones to the corresponding chiral alcohols (ref. 596). Analogs of DIOP with the phenyl groups on phosphorus replaced by ethyl, isopropyl or cyclohexyl groups are catalysts for the hydrogenation of ketones and α-ketoacids, -esters, -lactones and -amides to chiral hydroxy compounds. Optical yields of up to 77% have been observed (refs. 597, 598).

The catalyst derived from $[Rh(NBD)(dppb)]^+$ provides a highly selective reduction of 3-phenylbut-3-en-2-ol to *threo*-3-phenylbutan-2-ol. However significant isomerization to 3-phenylbutan-2-one also occurred. With 4-phenylpent-4-en-2-ol no isomerization was noted but the selectivity to the *threo*-alcohol over the *erythro*-form was poorer. The stereoselectivity is rationalized on the basis of a minimization of non-bonded interactions in the transition state (ref. 599). Analogous catalysts using DIOP and BPPM ligands effect the asymmetric reduction of prochiral α-β-unsaturated ketones to optically active allylic alcohols *via* initial asymmetric hydrosilylation. For example (R)-carvone is converted to a 3.5:1 mixture of *trans*-(5R, 1S)- and *cis*-(5R, 1R)-carveol and it may be noted that other routes to carveol, such as lithium aluminum hydride reduction give predominantly *cis*-product (ref. 600). The Schiff base ligands [236] (R = H, Me, Ph) and [237] (R = H, Me)



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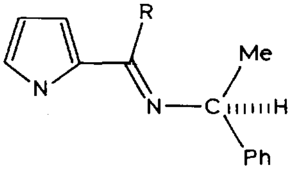
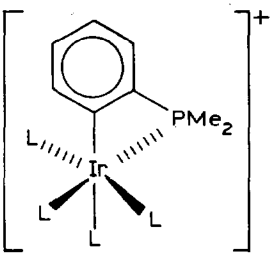


[237]

when used in excess with rhodium-diolefin complexes catalyze the asymmetric hydrosilylation of acetophenone by diphenylsilane. Moderate optical yields were obtained (ref. 601). A related study used *o*-(1-dimethylaminoethyl)phenyldiphenylphosphine and its arsenic analog as the ligand with the best optical yield obtained with the phosphine and 3,3-dimethylbutan-2-one as the substrate. Most others tried gave low optical yields and the arsenic ligand produced a totally unselective catalyst (ref. 602). Allyl amines can be catalytically isomerized to the corresponding enamines *via* a stereoselective 1,3-hydrogen shift using rhodium complexes of DIOP and 2,2'bis(diphenylphosphino)-1,1'binaphthyl (ref. 603, 604).

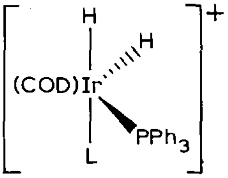
Hydrogenation of the bisdehydrodipeptide acetyl-(S)-phenylalanyl-(S)-phenylalanine methyl ester to its completely saturated analog is catalyzed by $[Rh(COD)(DIPAMP)]^+$ in high optical yield. Complexes with other ligands such as BPPM are also effective although the catalyst derived from $[Rh(C_2H_4)_2(DIOP)]^+$ is not as good (refs. 605-607). This last system has however been used to effect the stereospecific tritiation of the same substrate (ref. 608).

A high-yield synthesis of $[IrCl(COD)]_2$ used ammonium hexachloroiridate(IV) rather than hydrated iridium(III) chloride in refluxing aqueous isopropanol. The diene complex reacts with dimethylphenylphosphine in refluxing acetonitrile to give [238] (L = PMe_2Ph) (ref. 609). With triphenylphosphine, simple cleavage occurs to give $[IrCl(COD)(PPh_3)]$ which on treatment with silver tetrafluoroborate in the presence of nitriles yields $[Ir(COD)(PPh_3)L]BF_4$ (L = RCN (R = Me, *p*-anisyl, Ph,



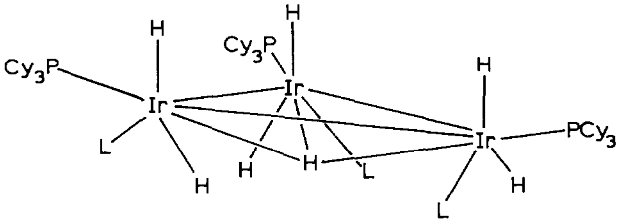
[238]

p-MeC(O)C_6H_4, p-$NO_2C_6H_4$)). These are active hydrogenation catalysts and at low temperature the hydrogen adduct [239] can be detected. From the ^{13}C NMR chemical



[239]

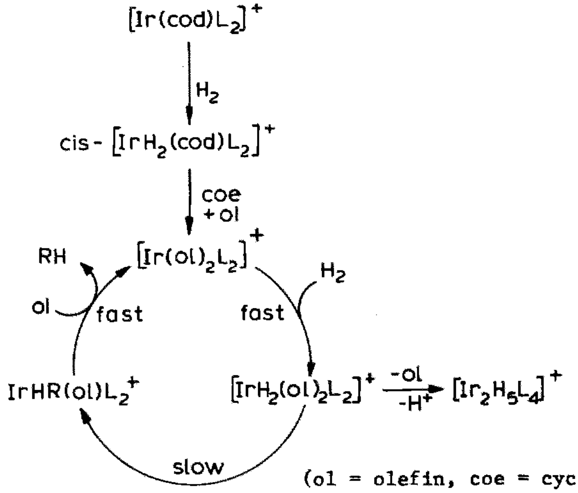
shifts of the vinyl carbon atoms of the COD ligand it appears that hydrogen addition has increased the electron density on the metal thus providing another example of the reductive addition of hydrogen previously reported by these authors. These chemical shifts are also affected by the nature of the nitrile ligand with the trans-influence being significantly greater than the cis-influence (ref. 610). By contrast, the related complex [Ir(COD)(Pcy_3)L]BF_4 (L = MeCN, py) reacts with hydrogen at room temperature in dichloromethane or even in the solid state to give the trinuclear hydride complex [240] which on further reaction with carbon monoxide or ethylene gives mixtures of cationic species while with borohydride it yields a



[240]

mixture of neutral hydrides. These were not separated (ref. 611). The same group has also made an extensive study of the complexes [Ir(COD)L_2]BF_4 (L = PPh_3, $PMePh_2$) and derivatives for olefin hydrogenation and dehydrogenation. Reaction with hydrogen in various solvents yields $[IrH_2S_2L_2]^+$ (S = H_2O, THF, Bu^tOH, Pr^iOH, acetone, EtOH, MeOH, MeCN) with the stability increasing with S in the order given.

At -80° C conversion of $[IrH_2(H_2O)_2(PPh_3)_2]^+$ into $[IrH_2S(olefin)(PPh_3)_2]^+$ and/or $[IrH_2(olefin)_2(PPh_3)_2]^+$ could be observed on addition of olefin. Bis(olefin) complexes were seen for simple olefins (except styrene which forms an arene complex) while bulky olefins gave only monosubstitution. Formation of the olefin complexes became increasingly difficult as the coordinating ability of the solvent increases. Hydrogenation occurs on warming and a further study of the system led to the proposed mechanism of Scheme LXIV for the catalysis of olefin hydrogenation

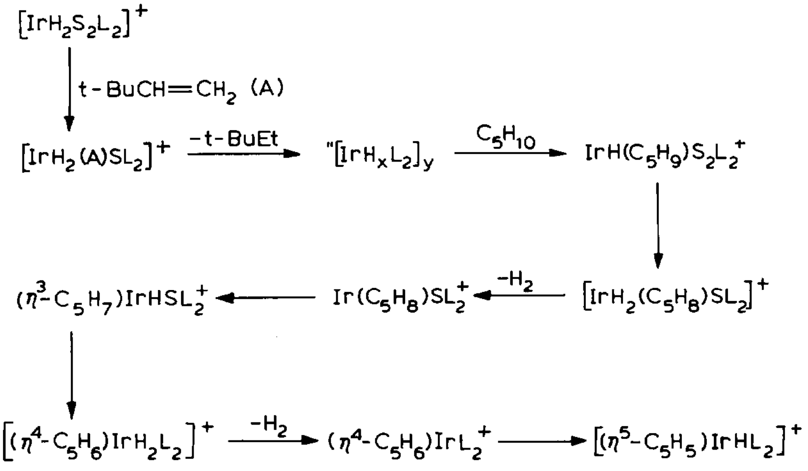


(ol = olefin, coe = cyclooctene)

Scheme LXIV

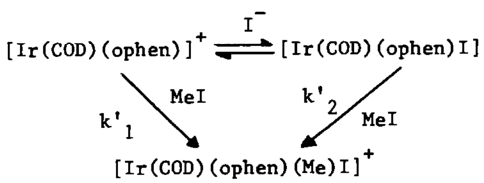
by $[IrH_2S_2L_2]^+$ (the bracketed species have been identified) (ref. 612). In the absence of additional hydrogen $[IrH_2S_2L_2]^+$ ($L = PPh_3$, $S = H_2O$) acts to dehydrogenate olefins. Thus reaction with cyclooctene or norbornene gave $[Ir(COD)L_2]^+$ or $[Ir(NBD)L_2]^+$ and two equivalents of cyclooctane or norbornane respectively. Direct attack on an unactivated carbon-hydrogen bond appears to occur. Similarly cyclopentene reacted to give $[cpIrHL_2]^+$ and cyclopentane. More importantly however, cycloalkanes could be dehydrogenated in the presence of tert-butylethene as a hydrogen acceptor to give $[IrH(diene)L_2]^+$. No reaction was observed with linear alkanes. The results here together with some of those reported in the previous paper suggest the reaction occurs according to Scheme LXV (bracketed species identified). In both studies extensive controls ruled out the participation of radicals, carbonium ions or heterogeneous species (ref. 613).

The complexes $[Ir(COD)(N\text{-}N)]^+$ (N-N = bipy, ophen) are formed from [IrCl(COD)L] or $[Ir(COD)L_2]^+$ (L = py, 2-picoline, 4-picoline) in methanol and kinetic studies show that in the first case the solvent-assisted path is unimportant and some associative character is detected while in the latter both direct and solvent-assisted



Scheme LXV

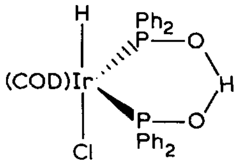
paths are followed (refs. 614, 615). The reactions of [Ir(COD)(ophen)]Cl with methyl iodide and oxygen have also been studied kinetically. For the former, iodide ion catalyzes the reaction and the mechanism of Scheme LXVI is proposed with the k'_2 path preferred. For the second, an analogous scheme is proposed for the



Scheme LXVI

formation of $[Ir(COD)(ophen)(O_2)]^+$ with the k'_1 path preferred. However with the iodide and thiocyanate analogs the k'_2 path predominates and at a significantly faster rate. This reaction is greatly inhibited by added triphenylphosphine and a possible initial end-on coordination of dioxygen is postulated (refs. 616, 617). These and other adducts of $[Ir(COD)(ophen)]^+$ have been studied by ESCA techniques with variations in the iridium $4f_{5/2}$ and $4f_{7/2}$ binding energies used to determine the extend of charge transfer to the added moiety. The results generally corroborate the conclusions reached previously by Vaska using variations in ν_{CO} for adducts of $[IrCl(CO)(PPh_3)_2]$ (ref. 618).

The phosphinite complex [241] (L_2 = COD) is synthesized from chlorodiphenylphosphine and $[IrCl(COD)]_2$ in aqueous methanol. Conversion to analogs with L_2 = diphos, DPAE and 1,2-bis(phenylthio)ethane occurs on addition of the appropriate ligand and these latter complexes react with tetrafluoroboric acid or boron trifluoride etherate to give [242] and [243]. Reaction of [241] (L_2 = COD) with



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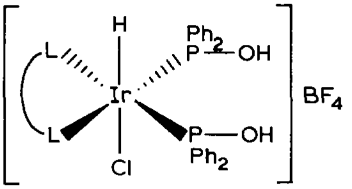

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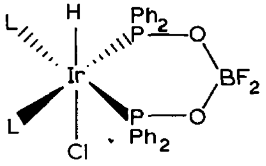
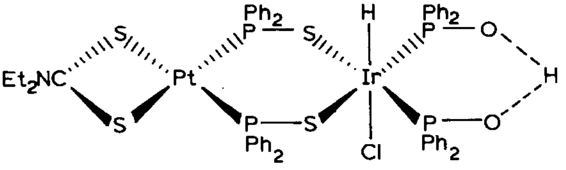
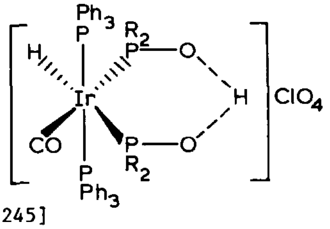


[243]

$[Et_2NH_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ yields [244] while $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ and dimethyl phosphonate give [245] (R = OMe). Analogous reactions with rhodium yield

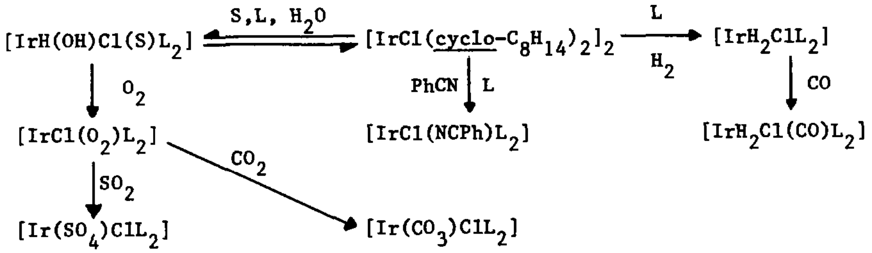


[244]



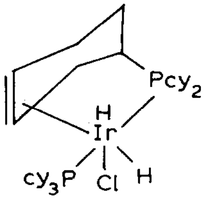
[245]

$[Rh(Ph_2P(OMe))_4]^+$ and $[RhHCl(Ph_2P(OMe))_4]^+$ at low water concentration while at higher concentration and with short reaction times $[Rh_2Cl_2((Ph_2PO)_2H)_2(\mu\text{-}Cl_3)]^-$ results (ref. 619). The five coordinate hydride $[IrHCl_2L_2]$ (L = Pcy_3) is formed from [IrCl(cyclo-$C_8H_{14})_2]_2$, the ligand and hydrogen chloride in toluene or by refluxing iridium tetrachloride with the ligand in 2-methoxyethanol. Carbon monoxide or DMA adds trans to the hydride ligand and the carbonyl complex isomerizes and then loses hydrogen chloride to finally yield trans-$[IrCl(CO)L_2]$. Dehydrohalogenation also occurs when the phosphine reacts with $[IrHCl_2(COD)]_2$ so that [IrCl(COD)L] is formed. Related chemistry is outlined in Scheme LXVII (L =

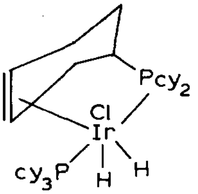


Scheme LXVII

Pcy_3; S = MeCN) while on refluxing [IrCl(cyclo-$C_8H_{14})_2]_2$ with the phosphine in toluene dehydrogenation of the ligand occurs to give a mixture of the isomers [246a] and [246b]. The same phosphine with hydrated rhodium(III) chloride in

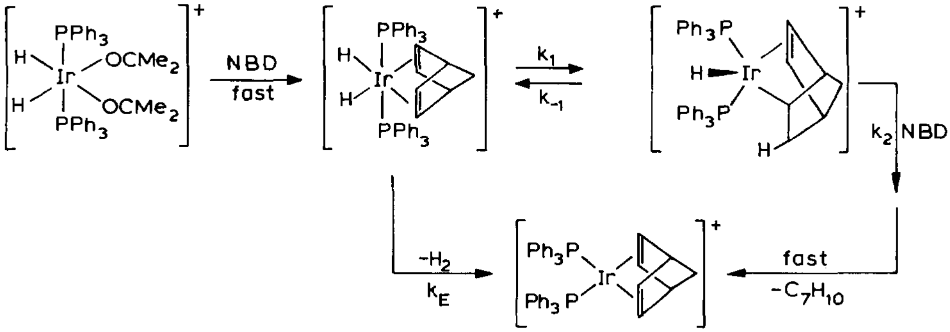


[246a]



[246b]

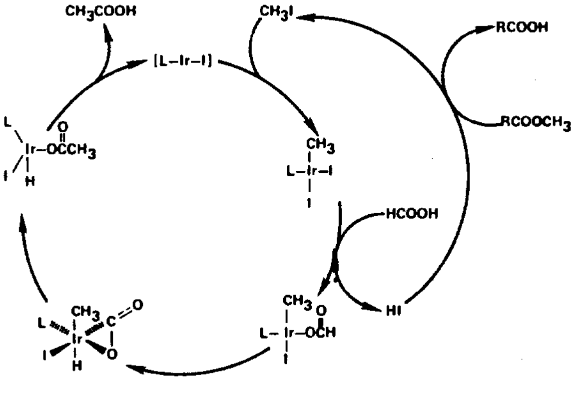
refluxing ethanol yields [$RhHCl_2L_2$] while the same reaction in the presence of formaldehyde and sodium borohydride gives trans-[$RhCl(CO)L_2$] (ref. 620). Kinetic studies demonstrate the presence of a significant inverse isotope effect in the hydrogenation of NBD by [$IrX_2(PPh_3)_2(acetone)_2]^+$ (X = H, D). NMR studies support the mechanism of Scheme LXVIII with the isotope effect attributed to a significant



Scheme LXVIII

difference in k_{-1} between the two isotopically substituted species (ref. 621). The kinetics of oxidative addition of TCNE, dimethylmaleate, MA and acetylene dicarboxylic acid and its dimethyl ester to [$IrX(CO)L_2$] (X = Cl, Br, I; L = PPh_3, $P(OPh)_3$, p-tolyl$_3$P, p-anisyl$_3$P) suggests a non-polar, concerted mechanism (ref. 622).

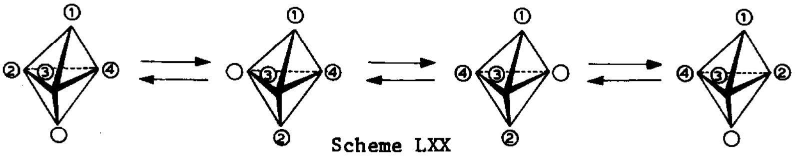
In DMA, [$IrHCl_2(COD)]_2$ or [$IrCl(COD)]_2$ plus hydrogen chloride is a modest catalyst for the oxidation of cyclooctene to cyclooctanone plus water in the presence of hydrogen-oxygen mixtures. The lack of reaction in the absence of hydrogen indicates free radical autooxidation is not occurring (ref. 623). The catalytic conversion of methyl formate to acetic acid in acetic or propionic acid as the solvent is effected by species derived from [$IrCl(COD)]_2$ plus methyl iodide as shown in Scheme LXIX (ref. 624). Although [$Ir(OClO_3)(CO)(PPh_3)_2$] does not catalyze acrylonitrile (AN) polymerization but only forms [$Ir(AN)(CO)(PPh_3)_2]ClO_4$, the species produced on chloride abstraction from [$IrCl(AN)(CO)(PPh_3)_2$] by silver perchlorate are active. One of these is thought to be [$Ir(OClO_3)(AN)(CO)(PPh_3)_2$] in which perchlorate could be replaced by a second molecule of AN (ref. 625).



Scheme LXIX

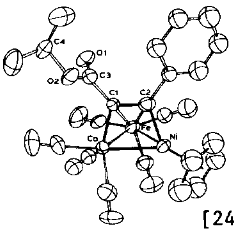
Metal Alkyne Complexes

Diphenylacetylene adds to $[CoBr(PMe_3)_3]$ in acetone-acetonitrile at -35° C to give $[Co(C_2Ph_2)(MeCN)(PMe_3)_3]$ while in acetone alone $[Co(C_2Ph_2)(PMe_3)_3]$ forms. The latter complex is considered to be pseudotetrahedral with the acetylene functioning as a four-electron donor (ref 626). The chiral complex $[cpNi(\mu\text{-}RC_2R')Co(CO)_3]$ (R = Ph; R' = CO_2Pr^i) synthesized from $[Co_2(CO)_8]$, $[cp_2Ni]$ and the acetylene in refluxing heptane readily racemized by an intramolecular process as depicted in Scheme LXX. Application of Wade's rules to the complex leads to considering it to be a

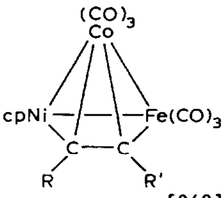


Scheme LXX

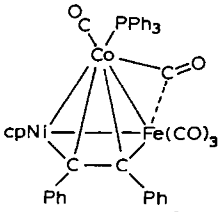
nido-trigonal bipyramid and the low barrier to rearrangement is then a consequence of a vacancy on the cluster surface denoted by the open circle in Scheme LXX. This complex reacts further with $[Fe_2(CO)_9]$ at 40° C to yield the fluxional species [247], while related species react with a large excess of $[Fe_2(CO)_9]$ at room temperature to give [248] ($R = R'$ = Ph. R = Ph; R' = Me. R = Me; R' = Ph). From



[247]



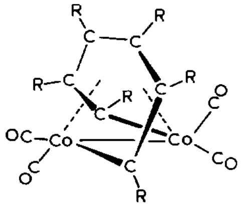
[248]



[249]

[248] (R = R' = Ph) [249] is formed on addition of triphenylphosphine. The fluxional behavior of [247] is also attributed to a vacancy on the cluster surface since it can be considered to be a nido octahedron (refs. 627-629).

The standard complex $[Co_2(CO)_6(\mu\text{-}(EtO)_2CHC_2CH(OEt)_2)]$ can be hydrolyzed with formic acid to $[Co_2(CO)_6(\mu\text{-}HC(O)C_2C(O)H)]$ which is an example of stabilized acetylenedicarbaldehyde (ref. 630). Other examples of $[Co_2(CO)_6(\text{acetylene})]$ complexes useful as intermediates in organic synthesis include the coupling of nucleophiles with cobalt-stabilized 1-alkynyl allyl cations in the regio- and stereoselective synthesis of (E)-1,3-enynes (ref. 631), the successive addition of electrophiles and nucleophiles to $[Co_2(CO)_6(\mu\text{-}HC_2CMe{=}CH_2)]$ to give $[Co_2(CO)_6\text{-}(\mu\text{-}HC_2CMe(R)CH_2X]$ (X = MeC(O), $Bu^tC(O)$, Me_3C, NO_2, 1-adamantyl; R = OMe, OH) (ref. 631) and the coupling of but-2-yne coordinated to cobalt with tetrahydro-2-(2-propenyloxy)pyran to give a functionalized cyclopentenone intermediate readily convertible to methylenomycin B (ref. 633). The $\{Co_2(CO)_6\}$ moiety has also been used to trap the unexpectedly unstable dineopentoxyethyne. Excess $[Co_2(CO)_8]$ must be used to avoid catalytic cyclotrimerization (ref. 634). Mono- and bis(phosphite) derivatives (one per cobalt) of the "flyover" complex [250] (R = CF_3) can be readily synthesized by controlled potential electrolysis in the presence of trimethylphosphite. The radical anion of [250] is thought to rearrange to [251]



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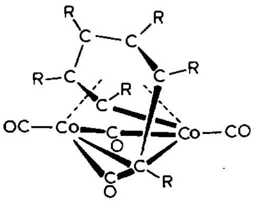
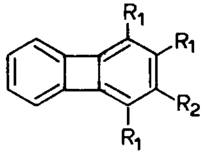


[251]

prior to substitution. The disubstituted species exists as the diequatorial isomer and on electrolysis converts to the axial-equatorial isomer (ref. 635). Electrochemical studies on $[Co_2(CO)_6(R_2C_2)]$ (R = Ph, Bu^t, CF_3) show initial formation of the radical anion which subsequently fragments except when R = CF_3. Under carbon monoxide $[Co(CO)_4]^-$ and $[(R_2C_2)Co(CO)_3]^-$ form as primary products however the reactive species are thought to be the fragments from the breakup of the radical anion rather than the anion itself. Similar behavior was noted for phosphine and phosphite derivatives (ref. 636).

Slow addition of $\underline{o}\text{-}(Me_3SiC{\equiv}C)_2C_6H_4$ to refluxing xylene containing a catalytic amount of $[cpCo(CO)_2]$ gives [252] (R_1 = $SiMe_3$, R_2 = $(\underline{o}\text{-}Me_3SiC{\equiv}C)C_6H_4$) while with stoichiometric quantities only a trace is formed together with five cobalt complexes of the oligomerized acetylene (ref. 637). A full report has now appeared on the use of $[Co_2(CO)_6(RC_2R')]$ (R,R' = H, Me, Et) as catalysts for the reactions of acetylenes with carbaboranes to give boron-substituted alkenylcarbaboranes. The

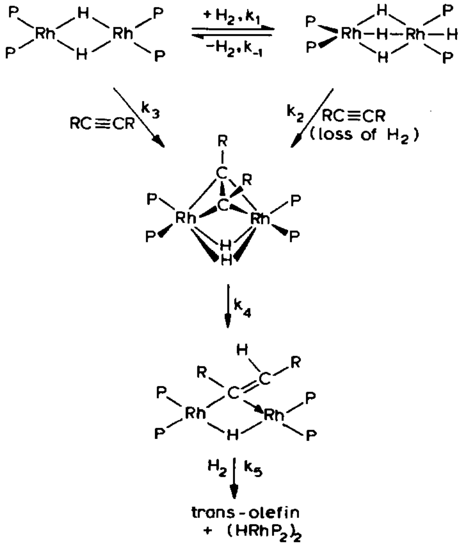


[252]

boron-hydrogen bonds add cis to the carbon-carbon triple bond and internal alkynes are more reactive than terminal ones. Although the cobalt dimer is thought to remain intact it was not established whether or not both metals are involved in the catalysis (ref. 638).

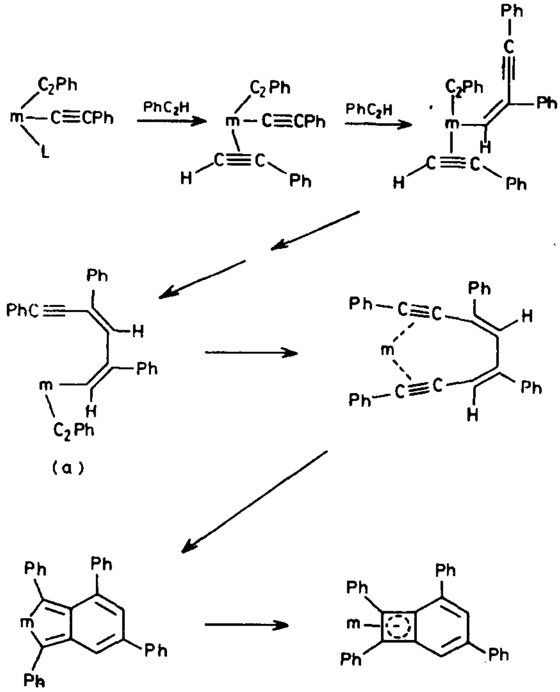
Molecular orbital calculations have been performed on $[\mathrm{cpCo(C_2H_2)_2}]$ and $[\mathrm{cp\overline{CoCH{=}CH{-}CH{=}C}H}]$, presumed to be intermediates in the cobalt-catalyzed oligomerization of acetylene, to determine their structures and preferred conformations (ref. 639). The photoelectron spectra of $[\mathrm{Co_2(CO)_6(PhC_2H)}]$, $[\mathrm{Co_4(CO)_{10}(PhC_2H)}]$ and $[\mathrm{PhCCo_3(CO)_9}]$ have been measured with the a_2 ionization potential of the phenyl group used as a probe of the extent of charge transfer between the cluster and the ligand. This value decreased over the set of complexes in the order listed indicating a net increase in π-donation to π* orbitals of the ligand as the number of bonded metal atoms increases. This was further suggested to indicate that alkyne cleavage on metal surfaces may be due to charge transfer to carbon and therefore those sites with the highest metal/carbon ratio would be most active (ref. 640).

Alkyne hydrogenation catalyzed by $[\mathrm{Rh_2(P(OPr^i)_3)_4(\mu\text{-}H)_2}]$ is considered to proceed via Scheme LXXI ($P = P(OPr^i)_3$, R = Ph, p-tolyl) with $k_1 > k_2 > k_4 > k_3 > k_5$ (ref.



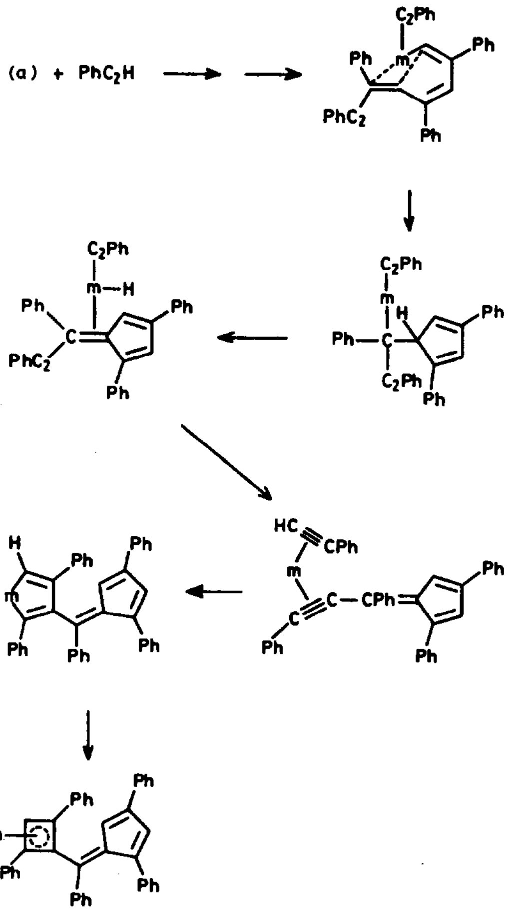
Scheme LXXI

641). Cyclooligomerization of phenylacetylene occurs in acetonitrile in the presence of $[cp'_2Rh_2Cl_4]$ and carbonate ion and two rhodium complexes containing oligomerized acetylene ligands are found among the products. Initial formation of $[cp'Rh(C_2Ph)_2MeCN]$ by attack of phenylacetylide ion (produced by carbonate deprotonation of the acetylene) on $[cp'Rh(MeCN)_3]^{2+}$ formed by solvolysis of the starting dimer is proposed. The rhodium complexes which appear as final products in Schemes LXXII and LXXIII (m = cp'Rh) are then thought to form from this common species as

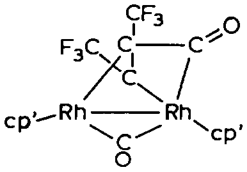


Scheme LXXII

indicated. In particular, the species labelled (a) in Scheme LXXII is proposed to be the branch point at which the process of Scheme LXXIII can begin (ref. 642). Treatment of $[cp_2Rh_2(\mu_2\text{-}\eta^2\text{-}CF_3C_2CF_3)(\mu\text{-}CO)]$ with various ligands causes rearrangement to the dimetallated olefin complex $[cpRh(L)(\mu\text{-}CF_3C{=}CCF_3)Rhcp(CO)]$ (L = CO, $CNBu^t$, PPh_3, $PMePh_2$, $P(OMe)_3$, $AsPh_3$, PF_3, PF_2NEt_2) which also contains a metal-metal bond. In the *tert*-butylisocyanide complex scrambling of the carbonyl and isocyanide ligands occurs (ref. 643). Hexafluorobut-2-yne reacts with $[cp'_2Rh_2(\mu\text{-}CO)_2]$ to give $[cp'Rh(\eta^4\text{-}C_6(CF_3)_6)]$ plus [253]. Analogs of [253] are also formed with dimethylacetylenedicarboxylate and diphenylacetylene. Complexes [254] and [255] are additional products of the latter reaction (ref. 644). $[RhCl(PPh_3)_3]$ is an effective catalyst for the [2+2+2] cycloaddition of $X(CH_2C{\equiv}CH)_2$ with $RC{\equiv}CH$ to give [256] (X = SO_2, NHCOMe; R = CH_2OH. X = O. R = Pr^n. X = $C(COMe)_2$; R = H) and

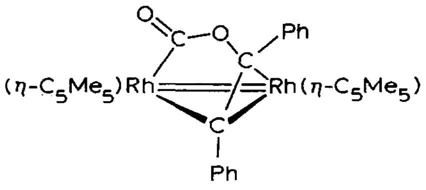


Scheme LXXIII

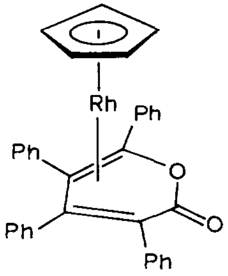


[253]

of [257] with acetylene to give [258] (ref. 645). Acetylenes add to $[Ir_2(CO)_2L_2(\mu\text{-}SBu^t)_2]$ (L = PPh_3, PMe_3) to yield $[Ir(CO)(L)(\mu\text{-}SBu^t)_2(\mu\text{-}RC{=}CR)Ir(CO)L]$ (R = CO_2Me, CF_3) which contain a dimetallated olefin and exist as isomers with *cis*- and *trans*-arrangements of the carbonyl ligands. These isomers interconvert in



[254]



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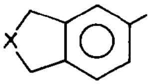

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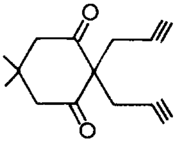

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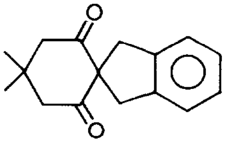


[258]

solution. Protonation with one equivalent of trifluoroacetic acid yields [$Ir_2(CO)_2L_2(\mu$-RC=CR)(μ-SBu^t)(μ-O_2CCF_3)] (R = CO_2Me, CF_3; L = PPh_3. R = CF_3; R = PMe_3). With the last complex [IrH(PMe_3)(CO)(μ-SBu^t)$_2$(μ-CF_3C=CCF_3)Ir(CO)(PMe_3)-(O_2CCF_3)] also is formed while with R = CO_2Me and L = PMe_3, [Ir(CO)(PMe_3)(O_2CCF_3)-(μ-H)(μ-SBu^t)(μ-MeO_2CC=CCO_2Me)Ir(SBu^t)(CO)(PMe_3)] is the product. Addition of two equivalents of acid yields both [$Ir_2(CO)_2L_2$(μ-RC=CR)(μ-SBu^t)(μ-O_2CCF_3)] and [Ir_2-$(CO)_2L_2(O_2CCF_3)_2$(μ-RC=CR)(μ-SBu^t)$_2$] when L = PPh_3 while with L = PMe_3 the product is [$Ir_2(CO)_2L_2(O_2CCF_3)_2$($\mu$-H)($\mu$-SBu^t)($\mu$-RC=CR)]. The first step in all the reactions is considered to be cleavage of a thiolate bridge by trifluoroacetate ion and surprisingly no protonation of the dimetallated olefin occurs (ref. 645).

Extended Hückel calculations have been performed to explore the adsorption and subsequent rearrangements of acetylene on cobalt, rhodium and iridium surfaces (ref. 647).

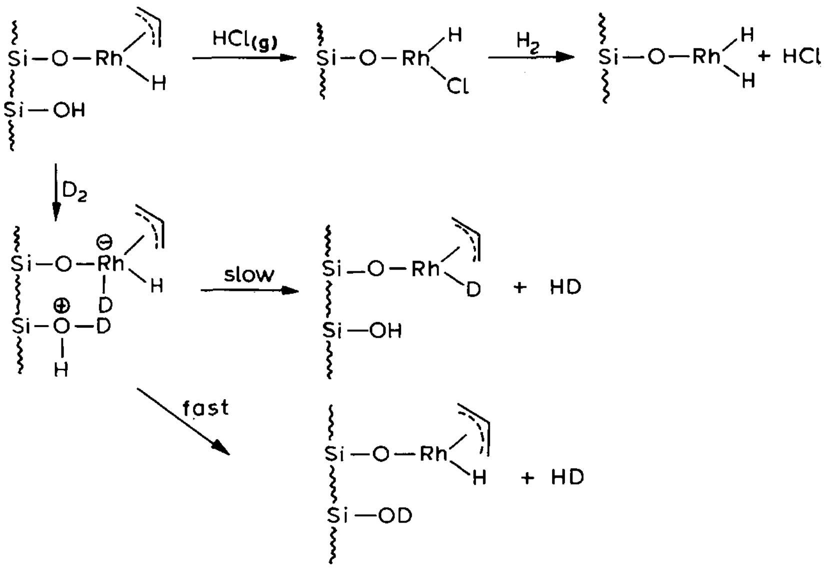
Metal π-allyl Complexes

Oxidative addition of 2-methylallyl iodide to [cpCo$(CO)_2$] yields [cpCo(η^3-C_3H_4Me)I] which is converted to [cpCo(η^3-C_3H_4Me)(C_6F_5)] by pentafluorophenylmagnesium bromide and to [cpCo(η^3-C_3H_4Me)(H_2O)]BF_4 by silver tetrafluoroborate in moist dichloromethane. The coordinated water is readily displaced by a variety of other ligands (ref. 648). In the reactions of [Zn$(Co(CO)_4)_2$] with allylic and propargylic amines and ethers, a variety of oligomeric organic products form and the only cleanly-produced cobalt complex is $[(\eta^3\text{-}C_3H_5)Co(CO)_3]$ which is formed with a stoichiometric quantity of N,N-diethylallylamine (ref. 649). The rate of benzene hydrogenation catalyzed by $[(\eta^3\text{-}C_3H_5)Co(P(OPr^i)_3)_3]$ is decreased in the presence of excess phosphite suggesting that the rate-determining step is either addition of hydrogen to a cobalt-benzene complex or a rearrangement of the species produced in this step (ref. 650).

The He(I) and He(II) photoelectron spectra of $[(\eta^3\text{-}C_3H_5)Co(CO)_3]$ have been measured from which it appears that π-backbonding to the carbonyl groups is more important than in related iron complexes. No determination could be made however of the extend of π-backbonding to the allyl ligand (ref. 651). Molecular orbital calculations have been performed on $[(\eta^3\text{-}C_3H_5)Co(CO)_3]$ and related species to determine preferred sites of attack by nucleophiles in polar solvents. Hard nucleophiles are predicted to attack a carbonyl group in preference to the metal while soft nucleophiles should preferentially attack the allyl group (ref. 652).

Reaction of 2-methylallylmagnesium chloride or 3-butenylmagnesium bromide with $[RhCl(COD)]_2$ produces $[(\eta^3\text{-}2\text{-}MeC_3H_4)Rh(COD)]$ and $[(\eta^3\text{-}1\text{-}MeC_3H_4)Rh(COD)]$ respectively. The COD ligand can be replaced by the chelating diphosphine ligands dmpe, dppp, vdiphos, CHIRAPHOS, ARPHOS, $HN(SiMe_2CH_2PPh_2)_2$ and $(MeO)_2PCH_2CH_2P(OMe)_2$. For the 1-methylallyl complexes the syn arrangement of the allyl ligand, predominates and when CHIRAPHOS is the ligand, both enantiomers of the syn and anti isomers are seen. These are proposed to be formed by different pathways since no syn→anti isomerization is noted. The complexes $[(\eta^3\text{-}2\text{-}MeC_3H_4)Rh(R_2PCH_2CH_2PR_2)]$ react with hydrogen in toluene to yield $[RhH(R_2PCH_2CH_2PR_2)]_x$ (R = OMe; x = 4. R = OPr^i; x = 2) which are fluxional and show equilibriation of all phosphorus and all hydrogen atoms. The extent of oligomerization appears to be determined by steric factors. The tetramer is proposed to possess a tetrahedral disposition of rhodium atoms with edge-bridging hydride ligands. The hydrides are effective catalysts for olefin hydrogenation and show facile H/D exchange however the integrity of the clusters in these reactions has not been established (refs. 653, 654). The reaction of hydrogen with $[(\eta^3\text{-}C_3H_5)Rh(L)_2]$ (L = $PPr^i{}_3$) yields $[Rh_2H_4L_4]$. Although the structural study failed to locate the hydride ligands it is proposed that three are bridging and one is terminal leading to the formulation of the dimer as a mixed valence rhodium(I)-rhodium(III) species. The dimer is also formed by sodium hydride reduction of $[RhH_2ClL_2]$ and reacts with nitrogen in the solid state and in toluene solution to give $[RhH(N_2)L_2]$ and $[(RhHL_2)_2(\mu\text{-}N_2)]$ respectively. Reaction with trimethylphosphite gives initially $[RhH_2(P(OMe)_3)_2]_n$ and ultimately $[RhH(P(OMe)_3)_4]$ (ref. 655).

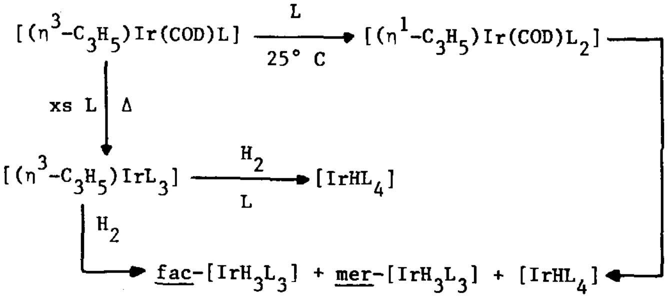
Support of $[(\eta^3\text{-allyl})_3Rh]$ on Linde 13-X molecular sieves provides $\{\text{-ORh(allyl)}_2\}$ moieties inside the cavities of the zeolite. These react with hydrogen to give $\{\text{-ORhH}(\eta^3\text{-allyl})\}$ species which are catalysts for the hydrogenation of olefins smaller than cyclohexene. Successive treatment with hydrogen chloride and hydrogen converts them to {-ORhHCl} and {-ORhH$_2$} moieties respectively while addition of trimethylphosphine yields {-ORh(allyl)H(PMe$_3$)$_2$} (ref. 656). In a related study {-ORh(allyl)$_2$} moieties supported on silica appeared to all be identical from proton NMR spectra. Reaction with hydrogen at 298 K generated propane and propene and NMR spectra showed signals attributable to adsorbed propene and surface hydroxyl groups. Although no reaction appeared to occur between the {-ORh(allyl)$_2$} moieties and carbon monoxide at 298 K, a sample so treated no longer reacted with hydrogen indicating that the hydrogenation of the original supported allylrhodium moieties occurs by activation of hydrogen at rhodium sites not containing allyl ligands with the protons so-formed spilling over to the support and hydrolyzing the allyl ligands. Addition of carbon monoxide evidently blocks these secondary sites (ref. 657). Silica-supported {-ORhH(allyl)} moieties catalyze H/D exchange between deuterium and butane and readily form HD on reaction with deuterium. The latter process is proposed to occur *via* Scheme LXXIV. All the reactions observed suggest



Scheme LXXIV

that the rhodium(III) species are coordinatively unsaturated and possess Lewis acid character (ref. 658).

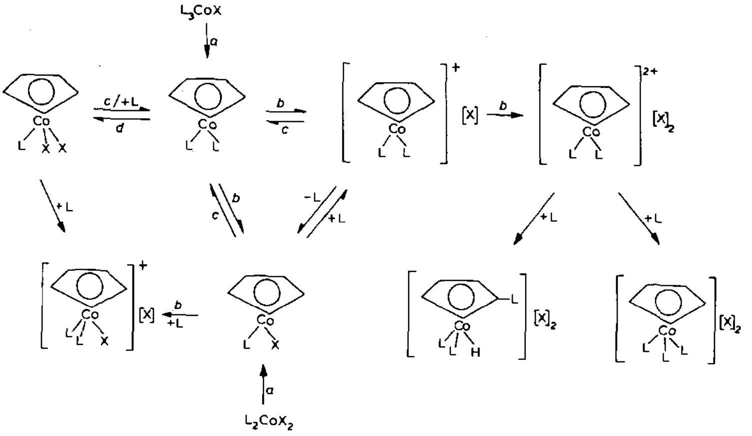
Successive additions of allyllithium and trimethylphosphite (L) to [IrCl(COD)]$_2$ at -78° C yields [(η^3-C_3H_5)Ir(COD)L] which reacts further as shown in Scheme LXXV. No exchange of ligand occurs with [(η^3-C_3H_5)IrL$_3$] nor is an η^1-allyl species formed. Also none of the complexes are precursors for arene hydrogenation catalysts although the η^3-allyls are good olefin hydrogenation catalysts (ref. 659). Coupling of diphenylacetylene with the allyl ligand in [cpIr(η^3-C_3H_5)Cl] occurs in the presence of silver tetrafluoroborate to give $[cpIr(\eta^5\text{-}C_5H_3Ph_2)]BF_4$ (ref. 660).



Scheme LXXV

Metal Carbocyclic Complexes

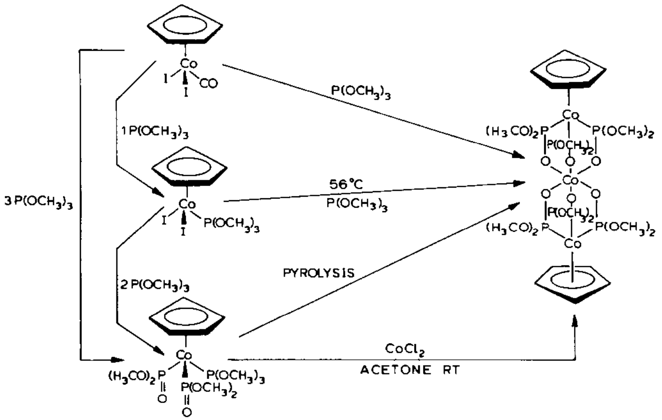
A number of thermally stable, paramagnetic, seventeen-electron cobalt complexes have been synthesized and the pertinent chemistry is detailed in Scheme LXXVI (L = PEt_3, $PEtPh_2$, PPh_3) (ref. 661). Oxidative addition of $(XCN)_2$ and $X(CN)_2$ (X = S, Se) to $[(\eta^5\text{-}C_5H_4R)Co(CO)_2]$ (R = H, $SiMe_3$) yields $[(\eta^5\text{-}C_5H_4R)Co(CO)Y_2]$ and $[(\eta^5\text{-}C_5H_4R)Co(CO)(CN)Y]$ (Y = NCS, NCSe) respectively. In acetone or acetonitrile solution the N-bonded thiocyanate complexes isomerise to the S-bonded species (ref. 662). Methyllithium converts $[(\eta^5\text{-}C_5H_3RR')CoL_2Me]I$ into $[(\eta^5\text{-}C_5H_3RR')CoMe_2(L)]$ (L = PMe_3;



a) Tlcp. b) AgX. c) Zn. d) X_2 or 2AgX

Scheme LXXVI

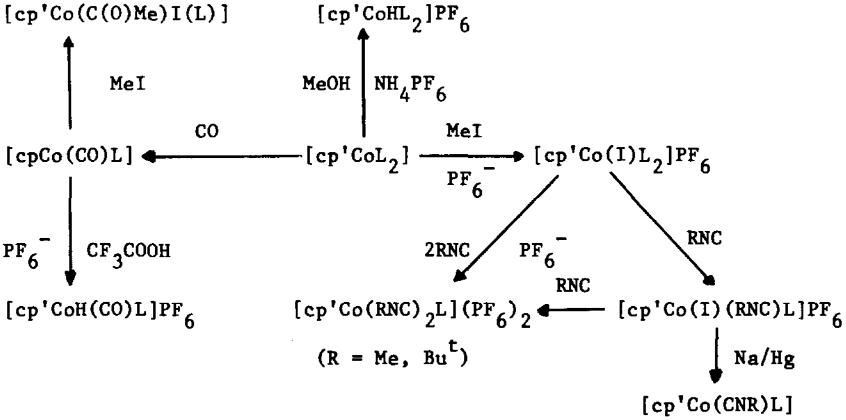
R = H; R' = H, Pr^i, Bu^t. R = Pr^i; R' = Pr^i, Bu^t. L = PEt_3; R = R' = H) which on treatment with two equivalents of trifluoroacetic acid forms $[(\eta^5\text{-}C_5H_3RR')Co(L)(O_2CCF_3)_2]$. The latter complex with R = R' = H reacts further with phenyllithium to give the labile $[cpCo(L)Ph_2]$. One equivalent of trifluoroacetic acid reacts with $[cpCoMe_2L]$ to yield $[cpCo(L)Me(O_2CCF_3)]$ which on successive treatment with phenyllithium and more acid yields $[cpCo(L)Me(Ph)]$ and then $[cpCo(L)Me(O_2CCF_3)]$ (ref. 663). Phosphine and phosphite ligands react with $[(\eta^5\text{-}C_5H_4R)Co(PMe_3)(O_2CCF_3)_2]$ in the presence of hexafluorophosphate ion to yield $[(\eta^5\text{-}C_5H_4R)Co(PMe_3)L_2](PF_6)_2$ (R = H, Pr^i, Bu^t; L = $P(OMe)_3$. R = H, Pr^i; L = PMe_3). The same reaction of $[(\eta^5\text{-}C_5H_3RR')Co(PMe_3)(O_2CCF_3)_2]$ with trimethylphosphite gives $[(\eta^5\text{-}C_5H_3RR')Co(PMe_3)(P(OMe)_3)(O_2CCF_3)]PF_6$ (R = R' = Pr^i) which with trimethylphosphine is further converted into $[(\eta^5\text{-}C_5H_3RR')Co(PMe_3)_2(P(OMe)_3)](PF_6)_2$. Reaction of sodium iodide with $[(\eta^5\text{-}C_5H_3RR')Co(PMe_3)(P(OMe)_3)L](PF_6)_2$ causes a Michael-Arbusov rearrangement of the phosphite ligand to give $[(\eta^5\text{-}C_5H_3RR')Co(PMe_3)L(P(O)(OMe)_2)]PF_6$ (L = PMe_3; R = R' = Pr^i. L = $P(OMe)_3$; R = H; R' = H, Pr^i, Bu^t). When L = $P(OMe)_3$ this rearrangement occurs a second time to yield $[(\eta^5\text{-}C_5H_3RR')Co(PMe_3)(P(O)(OMe)_2)_2Na]PF_6$. The last complex (R = R' = H) is protonated with hydrogen chloride to give $[cpCo(PMe_3)(P(O)(OMe)_2)_2H]PF_6$ which reacts with ammonia to give $[cpCo(PMe_3)(P(O)(OMe)_2)_2NH_4]PF_6$ and can be deprotonated to $[cpCo(PMe_3)(P(O)(OMe)_2)_2]$ with tetramethylammonium hydroxide (ref. 664). Other examples of Michael Arbusov rearrangement of phosphite ligands are found in the reactions of $[RM(P(OR')_3)_3](PF_6)_2$ (R = cp; M = Co; R' = Me, Et. R = cp'; M = Rh; R' = Me) with sodium iodide which yield $Na[RM(P(O)(OR')_2)_3]$. These form 2:1 complexes with a variety of di- and trivalent metal ions via coordination through the phosphonate oxygens. Also the rhodium complex reacts with $[cp'RhCl_2]_2$ to give $[cp'Rh(\mu\text{-}P(O)(OMe)_2)_3Rhcp']^+$ while the cobalt species adds to $[(\eta^6\text{-arene})RuCl_2]_2$ to give $[cpCo(\mu\text{-}P(O)(OMe)_2)_3Ru(\eta^6\text{-arene})]^+$ (ref. 665). The rearrangement can also occur in the absence of added iodide ion as shown in Scheme LXXVII (ref. 666) and by the successive reactions of



Scheme LXXVII

diphos and trimethylphosphite with [cpCo(CO)I_2] to yield first [cpCo(diphos)I]I and then [cpCo(diphos)(P(O)(OMe)$_2$)]I. The suggestion is made that any system where halide ion can be displaced from a metal by a phosphite ligand should provide favorable conditions for formation of phosphonate complexes by this route (ref. 667). The ^{59}Co NQR spectra of [cpCoI_2L] and [cpCoIL_2] (L = CO, P(OPh)$_3$, AsPh_3, SbPh_3, py, H_2NCH_2Ph. L_2 = en, bipy, o-phenylenediamine) together with those of a number of the phosphonate complexes just described have been obtained. The electric field gradient at cobalt is highest with σ-donor ligands and lowest with π-acceptor ligands. From these results, the phosphonate ligands are poor σ-donors but modest π-acceptors (ref. 668).

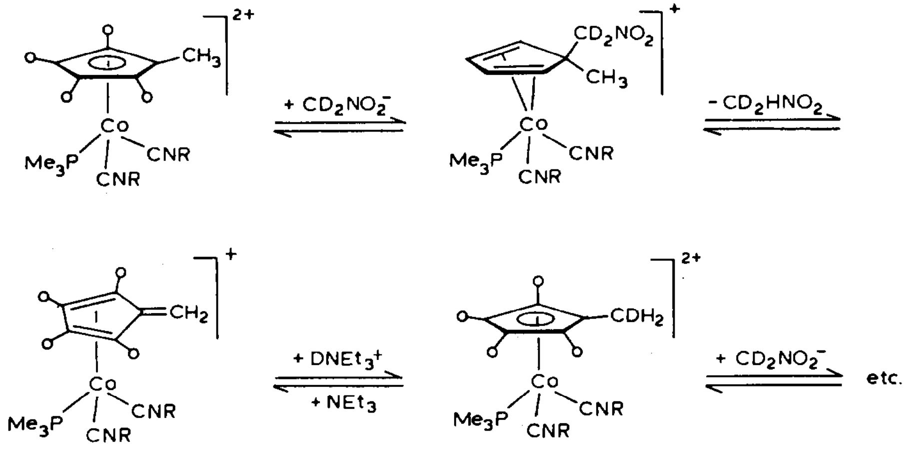
Addition of pentamethylcyclopentadienyllithium to [CoCl(PMe$_3$)$_3$] yields [cp'Co(PMe$_3$)$_2$] whose further chemistry is outlined in Scheme LXXVIII (L = PMe$_3$). An



Scheme LXXVIII

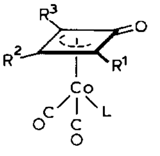
additional reaction of [cp'Co(PMe$_3$)$_2$] is that with [cpMn(CO)$_2$(THF)] which yields [cp'Co(PMe$_3$)(μ-CO)$_2$Mncp(CO)] which contains a Co→Mn bond. In deuteronitromethane solution containing triethylamine H/D exchange occurs between solvent and the methyl groups of the cp' ring in [cp'Co(RNC)$_2$(PMe$_3$)]$^{2+}$ as proposed is Scheme LXXIX (ref. 669). Reaction of equimolar quantities of [cpCo(CS)(PMe$_3$)] and [cpMn(CO)$_2$(THF)] yields [cpCo(PMe$_3$)(μ-CS)(μ-CO)Mncp(CO)] while with a two-fold excess of the manganese complex the same dimer with a {cpMn(CO)$_2$} moiety coordinated to the sulfur atom of the thiocarbonyl ligand results. This can be displaced on reaction with trimethylphosphine. The original dimer can be methylated at sulfur with methyl trifluoromethanesulfonate (ref. 670).

$$CD_3NO_2 + NEt_3 \rightleftharpoons CD_2NO_2^- + DNEt_3^+$$



Scheme LXXIX

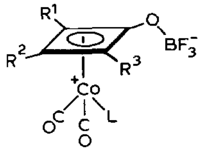
The η^3-oxocyclobutenyl complexes [259] (R_1, R_2, R_3 = various combinations of H, alkyl, aryl. L = CO, PPh_3, $PMePh_2$, PMe_2Ph) are formed from $[Co(CO)_3L]^-$ and the appropriate 2-cyclopropene-1-carbonyl chlorides. Initial formation of $[RC(O)Co(CO)_4]$ (R = 2-cyclopropenyl) followed by carbon monoxide loss to give $[RC(O)Co(CO)_3]$ and finally ring expansion is proposed as the reaction sequence. In THF or acetonitrile $[RC(O)Co(CO)_3]$ appears to dissociate to $[Co(CO)_4]^-$ and cyclopropenium ions. However since separate reaction of these two species gives $[RC(O)Co(CO)_3]$ and not an η^1-cyclopropenyl complex it is considered that electrophilic attack occurs at a carbonyl group rather than at the metal. Significantly no ring-expansion occurs on refluxing $[(\eta^3\text{-}C_3Ph_3)Co(CO)_3]$ with triphenylphosphine; $[(\eta^3\text{-}C_3Ph_3)Co(CO)_2(PPh_3)]$ forms instead. Complexes [259] react with boron trifluoride



[259]

etherate ($R_1 = R_2 = R_3$ = H; L = PPh_3) or trimethyloxonium hexafluorophosphate to yield [260] and [261] respectively while [261] (R_1 = H, $R_2 = R_3$ = Ph; L = PPh_3) reacts further with $[PhC(O)]SbF_6$ to give [262]. Refluxing [261] (L = CO) in benzene yields [263] (refs. 671-673).

The $[1,1'\text{-bicobaltocene}]^{n+}$ ions (n = 1,2) react with tetracyano-p,p'-quinodimethane (TCNQ) or bromoanil (BA) to yield $[1,1'\text{-bicobaltocene}]X_3$ (X = TCNQ, BA) while the dipositive ion with $(Et_3NH)[TCNQ]_2$ yields the same TCNQ salt rather than



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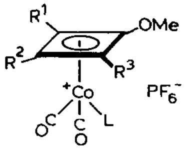

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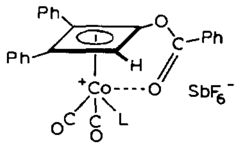

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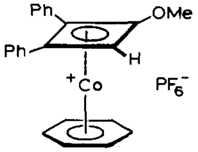
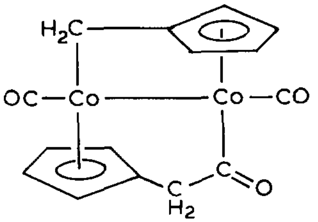


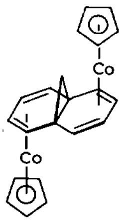
[263]

the desired [1,1'-bicobaltocene](TCNQ)$_2$ species. The compound is diamagnetic and an insulator (refs. 674-675). Although 6,6'-diphenylfulvene on successive treatment with butyllithium and cobalt(II) chloride yields $[(\eta^5\text{-}C_5H_4CHPh_2)_2Co]^+$, fulvene itself reacts with $[Co_2(CO)_8]$ to give [264] (ref. 676). Reaction of 1,6-methano-

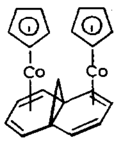


[264]

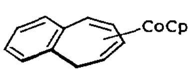
[10]annulene with $[cpCo(C_2H_4)_2]$ provides the first examples of the stabilization of the norcaradiene form of the molecule as the mixture of isomers [265a] and [265b] which react further with oxygen to yield [266] (ref. 677). At 110° C $[(\eta^4\text{-}C_4H_4)Fe\text{-}(CO)_3]$ and $[cpM(CO)_2]$ (M = Co, Rh) form [267] while the corresponding benzocyclobutadiene complex forms the isomeric mixture [268a, b]. The structural study of [267] showed the iron-carbon bonds to be rather short suggesting considerable π-delocalization in the ferracyclopentadiene ring. This complex also undergoes a reversible, one-electron reduction (ref. 678). A series of disubstituted thiophene 1,1-dioxides substitute in $[cpCo(CO)_2]$ to yield $[cpCo(\eta^4\text{-}C_4H_2R_2SO_2)]$ (R_2 = Me_2,



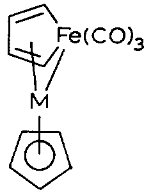
[265a]



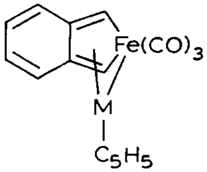
[265b]



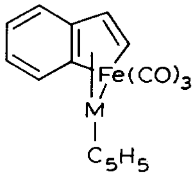
[266]



[267]



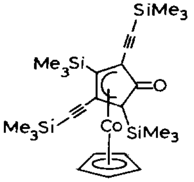
[268a]



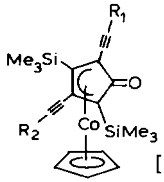
[268b]

MeEt) which on flash vacuum pyrolysis extrude sulfur dioxide to give the corresponding η^4-cyclobutadiene complexes. Labelling and crossover experiments indicate an intramolecular process possibly involving insertion of the metal into a carbon sulfur bond followed by ring contraction to a metallacyclopentadiene and then extrusion of metal (ref. 679).

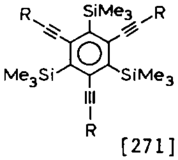
The use of [cpCo(CO)$_2$] to mediate transformations of acetylenic compounds with and without the formation of isolable cobalt complexes continues to be of considerable interest. In refluxing n-octane it reacts with bis(trimethylsilyl)-butadiyne to yield [269], [270] (R_1 = H; R_2 = SiMe$_3$ or the reverse), [271] (R =



[269]

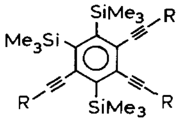


[270]

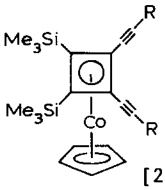


[271]

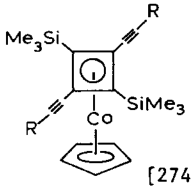
SiMe$_3$), [272] (R = SiMe$_3$) and traces of [273] (R = SiMe$_3$) and [274] (R = SiMe$_3$). The same reaction using a slow addition of reactants to boiling n-decane yields, after removal of the trimethylsilyl groups larger quantities of [273] (R = H) and particularly [274] (R = H) together with [271] (R = H), [272] (R = H) and [275].



[272]

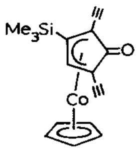


[273]



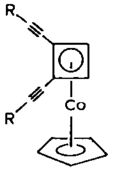
[274]

Using bis(trimethylsilyl)hexatriyne in refluxing BTMSA the product was [273] (R =



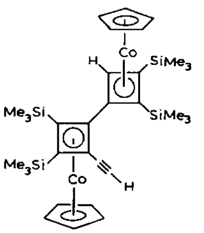
[275]

$SiMe_3$). Flash vacuum pyrolysis of [273] (R = H) produced [276] by what was characterized as a diethynylcyclobutadiene rearrangement while further reaction

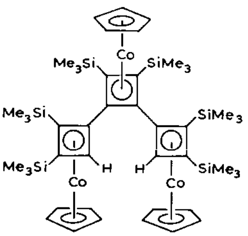


[276]

with [$cpCo(CO)_2$] in BTMSA yielded a mixture of diastereoisomers of [277] and [278] (ref. 680). Cocyclization of $NC(CH_2)_nC{\equiv}CH$ (n = 3-5) with $RC{\equiv}CR'$ (R, R' = various

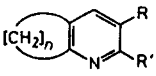


[277]

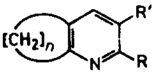


[278]

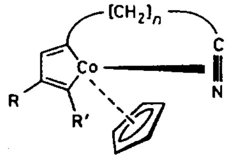
combinations of $SiMe_3$, CO_2Me, Bu^n, Me) occurs under photolysis in refluxing toluene in the presence of [$cpCo(CO)_2$] to yield [279] together with small amounts of [280] purportedly <u>via</u> [281] as an intermediate. Lower yields are obtained with terminal



[279]

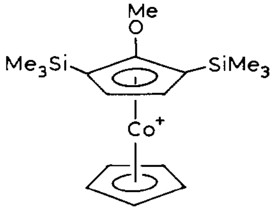


[280]



[281]

alkynes or with diphenylacetylene where cyclotrimerization of the terminal alkyne or formation of cyclobutadiene complexes occurs respectively (ref. 681). The same reaction with 1,2-bis(ethynyl)benzene in place of the cyanoacetylene yields disubstituted biphenylenes. When BTMSA is the coreactant, the trimethylsilyl groups can be readily hydrolyzed to give a good yield of biphenylene itself (ref. 682). A route to functionalized five-membered rings involves methylation of [cpCo-(η^4-$C_4H_2(SiMe_3)_2CO$)] with dimethyl sulfate to give [282] which on treatment with various organolithium reagents gives a mixture of [283] and [284] (R = Bu^t, Me, $R'C{\equiv}C$ (R' = n-hexyl, $SiMe_3$, OMe, OBu^t, SPh, Cl)). Unless R is bulky, attack on the substituted ring is preferred (ref. 683). Electrophiles react with [285] and for example when R = R' = H reaction with iodine in the presence of air and moisture, the analogs with R = H, R' = I and R = R' = I are formed. The former reacts with silver tetrafluoroborate in benzene-methanol to yield the derivative with R = H, R' = OMe (ref. 684).



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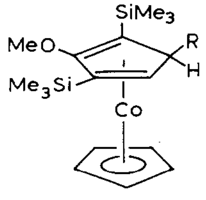
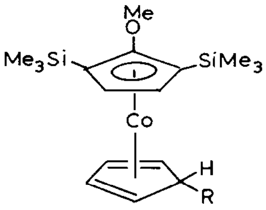
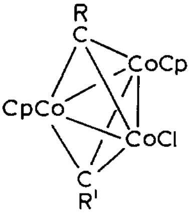


[283]

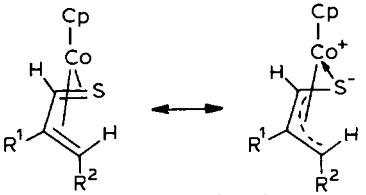


[284]

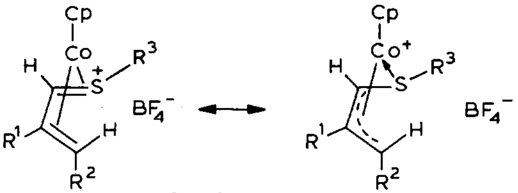


[285]

The enethial complexes [286] are alkylated at sulfur by triethyl- or trimethyloxonium tetrafluoroborate to give the hygroscopic salts [287] (R^3 = Me; R^1 = R^2 =

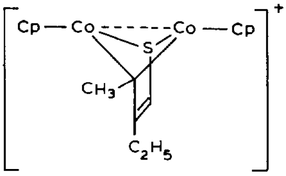


[286]



[287]

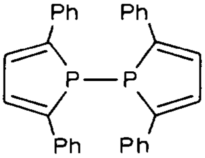
H, $(CH_2)_5$; R^1 = Ph, R^2 = H; R^1 = Et, R^2 = Me; R^1 = 2-naphthyl, R^2 = H. R^3 = Et; R^1 = Ph, R_2 = H; R^1 = Et, R^2 = Me). Methylation of [286] (R^1 = Et, R^2 = Me) also occurs with methyl iodide but more slowly and the resulting iodide can be metathesized to [287] with silver tetrafluoroborate. However reaction of [286] (R^1 = Et, R^2 = Me) with the silver salt gives [288] whether or not methyl iodide is present.



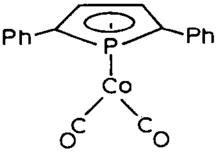
[288]

Complexes [286] (R^1 = Ph, R^2 = H, R^3 = Me, Et) react with cyanide ion in acetonitrile to give mixtures of allyl and vinyl sulfides plus $[cpCo(CN)_3]^-$ (ref. 685, 686).

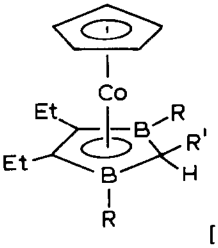
A number of heterocyclic rings form π-complexes with cobalt and rhodium. The biphosphine [289] prepared from 1,2,5-triphenyl-1-phosphacyclopentadiene reacts with $[Co_2(CO)_8]$ in refluxing toluene to give [290] (ref. 687). Complex [291] (R = Et; R' = Me. R = Me, R' = H) is prepared from $[cpCo(C_2H_4)_2]$ and the appropriate diboroline and reacts further with $[cpCo(C_2H_4)_2]$ to yield the "triple-decker" sandwich compound [292] (X = cpCo). Analogs of [292] (X = cpFe, $Mn(CO)_3$, cpNi) were also prepared and the last (R = Me, R' = H) is reduced by potassium in diethyl ether to give [293]. Further reduction of [293] by potassium in THF yields its dianion which then loses nickel to give the monoanion of [291] (R = Me, R' = H). Salts of this ion with zinc(II), iron(II) and cobalt(II) can be prepared. If [291] (R = Et, R' = Me) is heated in toluene with $[Ni(CO)_4]$, [294] forms which reacts



[289]



[290]



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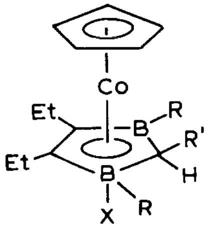

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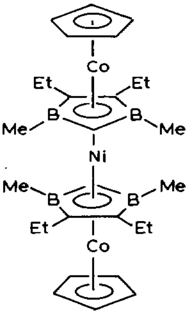
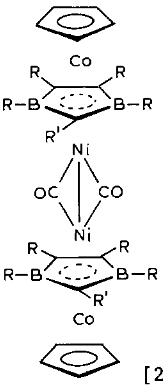


[293]

further with the diboroline $[C_2Et_2B_2Me_2CH_2]$ to give [295] (refs. 688-690). Reaction of cobalt atoms with 1-trimethylsilyl-2-methyl-Δ^3-1,2-azaboroline or of cobalt(II) chloride with the anion of the azaboroline yields $[(\eta^5\text{-}C_3H_3N(SiMe_3)\text{-}BMe)_2Co]$ which exists in staggered and eclipsed rotamers and in which the cobalt is displaced slightly towards the carbon atoms of the ring. The analogous 1-*tert*-butyl species has also been prepared by the latter route (refs. 691-693). The related complex $[cpCo(\eta^4\text{-}\overline{N(Me)B(Et)C(Et)C(Me)Si}Me_2)]$ is obtained from $[cpCo(C_2H_4)_2)]$ and 4,5-diethyl-1,2,2,3-tetramethyl-Δ^3-1,2,5-azasilaboroline (ref. 694). Methoxydivinylborane reacts with $[cp'_2Rh_2Cl_4]$ in the presence of $[cp_2Co]^+$ to give $[cpRh(\eta^5\text{-}C_4H_4BOMe)]$ and traces of $[cpCo(\eta^4\text{-}C_4H_4CH(CH_2Cl))]$. The rhodium complex can be alkylated at boron by Grignard reagents and can be hydrolyzed to $[cp'Rh(\eta^5\text{-}C_4H_4B\text{-}O\text{-}BC_4H_4\text{-}\eta^5)Rhcp']$ and then $[cp'Rh(C_2H_4)_2]$ (ref. 695). Reduction of 1,4-bis(ferrocenyl)-1,4-diboracyclohexa-2,5-diene with sodium amalgam generates its dianion which reacts with $[cpCo(CO)_2]$ and $[cp'_2Rh_2Cl_4]$ to give [296] and [297] (R = ferrocenyl) respectively (ref. 696). The He(I) PES of [296] (R = Me) has been measured (ref. 697).



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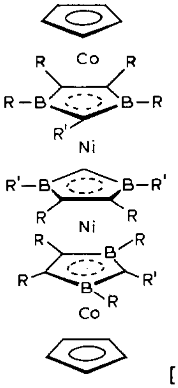

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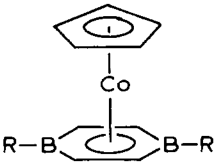

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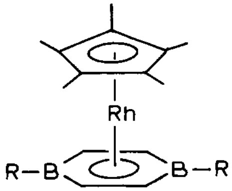
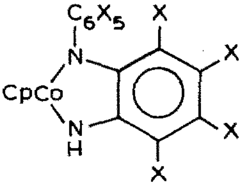


[297]

In refluxing benzene $[cpCo(CO)_2]$ and tetrasulfurtetranitride form $[cp\overline{CoS\text{-}N\text{=}S\text{=}N}]$ (ref. 698) while in refluxing toluene the tetraazadiene complex $[cpCo(RN_4R)]$ (R = *p*-tolyl) reacts with 3,5-dimethylphenyl azide to give the analog with R = 3,5-$Me_2C_6H_3$ (ref. 699). Further examples of the tetraazadiene complexes (R = Me, Ph,

C_6F_5, 2,4-$F_2C_6H_3$, 2,6-$Me_2C_6H_3$) have been prepared and from the structure of the pentafluorophenyl derivative it was concluded that considerable π-delocalization exists in the CoN_4 ring. The electronic spectra are dominated by an intense π-π* transition of the metallocycle. Photolysis of the phenyl and pentafluorophenyl complexes causes extrusion of dinitrogen and the formation of [298] (X = F, H) (refs. 700, 701).



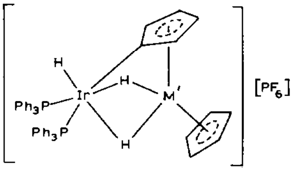
[298]

Pentamethylcyclopentadienyllithium reacts with $[Co(NH_3)_6]Cl_2$ followed by oxidation by iron(III) to yield $[cp'Co(\mu\text{-}NH_2)_2(\mu\text{-}Cl)Cocp']^+$ while in the absence of oxidation $[cp'Co(\mu\text{-}NH_2)_2Cocp']$ is formed from $[Co(NH_3)_6](BF_4)_2$. Analogs of both species with three and two bridging halide ligands can be prepared from anhydrous cobalt(II) halides. Reaction of $[cp'Co(\mu\text{-}X)_2Cocp']$ (X = Cl, Br, I) with carbon monoxide gives $[cp'Co(CO)_2]$ plus $[cp'Co(CO)X_2]$ while with sodium amalgam in the presence of ethylene $[cp'Co(C_2H_4)_2]$ forms. Dienes react to give [cp'Co(diene)] (diene = COD, butadiene, tetraphenylcyclobutadiene) plus $[cp'CoX(\mu\text{-}X)]_2$ (ref. 702). In a related reaction, $[CoBr_2(DME)_2]$ (DME = dimethoxyethane) and sodium cyclopentadienide at -80° C in the presence of other ligands gives low yields of $[cpCoL_2]$ (L_2 = $(CO)_2$, COD, cycloheptatriene). The initial formation of $[cpCoBr]_2$ is proposed (ref. 703). The complexes $[cp'_2Co]^n$ (n = 0, +1) have been prepared by standard routes and the interconversion studied by cyclic voltammetry. The ESR spectrum of the neutral species showed it to have a $^2E_{1g}$ ground state (ref. 704). Reaction of $[cp_2Zn]$ with $[CoH(N_2)(PPh_3)_3]$ or $[Zn(Co(CO)_4)_2]$ yielded $[cpCo(Zncp)_2(PPh_3)]$ and $[cpZn(Co(CO)_4)]$ respectively which are said to be considerably more stable than expected (ref. 705).

Vinylcyclopentadienyllithium reacts with $[Co_2(CO)_8]$ in the presence of iodine or with $[RhCl(CO)_2]_2$ or $[IrCl(CO)_3]_n$ to yield $[(\eta^5\text{-}C_5H_4CH{=}CH_2)M(CO)_2]$ (M = Co, Rh, Ir) with the yields increasing from 15% to 95% in the order listed. The iridium complex could be polymerized or copolymerized with styrene to give a supported complex which on reduction with sodium triethylborohydride catalyzed the hydrogenation of COD at 100° C (ref. 706). Electrolysis of cyclopentadiene or methylcyclopentadiene at a cobalt anode in DMSO yielded the corresponding cobaltacinium ions (ref. 707). A catalyst system derived from $[Co(acac)_2]$, tributylphosphine and triethylaluminum is effective for the conjugate hydrogenation of styrene and benzene although the relative consumption of the two substrates is about 20:1. Nevertheless no benzene hydrogenation (to primarily cyclohexene) occurs in the absence of styrene. Intermediate η^4-benzene complexes are proposed (ref. 708). Poly(2,6-dimethyl-1,4-phenylene oxide) functionalized with cyclopentadienyl groups at either benzylic or aromatic sites has been used to bind $\{M(CO)_2\}$ groups (M = Co, Rh). Both catalyze oct-1-ene hydroformylation but with little or no selectivity and show no Fischer-Tropsch activity (ref. 709). The cobalticinium ion $[(\eta^5\text{-}C_5H_4\text{-}CO_2H)_2Co]^+$ in the presence of a platinum colloid serves as a catalytic electron relay for the photolytic production of hydrogen from water (ref. 710). ESR spectra of mixtures of cobalt(II) chloride, aluminum tribromide and arenes indicate the formation of cobalt-arene complexes when the arenes are alkylated benzenes (ref. 711). Photoacoustic spectra in the 1000-2600 nm region have been obtained for a variety of complexes including $[cpCo(\eta^4\text{-}C_4Ph_4)]$ and $[cpCo(CO)_2]$ (ref. 712). Multiple scattering Xα molecular orbital calculations on $[cp_2Co]$ are said to give good theoretical values for a variety of observable parameters including electronic, photoelectron and electron spin resonance spectra (ref. 713). From molecular orbital calculations on $[cp_3Co_3(\mu_3\text{-}S)]^n$ (n = 0, +1) and $[cp_3Co_3(\mu_3\text{-}S)(\mu_3\text{-}CO)]$ it was concluded that the differences in magnetic and structural properties arise from the different bonding capabilities of the μ_3-S and μ_3-CO ligands. An analysis of the metal-metal interactions suggested that no net occupation of direct metal-metal bonding orbitals occurs but rather it is dominated by the occupation of orbitals mainly s and p in character, a situation much like that presumed to occur on the corresponding metal surface (ref. 714).

Cyclohexa-1,3-diene is stoichiometrically converted to benzene and $[(\eta^3\text{-}C_6H_9)\text{-}RhL_2]$ by $[RhHL_2]_2$ (L = $P(OPr^i)_3$). Hydrogenation of the rhodium complex regenerates $[RhHL_2]_2$ and produces cyclohexene and cyclohexane neither of which participates in the original reaction. By contrast $[RhH_2L_2]$ and the diene give only the cyclohexenyl complex; no benzene is formed. The results suggest that $[RhHL_2]_2$ dehydrogenates the diene forming benzene and $[RhH_2L_2]_2$ which then adds more diene to give the cyclohexenyl complex. Addition of triisopropoxyborohydride to $[(\eta^6\text{-}C_6D_6)RhL_2]^+$ (L = $P(OPr^i)_3$) gave $[RhHL_2]_2$ and predominantly C_6D_6 indicating that little hydride attack on the coordinated arene occurred although this conclusion must be tempered with the fact that the arene dissociates to a substantial extent in solution. The same reaction with $[(\eta^6\text{-}C_6Me_6)RhL_2]^+$ yielded $[(\eta^3\text{-}C_6Me_5CH_2)RhL_2]$ (ref. 715).

The solvates $[MH_2(PPh_3)_2(acetone)_2]PF_6$ combine with $[cp_2M'H_2]$ (M' = Mo, W) to yield $[(Ph_3P)_2Rh(\mu\text{-}H)_2M'cp_2]PF_6$ and $[(Ph_3P)_2H_2Ir(\mu\text{-}H)_2M'cp_2]PF_6$ respectively. In the rhodium complex the bridge is cleaved by pyridine giving $[Rhpy_2(PPh_3)_2]PF_6$ and $[cp_2M'H_2]$ while with hydrogen chloride $[RhCl(PPh_3)_2]_2$ and $[cp_2M'H_3]PF_6$ (M' = W) result. The rhodium complex undergoes H/D exchange in d_6-acetone/D_2O solution and deuterium incorporation into the cyclopentadienyl rings is also seen. An insight into the process whereby this latter exchange occurs is provided by a further reaction of the iridium complex from which [299] is formed. Complex [299] is fluxional with all three hydride ligands equilibrating and when M' = W reacts with



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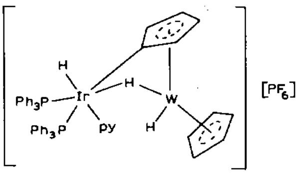

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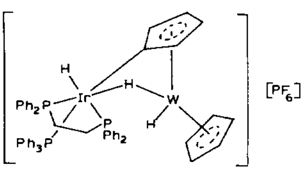


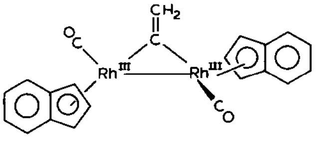
[301]

pyridine or diphos to form [300] and [301] respectively (ref. 716). Some chemistry of $[cp'Rh(CO)_2]$ is outlined in Scheme LXXX. The iridium analog by contrast does

$$\begin{tikzcd}
 & {[cp'_2Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}H)]BF_4} \arrow[r, "OMe^-"] & {[cp'_2Rh_2(CO)_2(\mu\text{-}CO)]} \arrow[dl, "h\nu"'] \arrow[d, shift left, "h\nu\ \text{or}\Delta"] \\
{[cp'Rh(\mu\text{-}Br)_2Rh(CO)Br_2]^+} & {[cp'Rh(CO)_2]} \arrow[l, "HBr"'] \arrow[u, "HBF_4"'] \arrow[d, "Br_2"] & {[cp'_2Rh_2(\mu\text{-}CO)_2]} \arrow[l, "CO"'] \arrow[u, shift left, "CO"] \arrow[d, "SO_2"] \\
{[cp'Rh(CO)Br_2]} & {[cp'Rh(CO)_2Br]Br} \arrow[l] & {[cp'_2Rh_2(CO)_2(\mu\text{-}SO_2)]}
\end{tikzcd}$$

Scheme LXXX

not dimerize on acidification but simply protonates to $[cp'IrH(CO)_2]BF_4$ (ref. 717). Although a dimeric species may form in the thermolysis of the analogous $[(\eta^5\text{-}C_9H_7)\text{-}Rh(CO)_2]$, the isolated product is $[(\eta^5\text{-}C_9H_7)_3Rh_3(\eta\text{-}CO)_3]$. This reacts with ethylene under pressure at 80° C to give $[(\eta^5\text{-}C_9H_7)Rh(CO)(C_2H_4)]$ which after isolation slowly reconverts to the trimer. The ethylene complex reacts with acetylene to yield [302], $[(\eta^5\text{-}C_9H_7)_2Rh_2(CO)_2(\mu\text{-}CO)]$ and traces of [303] while [302] is protonated, presumably first at the metal-metal bond, by tetrafluoroboric acid in ether to yield [304]. The formation of [302] is thought to proceed as shown in



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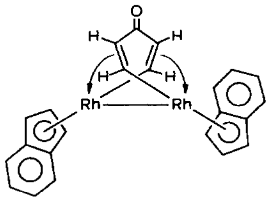
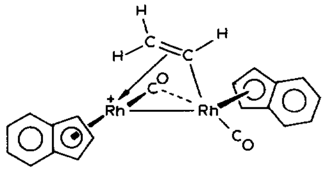
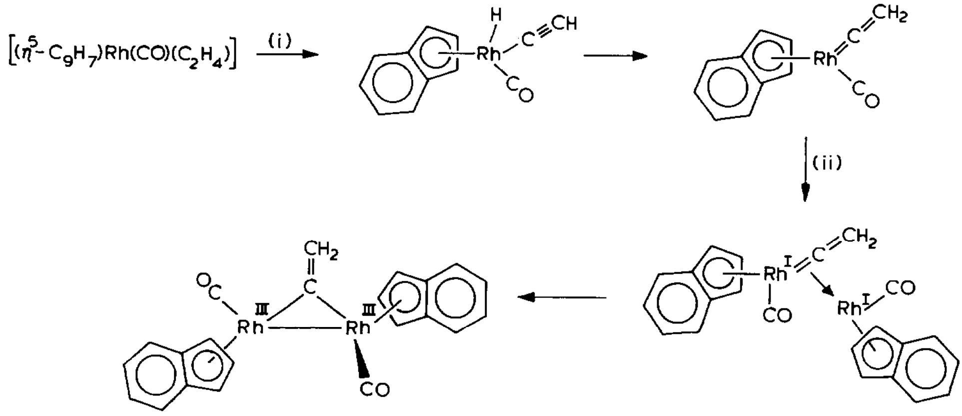


[303]



[304]

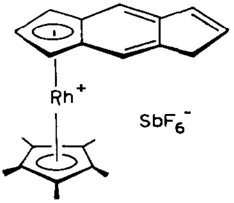
Scheme LXXXI. Complex [303] together with $[(\eta^5\text{-}C_9H_7)Rh(\eta^4\text{-}C_4H_4CO)]$ are formed directly from the trimer and acetylene on heating in toluene (ref. 718).



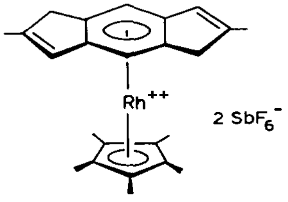
(i) HC_2H. (ii) $[(\eta^5\text{-}C_9H_7)Rh(CO)(C_2H_4)]$

Scheme LXXXI

Several papers have reported further chemistry of $[cp'_2M_2X_4]$ (M = Rh, Ir; X = Cl, I) and their derivatives. The iodide derivatives react with iodine to give $[cp'_2M_2I_6]$ and $[cp'_2M_2I_8]$. The structure of the former (M = Ir) shows it to contain $[cp'_2Ir_2I_4]$ units bridged by iodine molecules rather than a complex of the triiodide ion (ref. 719). The rhodium chloride complex reacts with the tripod phosphines, L(= $E(CH_2CH_2PPh_2)_3$ (E = N,P)) in the presence of hexafluorophosphate ion to give $[cp'RhCl(L)(cp'RhCl_2)_2]PF_6$ in which the ligand chelates to the first metal and coordinates the other two with the two remaining arms. Addition of chloride ion displaces rhodium from the bridgehead atom to give $[(cp'RhCl_2)_3L]$. With the ligands $R_2P(CH_2)_nNR'_2(PN)$ (n = 2; R = Ph, cy; R' = H, Me, Et. n = 3; R = Ph; R' = H, Me, Et; R = cy; R' = H, Me) are obtained $[cp'RhCl(PN)]^+$ containing chelate PN ligands. Addition of chloride ion displaces the nitrogen to give $[cp'RhCl_2(PN)]$. In some instances addition of excess ligand affords $[cp'RhCl(PN)_2]^+$ where only the phosphorus end is bound (ref. 720). Formation of $[cp'M(\eta^6\text{-}C_6H_6)]^{2+}$ occurs on addition of benzene to $[cp'M(H_2O)_3]^{2+}$ (M = Rh, Ir) and this can be sequentially reduced to $[cp'M(\eta^5\text{-}C_6H_7)]^+$ and $[cp'M(\eta^4\text{-}C_6H_8)]$ by borohydride in water and $AlH_2(OCH_2CH_2OMe)_2^-$ in toluene respectively. Treatment of the diene complex with hydrogen chloride in benzene regenerates the original benzene complex together with cyclohexene and therefore provides a possible catalytic cycle for the hydrogenation of benzene to cyclohexene although it appears that the incompatability of the reagents used would prevent the complete cycle being carried out in a single system (ref. 721). Under carefully controlled conditions, a 10% solution of trimethylaluminum in benzene reacts with finely divided solid $[cp'_2Rh_2Cl_4]$ to give, after extensive workup, $[cp'_3Rh_3(\mu\text{-}CH)_2]$. Under more dilute conditions the product is <u>cis</u>-$[cp'_2Rh_2Me_2(\mu\text{-}CH_2)_2]$ (ref. 722). Only one ring of 1,5-dihydro-S-indacene complexes to rhodium on reaction with $[cp'_2Rh_2Cl_4]$ in the presence of silver hexafluoroantimonate and the product is [305]. The 2,6-dimethyl analog however forms [306]. The same route using 18,22-dihydro-[2](4,4')-biphenylo-[2](2,6)-S-indacenophane gives a paracyclophane-type analog of [306] while with 2-methylindene the



[305]

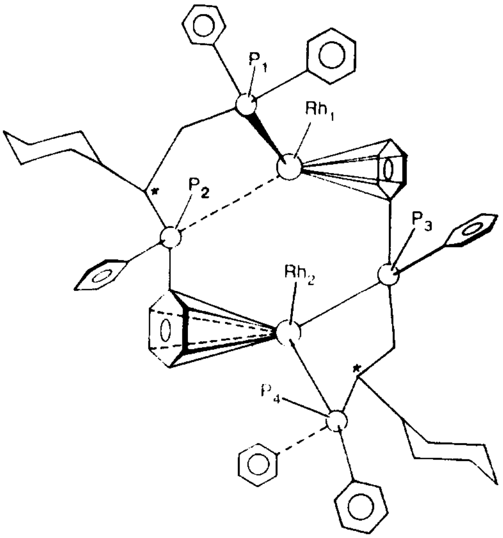


[306]

initial product is $[cp'Rh(\eta^6\text{-}C_9H_7Me)](SbF_6)_2$ but with longer reaction times $[cp'Rh(\eta^5\text{-}C_9H_6Me)]SbF_6$ is formed (ref. 723). An unusual example of a formally rhodium(V) organometallic complex is $[cp'RhH_2(SiEt_3)_2]$ which is prepared from $[cp'_2Rh_2Cl_4]$ and triethylsilane in the presence of triethylamine (ref. 724). In isopropanol, $[cp'_2Rh_2(\mu\text{-}OH)_3]Cl$ is an effective olefin hydrogenation catalyst whose activity is increased by addition of up to 20% of $[RhCl(COD)]_2$. The presence of chloride is required suggesting fragmentation of the dimer to monomeric species <u>via</u> chloride attack (ref. 725).

A number of arene complexes of rhodium of the type $[(\eta^6\text{-arene})RhL_2]X$ (arene = benzene, toluene, durene, mesitylene, xylenes, hexamethylbenzene; $L_2 = (CO)_2$, TFB, Me_3TFB; $X = ClO_4^-$, PF_6^-) have been prepared from the appropriate $[RhClL_2]_2$ complex and AgX in acetone solutions of the arene (arene in large excess). In general, dissolution of the complexes in polar solvents leads to replacement of the arene ligand by solvent except when four or more methyl groups are attached to the arene (refs. 726-730). Hydrogenation of $[Rh(NBD)(cycphos)]PF_6$ (cycphos = $Ph_2PC(cy)HCH_2\text{-}PPh_2$) yields the dimer [307] which adds (Z)-ethyl-α-benzamidocinnamate to give two regioisomers depending on whether the cyclohexyl substituent is <u>cis</u> or <u>trans</u> to the coordinated double bond. Complex [307] also reacts with toluene to give $[(\eta^6\text{-}C_6H_5Me)Rh(cycphos)]PF_6$ (ref. 731). The diphenylacetylene complex $[cpRh(PPr^i_3)\text{-}(Ph_2C_2)]$ converts to $[cpRh(PPr^i_3)(O_2CCF_3)]$ on treatment with trifluoroacetic acid and then forms $[cpRhH_2(PPr^i_3)]$ on reaction with $AlH_2(OCH_2CH_2OMe)_2^-$. The dihydride is unreactive towards olefins and acetylenes but does react with trifluoroacetic acid in methanol to give $[cp_2Rh_2(PPr^i_3)_2(\mu\text{-}H)_3]^+$ (ref. 732).

Cocondensation of rhodium and toluene vapors gives a species considered to be a toluene-solvated rhodium atom which catalyzes olefin hydrogenation. In the absence of olefin the species will hydrogenate toluene to methylcyclohexane (ref. 733).



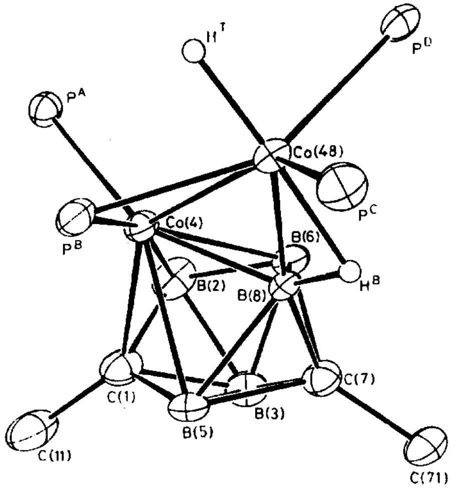
[307]

Another catalyst for arene hydrogenation under mild conditions is formed from hydrated rhodium(III) chloride and sodium borohydride in ethanol. The requirement of incubating the rhodium salt with the arene prior to adding borohydride suggests the possibility of arene coordination prior to reduction (ref. 734). An ion-cyclotron resonance study of the reaction of $Rh^+_{(g)}$ with $[cp_2M]$ (M = Fe, Ni) showed significant amounts of $[cp_2Rh]^+$ were formed (ref. 735).

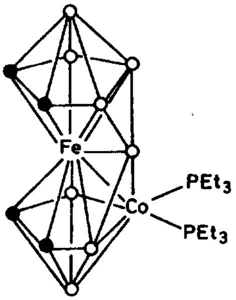
Reduction of $[cpIr(CO)Br_2]$ with zinc in methanolic acetic acid produces $[cpIr(CO)H_2]$ which in refluxing toluene or at room temperature in THF gives a mixture of clusters including $[cp_3Ir_3(CO)_3]$. Carbonylation of the trimer with ^{13}CO in refluxing xylene gives $[cpIr(^{13}CO)_2]$ plus *unlabelled* residual trimer. Reaction of the hydride with ligands gives $[cpIr(CO)L]$ (L = PPh_3, PMe_2Ph, $CNBu^t$, CO) while with $[cpIr(CO)_2]$ the product is $[cp_2Ir_2(CO)_3]$. All of the results suggest that the hydride can reductively eliminate hydrogen to give a reactive $\{cpIr(CO)\}$ fragment (ref. 736).

Metal Carbaborane Complexes

Reaction of $[Co(PEt_3)_4]$ with *closo*-$[2,4\text{-}Me_2\text{-}2,4\text{-}C_2B_5H_5]$ yields [308] while with $[FeH_2(2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_2)_2]$ the product is [309] (refs. 737, 738). Oxidative fusion of two carbaborane units occurs on reaction of $[CoH(Et_2C_2B_4H_4)_2]$ with $Na[Me_2C_2B_4H_5]$ followed by acidification and oxygenation. The product is $[Et_4C_4B_8H_8]$ and appears to form in an intramolecular process (ref. 739). The low-temperature reaction of cobalt(II) chloride, sodium pentamethylcyclopentadienide and $[B_5H_8]^-$ gives a low yield of $[2\text{-}cp'CoB_4H_8]$ and traces of five more di- and tricobaltaboranes. The same reaction with $[B_9H_{11}]^-$ gives a moderate yield of



[308]



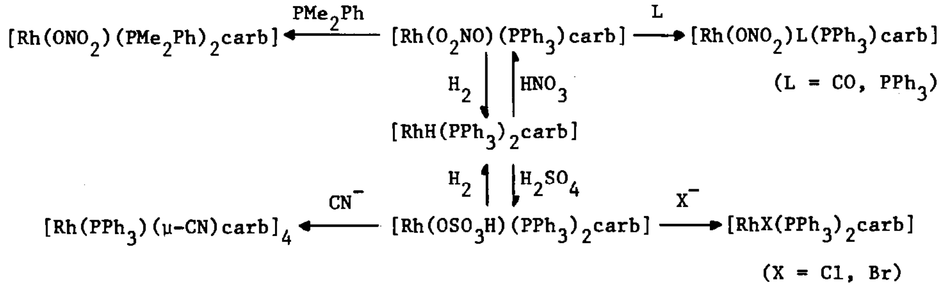
● = CMe, O = BH

[309]

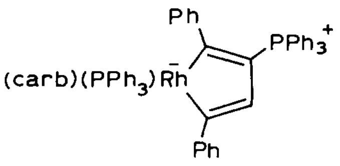
[6-cp'CoB_9H_{13}] and traces of three more dicobaltaboranes (ref. 740). In an attempt to prepare a mixed metallacarbaborane complex, cobalt(II) chloride was reacted with a mixture of $[1,2\text{-}C_2B_9H_{11}]^-$ and $[Me_2C_2B_4H_5]^-$ but only the symmetrical product $[Co(1,2\text{-}C_2B_9H_{11})_2]^-$ was obtained (ref. 741). Mixed metallaborane-carbaboranes have been synthesized in low yield by reacting cobalt(II) chloride with $[B_5H_8]^-$ in THF followed by cooling to -30° C, addition of $[R_2C_2B_4H_5]^-$ (R = Me, Et), hydrolysis and finally oxygenation. Identified products were $[R_2C_2B_4H_4\text{-}2\text{-}CoB_5H_{10}]$, $[R_2C_2B_4H_4\text{-}5\text{-}CoB_9H_{12}\text{-}1\text{-}THF]$ and $[R_2C_2B_3H_5\text{-}5\text{-}CoB_9H_{12}\text{-}1\text{-}THF]$. The same reaction using $[B_9H_{14}]^-$ in the initial stage yielded small amounts of $[R_2C_2B_3H_5\text{-}6\text{-}CoB_9H_{12}\text{-}2\text{-}THF]$ and $[R_2C_2B_7\text{-}H_7\text{-}6\text{-}CoB_9H_{12}\text{-}2\text{-}THF]$ plus traces of the three species listed above (ref. 742). Under thermal or photochemical conditions $[2\text{-}((OC)_4Co)B_5H_8]$ forms from $[Co_2(CO)_8]$ and $[B_5H_9]$. The $\{B_5H_8\}$ moiety appears to occupy an equatorial position on cobalt (ref. 743). Extended reaction of cobalt(II) chloride with $[1,2\text{-}C_2B_9H_{12}]^-$ or $[1,2\text{-}C_2B_9H_{11}]^{2-}$ in aqueous base gives a mixture of complexes some of which are proposed to have the formula $Cs_n[(B_9H_{11}C_2)_2Co_n(B_8C_2H_{10})_{n-1}]$ (n = 2-4). That with n = 4 appears to have been well-characterized but the data on the others are quite limited (refs. 744-746). Bromination of $[1,2,3\text{-}cpCoC_2B_8H_{10}]$ at room temperature yields $[10\text{-}Br\text{-}1,2,3\text{-}cpCoC_2B_8H_9]$ and some of the 4-bromo isomer while at reflux in the presence of aluminum trichloride the product is $[4,5,6,10,11\text{-}Br_5\text{-}1,2,3\text{-}cpCoC_2B_8H_5]$ (ref. 747).

Electrochemical studies on $[1,2,3\text{-}cpCoC_2B_4H_6]$, $[1,2,4\text{-}cpCoC_2B_4H_6]$, $[1,2,3\text{-}cpCoC_2Me_2B_4H_4]$ and $[2\text{-}cpCoB_4H_8]$ show all to undergo reversible, one-electron reductions and oxidations. A second irreversible one-electron reduction step is also seen. The data are interpreted to support the analogy between metallacarbaboranes and metallocenes (ref. 748). Analogous studies on $[cpCo(B_{10}H_{10}As)]^-$, $[cpCo(B_9H_9As_2)]$, $[cpCo(B_{10}H_{10}P)]^-$ and $[(1\text{-}Me\text{-}1,7\text{-}PCB_9H_{10})_2Co]$ showed similar behavior although only the first reduction step was reversible (ref. 749). Two considerations of bonding in metalloboranes include comments on $[cp_4Co_4B_4H_4]$ which has previously been considered to violate Wade's rules. If it is considered to have eight 3-center bonds and no 2-center bonds the sixteen skeletal electrons can be readily accommodated (refs. 750-751).

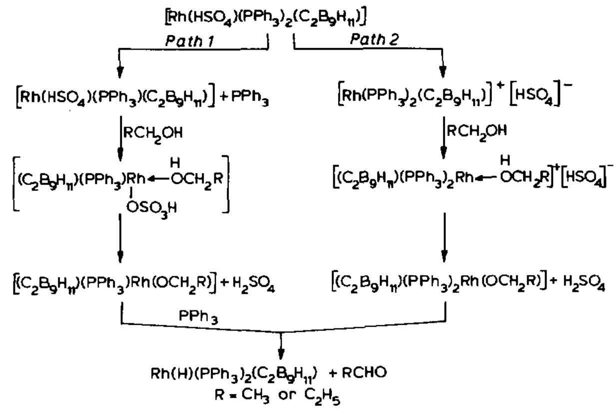
Some chemistry of closo-$[3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ is outlined in Scheme LXXXII (carb = $C_2B_9H_{11}$). Two other reactions of the bisulfate derivative shown in the lower portion of the Scheme are with phenylacetylene to give [310] and with alcohols to oxidize them to aldehydes as shown in Scheme LXXXIII (ref. 752).



Scheme LXXXII

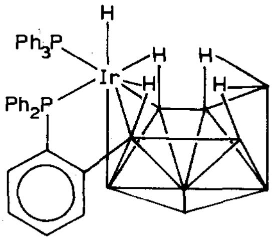


[310]

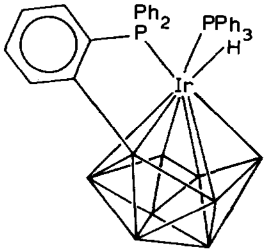


Scheme LXXXIII

Reaction of $[Ir(CO)Cl(PMe_3)_2]$ with nido-$[B_9H_{12}]^-$ yields arachno-$[H(CO)(PMe_3)_2\text{-}IrB_8H_{12}]$, which loses hydrogen on heating to give nido-$[(CO)(PMe_3)_2IrB_8H_{11}]$, and $[1\text{-}Cl\text{-}4,4,4,4\text{-}(CO)H(PMe_3)_2\text{-}4\text{-}IrB_8H_{11}]$. The last on mild heating converts to nido-$[(CO)(PMe_3)_2IrB_8H_{10}Cl]$ and at higher temperature to closo-$[H(PMe_3)_2IrB_8H_7Cl]$. Also, heating nido-$[H(PMe_3)_2IrB_9H_{13}]$ converts it to closo-$[H(PMe_3)_2IrB_9H_9]$ (ref. 753). By contrast, $[IrCl(PPh_3)_3]$ reacts with nido-$[B_9H_{12}]^-$ to give the ortho-cycloboronated complex [311] which on heating loses hydrogen and rearranges to [312]. The latter can also be prepared by heating $[6,6,6\text{-}H(PPh_3)_2\text{-}6\text{-}IrB_9H_{12}]$ at

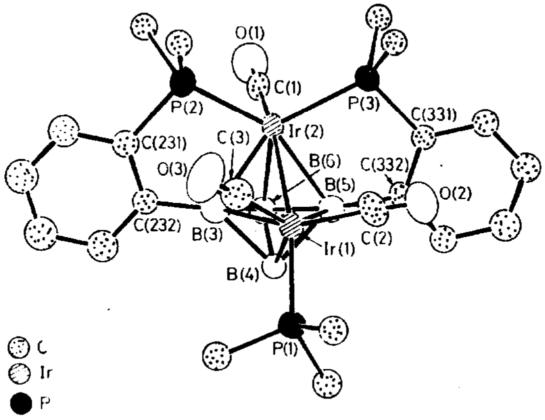


[311]



[312]

85° C (ref. 754). With arachno-$[B_9H_{14}]^-$, $[IrCl(CO)L_2]$ (L = PPh_3, PMe_3) forms nido-$[6\text{-}H\text{-}6,6\text{-}L_2\text{-}6\text{-}IrB_9H_{13}]$ while $[MCl(COD)]_2$ forms nido-$[6\text{-}(\eta^2\text{:}\eta^2\text{-}COD)\text{-}6\text{-}Cl\text{-}6\text{-}MB_9H_{13}]$ (M = Rh, Ir). The coordination of the metal is approximately octahedral with the borane moiety bound by one Ir-B and two Ir-H-B bonds but only very low yields were obtained (ref. 755). Other low-yield products reported are $[1,1,1\text{-}(CO)(PMe_3)_2\text{-}1\text{-}IrB_4H_9]$ from $[IrCl(CO)(PMe_3)_2]$ and $(Et_4N)[B_9H_{12}]$ and [313] from $[IrCl(CO)(PPh_3)_2]$ and $[B_{10}H_{10}]^{2-}$ (refs. 756, 757). Maleic anhydride can be hydrogenated to succinic anhydride by $[IrH_2(\sigma\text{-carb})(CO)(RCN)(PPh_3)]$ (σ-carb = 7-Ph-1,7-$C_2B_{10}H_{10}$; R = Me, Ph) and the intermediate alkyl hydride species has been isolated. With acrylic acid esters $[IrH(CH_2CH_2CO_2R)(CO)(\sigma\text{-carb})(PPh_3)]$ (R = Me, Et) forms where the ester



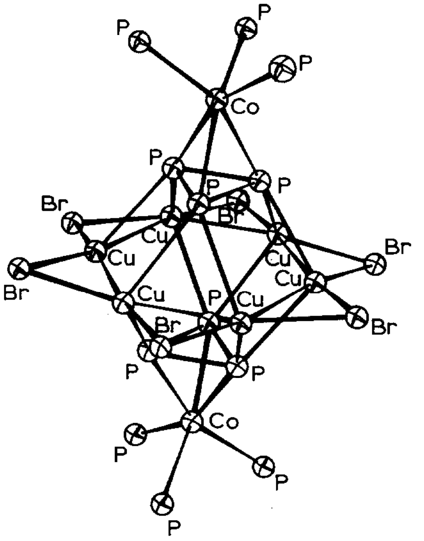
[313]

carbonyl group also coordinates to replace nitrile. Treatment of these complexes with carbon monoxide forms $[IrH(CH_2CH_2CO_2R)(CO)_2(\sigma\text{-carb})(PPh_3)]$ which then reductively eliminates $CH_3CH_2CO_2R$ and adds more carbon monoxide to finally form $[Ir(CO)_3(\sigma\text{-carb})(PPh_3)]$. At low temperature, the dihydride reacts with alkynes to yield alkenyl hydride complexes but these reductively eliminate alkene on warming to room temperature except when the acetylene is ethylphenylpropiolate or dimethylacetylene dicarboxylate when heating above room temperature is required for reductive elimination. The dihydride is also involved in catalytic hydrogenation of terminal olefins (refs. 758, 759).

Miscellaneous Complexes

As in the previous Annual Survey, this section includes complexes which are not strictly organometallic but which are likely to be of interest. A previous report that $[HCoL_4]$ and $[Co_2L_8]$ ($L = P(OPr^i)_3$), when synthesized by sodium amalgam reduction of cobalt(II) chloride in the presence of ligand are formed by reactions of the radical $[\cdot CoL_4]$ has been shown to be incorrect. In the same reaction using trimethylphosphite (L) the products are $[Co(P(O)(OMe)_2)(L_4)]$, $[Hg(CoL_4)_2]$ and $[CoL_5]^+[CoL_4NaL_4Co]^-$ at low temperature. On warming, the last converts into the first two with $[CoL_5]^+$ rearranging to the phosphonate complex and the anion fragmenting to $Na[CoL_4]$ and $[\cdot CoL_4]$. The $[Hg(CoL_4)_2]$ then results from reaction of the radicals with mercury. The absence of $[HCo(P(OMe)_3)_4]$ and $[Co_2(P(OMe)_3)_8]$ is taken to indicate that the radicals produced do not react to form these products. In the original study the products are proposed to form from $[CoL_4]^-$ ($L = P(OPr^i)_3$) (ref. 760). The formally cobalt(II)-cobalt(I) dimer $[CoCl(PMe_3)(\mu\text{-}PBu^t_2)_2Co(PMe_3)]$ is formed from $[CoCl_2(PMe_3)_2]$ and $Li[PBu^t_2]$ at -78° C and contains a planar Co_2P_2 ring (ref. 761). The phosphorus ylide $Me_3P{=}C(PMe_2)_2(L_2)$ reacts with $[Co(PMe_3)_4]PF_6$ to coordinate as a diphosphine and form $[(Me_3P)_3Co(L_2)]PF_6$ (ref. 762).

Copper(I) bromide adds to $[(\mathrm{triphos})\mathrm{Co}(\eta^3\text{-}\mathrm{P}_3)]$ (triphos = $\mathrm{MeC(CH_2PPh_2)_3}$) to yield [314] (ref. 763), while cobalt(II) tetrafluoroborate reacts with triphos and



[314]

$\mathrm{P_4S_3}$ to give $[(\mathrm{triphos})\mathrm{Co}(\eta^3\text{-}\mathrm{P_2S})]\mathrm{BF_4}$ (ref. 764). Reactions of $[(\mathrm{triphos})\mathrm{Co}(\mathrm{S_2CPEt_2})](\mathrm{BPh_4})_2$ are shown in Scheme LXXXIV (ref. 765).

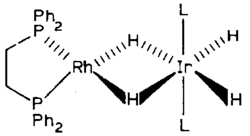
$$\begin{tikzcd}
& {[(\mathrm{triphos})\mathrm{Co}(\mathrm{S_2CS})]} & \\
{[(\mathrm{triphos})\mathrm{Co}(\eta^2\mathrm{CS_2})]} & {[(\mathrm{triphos})\mathrm{Co}(\mathrm{S_2CPEt_3})]^{2+}} \arrow[l, "\mathrm{Na}"', "\mathrm{THF}"] \arrow[u, "\Delta", "\mathrm{EtO^-},\ \mathrm{S_8}"'] \arrow[r, "\mathrm{BH_4^-}"] \arrow[dr, "\mathrm{EtO^-},\ \mathrm{O_2}", "\Delta"'] & {[(\mathrm{triphos})\mathrm{Co}(\mathrm{S_2CHPEt_3})]^{+}} \arrow[d, phantom, "\mathrm{O_2}"] \\
& & {[(\mathrm{triphos})\mathrm{Co}(\mathrm{S_2CO})]}
\end{tikzcd}$$

Scheme LXXXIV

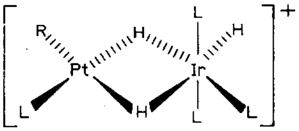
The cyano groups of alkyl and aryl nitriles can be cleaved by $[\mathrm{Li(Et_2O)_3}]$-$[\mathrm{Co(N_2)(PPh_3)_3}]$ to yield hydrocarbons and the complex also appears to catalyze the isomerization of allyl cyanide to crotononitrile (ref. 766).

Acetylacetone reacts with $[\mathrm{RhCl(O_2)(PPh_3)_3}]$ in the presence of triphenylphosphine to give the hydroperoxo complex $[\mathrm{RhCl(OOH)(acac)(PPh_3)_2}]$. In chloroform this reacts with more phosphine to give $[\mathrm{RhCl(OH)(acac)(PPh_3)_2}]$ plus triphenylphosphine oxide and finally $[\mathrm{RhCl_2(acac)(PPh_3)_2}]$ (ref. 767). The iridium pentahydride

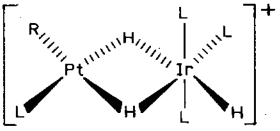
$[IrH_5L_2]$ reacts with $[Rh(diphos)(MeOH)_2]^+$ to give [315] (L = PPr^i_3) while with trans-$[PtR(MeOH)L_2]$ the isomeric mixture [315a, b] (L = PEt_3; R = H, Ph) is formed.



[315]



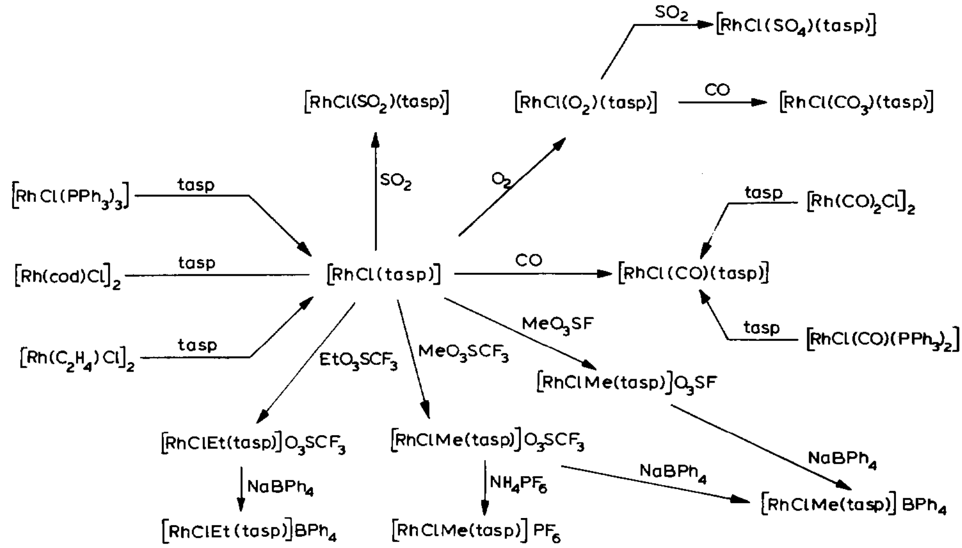
[315a]



[315b]

Isomers [315a, b] interconvert in solution possibly via an opening of one of the hydride bridges to give a three-coordinate platinum atom which can rearrange. Complex [315] is unreactive towards ethylene but with carbon monoxide forms $[IrH_3(CO)(PPr^i_3)_2]$ among other products. When R = H, [315] reacts with carbon monoxide to give $[IrH_2(CO)L_3]^+$, $[Pt_5(CO)(\mu\text{-}CO)_5L_4]$ and $[Pt_4(CO)_5L_4]$ (refs. 768, 769).

One chloride ligand is replaced when $[RhCl_3(PBu^n_3)_2]_2$ reacts with N-(3-thienyl)-pyrazole (3-tpz) in refluxing toluene and the resulting dimer is cleaved by tributylphosphine to give $[RhCl_2(PBu^n_3)_2(3\text{-tpz})]$ as a mixture of isomers metallated at either the 2- or 4- position of the thienyl ring (ref. 770). The synthesis and chemistry of some rhodium complexes of the ligand bis(3-dimethylarsinopropyl)-phenylarsine (tasp) are shown in Scheme LXXXV while with 1,2-bis(methylphenyl-arsino)ethane (L_2), $[RhCl(PPh_3)_3]$ reacts to give $[RhCl(L_2)_2]$ which can be

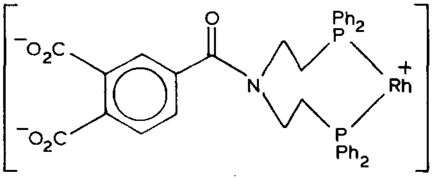


Scheme LXXXV

methylated by methyl trifluoromethanesulfonate to give $[RhCl(Me)(L_2)_2](O_2SOCF_3)$ (ref. 771). The ligands o-$(R_2As)_2C_6H_4$ react with hydrated rhodium(III) halides to give $[RhX_3(\text{o-}(R_2As)_2C_6H_4)]_2$ (X = Cl, Br; R = p-tolyl) or $[RhX_2(\text{o-}(R_2As)_2C_6H_4)_2]X$ (X

= Cl, Br; R = Ph, Me) (ref. 772). Tin(II) chloride is reported to react with hydrated rhodium(III) chloride in a DMF solution containing hydrochloric acid to give $[RhH(SnCl_2\ DMF)_4]^{2+}$ but the characterizational data are very limited (ref. 773). The enthalpies of oxidative addition of tetrachloro-o-benzoquinone to $[M(vdiphos)_2]BF_4$ (M = Co, Rh, Ir) have been measured and found to be in the order Co>Ir>Rh. This is also the order of reactivity of the parent complexes (ref. 774). A reexamination of the reduction of $[M(diphos)_2]^+$ (M = Rh, Ir) in acetonitrile containing tetraethylammonium perchlorate shows it to occur in a single, two-electron step which is essentially reversible. This is taken to confirm that it is an EC process and to preclude the possibility of an ECE mechanism as proposed (1980 Annual Survey ref. 294) subsequent to the original work of the present authors (ref. 775). On the other hand, $[Rh(diphos)_2]^+$ is converted to $[Rh(H)(diphos)_2]$ by sodium amalgam in methanol presumably by reaction of $[Rh(diphos)_2]$ with solvent (ref. 776).

A mixture of rac-sodium lactate, NAD^+, horse liver alcohol dehydrogenase (HLADH), D- and L-lactate dehydrogenase and [317] catalyzes the asymmetric hydrogenation of

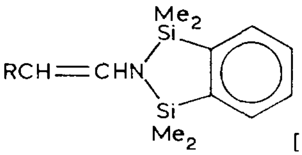


[317]

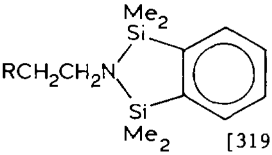
(±)-2-norbornanone to a 3:1 mixture of endo- and exo-norbornanol however the catalyst lifetime is limited. The catalyst system containing everything but HLADH catalyzes the reduction of NAD^+ to NADH by hydrogen (ref. 777).

$[RhCl(PPh_3)_3]$ continues to be used as a catalyst for a wide variety of transformations including the hydrosilylation of vinyl trichlorosilane with trichlorosilane (ref. 778), the hydrogenation of terminal double bonds in side chains attached to the A and E rings of pentacyclic triterpenoids (ref. 779) and the decarbonylation of phenoxyacetyl chlorides to chloromethyl aryl ethers (ref. 780). In refluxing acetonitrile it effects the stepwise decarbonylation of $[M(CO)_6]$ (M = Mo, W) to give $[M(PPh_3)_x(MeCN)_{3-x}(CO)_3]$ (x = 1,2) and $[Mo(PPh_3)_2(MeCN)_2(CO)_2]$ plus $[RhCl(CO)(PPh_3)_2]$ (ref. 781). Other examples are the alkysilane reduction of 4-tert-butylcyclohexanone to the alcohol (ref. 782), the isomerization of cyclohexa-1,4-dienes to their 1,3-isomers for the synthesis of phthalates and phthalides from dienes and acetylenic esters (ref. 783), the carboxylation of ethylene by carbon dioxide (ref. 784) and the deuteration and tritiation of methadone and its metabolites (ref. 785). In toluene it facilitates the condensation of alkyl nitriles with o-$(HMe_2Si)_2C_6H_4$ to give predominantly [318] together with some [319] (R = Ph, Me, H). These products were not formed in the presence of

$[MCl(CO)(PPh_3)_2]$ (M = Rh, Ir) or $[RhCl(\textit{cyclo}\text{-}C_8H_{14})_2]_2$ but $[Rh(COD)(PPh_3)_2]BPh_4$ yielded a small amount. With $NC(CH_2)_4CN$ a 2:1 mixture of [318] and [319] (R =



[318]



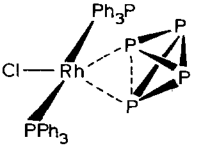
[319]

$NC(CH_2)_3$) was formed (ref. 786). Aldehydes can be catalytically decarbonylated by $[Rh(L_2)_2]^+$ (L_2 = DPM, diphos, dppp, dppb) with the best being the dppp complex which is superior to $[RhCl(PPh_3)_3]$ in reaction rate and selectivity to alkane. The proposed mechanism involves a rapid preequilibrium giving $[Rh(OCHR)(L_2)_2]^+$ followed by a rate-determining oxidative addition of the aldehyde carbon-hydrogen bond (ref. 787).

The hydride complex $[RhH(PPh_3)_4]$ catalyzes hydrogen transfer from alcohols, particularly PhCH(OH)Me to benzalacetone or cyclohexenone. Weak coordination of the alcohol to a $\{RhH(PPh_3)_3\}$ moiety has been demonstrated and labelling studies indicate a selective transfer of the hydroxylic hydrogen to the α-carbon of the ketone (refs. 788-790). Rhodium(I) complexes of the 2-diphenylphosphinoethyltrimethylammonium ion are catalysts for the hydrogenation and hydroformylation of water-soluble olefins in aqueous solution and for hydrophobic substrates in two-phase systems. They can also be supported on macroreticular cation-exchange resins (ref. 791). The alkylation of benzyl cyanide by alcohols to yield PhCHRCN (R = Me, Et, $PhCH_2$) is catalyzed by $[RhH(PPh_3)_4]$, $[RhCl(PPh_3)_3]$ or mixtures of $[MCl_3 \cdot xH_2O]$ (M = Rh, Ir), triphenylphosphine and sodium carbonate. Cyclization and alkylation occurs with $\textit{o}\text{-}(NCCH_2)_2C_6H_4$ to give enaminonitriles while with *o*-cyanobenzyl cyanide, mixtures of monoalkylated products and isoquinolines are formed. The reaction is thought to involve oxidation of the alcohol by the metal complex to give aldehyde and a metal-dihydride species, reaction of the aldehyde with the nitrile and hydrogenation of the arylacrylonitrile so formed by the hydride complex (ref. 792).

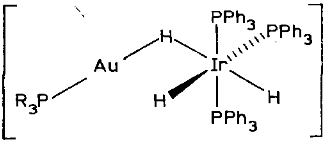
Atomic absorption techniques can be used to determine the rhodium content of polymer-supported catalysts employing $[RhH(CO)(PPh_3)_3]$ as a standard (ref. 793). Analogs of $[RhCl(PPh_3)_3]$ anchored to polysiloxyalkylphosphine supports appears to be no different from their homogeneous counterparts for olefin hydrosilylation (ref. 794). If anchored to silica *via* $\text{-O-SiMe}_2(CH_2)_nPPh_2$ (n = 1,3,7,9) groups they catalyze the isomerization of pent-1-ene to internal olefins with the longest chain showing the best activity presumably because it provides the best access to the metal. On attempted hydrogenation some rhodium metal was formed (ref. 795). Support of $[RhH_2(O_2COH)(PPr^i{}_3)_2]$ on silica using an $(\text{-O})_3Si(CH_2)_3PPh_2$ group provided a good catalyst for the hydrogenation of methylcinnamate under water-gas-shift conditions (ref. 796). Silver ions adsorbed on macroreticular polystyrenesulfonate resins is effective for the removal of excess triphenylphosphine from solutions of $[RhCl(PPh_3)_3]$ thereby providing a means of regenerating phosphine-poisoned catalysts but it does but it does not accelerate the rate of alkene hydrogenation (ref. 797).

The two-dimensional δ/J resolved ^{31}P NMR spectrum of $[RhCl(PMe_3)(DPM)]$ has been measured (ref. 798) as has the low temperature ^{31}P NMR spectrum of $[RhCl(P_4)(PPh_3)_2]$. The latter is thereby said to have the structure [320] (ref. 799).



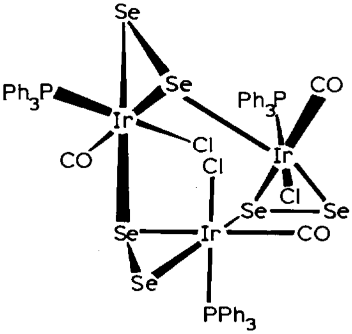
[320]

Reaction of $[AuCl(PR_3)]$ (R = Ph, Et) with silver tetrafluoroborate followed by addition of mer-$[IrH_3(PPh_3)_3]$ yields [321] whose NMR spectrum indicates only a



[321]

single bridging hydride ligand (ref. 800). The complex $[IrH_2L_2S_2]BF_4$ (L = PPh_3; S = acetone) forms adducts with o-diiodobenzene and o-bromoiodobenzene (L') formulated as $[IrH_2L_2L']BF_4$ in which the dihalobenzenes coordinate through the halogen atoms. No adducts formed with iodobenzene or alkyl iodides. However hydrogenation of $[Ir(COD)L_2]BF_4$ in the presence of organic iodides yielded $[IrH_2L_2(L')_2]BF_4$ (L' = PhI; L = PPh_3, $PMePh_2$, P-p-tolyl$_3$. L' = MeI; L = PPh_3). One-to-one adducts also formed with o-$X_2C_6H_4$ (X = Cl, Br) (ref. 801). The ligands bis(o-diphenylphosphinophenyl)phenylphosphine, its all-arsenic analog, bis(o-diphenylarsinophenyl)phenylphosphine and bis(o-diphenylphosphinophenyl)phenylarsine (L_3) react with $[IrHX_2(PPh_3)_3]$ in refluxing chlorobenzene to give $[IrHX_2(L_3)]$ (X = Cl, Br) except for the all-arsenic ligand which formed $[IrBr_3(L_3)]$. In several cases, mixtures of isomers were obtained (ref. 802). Reaction of elemental sulfur or selenium with $[M(L_2)_2]Cl$ gave $[M(X_2)(L_2)_2]Cl$ (M = Rh, Ir; X = S, Se; L_2 = diphos, dmpe) from which $[M(L_2)_2]Cl$ could be regenerated by treatment with mercury. Removal of the X_2 moiety from $[Ir(X_2)(diphos)_2]^+$ could be effected by reaction with ethyldiphenylphosphine while when X = S reaction with iodine gave $[Ir(\eta^2\text{-}S_2I_2)(diphos)_2]^+$. Reaction of $[M(S_2)(L_2)_2]^+$ with one equivalent of $[Pt(PPh_2R)_3]$ gave $[(L_2)_2M(\mu\text{-}S)_2Pt(PPh_2R)_2]^+$ (R = Ph, Et. M = Ir; L_2 = diphos. M = Rh; L_2 = dmpe). With $[Ir(Se)_2(dmpe)_2]^+$ one equivalent of $[IrCl(CO)(PEt_2Ph)_2]$ yielded $[(dmpe)_2Ir(\mu\text{-}Se)_2IrCl(CO)(PEt_2Ph)_2]^+$ by oxidative addition across the selenium-selenium bond while with two equivalents $[Ir_2(CO)_2Cl_2(PEt_2Ph)_2(\mu\text{-}Se)_2]$ formed. Although the diphos analog was unreactive in the above reaction, it did react with $[PtL_3]$ (L = PPh_3, $PEtPh_2$) to give $[Ir(diphos)_2]^+$ and $[Pt_2L_4(\mu\text{-}Se)_2]$. Reaction of $[Ir(CO)Cl(PPh_3)_2]$ with elemental sulfur yielded a polymer of empirical formula $[Ir(S_6)(CO)Cl(PPh_3)_2]$ while with selenium a trimer thought to be [322] formed. The same reactions with $[RhX(PPh_3)_3]$



[322]

(X = Cl, Br) gave species proposed to be $[RhX(Y_3)Cl(PPh_3)]_4$ (Y = S, Se) with bridging $\eta^2\text{-}Y_3$ units (ref. 803). The structures of fac- and mer-$[IrCl_3L_3]$, mer-$[IrHCl_2L_3]$ (both cis- and trans- chlorides), mer-$[IrH_2ClL_3]$ (cis-hydrogens) and fac-$[IrH_3L_3]$ (L = PMe_2Ph) have been determined. The trans-influence series appears to be H>L>Cl however the variations in the iridium-phosphorus distances as a function of the types of other ligands present indicate the presence of steric effects as well (ref. 804). Mixtures of $[MCl_3 \cdot xH_2O]$ (M = Rh, Ir) or $[H_3IrCl_6]$ with tin(II) chloride and lithium chloride or hydrochloric acid catalyze the hydrogen transfer from isopropanol to cyclohexanone (ref. 805).

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