COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1983*

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

CONTENTS

Introduction

The format used in previous Surveys will be retained with the exception that a single list of all abbreviations used will be included at the end. Articles appearing in less-available journals have been covered in abstract form and are so indicated in the list of references while those reporting only the results of crystal structure determinations are not included.

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* No reprints available. Previous Survey, J. Organometal. Chem., 261(1984) 103.

Reviews have appeared on trifluoromethyl (ref. 1) vinylidene (ref. 2) and other complexes containing metal-carbon σ-bonds (ref. 3) which include those of the cobalt group. Also reviewed are methylene-bridged complexes (ref. 4), complexes containing agostic hydrogens (ref. 5), the formation of rhodium and iridium alkyl complexes by C-H oxidative addition (ref. 6) and formyl, hydroxymethyl and carbene complexes of iridium (ref. 7). Three further reviews cover the electrochemistry of vitamin B_{12} and related compounds (ref. 8), selected chemistry of cobaloximes (ref. 9) and the use of vitamin B_{12} and related cobalt complexes in organic synthesis (ref. 10). The use of iridium complexes in catalysis has been covered (ref. 11) as have hydrocarbyl and hydrocarbon-bridged binuclear compounds (ref. 12), isocyanide complexes (ref. 13), the effects of various ligands in substitution reactions of $[M_4(CO)_{12}]$ (M = Co, Ir) (ref. 14) and carbido carbonyl clusters (ref. 15). The reactivity of basic metal clusters has been reviewed (ref. 16) together with reports on the synthesis of heteronuclear clusters (refs. 17, 18), catalysis by clusters (refs. 19, 20), the use of cobalt and rhodium complexes for the homogeneous catalytic hydrogenation of carbon monoxide (ref. 21) and ways to produce oxygenated products from these systems (ref. 22). Also reported are the results of multinuclear NMR studies on rhodium carbonyl clusters (ref. 23).

Some cobalt complexes appear in a review of substitution reactions of low-valent four-, five- and six-coordinate compounds (ref. 24), in two on the activation of carbon dioxide by metal complexes (refs. 25, 26) and in one on complexes of bis(diphenylphosphino)methane (ref. 27). Also covered are examples of catalysis by rhodium complexes of bis(diphenylphosphino)methane (ref. 28), the synthesis of phosphine and phosphite derivatives of $[Rh(CO)_2(acac)]$ (ref. 29), complexes of diolefins (ref. 30) and olefin complexes of Co(I) (ref. 31).

Four reviews describe aspects of asymmetric hydrogenation catalyzed by chiral rhodium complexes (refs. 32-35) while another is concerned with related complexes as catalysts for enantioselective hydrosilylation (ref. 36).

Cobalt-group complexes are included in reviews on acetylene derivatives of carbonyl clusters (ref. 37), metalloborane clusters (ref. 38), the coordination chemistry of ylides (ref. 39), bimetallic hydride complexes (ref. 40) and the activation of dioxygen by metal complexes (ref. 41).

Dissertations

One dissertation reports the formation of binuclear metallacycles from α,ω-dihaloalkanes and $[cp_2Co_2(CO)_2]^{a}$ (ref. 42) while two more are concerned with the hydrogenolysis of $[cpCoMe_2(PPh_3)]$ and the activation of carbon-hydrogen bonds by the $\{cp'Ir(PMe_3)\}$ moiety (ref. 43) and by $[IrH_2S_2(PPh_3)_2]^+$ (S = solvent) (ref. 44). Another describes the synthesis and chemistry of the alkylidene-bridged dimers $[cp'_2Rh_2(CO)_2(\mu\text{-}CRR')]$ (ref. 45). Three more describe aspects of the chemistry of organocobalamins and related vitamin B_{12} model compounds (refs. 46-48). The activation of small molecules by [M(OEP)] (M = Rh, Ir) is also reported (refs. 49-50). One dissertation discusses the synthesis and chemistry of cationic rhodium complexes of the bidentate ligands 1,2-bis(2-isocyano-3-trimethylsiloxyphenoxy)ethane and -propane (ref. 51).

The activation of cobalt carbonyls by ultrasound (ref. 52), the flash photolysis of a mixture of $[HCo(P(OEt)_3)_4]$ and $[Re_2(CO)_{10}]$ to give $[HCo(P(OEt)_3)_3(CO)]$ (ref. 53) and the reaction of $[Co_2(CO)_8]$ with alkyl peroxides and hydroperoxides (ref. 54) have been reported. Other dissertations are concerned with molecular orbital calculations and photoelectron spectroscopic measurements on cobalt carbonyl clusters (ref. 55), the infrared spectra of cobalt and rhodium carbonyl complexes on solid supports (refs. 56, 57), the use of rhodium complexes supported on silica gel as hydroformylation and oxidation catalysts (refs. 58, 59) and $[Ir_4(CO)_{12}]$ in a $NaCl/AlCl_3$ melt as catalyst for the hydrogenation of carbon monoxide (ref. 60).

A number of reports of the synthesis of mixed-metal clusters including $[RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$ (ref. 61), $[Fe_2Rh(\mu\text{-}PPh_2)(CO)_6(PR_3)]$ (R = Et, Ph) and $[MIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$ (M = Mo, W) (ref. 62) and the use of photolytic methods for obtaining related species (ref. 63) have appeared. Rhodium and iridium complexes of nitrogen-containing heterocycles (ref. 64), 2-pyridyldiphenylphosphine (ref. 65) and $HN(SiMe_2CH_2PPh_2)_2$ (ref. 66) are described as are molecular orbital calculation on A-frame-type binuclear complexes (ref. 67). Further dissertations report on the reactions of $[IrCl(CO)(PPh_3)_2]$ with fused cyclopropanes (ref. 68), the synthesis and structure of $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-}pz)_2]$ (ref. 69) and the formation of substituted cyclopropyl complexes of rhodium and iridium (ref. 70).

One report on nitrosyl complexes concerns the use of $[cpCo(NO)]_2$ for the conversion of olefins to vicinal aliphatic diamines (ref. 71).

The use of deuterium labelling in mechanistic studies on the catalytic hydrogenation of olefins using rhodium phosphine complexes is described (ref. 72) as is the synthesis of $[Ir(COD)(PPh_3)(Tcbiim)]^-$ (ref. 73).

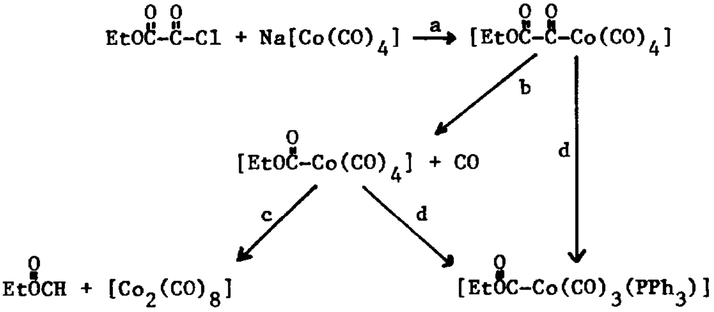
Four dissertations concern cobalt acetylene complexes including electrochemical studies on $[Co_2(CO)_6(RC_2R)]$ (ref. 74), the stabilization of propargyl cations by coordination to the $\{Co_2(CO)_6\}$ moiety (ref. 75) and the use of $[cpCo(CO)_2]$ and $[Co_2(CO)_8]$ to mediate the cyclization of α,ω-enynes (ref. 76) and diynenes (ref. 77).

The synthesis and chemistry of cobalt and rhodium borane and carbaborane clusters are covered in other dissertations (refs. 78-81).

Finally there are dissertations describing cobalt complexes of ferrocenylphosphines (ref. 82), the decarbonylation of aldehydes catalyzed by $[Rh(L_2)_2]^+$ (L_2 = chelating di(tertiary)phosphine) (ref. 83), the synthesis of the coordinatively unsaturated clusters $[H_mRhL_2]_n$ (L = tertiary phosphine or phosphite) (ref. 84) and rhodium and iridium complexes of chelating phosphine ligands containing both tertiary and secondary phosphorus atoms (ref. 85).

Metal-carbon σ-bonded Complexes

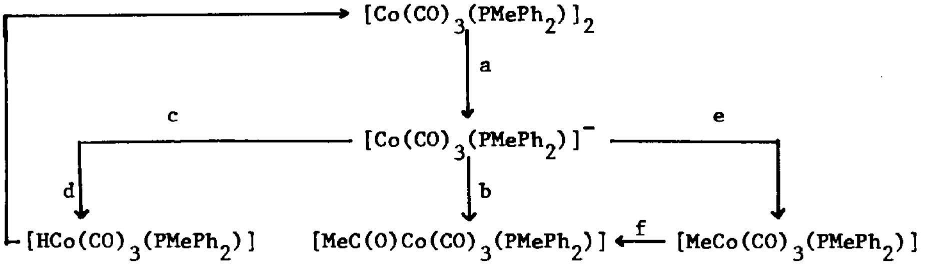
Bromoacetonitrile reacts with $Na[Co(CO)_4]$ at low temperature to yield the expected $[NCCH_2Co(CO)_4]$ which on treatment with sodium methoxide is converted to $[NCCH_2Co(CO_2Me)(CO)_3]^-$. Carbonylation of this species in methanol at room temperature yields $[Co(CO)_4]^-$ and acetonitrile. The results are interpreted to suggest that analogous species may form during the cobalt carbonyl-catalyzed carbonylation of alkyl halides where the alkyl group is electron-withdrawing and renders CO "insertion" difficult (ref. 86). The final step in the usual mechanism proposed for the cobalt carbonyl-catalyzed hydroformylation of olefins is hydrogenolysis of an acyl cobalt carbonyl species. This part of the mechanism has been probed using the reaction sequence outlined in Scheme I. In a separate experiment $[EtOC(O)Co(CO)_4]$ was found to also react with $[HCo(CO)_4]$ to give ethyl formate and $[Co_2(CO)_8]$. Since the rate of this reaction was only twelve times faster than that of the same complex with dihydrogen it was concluded that the hydrogenolysis of acyl species in hydroformylation systems may follow parallel paths involving either dihydrogen or $[HCo(CO)_4]$. In these reactions, as well as those with triphenylphosphine, the formation of $[EtOC(O)Co(CO)_3]$ as



a) Et_2O, 0°C. b) 25°C. c) H_2. d) PPh_3

Scheme I

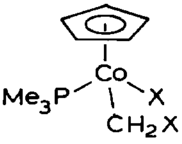
a reactive intermediate is proposed (ref. 87). In a related study, the role of acetyl cobalt carbonyl complexes in the cobalt-catalyzed homologation of methyl to ethanol has been investigated using the system outlined in Scheme II. Attempted reaction of [$HCo(CO)_3(PMePh_2)$] with [$MeC(O)Co(CO)_3(PMePh_2)$] in methanol showed the primary process to be the slow decomposition of the hydride complex to [$Co(CO)_3(PMePh_2)$]$_2$ while the acetyl complex eventually reacted with solvent to form methyl acetate. This result indicates that the homologation reaction evidently does not involve reaction of a cobalt hydride complex with the acetyl complex. No reaction between [$MeC(O)Co(CO)_3$-$(PMePh_2)$] and dihydrogen occurs under ambient conditions but at 35 atm dihydrogen pressure ethanol, acetaldehyde and [$Co(CO)_3(PMePh_2)$]$_2$ form with the yield of ethanol increasing with increasing temperature. In this system acetaldehyde is considered to be the immediate precursor to ethanol and since the product distribution is comparable to that observed in catalytic systems using [$Co(CO)_3L$]$_2$ (L = tertiary phosphine), MeI and CO/H_2 mixtures it is proposed that [$MeC(O)Co(CO)_3L$] is an intermediate in the homologation process (ref. 88).



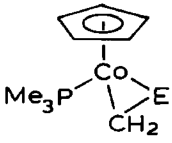
a) Na/Hg. b) CO, MeI. c) H_2, -35°C. d) H_3PO_4. e) MeI, -78°C. f) CO.

Scheme II

Whilst Na[$Co(CO)_4$] reacts with $BrCHRCO_2R'$ to yield [$RCH(CO_2R')Co(CO)_4$] (R = Me, Bu^t, Ph; R' = Me, Et) as the major product, when R = Ph and R' = Et, the η^3-benzyl isomer was also formed. The complexes are only moderately stable and some could only be identified in solution. Decomposition appears to occur by a radical process (ref. 89). Reaction of [$cpCo(CO)(PMe_3)$] with dihalomethanes at low temperature forms [1] (X = Br, I) which further reacts

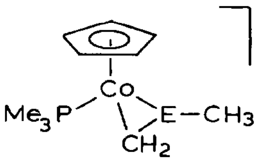


[1]



[2]

with NaEH to give [2] (E = S, Se). Complexes [2] can be alkylated to give [3] which, when E = S, form [4] on treatment with acid and sodium iodide. Bromine reacts with $[cpCo(CO)(PMe_3)]$ to give $[cpCo(CO)(PMe_3)Br]Br$ which undergoes nucleophilic attack by methoxide ion on the carbonyl carbon to



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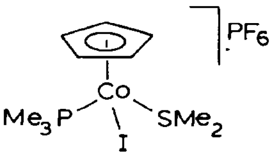
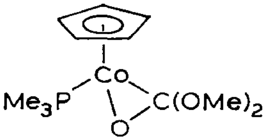


[4]

form the carboxymethyl complex $[cpCo(Br)(PMe_3)(CO_2Me)]$. This in turn reacts further with methoxide ion forming [5]. Treatment of [5] with trifluoroacetic acid or methyl trifluoromethanesulfonate converts it to [6] from



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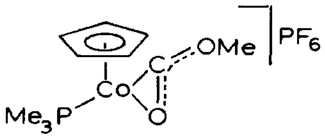
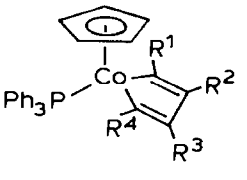


[6]

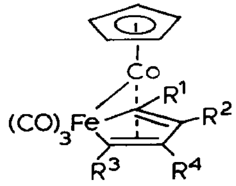
which $[cpCo(I)(PMe_3)(CO_2Me)]$ can be obtained on reaction with sodium iodide (ref. 90).

Toluene is displaced from $[(C_6F_5)_2Co(\eta^6-C_6H_5Me)]$ by a variety of ligands at 0°C to give $[(C_6F_5)_2CoL_2]$ (L = py, THF, THT, ½ bipy) and $[(C_6F_5)_2Co(CO)_3]$. The last is a rare example of a mononuclear Co(II) carbonyl complex. It decomposes at 25°C to $[(C_6F_5)Co(CO)_4]$ and perfluorobenzophenone. The tetracarbonyl complex undergoes carbonyl replacement by various phosphorus ligands to give $[(C_6F_5)Co(CO)_3L]$ (L = PMe_2Ph, $PMePh_2$, $P(OR)_3$ (R = Me, Et, Ph)), $[(C_6F_5)Co(CO)_2L_2]$ (L = PEt_3, PBu^n_3, PPh_3, $PMePh_2$, PMe_2Ph, $P(OR)_3$ (R = Me, Et, Ph)) and $[((C_6F_5)Co(CO)_3)_2(\mu\text{-DPPE})]$. The arene complex decomposes in hot toluene under dinitrogen to cobalt metal, pentafluorobenzene and perfluorobiphenyl. It also causes the polymerization of NBD and propyne. In both instances the polymer contains cobalt and pentafluorophenyl groups (refs. 91-93). The complex $[(C_6F_5)_2Co(PEt_3)_2]$ can be prepared by the successive treatment of a cobalt slurry, generated from cobalt(II) chloride, lithium and naphthalene in glyme, with pentafluoroiodobenzene and triethylphosphine (ref. 94).

Reaction of *cis*-$[CoMe_2(PMe_3)_4]PF_6$ with dmpm gives *trans*-$[CoMe_2(PMe_3)_2(dmpm)]PF_6$ while with dmpp the product is *cis*-$[CoMe_2(PMe_3)_2(dmpp)]PF_6$. The same reaction with dmpe gives both *trans*-[CoMe$_2$(PMe$_3$)$_2$(dmpe)]PF$_6$ and *cis*-[CoMe$_2$(dmpe)$_2$]PF$_6$ (ref. 95). The cobaltacycle [7] reacts with [Fe$_2$(CO)$_9$] in

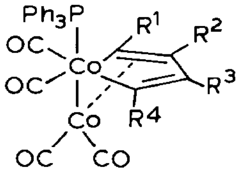


[7]

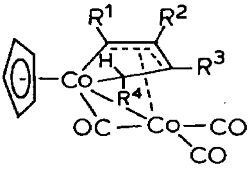


[8]

refluxing benzene to yield [8] (R^1 = R^2 = R^3 = R^4 = H, Me, Ph. R^1 = R^3 = Ph; R^2 = R^4 = H, CO$_2$Me. R^1 = R^4 = Ph; R^2 = R^3 = H, CO$_2$Me. R^1 = R^2 = Ph; R^3 = R^4 = CO$_2$Me). The rearrangement to the ferracyclopentadiene rather than retention of the cobaltacyclopentadiene moiety is attributed to the ability of the iron to form stronger σ-bonds to carbon. Complex [7] (R^1 = R^3 = Ph; R^2 = R^4 = CO$_2$Me) forms a mixture of [9] and [10] (R^1 = R^3 = Ph; R^2 = R^4 =

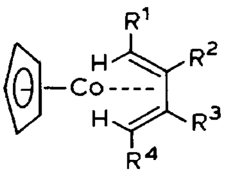


[9]



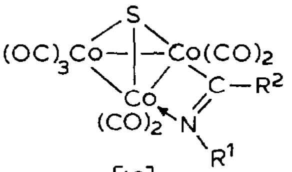
[10]

CO$_2$Me) when reacted with [Co$_2$(CO)$_8$] in benzene but when R^1 = R^4 = Ph and R^2 = R^3 = CO$_2$Me or R^1 = R^2 = Ph and R^3 = R^4 = CO$_2$Me, only [9] was formed. On the other hand if the reaction is run in benzene/ethanol the products are [10] and [11] (R^1 = R^3 = Ph; R^2 = R^4 = CO$_2$Me) while if R^1 = R^4 = Ph and R^2 = R^3 = CO$_2$Me only [10] forms and if R^1 = R^2 = Ph and R^3 = R^4 = CO$_2$Me only [11] results. The reasons for the change in the product distribution with



[11]

changes in the positions of the substituents on the cobaltacyclopentadiene ring were not explained (ref. 96). The cluster [12] (R^1 = cy, α-cholestanyl, R^2 = Ph) and [*p*-MeOC$_6$H$_4$CCo$_3$(CO)$_9$] have been electrochemically reduced in the presence of oxygen. From [12] is recovered the thioamide from which it was originally prepared while from the last was obtained p-methoxybenzoic acid. It is suggested that dioxygen initially coordinates to the cluster radical anion formed on reduction (ref. 97). Complex [12] (R^1 = Me, R^2 = cy) reacts with $[cpMo(CO)_3]^-$ to give [13] which spontaneously forms



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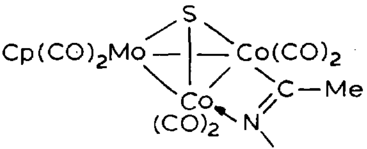
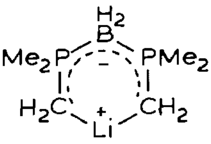


[13]

optically active crystals. The compound, however, is catalytically inactive (ref. 98). Anhydrous cobalt(II) chloride reacts with lithium bis(dimethylmethylenephosphoranyl)dihydroborate ([14]) at low temperature to give the tetrahedral, paramagnetic complex [15]. Surprisingly an ESR signal could



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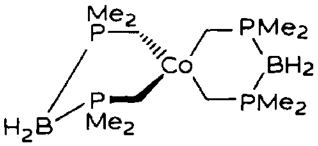


[15]

not be observed despite the observation of the expected spin-only magnetic moment and an NMR spectrum showing paramagnetic contact shifts (ref. 99). Complexes of the type $[ArCo(CN)_5]^{3-}$ (Ar = o-tolyl, m-tolyl, p-tolyl, Ph, p-$H_2NC_6H_4$, p-anisyl, α-naphthyl, β-naphthyl) are formed from the corresponding aryl bromides and $[Co(CN)_4]^{3-}$ in aqueous base under hydrogen and were identified in solution. The proposed mechanism for formation is shown in Scheme III (ref. 100).

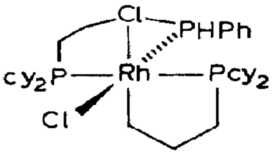
$$\begin{tikzcd}
{[Co(CN)_4]^{3-} + ArX} \arrow[r] & \{ArX,{}^{\cdot -}[Co(CN)_4]^{2-}\} \arrow[r] & \{Ar\cdot,[XCo(CN)_4]^{3-}\} \arrow[dl] \\
X^- + [ArCo(CN)_5]^{3-} & {[ArCo(CN)_4X]^{3-}} \arrow[l, "CN^-"'] &
\end{tikzcd}$$

Scheme III

The formation of cobalt-carbon σ-bonds is proposed to occur in several reactions mediated by cobalt complexes including the conversion of bromohydrins to the corresponding ketones by $[CoCl(PPh_3)_3]$ (ref. 101), the $[CoCl_2(PPh_3)_2]$-catalyzed cross-coupling of Grignard reagents and organotellurides (ref. 102) and in the reduction of $[Co(acac)_3]$ by triethylaluminum where a stepwise replacement of acetylacetonate ligands by ethyl groups is suggested (ref. 103).

In refluxing toluene [Rh(PMe$_3$)$_4$]Cl reacts with DPM to produce [RhCl(PMe$_3$)-(DPM)] which can be alkylated with alkyllithium compounds to form [Rh(R)-(PMe$_3$)(DPM)] (R = CH$_2$SiMe$_3$, CH$_2$Bu^t, CH$_2$CMe$_2$Ph) and with sodium cyclopentadienide to give [cpRh(PMe$_3$)(DPM)]. In the last, the DPM ligand is monodentate. By contrast, [RhCl(PPh$_3$)$_3$] is converted by DPM into [RhCl(DPM)$_2$] which can be alkylated by methyllithium to give the five coordinate species [Rh(Me)(DPM)$_2$] (ref. 104). A similar system involves alkylation of [RhCl-(bdpp)] with organolithium reagents to yield [Rh(R)(bdpp)] (R = CH$_2$Bu^t, CH$_2$SiMe$_3$, o-tolyl, p-tolyl, o-xylyl, mesityl). A trans influence of the R group on the ^{31}P NMR chemical shifts of the central phosphorus atom is seen. Some of these (R = o-tolyl, p-tolyl, CH$_2$SiMe$_3$) react with phenylacetylene forming the acetylide complex [Rh(C$_2$Ph)(bdpp)] and eliminating RH (ref. 105). Two fluorophenyl rhodium complexes, trans-[Rh(R)(CO)(PPh$_3$)$_2$] have been obtained from R$_2$Yb (R = C$_6$F$_5$, p-C$_6$F$_4$H) and [RhCl(CO)(PPh$_3$)$_2$] (ref. 106).

The phosphine cy$_2$P(CH$_2$)$_3$Cl cleaves [RhCl(COD)]$_2$ to form [RhCl(COD)(cy$_2$-P(CH$_2$)$_3$Cl)] which can then react with cy$_2$P(CH$_2$)$_3$PHPh at -78°C in the presence of triethylamine followed by warming to ambient temperature to provide a template synthesis of [RhCl(cyttp)]. If the same reaction is carried out at 25°C in the absence of base, an internal oxidative addition reaction occurs to form [16] (ref. 107). Dehydrohalogenation of [17] with sodium bis(trimethylsilyl)amide in hydrocarbon solvents (RH) generates the weakly solvated and evidently reactive [18]. Other species identified in this reaction are [19] and [20] which arise from [18] by oxidative addition of a



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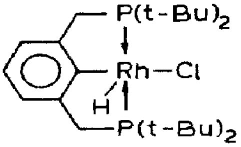

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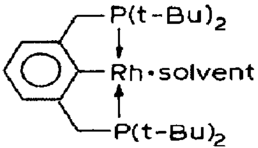
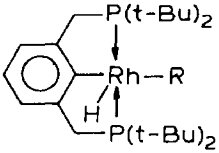


[18]

C-H bond of the solvent and internal metallation of the ligand respectively. If the dehydrohalogenation is carried out under hydrogen a dihydrido complex forms which on photolysis eliminates dihydrogen and a mixture of [18] and [19] again is seen. Generation of [18] in the presence of carbon monoxide or ethylene permits trapping of the coordinatively unsaturated species before it can react with the solvent and [21] (L = CO, C_2H_4) forms. In a similar fashion [22] can be formed from $[Me_4P]Br$ by C-H oxidative addition or from [17] and methylenetrimethylphosphorane by replacement of chloride (ref. 108). Benzoyl azide and $[cpRh(CO)(PMe_3)]$ react, possibly via an intermediate nitrene complex, to form [23] which reacts with trimethyloxonium tetrafluoroborate or trifluoroacetic acid to give [24] (R = Me or H respectively) (ref. 109). Treatment of $[cpRh(CH_2I)(PMe_3)I]$ with sodium hydrogen sulfide in THF affords the thioformaldehyde complex $[cpRh(PMe_3)(\eta^2-H_2CS)]$ which can be alkylated by methyl trifluoromethanesulfonate to form $[cpRh(PMe_3)(\eta^2-CH_2SMe)]^+$. The selenium and tellurium analogs were also prepared (ref. 110).



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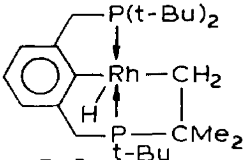

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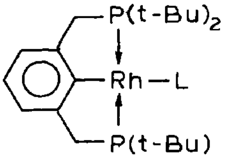
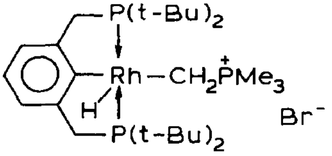


[21]



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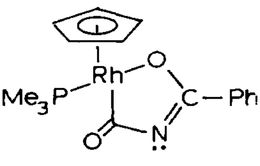

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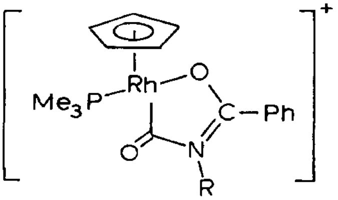
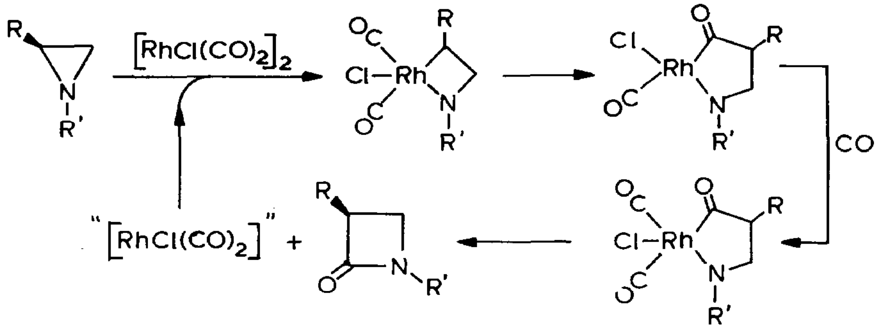


[24]

The formation of species containing rhodium-carbon σ-bonds is proposed to occur in two systems involving catalysis by rhodium complexes. In the first a regiospecific carbonylation of aziridines to β-lactams is catalyzed by

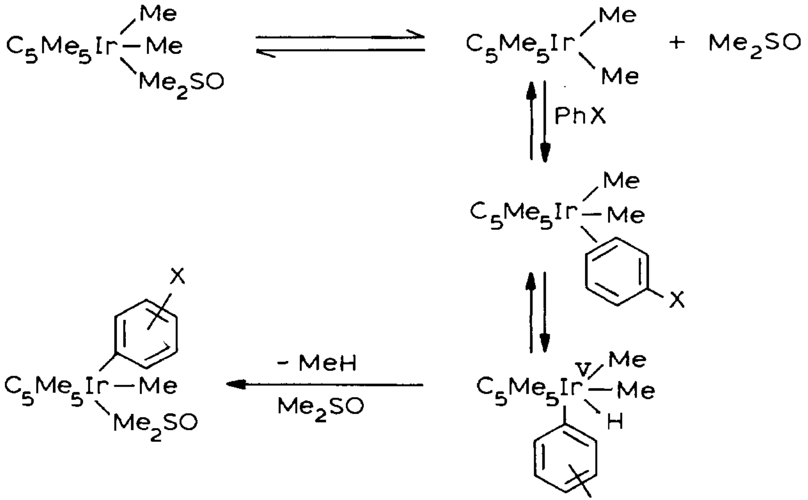
$[RhCl(CO)_2]_2$ and proposed to occur as shown in Scheme IV (R = Ph; R' = Bu^t.



Scheme IV

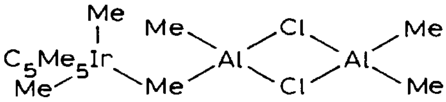
R = p-tolyl, p-BrC_6H_4; R' = adamantyl) (ref. 111). In the second, aryl mercury compounds can be cross coupled with vinyl halides in reasonable yields in the presence of $[RhCl(PPh_3)_3]$. The proposed mechanism envisages oxidative addition of the vinyl halide to rhodium followed by arylation of the vinyl complex by the mercury compound and finally reductive elimination to give the coupling product (ref. 112).

Heating $[IrCl(CO)(PPh_3)_2]$ with neat alkyl chlorides ($Me(CH_2)_nCH_2Cl$; n = 4-7) affords $[IrHCl_2(CO)(PPh_3)_2]$ and the corresponding terminal olefin. It is proposed that the alkyl chloride oxidatively adds and the iridium alkyl complex then decomposes by β-hydrogen abstraction (ref. 113). Thermolysis of $[cp'IrMe_4]$ generates methane as the principal volatile product while decomposition by $[IrCl_6]^{2-}$ in acetonitrile at room temperature forms some ethylene and ethane in addition to methane. In related work, one equivalent of halogen reacts with $[cp'_2Rh_2Me_2(\mu\text{-}CH_2)_2]$ to form $[cp'_2Rh_2X_2(\mu\text{-}CH_2)_2]$. (X = Br, I) and the appropriate methyl halide. Addition of a second equivalent of halogen forms $[cp'_2Rh_2X_2(\mu\text{-}X)_2]$ and ethylene. If the oxidation of $[cp'_2\text{-}Rh_2Me_2(\mu\text{-}CH_2)_2]$ is performed using $HBF_4/AgBF_4$, Ce(IV) or $[IrCl_6]^{2-}$, the major volatile product is methane together with small amounts of ethylene, ethane and propylene. No detectable abstraction of hydrogen from the cp' ligand occurred. The observation that reaction of these iridium and rhodium complexes with electrophiles promotes the formation of carbon-carbon bonds was taken to indicate that in the Fischer-Tropsch reaction carbon-carbon bond formation may similarly be promoted by electrophilic sites in the catalyst support (ref. 114). Heating $[cp'IrMe_2(DMSO)]$ with PhX (X = I, NO_2, CF_3, Br, H, OMe, Cl, F, Me) initially forms methane and $[cp'IrMe(C_6H_4X)\text{-}(DMSO)]$ with the rate decreasing in the order shown. For X = H a second and slower step occurs to give [cp'Ir(Ph)$_2$(DMSO)] and methane. Of particular note is the preference for C-H activation over C-I activation with iodobenzene. In this case the product is a 3:1 mixture of the m-iodophenyl and p-iodophenyl derivatives. The rhodium analog reacts similarly but much more slowly. The participation of radical processes was ruled out and with C_6D_6, [cp'IrMe$_2$(DMSO)] gives only [cp'IrMe(C_6D_5)(DMSO)] and CH_3D. All the results are consistent with the reaction proceeding via Scheme V (ref. 115). The



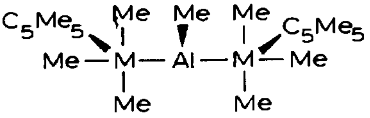
Scheme V

reaction of [cp'$_2$M$_2$Cl$_4$] (M = Rh, Ir) with trimethylaluminum gives a species originally formulated as [25] (ref. 116) but further work indicates it



[25]

should be formulated as either [26] or [27] (ref. 117). Treatment of this species (M = Ir) with oxygen generates [cp'IrMe$_4$] while in acetone it forms



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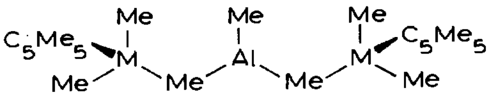
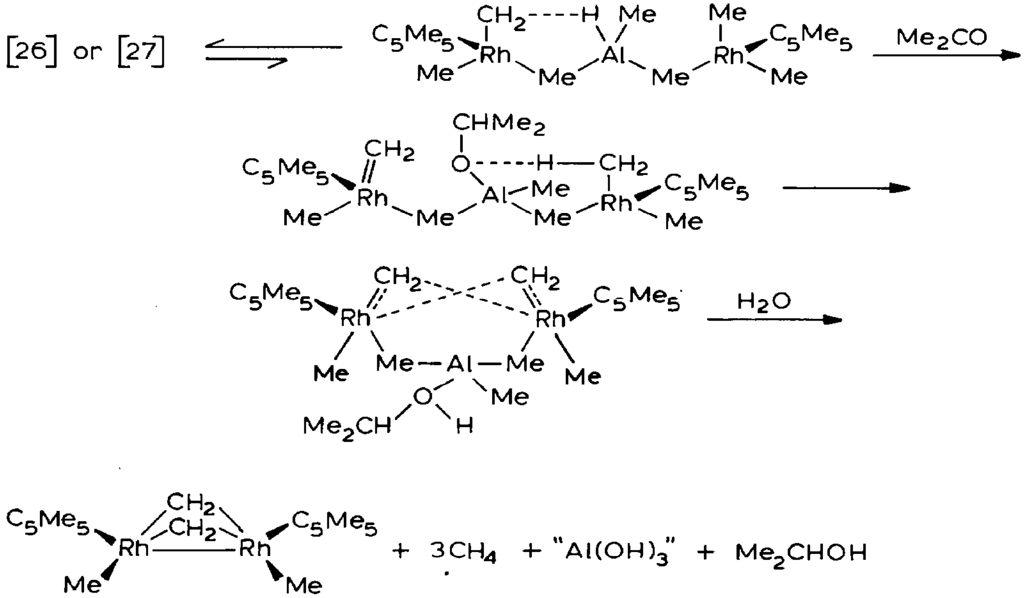


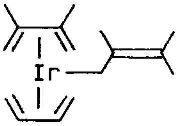
[27]

cis- and trans-[cp'$_2$Ir$_2$Me$_2$(μ-CH$_2$)$_2$]. In acetone solution containing added benzene or biphenyl the product is [cp'Ir(C$_6$H$_4$R)(μ-CH$_2$)$_2$Ir(Me)cp'] (R = H, Ph) while in benzene solution under carbon monoxide low yields of [cp'IrMe$_2$(CO)], [cp'Ir(CO)(Me)Ph] and [cp'Ir(CO)(Ph)$_2$] were obtained. In pentane solution the same reaction gave only [cp'IrMe$_2$(CO)]. Since phenyl complexes but no methylene-bridged species were formed in benzene under carbon monoxide, it appears that the formation of the aryl-iridium bond must occur prior to formation of any methylene-bridged species (ref. 116). Reaction of [cp'$_2$M$_2$Me$_4$AlMe] ([26] or [27]) with triphenylphosphine yields [cp'MMe$_2$(PPh$_3$)] (M = Rh, Ir). With DPM the product is [cp'$_2$M$_2$Me$_4$(μ-DPM)]. This can also be formed from [cp'MMe$_2$(DMSO)] which in turn is obtained from [cp'$_2$M$_2$Me$_4$AlMe] and DMSO. Since [cp'RhMe$_2$(DMSO)] does not react with acetone to form [cp'$_2$Rh$_2$Me$_2$(μ-CH$_2$)$_2$] but [cp'$_2$Rh$_2$Me$_4$AlMe] does is taken to indicate that the aluminum is important in the formation of the methylene-bridged species, possibly as shown in Scheme VI (ref. 117). The first example of the oxidative addition of methane to a metal complex has been reported. Photolysis of a solution of [cp'Ir(CO)$_2$] in perfluorohexane under 8 atm pressure of methane forms [cp'Ir(CO)H(Me)] which was identified in solution and converted to the more stable [cp'Ir(CO)Cl(Me)] by reaction with carbon tetrachloride for complete characterization (ref. 118).



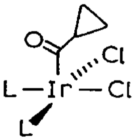
Scheme VI

Alkylation of the diene complexes [Ir(diene)$_2$Cl] (diene = buta-1,3-diene, 2,3-dimethylbuta-1,3-diene, hexa-2,4-diene, isoprene, piperylene) with organolithium reagents provides [RIr(diene)$_2$] (R = Me, Ph). The 2,3-dimethylbuta-1,3-diene complex also forms *n*-propyl and *n*-butyl derivatives since decomposition by β-elimination appears to be hindered for steric reasons. The same complex on reduction with lithium aluminum hydride in the presence of excess diene yields [28] possibly <u>via</u> initial formation of [Ir(diene)$_2$H] (ref. 119). An infrared study of the coordination of Lewis acids (AlR$_3$ (R = Et, F, Cl)) to the ester group of [Ir(CO)$_2$(PPh$_3$)$_2$CO$_2$Me] shows that aluminum trichloride coordinates most strongly (ref. 120).



[28]

Addition of four equivalents of methyldiphenylphosphine (L) and two equivalents of cyclopropylmethanoic chloride to [Ir$_2$Cl$_2$(cyoct)$_4$] in toluene forms a 2:1 equilibrium mixture of [29] and [30]. Heating the solution converts the mixture to [31]. Complex [31] can be partially reduced to trans-[Ir(CO)(cyclo-C$_3$H$_5$)(PMePh$_2$)$_2$] with potassium benzophenone ketyl. If the original reaction is carried out using an excess of the phosphine [32] is formed from which [33] can be obtained on treatment with hexafluorophosphate ion in acetone. The rhodium analog of [29] is prepared in like



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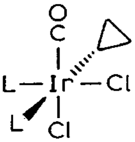

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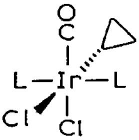

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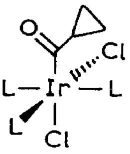
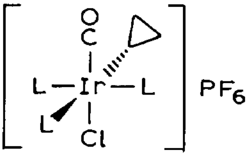
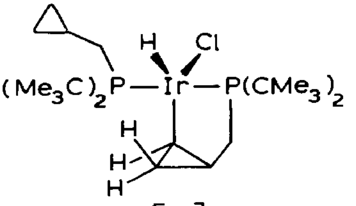


[32]



[33]

fashion but no migration of the cyclopropyl group to the metal occurs on treatment with silver tetrafluoroborate or on heating. In the latter experiment only isomerization to the trans isomer occurred. The considerable stability of the iridium-cyclopropyl bond evident from the first part of this study implies that it is unlikely that cyclopropyl iridium hydride species are intermediates in iridium-catalyzed isomerizations of substituted cyclopropanes (ref. 121). Despite this suggestion, oxidative addition of a carbon-hydrogen bond of the cyclopropyl group in cyclopropylmethyldi(tert-butyl)phosphine does occur when this ligand is reacted with $[Ir_2Cl_2(cyoct)_4]$. The product is an equilibrium mixture of the diastereomers [34] and [35] which isomerize in polar solvents to a single species which is as yet



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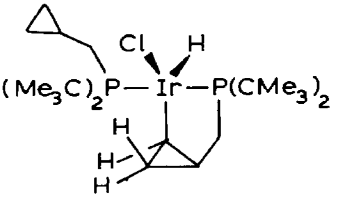
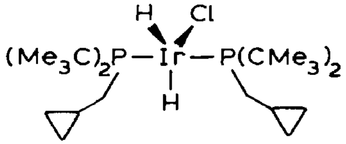


[35]

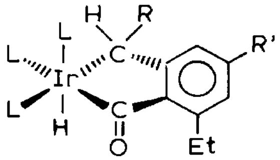
unidentified. Treatment of [34], [35] with dihydrogen forms [36]. The corresponding dideuteride results from treatment with deuterium indicating



[36]

that reductive elimination of the cyclopropane moiety precedes reaction with dihydrogen or deuterium. This apparently also occurs when [34], [35] reacts with carbon disulfide and carbonyl sulfide as the products are η^2-(C-S) adducts of these complexes in which the phosphine ligands are no longer metallated. By contrast, carbon monoxide merely adds to give a six-coordinate complex in which the metallated ligand is retained (ref. 122).

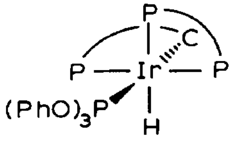
Cyclometallation of σ-bonded aryl groups in $[Ir(Ar)(CO)(PPh_3)_2]$ (Ar = o-tolyl, 2,4-$Me_2C_6H_3$, 2,6-$Et_2C_6H_3$, 2-Me-6-EtC_6H_3) occurs on reaction with an excess of a phosphite, phosphonite or phosphinite (L). When Ar = 2,6-$Et_2C_6H_3$ or 2-Me-6-EtC_6H_3 and L = $P(OMe)_3$ the product is [37] (R = H, Me; R' = H). Analogous complexes result when Ar = o-tolyl and L = $PPh(OMe)_2$ or when Ar = 2,4-$Me_2C_6H_3$ and L = $PPh(OR)_2$ or $PPh_2(OR)$ (R = Me, Et). With the last, the cyclometallation reaction is reversible and the product is



[37]

obtained only in the presence of excess ligand (refs. 123, 124). The mechanism of this reaction has been investigated using stoichiometric quantities of triphenylphosphite and $[Ir(Ar)(CO)(PPh_3)_2]$ (Ar = mesityl). With one equivalent of phosphite an equilibrium mixture of the starting complex and $[Ir(Ar)(CO)(PPh_3)(P(OPh)_3)]$ is formed with the position of the equilibrium markedly favoring the mixed complex. The latter complex can also be generated from $[Ir(CO)Cl(PPh_3)(P(OPh)_3)]$ and mesityllithium while the same reaction using $[Ir(CO)Cl(P(OPh)_3)_2]$ forms $[Ir(Ar)(CO)(P(OPh)_3)_2]$. No evidence for cyclometallation in this last complex was found so it is evidently not an intermediate in the cyclometallation reaction which occurs when $[Ir(Ar)(CO)(PPh_3)_2]$ reacts with excess triphenylphosphite to form [37] (R = H; R' = Me). Rather it is proposed that $[Ir(C(O)Ar)(P(OPh)_3)_3]$ forms first and that this species undergoes cyclometallation. Related complexes, $[Ir(C(O)R)(CO)_m(PPh_3)_n]$ (m = n = 2; R = CH_2Bu^t, CH_2SiMe_3, o-tolyl, 2,4-Me_2-C_6H_3. m = 3, n = 1; R = 2,6-$Me_2C_6H_3$) were prepared from $[IrR(CO)(PPh_3)_2]$ and carbon monoxide. These fluxional molecules are proposed to be approximately trigonal bipyramidal with the acyl group in an axial position (ref. 125). Reaction of $[IrCl(PPh_3)_3]$ with organolithium compounds at 0°C yields $[IrR(PPh_3)_3]$ (R = Ph, Me, o-tolyl) which were not isolated. The methyl complex on standing underwent o-metallation of a phosphine ligand to give a mixture of $[IrH(Me)(o\text{-}C_6H_4PPh_2)(PPh_3)_n]$ (n = 1,2) and on warming eliminated methane. If an excess of the organolithium was not used the product obtained was $[IrHCl(o\text{-}C_6H_4PPh_2)(PPh_3)_2]$. The alkylidene complexes $[Ir(CHEMe_3)(o\text{-}C_6H_4PPh_2)(PPh_3)]$ were obtained from $[IrCl(PPh_3)_3]$ and excess $LiCH_2EMe_3$ (E = C, Si) under similar conditions. Reaction of the alkylidene complexes with triphenylphosphine gave initially $[Ir(o\text{-}C_6H_4PPh_2)(PPh_3)_2]$ and then $[IrH(o\text{-}C_6H_4PPh_2)_2(PPh_3)]$ (ref. 126). Triphenylphosphite adds to $[Ir(CH_2EMe_3)(CO)$-$(PPh_3)_2]$ (E = C, Si) to give [38] ($P\frown C$ = o-metallated $P(OPh)_3$), possibly via an unstable species such as $[Ir(CH_2EMe_3)(CO)(P(OPh)_3)_3]$. This proposal was supported by the isolation of the fluxional complex $[Ir(CH_2SiMe_3)(CO)(P$-

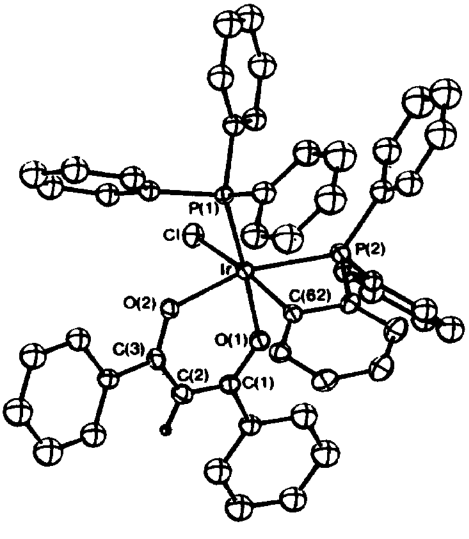
$(OMe)_3)_3]$ from an analogous reaction (ref. 127). Square planar complexes of



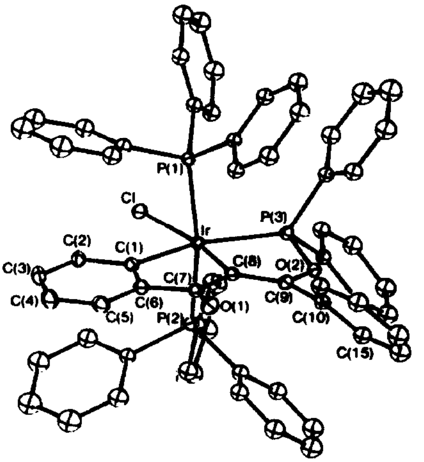
[38]

the formula [Ir(R)(bdpp)] (R = CH_2Bu^t, CH_2SiMe_3, o-tolyl, p- tolyl, mesityl) can be prepared from [IrCl(bdpp)] and the appropriate organolithium reagent (ref. 128).

A variety of other cyclometallated iridium complexes have been studied. Reaction of dibenzoyldiazomethane with $[IrCl(N_2)(PPh_3)_2]$ in refluxing toluene yields [39] which contains an o-metallated triphenylphosphine ligand. With $[IrCl(PPh_3)_3]$ in refluxing THF dibenzoyldiazomethane yields a species thought to be an isomer of [39] together with a small amount of a species characterized as [40] in which the dibenzoyldiazomethane has lost

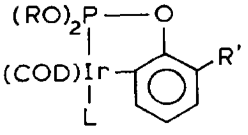


[39]



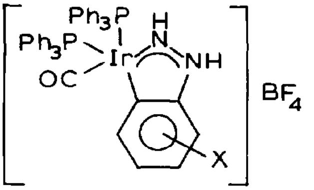
[40]

dinitrogen, coupled to a phosphine ligand and undergone metallation of one of its phenyl groups. The central carbon atom is considered to be bound as a carbene (ref. 129). The complex [41] (R = Ph; R' = H; L = P(OPh)$_3$. R =



[41]

o-tolyl; R' = Me; L = P(O-*o*-tolyl)$_3$, PMe$_3$, PMe$_2$Ph) reacts with hexafluorophosphoric acid to give cyclometallated Ir(III) hydride complexes while with hydrohalic acids the iridium-carbon bond is cleaved and non-cyclometallated Ir(III) hydride complexes result. With chlorine are obtained Ir(III) chloro complexes which retain the *o*-metallated ligand but in which the metallated phenyl group is completely chlorinated (ref. 130). The same result is seen in the chlorination of [Ir(P$\frown$C)Cl$_2$(PMe$_3$)(py)] (P$\frown$C = *o*-metallated P(O-*o*-tolyl)$_3$) (ref. 131). The *o*-metallated aryl hydrazido complexes [42] (X = H, *o*-F, *m*-F, *p*-F, *o*-OMe, *p*-OMe, *o*-NO$_2$, *p*-NO$_2$, *m*-Me, *p*-Me, *o*-CF$_3$) are converted to the aryl diazene complexes [43] (Y = Cl, Br, I) by halogens and to analogous species (Y = F, FBF$_3$) by dioxygen. The yields are generally low however. Reaction of [42] with base generates [44] while with hydrogen chloride in chloroform the product is [45] (X = *o*-NO$_2$). The latter reaction



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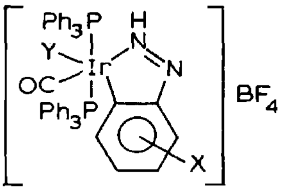
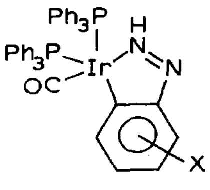


[43]



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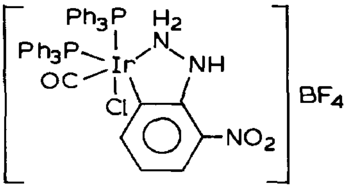
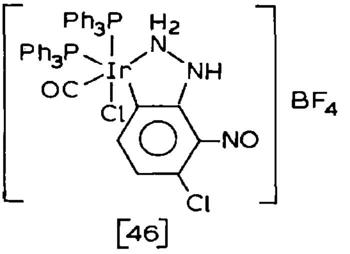
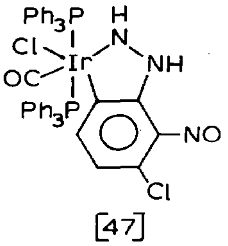


[45]

is reversed upon dissolution in hydroxylic solvents. While [45] is unreactive towards liquid hydrogen chloride, [42] (X = o-NO_2) is converted to [46] which on reaction with base gives [47]. Complex [46] can be regenerated by reaction of [47] with tetrafluoroboric acid. Although it was not



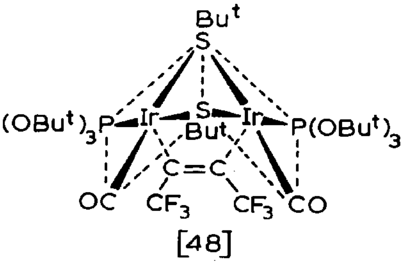
[46]



[47]

unequivocally determined, the formulation of [46] as a nitroso complex was preferred to formulation as an oxime (refs. 132, 133). Extended reaction of hydrated iridium(III) chloride with 2,2'-bipyridine in water at 170°C followed by addition of sodium perchlorate afforded a small amount of [Ir(bipy-N,N')$_2$(bipy-C,N')](ClO_4)$_2$ in addition to the expected [Ir(bipy-N,N')$_3$]-(ClO_4)$_3$ (ref. 134). The related complex [Ir(bipy-N,N')$_2$(Hbipy-C,N')](ClO_4)$_3$ has been studied by high field proton and ^{13}C NMR spectroscopy and the C-metallation of one of the rings which was not definitely established crystallographically is confirmed (ref. 135).

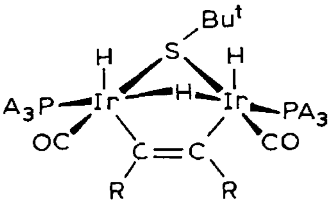
Addition of tri(tert-butyl)phosphite (L) to [Ir_2(μ-SBu^t)$_2$(CO)$_4$] yields [Ir(CO)L(μ-SBu^t)$_2$Ir(CO)L] which reversibly adds dihydrogen in a stepwise fashion to give [Ir(H)$_2$(CO)L(μ-SBu^t)$_2$Ir(CO)L] and then [Ir(H)$_2$(CO)L(μ-SBu^t)$_2$-Ir(H)$_2$(CO)L]. Hexafluorobut-2-yne adds to the dihydride complex to form [Ir(H)$_2$(CO)L(μ-SBu^t)$_2$Ir($CF_3C_2CF_3$)(CO)L] which reversibly loses dihydrogen to give [Ir(CO)L(μ-SBu^t)$_2$Ir($CF_3C_2CF_3$)(CO)L]. This last species slowly converts to [48]. Apparently in these systems the ligands can be quite bulky and not

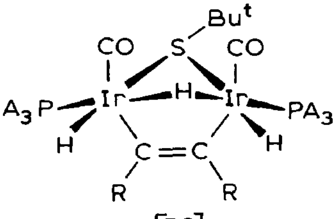


[48]

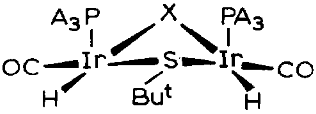
prevent the addition of small molecules (ref. 136). While [Ir(CO)(P(OBu^t)$_3$)-(μ-SBu^t)$_2$Ir($CF_3C_2CF_3$)(CO)(P(OBu^t)$_3$)] simply forms a dihydride on reaction with dihydrogen, [Ir(CO)(PMe_3)(μ-SBu^t)$_2$(μ-RC≡CR)Ir(CO)(PMe_3)] (R = CO_2Me,

CF_3) which are analogs of [48] convert to [49] (R = CO_2Me; A = Me) and [50] (R = CF_3; A = Me) respectively with the elimination of Bu^tSH. At 40°C,

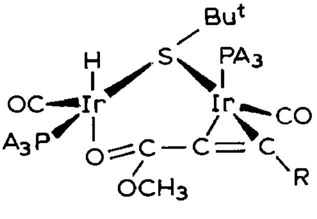

[49]

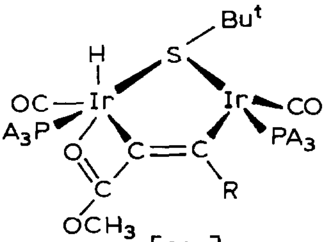

[50]

$[Ir(CO)(PPh_3)(\mu\text{-}SBu^t)_2(\mu\text{-}RC{=}CR)Ir(CO)(PPh_3)]$ (R = CO_2Me) is hydrogenated to $[IrH(CO)(PPh_3)(\mu\text{-}SBu^t)_2IrH(CO)(PPh_3)]$ with elimination of dimethylmaleate. The analog with R = CF_3 is partially hydrogenated at 60°C in like fashion but also formed is an isomer of [49] (R = CF_3; A = Ph). Under the same conditions, $[Ir(CO)(PPh_3)(\mu\text{-}O_2CCF_3)(\mu\text{-}SBu^t)(\mu\text{-}RC{=}CR)Ir(CO)(PPh_3)]$ (R = CF_3, CO_2Me) forms [51] (X = O_2CCF_3; A = Ph). No reaction occurs between $[Ir(CO)(PA_3)(\mu\text{-}SBu^t)_2(\mu\text{-}RC{=}CR)Ir(CO)(PA_3)]$ (R = CF_3; A = Ph) and formic acid but

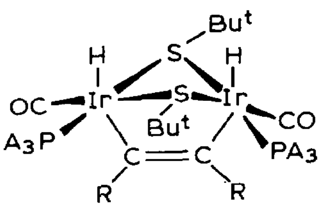

[51]

when R = CO_2Me and A = Ph or R = CF_3 and A = Me a slow conversion to [52a] or [52b] and finally to [53a] or [53b] is observed. In both cases the

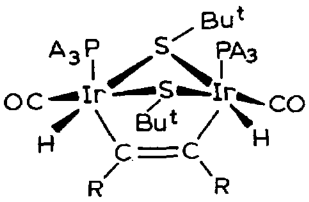

[52a]


[52b]

spectroscopic data were insufficient to distinguish between the possible structures. When R = CO_2Me and A = Me the reaction with formic acid produced a complex product mixture. When run at -30°C it was possible to isolate one species which is formulated as either [54a] or [54b]. This last complex is considered to be a key intermediate in the reactions with dihydrogen described earlier and it is suggested that that process proceeds <u>via</u> an

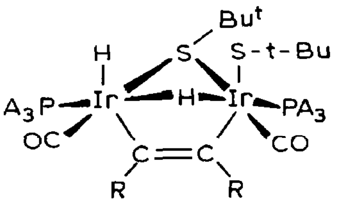


[53a]

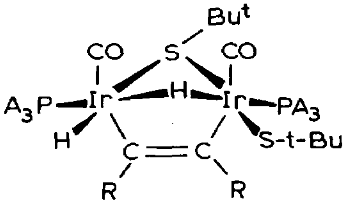


[53b]

initial opening of one thiolate bridge followed by oxidative addition of dihydrogen to one metal. The subsequent course of the reaction is depicted

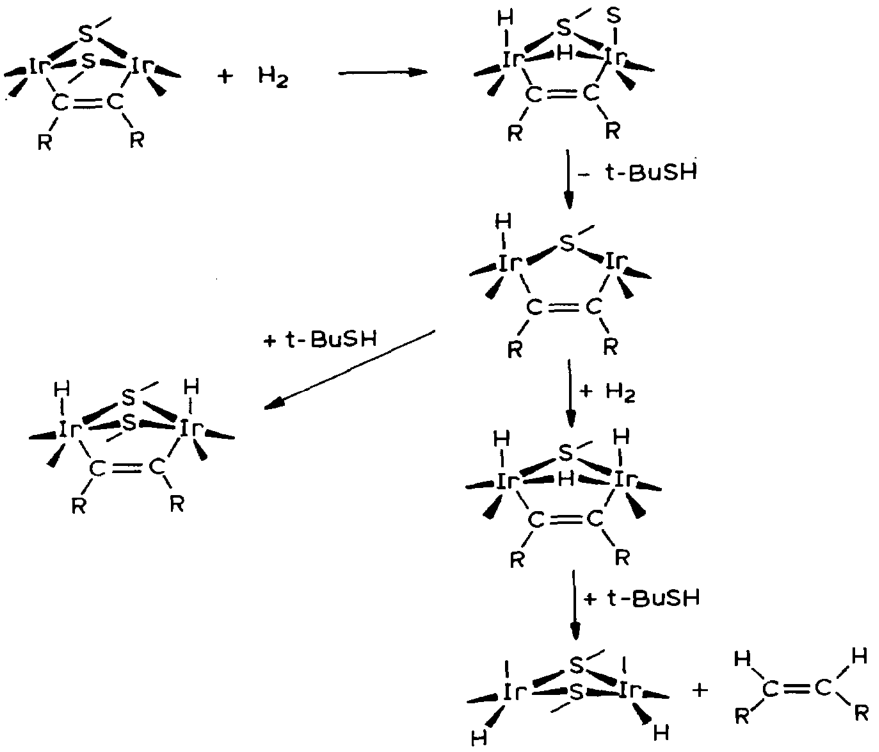


[54a]



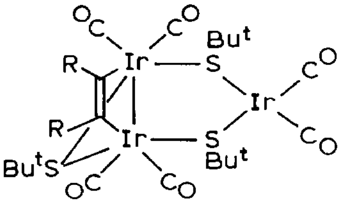
[54b]

in Scheme VII (ref. 137). The trinuclear complexes [55] (R = CF_3, CO_2Me)

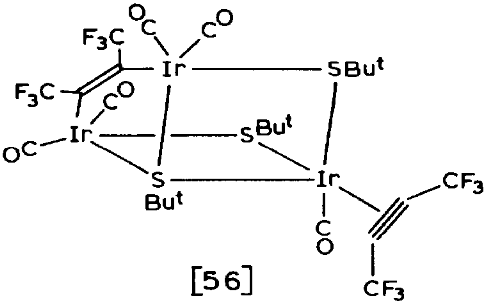


Scheme VII

and [56] show irreversible, one-electron oxidation and reduction steps in cyclic voltammetric studies. Decomposition follows electron transfer and it



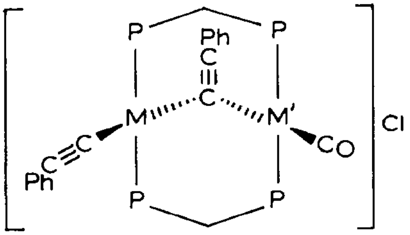
[55]



[56]

is suggested that the iridium atom not bridged by the dimetallated olefin is cleaved from the molecule (ref. 138).

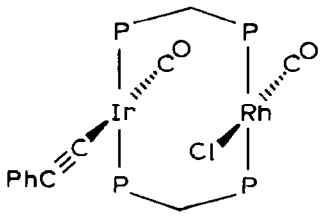
Several additional reports of the synthesis of heterobinuclear complexes bridged by DPM ligands have appeared. These involve reaction of $[Pt(C{\equiv}CPh)_2(\mu\text{-}DPM)_2MCl_n]$ (M = Cu, Ag, Au; n = 1. M = Hg; n = 2) or $[Pd(C{\equiv}CPh)_2(DPM)_2]$ (prepared from $[Pd(C{\equiv}CPh)_2(\mu\text{-}DPM)_2HgCl_2]$ and sodium sulfide at low temperature) with $[RhCl(CO)_2]_2$ or with $[IrCl(cyoct)_2]_2$ under carbon monoxide and the products have the structure [57] (M = Pd, Pt; M' = Rh, Ir). A "one pot"



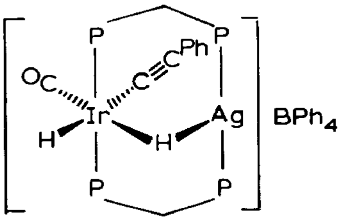
[57]

synthesis of the platinum-rhodium complex can be achieved by reaction of $[Pt(DPM)_2]Cl_2$ with a mixture of mercury(II) acetate and phenylacetylene followed by addition of $[RhCl(CO)_2]_2$. In the absence of carbon monoxide, $[IrCl(cyoct)_2]_2$ reacts with $[Pt(C{\equiv}CPh)_2(\mu\text{-}DPM)_2AgI]$ to give $[Pt(C{\equiv}CPh)_2(\mu\text{-}DPM)_2IrCl]$ while $[PtCl(C{\equiv}CR)(\mu\text{-}DPM)_2AgCl]$ reacts with $[RhCl(CO)_2]_2$ to yield $[PtCl(\mu\text{-}C{\equiv}CR)(\mu\text{-}DPM)_2Rh(CO)]AgCl_2$ (R = Me, Ph, *p*-tolyl). The last complexes have structures analogous to [57] (refs. 139, 140). Reaction of $[Ir(DPM)_2(CO)]Cl$ with $MC{\equiv}CR$ provides $[Ir(CO)(C{\equiv}CR)(\mu\text{-}DPM)_2MCl]$ (M = Cu; R = Ph. M = Ag; R = Me, Ph, *p*-tolyl). With $[AuC{\equiv}CPh]$ the ionic complex $[Ir(CO)(C{\equiv}CPh)(\mu\text{-}DPM)_2Au]Cl$ is formed. Treatment of $[Ir(CO)(C{\equiv}CPh)(\mu\text{-}DPM)_2MCl]$ (M

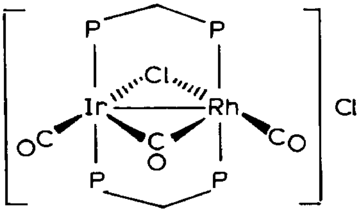
= Cu, Ag) with $[RhCl(CO)_2]_2$ yields [58] while treatment with sodium tetraphenylborate (M = Ag) gives $[Ir(CO)(C{\equiv}CPh)(\mu\text{-}DPM)_2Ag]BPh_4$ which adds dihydrogen to give [59]. Reaction of $[M(CO)(DPM)_2]Cl$ with copper(I) chloride or $[AgCl(PPh_3)]_4$ yields $[M(CO)Cl(\mu\text{-}DPM)_2M'Cl]$ (M = Ir; M' = Cu, Ag. M = Rh; M' = Ag). Subsequent treatment (M = Ir; M' = Ag) with $[RhCl(CO)_2]_2$ provides a mixture of [60] and [61]. Finally, $[Ir(CO)(DPM)_2]Cl$ reacts with $[AuCl(PPh_3)]$ in refluxing acetone to form $[Ir(CO)Cl(\mu\text{-}DPM)_2Au]Cl$ (ref. 141).



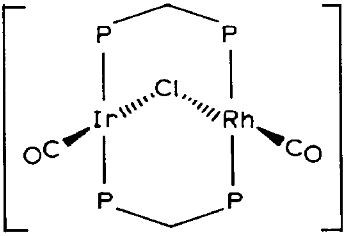
[58]



[59]

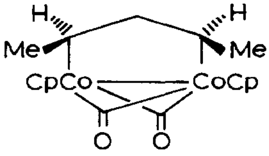


[60]

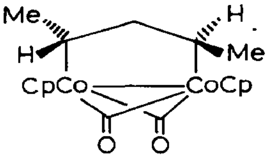


[61]

The mechanism of the formation of dicobaltacyclopentanes has been probed with the reaction of meso- and d,ℓ-2,4-diiodopentane and $PPN^+[cp_2Co_2(\mu\text{-}CO)_2]^{\dot{-}}$. The product is a 45:55 mixture of [62] and [63] indicating loss of stereochemistry at at least one center. Control experiments confirmed that this occurred during the reaction and was not due to prior or subsequent epimerization. The same experiment using *syn*-2-[^{2}H]-1,3-diiodobutane

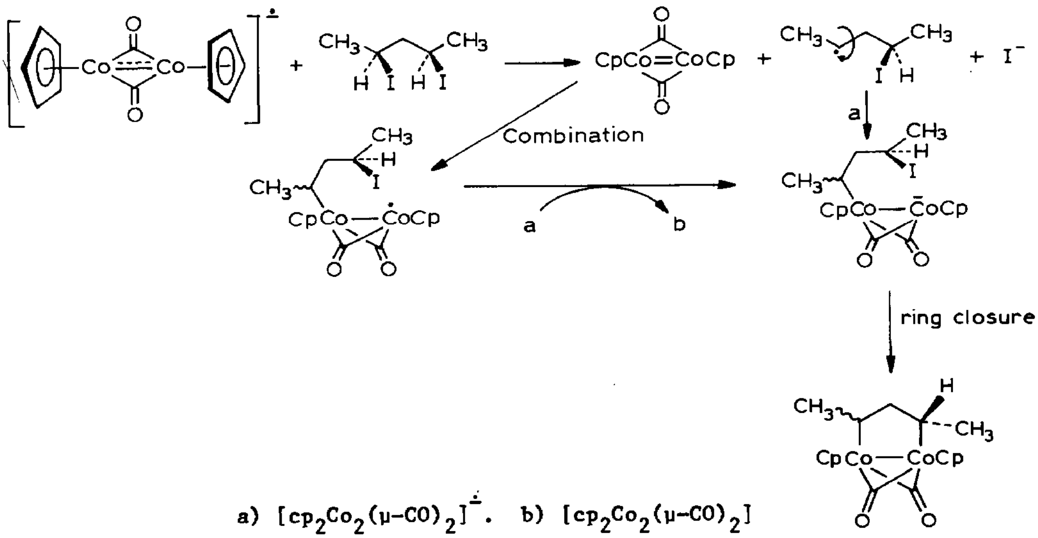


[62]



[63]

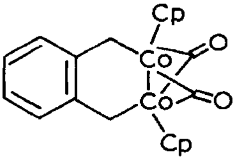
gave a 1:5 mixture of the *syn* and *anti* forms of the corresponding dimetallacyclopentane. This result suggested that the formation of the second cobalt-carbon bond occurs with some stereospecificity since controls indicate that substitution at the primary iodide center occurs much more rapidly than at the secondary center. The data suggest the mechanism of Scheme VIII



a) $[cp_2Co_2(\mu\text{-}CO)_2]^{\dot{-}}$. b) $[cp_2Co_2(\mu\text{-}CO)_2]$

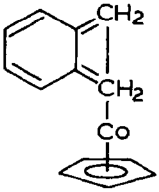
Scheme VIII

(ref. 142). In related work, a full account of the preparation of the first six-membered bimetallacycle, [64], has appeared. This is formed from $[cp_2Co_2(\mu\text{-}CO)_2]^{\dot{-}}$ and α,α'-dibromo-*o*-xylene. At room temperature in benzene it decomposes to $[cpCo(CO)_2]$ and [65] by a process proposed to involve an initial reversible binuclear elimination with the formation of *o*-xylylene and $[cp_2Co_2(\mu\text{-}CO)_2]$. The reversibility of this step was shown by the separate reaction of $[cp_2Co_2(\mu\text{-}CO)_2]$ with *o*-xylylene generated *in situ*



[64]

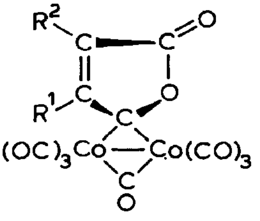
whereupon [64] was formed. This has been termed a dimetalla-Diels-Alder



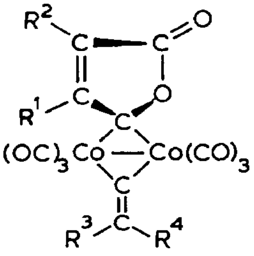
[65]

reaction since the starting cobalt complex formally contains a cobalt-cobalt double bond (refs. 143, 144).

The study of alkylidene-bridged binuclear complexes also continues unabated. α-Halo acetylenes react with [66] to generate [67] (R^1 = H; R^2 =



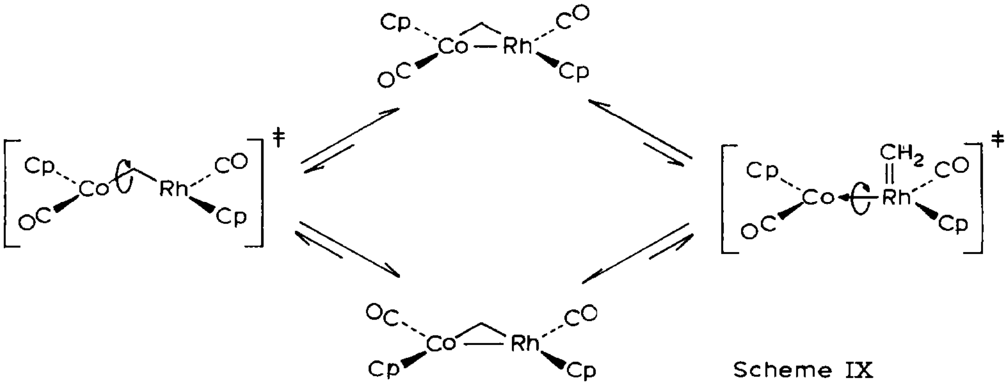
[66]



[67]

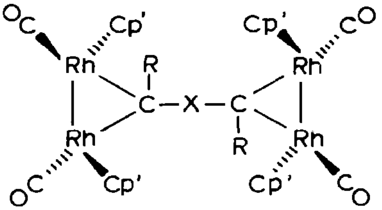
H, Pr^n, Ph; R^3 = Bu^n; R^4 = Cl, Br; R^3 = Ph; R^4 = Br; R^3 = R^4 = I) (ref. 145). The first example of an alkylidene-bridged complex formed by displacement of a bridging carbonyl ligand is $[Co_2(CO)_4(\mu\text{-}CO)(\mu\text{-}CHR)(DPM)]$ (R = H, CO_2Et) obtained from $[Co_2(CO)_4(\mu\text{-}CO)_2(DPM)]$ and the appropriate diazoalkane. When R = H, $[Co_2(CO)_4(\mu\text{-}CH_2)_2(DPM)]$ is also formed. Diazomethane reacts with $[Co_2(CO)_4(\mu\text{-}CO)(\mu\text{-}CH(CO_2Et))(DPM)]$ to give $[Co_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CH(CO_2Et))(DPM)]$. The two methylene-bridged complexes are fluxional. Rearrangement is proposed to occur via reversible opening of the methylene bridges (ref. 146). A full paper has now appeared on the reaction of $[cp_2Co_2(\mu\text{-}CO)_2]^-$ with *gem*-diiodoalkanes. With $RCHI_2$ (R = H, Et, Bu^n, Bu^t)

the product is trans-[$cp_2Co_2(CO)_2(\mu$-CHR)] together with a small amount of the cis isomer. With RR'CI_2, however, the same initial product forms but then reversibly converts into [$cp_2Co_2(\mu$-CO)$_2(\mu$-CRR')] (R = R' = Me, Et, CD_3, CD_3CH_3. R = Me, R' = Pr^n) or [$cp_2Co_2(\mu$-CO)(μ-CRR')] (R = R' = Me, Et. R = Me; R' = Pr^n). Scrambling of [$cp_2Co_2(CO)_2(\mu$-CH_2)] and [(cpMe)$_2Co_2(CO)_2$-(μ-CH_2)] occurs with the formation of [cpCo(CO)(μ-CH_2)Co(cpMe)(CO)] while the first complex also reacts with [cpRh$(CO)_2$] to give a mixture of [cpRh-(CO)(μ-CH_2)Co(cp)(CO)], [$cp_2Rh_2(CO)_2(\mu$-CH_2)] and [cpCo$(CO)_2$]. The results of these crossover experiments were taken to indicate that the cis↔trans isomerization observed here and in the previous paper may proceed as depicted in Scheme IX. At low temperature the diastereotopic protons of the



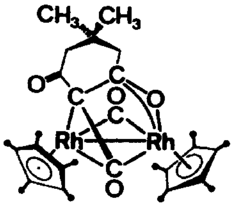
Scheme IX

methylene group in trans-[cpRh(CO)(μ-CH_2)Co(cp)(CO)] show separate signals but these coalesce on warming. The equilibration of these protons is thought to occur via a carbonyl-bridged intermediate. Further details have appeared on the reaction of [$cp_2Co_2(CO)_2(\mu$-CH_2)] with ethylene and the thermal isomerization of [$cp_2Co_2(CO)_2(\mu$-CMe_2)] to [$cp_2Co_2(CO)_2(\mu$-CHEt)] which have been described in previous Annual Surveys (J. Organometal. Chem., 242(1983)241 (Scheme XII) and J. Organometal. Chem., 261(1984)103 (Scheme XVI) respectively) (ref. 147). The more commonly employed synthesis of alkylidene-bridged cobalt dimers, namely the reaction of [$cp'_2Co_2(\mu$-CO)$_2$] with diazoalkanes, has been used to prepare [$cp'_2Co_2(\mu$-CO)$_2$(CRR')] (R = H; R' = H, CF_3, Me, Pr^n, C(OEt)=NC≡N, CO_2Et. R = R' = Me, CO_2Et, Ph. RR' = CX=CX-CX=CX (X = H, Cl), 2,2'-biphenylyl). Most give [$cp'_2Co_2(\mu$-CO)-(μ-CRR')] on heating and a few rearrange to [$cp'_2Co_2(CO)_2(\mu$-CRR')] (R = R' = H. R = H; R' = CF_3, Pr^1) (ref. 148). More elaborate species of this type are those prepared from [$cp'_2Rh_2(\mu$-CO)$_2$] and RC(=N_2)-X-C(=N_2)R ([68]) (R = Me; X = $(CH_2)_4$. R = Ph, X = C_6H_4), α-diazopropionaldehyde ([$cp'_2Rh_2(CO)_2$-(μ-C(Me)CHO)], an example of a μ-η^1 formylmethylene ligand) or diazodimedone ([69]). In [69] an interesting feature is the formation of a ketenyl moiety by coupling of the organic molecule with a carbonyl group (refs. 149, 150). The reaction of $[cp'_2Rh_2Cl_2(\mu-Cl)_2]$ with methyllithium or trimethylaluminum



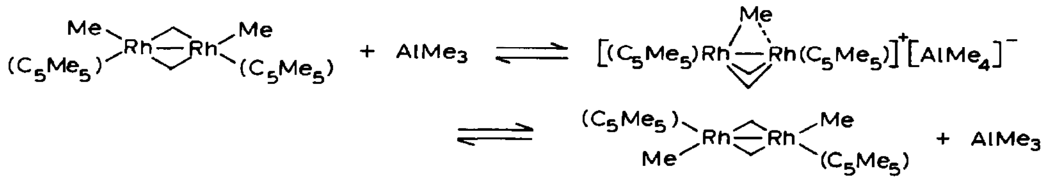
[68]

followed by quenching with either dioxygen or acetone yields a mixture of



[69]

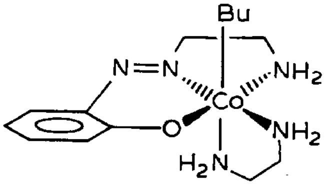
cis- and trans-$[cp'_2Rh_2Me_2(\mu-CH_2)_2]$. The same experiments using highly deuterated $[cp'_2Rh_2Cl_2(\mu-Cl)_2]$ showed considerable scrambling of deuterium throughout the product when dioxygen was used to quench the reaction but with acetone, only minimal deuterium incorporation in the rhodium-bound methyl and methylene groups was seen. Thus it appears that the hydrogen-transfer reaction that must occur to generate the methylene groups can occur in different ways depending on the mode of workup and it is considered to be the slowest or most difficult step in the transformation. A cis→trans isomerization of $[cp'_2Rh_2Me_2(\mu-CH_2)_2]$ is effected by Lewis acids. Scheme X



Scheme X

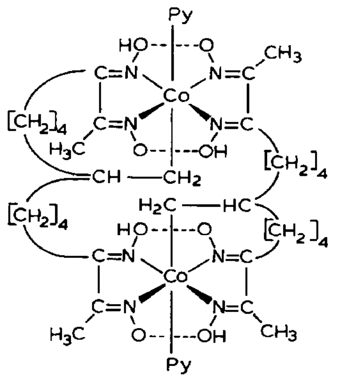
is proposed for the case where the acid is trimethylaluminum (ref. 151). Reaction of trans-$[cp'_2Rh_2Me_2(\mu-CH_2)_2]$ with p-toluenesulfonic acid followed by addition of a Lewis base and hexafluorophosphate ion yields a mixture of cis- and trans-[cp'RhMe(μ-CH_2)$_2$Rh(cp')L]PF_6 (L = MeCN, py, 2-Mepy, CO). The acetonitrile complex is fluxional at room temperature while the others are not. It is suggested that the fluxional process involves loss of acetonitrile followed by migration of the methyl group between the rhodium atoms via [cp'$_2$$Rh_2$(μ-$CH_2$)$_2$(μ-Me)]$^+$ as an intermediate (ref. 152). Treatment of [cp'$_2$$Rh_2$$Cl_2$(μ-$CH_2$)$_2$] with sodium carbonate in methanol yields [cp'$_2$$Rh_2$(μ-$CH_2$)$_2$(μ-$O_2$C=O)] which reacts with aqueous tetrafluoroboric acid to first give [cp'$_2$$Rh_2$(μ-$CH_2$)$_2$(μ-$O_2$C-OH)]$BF_4$ and then [cp'$_2$$Rh_2$($OH_2$)$_2$(μ-$CH_2$)$_2$]($BF_4$)$_2$. The methylene bridges are unaffected by acid up to pH 1 (ref. 153).

Complex [70] is susceptible to cobalt-carbon bond homolysis in weakly acidic solution as indicated by its ability to initiate the polymerization of methylmethacrylate (ref. 154). The alkyl cobaloximes [(CH_2=CHCH$_2$CH(CO_2Et))Co(dmgH)$_2$py] and [(CH_2=CHCH(CO_2Et)CH_2)Co(dmgH)$_2$py] are synthesized from [Co(dmgH)$_2$py]$^-$ plus CH_2=CHCH$_2$CHBrCO$_2$Et and CH_2=CHCH(CH_2I)CO_2Et respectively. The second complex slowly converts to the first in aqueous trifluoroacetic acid. The first complex is also formed as the major product of the reaction of [Co(dmgH)$_2$py]$^-$ with either cis- or trans-ethyl 2-(iodomethyl)cyclopropanecarboxylate suggesting that the initial step is an electron transfer to form cyclopropylmethyl radicals which equilibrate before combining with the cobalt moiety (ref. 155). Alkylation of cob(I)-alamin with 2-(R)- or 2-(S)-2-hydroxy-1-chloropropane or the corresponding 2,3-dihydroxy-1-chloropropanes yields stereoisomerically pure alkylcobalamins. Use of racemic alkylating agents shows a slight enantioselectivity in some instances (ref. 156). A ready conversion of 1,1-dichloro-2,2-diarylethanes to the corresponding trans-stilbenes is effected by reaction with [Co(dmgH)$_2$]$^-$, [Co(salen)]$^-$ or vitamin B_{12s} (ref. 157). Trichloroacetonitrile couples with the alkenyl group in [(RR'C=CR"CH_2)Co(dmgH)$_2$py] (R = R' = R" = H. R = R' = H; R" = Me. R = R" = H(trans); R' = Me. R = R' = Me; R" = H) to give NCCCl$_2$CRR'CR"=CH_2 (ref. 158). Perfluoroalkyl iodides add to [Co(salophen)] in aqueous DMSO to give [RCo(salophen)(H_2O)] (R = CF_3, C_2F_5, C_3F_7). The corresponding derivatives of [Co(acen)] and [Co(tfacen)] were also prepared and all were studied by cyclic voltammetry. The salophen

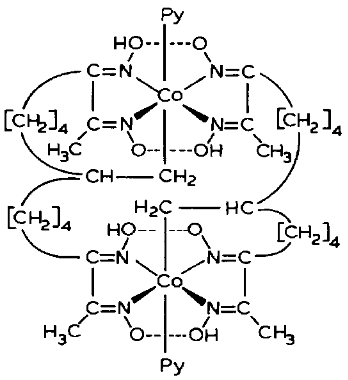


[70]

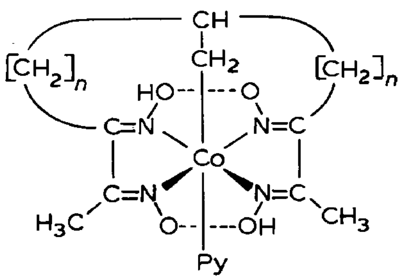
complexes dissociate less readily than their hydrocarbon analogs on reduction (ref. 159). Alkylation of $[ClCo(GH)_2py]$ by alkyl halides occurs in basic methanol in the presence of sodium borohydride to give $[RCo(GH)_2py]$ (R = Me, Et, Pr^i). The rates of axial ligand substitution in the alkyl complexes were determined and found to be much slower than in the analogous dmgH complexes. The difference was attributed primarily to electronic factors (ref. 160). The tetraoximes $MeC(=NOH)C(=NOH)(CH_2)_nCH(CH_2X)(CH_2)_n$-$C(=NOH)C(=NOH)Me$ (n = 4,6; X = Br. n = 7; X = Cl) react with cobalt(II) chloride and sodium borohydride in the presence of pyridine and base to give the intramolecularly alkylated cobaloximes [71] - [73] (n = 6,7) and [74]



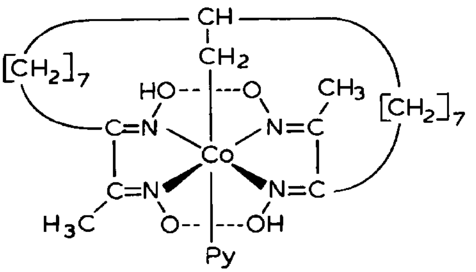
[71]



[72]



[73]

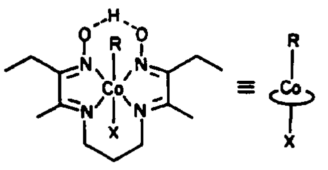


[74]

(ref. 161). Unlike many dmgH complexes, $[MeCo(ADDH)_2(H_2O)]$, prepared by standard methods is photochemically stable (ref. 162).

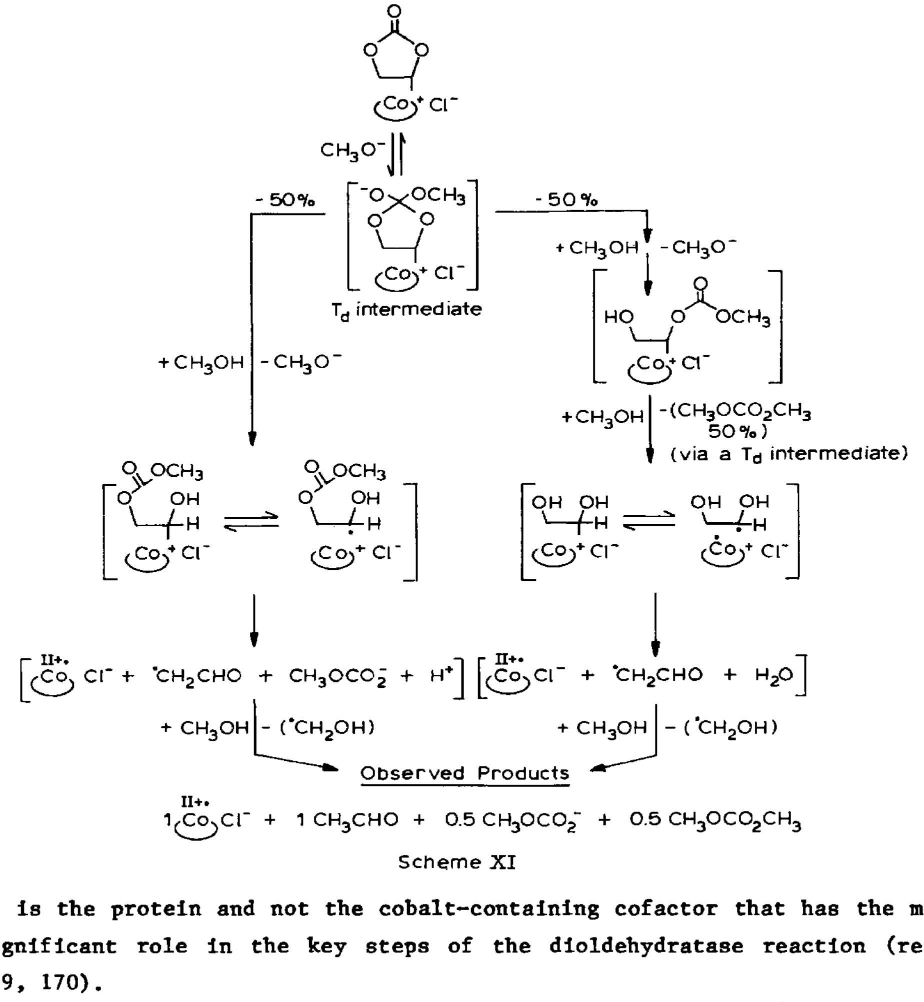
The kinetics of substitution of axial base ligands in organocobaloximes have been studied. Replacement of water in $[RCo(dmgH)_2(H_2O)]$ (R = Me, CH_2Cl, CH_2CF_3) by ammonia, imidazole, morpholine and the thiocyanate ion appears to proceed by an I_d mechanism although at high concentration some evidence of an associative process was obtained (ref. 163). However when the reaction with ammonia (R = Me, Et, CH_2Cl) was studied as a function of pH it appeared to proceed <u>via</u> a conjugate base mechanism. Two opposing factors appear to operate: an inhibition by formation of the substitution-inert $[RCo(dmgH)_2(OH)]^-$ and a rate enhancement by formation of the conjugate base complex where a dmgH ligand is deprotonated (ref. 164). The complexes $[RCo(dmgH)_2L]$ (R = Me, Et, Pr^i, Bu^i, $\underline{neo}$-C_5H_{11}, CH_2Br, CH_2CF_3; L = $PhNH_2$, PhNHMe, 2-Xpy (X = NH_2, MeNH, bzNH), 3-NH_2py) have been prepared from the corresponding aquo species (ref. 165). Diaquocobinamide reacts with acetylene in the presence of catalytic amounts of copper(II) salts to give two isomers of ethynylaquocobinamide. In the replacement of water by hydroxide ion or imidazole it appears that the ethynyl ligand exerts a trans-effect between that for cyanide ion and the vinyl group in these complexes (ref. 166).

The decomposition of $[(PhCHMe)Co(dmgH)_2L]$ (L = tertiary phosphine) to $[Co(dmgH)_2L]$, styrene and dihydrogen has been studied kinetically to determine the factors affecting the cobalt-carbon bond dissociation energy. In contrast to previous systems where the axial base is pyridine or its derivatives, there is no dependence of the rate or bond dissociation energy on the pKa of the phosphine. Here the rates increase and the bond dissociation energies decrease as the cone angle of the phosphine increases (ref. 167). A related study used the thermal decomposition of $[RCo(C_2(DO)(DOH)_{pn})I]$ ([75]; R = bz, CH_2Bu^t; X = I) in the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy as a radical trap to obtain other cobalt-carbon bond



[75]

energies (ref. 168). The same group has used [75] (R = $\overline{CHCH_2OC(O)O}$; X = Cl, H_2O, 1,5,6-trimethylbenzimidazole, MeCN. R = CH_2CHO; X = I) to conduct a model study for probing the question of the participation of cobalt in the coenzyme B_{12}-dependent diol dehydratase rearrangement (dehydration of ethylene glycol to acetaldehyde). The carbonate-protected diol complex (X = Cl) was synthesized from $\overline{CHClCH_2OC(O)O}$ and $[(OC)Co^I(C_2(DO)(DOH)_{pn})]$ and the derivatives with neutral axial base ligands generated from this on treatment with silver hexafluorophosphate or sodium tetraphenylborate in the presence of the desired ligand. Complex [75] (R = $\overline{CHCH_2OC(O)O}$; X = Cl) in methanol containing a catalytic amount of methoxide ion quantitatively decomposes to $[Co^{II}(C_2(DO)(DOH)_{pn})]Cl$, acetaldehyde and roughly equal amounts of $(MeO)_2C{=}O$ and $MeOCO_2^-$. The source of hydrogen for the formation of the acetaldehyde was shown to be the solvent and the intermediacy of a formylmethyl-cobalt complex was ruled out since the separately-prepared $[(OHCCH_2)Co(C_2(DO)(DOH)_{pn})I]$ was shown to be too stable. The mechanism of Scheme XI was proposed. The results of the study suggest that in the enzymatic reaction



Scheme XI

it is the protein and not the cobalt-containing cofactor that has the more significant role in the key steps of the dioldehydratase reaction (refs. 169, 170).

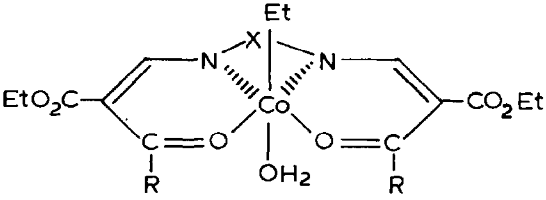
The acid-induced decomposition of mer-$[RCo(7\text{-Mesalen})(en)]^+$ (R = Me, Et, Pr^i, Bu^n) produces alkanes, alkenes and coupling products with the first predominating. Most of the hydrogen incorporated into the alkane product comes from the ligands and not the solvent. No significant decomposition by β-elimination appears to occur (ref. 171). With $[(PhMeHC)Co(dmgH)_2(H_2O)]$ on the other hand decomposition in acid proceeds both by homolysis of the cobalt-carbon bond and by β-elimination (ref. 172).

Several groups have studied the oxidative dealkylation of alkylcobalamins and related complexes by various metal compounds. The course of the reaction of [MeCo(chel)B] (chel = $(dmgH)_2$, salen, $C_2(DO)(DOH)_{pn}$, BAE; B = SMe_2, substituted pyridines) with methyltrichlorotin or dimethyldichlorotin depends both on the electron donor ability of chel and on the nature of the tin center. In some cases dealkylation occurred but in others the tin species merely added to the cobalt complex or failed to react (ref. 173). Oxidative demethylation of methylcobalamin with an excess of $[IrCl_6]^{2-}$ generates mostly methyl chloride while with a limited amount the major product is ethane. The process is proposed to involve initial electron transfer to the cobalamin with formation of a methyl radical. In the presence of excess $[IrCl_6]^{2-}$, chloride abstraction can then occur; otherwise the radicals dimerize (ref. 174). The same process using a mixture of Pt(II) and Pt(IV) complexes (e.g. $[PtCl_6]^{2-}$, $[Pt(CN)_4Cl_2]^{2-}$, $[Pt(CN)_5Cl]^{2-}$, $[PtCl_4]^{2-}$, $[Pt(CN)_4]^{2-}$) appears to involve an initial association of the Pt(II) complex with the methyl cobalamin followed by a further association of this adduct with the Pt(IV) complex *via* a bridging ligand originally part of the Pt(IV) coordination sphere. This is followed by transfer of a methyl radical to the original Pt(II) center and finally its oxidation to a Pt(IV)-methyl species by the second platinum center (refs. 175-177). An electron-transfer reaction also appears to be involved in the dealkylation of ethylcobalamin by $[AuCl_4]^-$ (ref. 178).

Organic radicals show some rather specific reactivity towards $[RCo(dmgH)_2(H_2O)]$ (R = Me, Et, Pr^i, bz). For example the benzyl complex reacts with $\{\cdot CMe_2OH\}$ to give the coupling product $PhCH_2CMe_2OH$ (ref. 179). In a pulse radiolysis study, [Co(TPPS)] was reacted with pulse-generated radicals to give the alkyl derivatives [RCo(TPPS)]. When R = Me the product was stable but with R = Pr^i decomposition occurred by a β-elimination process (ref. 180).

In a continuation of studies of electronic effects in alkyl and arylcobaloximes, the pKa's of the conjugate acids of $[ArCo(dmgH)_2L]$ (Ar = *m*-$Me_2NC_6H_4$, *p*-$Me_2NC_6H_4$; L = H_2O, SCN^-, NCS^-, CN^-, N_3^-) were measured and correlated with those of a variety of dimethylanilinium ions by a dual substituent parameter equation. The results suggest that resonance interactions of the aryl group with the cobalt are insignificant (ref. 181). Photolysis of [RCo(salen)] (R = Me, Et, Pr^n, Bu^n, Bu^i) in dichloromethane or DMF matrices at 77 K involves cobalt-carbon bond homolysis as the primary process (ref. 182). The same process appears to occur with $[MeCo(dmgH)_2py]$ in d_4 methanol while electron capture in 2-methyltetrahydrofuran at 77 K gives a σ* anion with the odd electron largely localized in the cobalt d_{z^2} orbital (ref. 183). Electrochemical studies on methylcobalamin and coenzyme B_{12} at pH 11.7 show that the base-off form of the former undergoes a reversible one-electron reduction followed by cleavage of the cobalt-methyl bond while the second undergoes an irreversible one-electron reduction (ref. 184). Electrochemical oxidation of $[bzCo(dmgH)_2]$ and [bzCo(salophen)] occurs by an

ECE process with the irreversible decomposition following the oxidation being significantly diminished at temperatures below -20°C. The initial step is proposed to be the formation of a benzyl-Co(IV) species (ref. 185). The electrochemical reduction of vitamin B_{12a} under photolytic conditions generates a catalytic system for the reaction of carboxylic acid anhydrides with activated olefins to give 4-oxo aldehydes, esters, ketones and nitriles. It is proposed that the reduced B_{12} species forms an acyl complex on reaction with the anhydride which is then cleaved by photolysis. The resulting acyl fragment then adds to the olefin (ref. 186). Complexes [76]



[76]

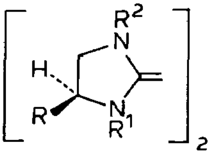
($X = (CH_2)_2$; R = Me. $X = 1,2\text{-}C_6H_4$; R = Me, OEt) have been studied by field desorption mass spectroscopy (ref. 187).

Reaction of [RhCl(OEP)] with silver perchlorate in benzene forms [Rh(Ph)-(OEP)]. The same product results if $[Rh(OEP)]ClO_4$ is formed separately and then reacted with benzene. Related complexes are formed in toluene, chlorobenzene and anisole and here attack occurs exclusively in the para position. The rate of the reaction increases with increasing electron-donating ability of the substituent on the benzene ring leading to a characterization of the process as an electrophilic aromatic metallation (ref. 188).

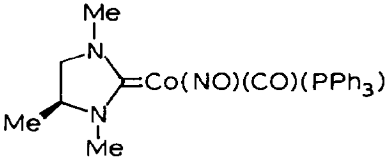
The thermodynamically stable formyl complex $[Rh(L_4)(CHO)]$ (L_4 = TPP, OEP) can be prepared directly from $[RhCl(CO)(L_4)]$, carbon monoxide and potassium hydroxide in deuterobenzene thereby avoiding the separate preparation of $[Rh(L_4)]_2$ or $[RhH(L_4)]$ as has been required in previous syntheses. The reaction is proposed to involve initial formation of $[Rh(CO_2H)(L_4)]$ by hydroxide ion attack on the carbonyl group followed by extrusion of carbon dioxide to form $[RhH(L_4)]$ which can then react with carbon monoxide to form the formyl complex (ref. 189).

Metal Carbene Complexes

The preparation of optically active carbene complexes using the well-established route of cleaving electron-rich olefins by low-valent transition metal compounds has been reported. For example [77] ($R = R^1 = R^2$ = Me) reacts with $[Co(CO)_3(NO)]$ and the triphenylphosphine to give [78] ($[(carbene)$-$Co(CO)(NO)(PPh_3)]$). Similarly $[RhCl(PPh_3)_3]$ reacts with [77] ($R = Bu^i$; $R^1 = R^2 = Et$. $R = H$; $R^1 = R^2 =$ (-)-cis-myrtanyl) to furnish the derivatives

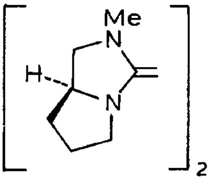


[77]

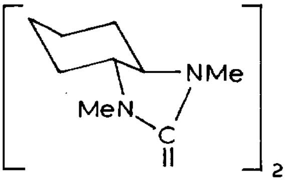


[78]

$[(carbene)RhCl(PPh_3)_2]$ while $[(carbene)RhCl(COD)]$ is formed from $[RhCl$-$(COD)]_2$ plus [79] or [80] (ref. 190). The phosphide-bridged complex $[(OC)_4$-$W(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3)]$ is readily obtained from $Li[W(CO)_4(PPh_2H)(PPh_2)]$



[79]



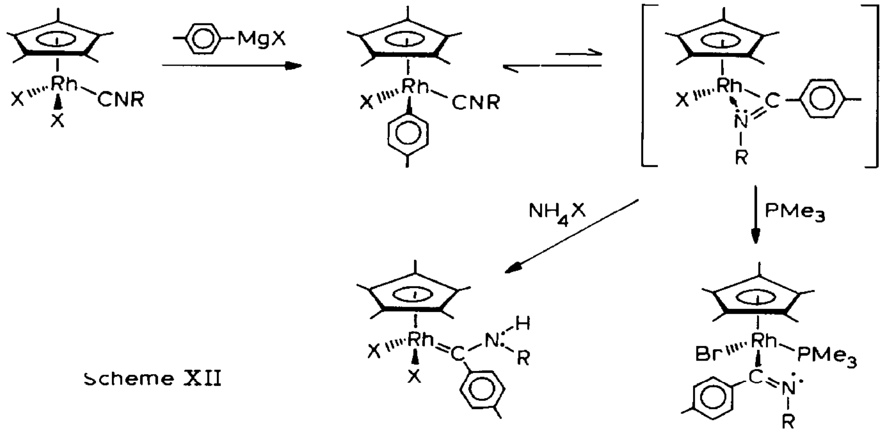
[80]

and $[IrCl(CO)(PPh_3)_2]$. Reaction with organolithium reagents generates the acyl complex $Li[(OC)_3W(C(O)R)(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3)]$ ($R = Me$, Ph) which on treatment with trimethyloxonium tetrafluoroborate gives $[(OC)_3W(=C(OMe)R)$-$(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3)]$ as the first example of a heterobimetallic carbene hydride complex. This reverts to $[(OC)_4W(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3)]$ on heating and is hydrolyzed to $[(OC)_3W(=C(OH)R)(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3)]$ by trifluoracetic acid at low temperature. While all of the above complexes appear to contain metal-metal bonds, none is present in $K[(OC)_4W(\mu\text{-}PPh_2)_2IrH_2(CO)$-$(PPh_3)]$ which resulted from an attempt to generate a formyl complex by the reaction of $[(OC)_4W(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3)]$ with $K[BHBu^i_3]$. Attempts to cause hydride migration from iridium to the tungsten-bound acyl or carbene moieties were unsuccessful presumably because the tungsten center is coordinatively saturated (ref. 191).

Metal Isocyanide Complexes

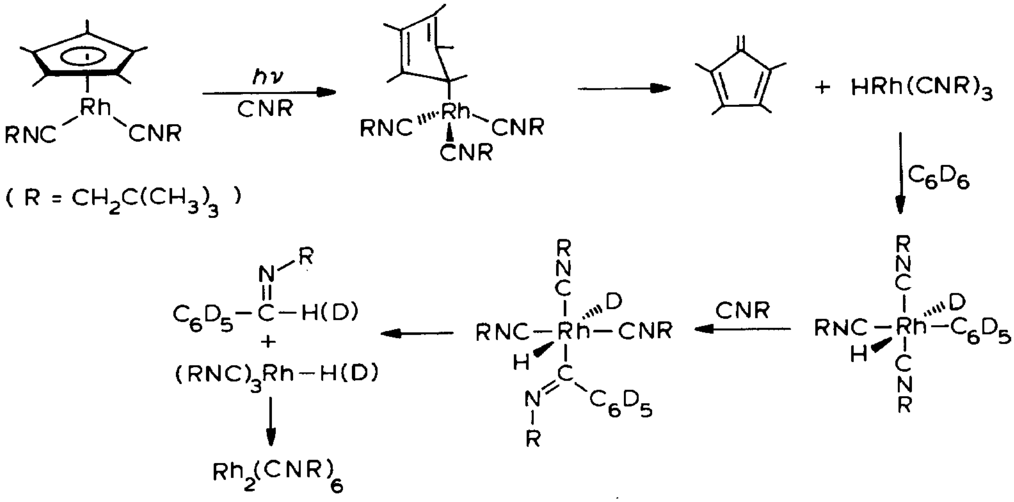
Phenyl isothiocyanate replaces a carbonyl group in $[cpCo(CO)(PPh_3)]$ to form $[cpCo(PPh_3)(\eta^2\text{-}SCNPh)]$ but desulfurization also occurs to yield $[cp_3Co_3$-$(\mu_3\text{-}S)(\mu_3\text{-}CNPh)]$. The methyl and cyclohexyl analogs of the latter complex were also prepared. These are claimed as the first examples of an isocyanide acting as a triply-bridging, two-electron ligand (ref. 192). Further studies on the substitution of phosphine for isocyanide ligands in $[Co(CNR)_5]^+$ (R = *p*-ClC_6H_4, 2,6-$Et_2C_6H_3$, *o*-tolyl) to produce mono- and/or disubstituted species tend to confirm earlier conclusions that monosubstitution is favored by electron-withdrawing substituents on the phosphine (ref. 193). The complex *trans*-$[CoBr_2$(*t*-buDiNC)$_2]$ is formed from the ligand and $[Co(H_2O)_6]Br_2$ in acetone and is oxidized to $[CoBr_2$(*t*-buDiNC)$_2]Br_3$ with excess bromine. Oxidation with a stoichiometric quantity of bromine followed by treatment with silver hexafluorophosphate and one equivalent of the ligand forms [Co(*t*-buDiNC)$_3$]$(PF_6)_3$. Reduction of $[Co(H_2O)_6]Cl_2$ with zinc in ethanol in the presence of a stoichiometric quantity of the ligand and hexafluorophosphate ion forms [((*t*-buDiNC)$_2$Co)$_2$(μ-*t*-buDiNC)]$(PF_6)_2$ (ref. 194). Formation of [Rh(*t*-buDiNC)$_2$]Cl from the ligand and $[RhCl(COD)]_2$ occurs readily and oxidation with iodine gives [IRh(*t*-buDiNC)$_2$]$_2^{2+}$ containing a rhodium-rhodium bond. In concentrated solution, [Rh(*t*-buDiNC)$_2$]$^+$ oligomerizes more readily than does $[Rh(CNPh)_4]^+$ presumably because less steric hindrance is present. The oligomers dissociate on photolysis (ref. 195).

Cyclooctadiene is displaced from $[Rh(COD)(S_2P(OEt)_2)]$ by isocyanides to give $[Rh(CNR)_2(S_2P(OEt)_2)]$ (R = Ph, *p*-tolyl, *p*-anisyl). The phenylisocyanide complex reacts with TCNE giving $[Rh(TCNE)(CNPh)_2(S_2P(OEt)_2)]$ and with TCNQ in refluxing THF to form $[Rh(CNPh)_2(S_2P(OEt)_2)]_2^{2+}(TCNQ^{\overset{\cdot}{-}})_2$ which contains a metal-metal bond (ref. 196). Reaction of six equivalents of 4-bromo-2,6-dimethylphenylisocyanide (L) with $[RhCl(COD)]_2$ yields a complex of empirical formula $[RhClL_3]$. Rapid crystallization provides a brown crystalline material which is characterized as a monomer while slow crystallization yields purple crystals of the metal-metal bonded dimer. The equilibrium constant for the dimerization was measured and found to be less than that for the corresponding $[RhL_4]Cl$ species (ref. 197). In a previous paper (J. Organometal. Chem., 261(1984)103 (ref. 119)) it was reported that reaction of $[Rh_2(CNBu^t)_4(DPM)_2]A_2$ (A = BPh_4, PF_6) with electrophilic acetylenes gave brownish crystals of $[Rh_2(CNBu^t)_4(\mu\text{-}RC{\equiv}CR)(DPM)_2]A_2$ (R = CF_3, CO_2Me) which became yellow on contact with carbon monoxide although no evidence of a coordinated carbonyl group could be found. The structures of both brown and yellow forms of $[Rh_2(CNBu^t)_4(\mu\text{-}F_3CC{\equiv}CCF_3)(DPM)_2](PF_6)_2$ have now been determined and shown to be identical. The brown crystals were found to contain a small quantity (crystallographically undetectable) of cocrystallized $[Rh(CNBu^t)_4(DPM)_2](PF_6)_2$ and the color change on carbonylation is the result of conversion of this purple complex to yellow $[Rh_2(\mu\text{-}CO)(CNBu^t)_4(DPM)_2](PF_6)_2$ (ref. 198). The dimer $[cp'_2Rh_2X_4]$ is cleaved by neopentylisocyanide to give $[cp'RhX_2(CNR)]$ (X = Cl, Br; R = CH_2Bu^t) whose further reactions are depicted in Scheme XII. In the same fashion, $[cp'RhI_2(CNR)]$ can be synthesized which on reduction by sodium amalgam in benzene/THF yields [cp'$_2$Rh$_2$(μ-C=NR)$_2$] proposed to contain a rhodium-rhodium double bond. The chloro and bromo



Scheme XII

analogs decompose under the same conditions. If the reduction of [cp'RhI$_2$-(CNR)] is carried out in the presence of more isocyanide the product is [cp'Rh(CNR)$_2$] which undergoes photolysis in deuterobenzene containing excess isocyanide according to Scheme XIII (ref. 199).



Scheme XIII

Cyclic voltammetric studies on [Rh$_2$(CNR)$_4$(DPM)$_2$](PF$_6$)$_2$ (R = Pr^i, Bu^n, Bu^s, Bu^t, cy) in dichloromethane show evidence for quasi-reservible, one-electron oxidation steps. Although most oxidized species appear to undergo subsequent chemical reactions, in some instances it is possible to reduce these products back to the starting dimers. In acetonitrile two oxidation processes are seen and in one instance the final product is proposed to be [Rh$_2$(CNBu^n)$_4$(MeCN)$_2$(DPM)$_2$]$^{4+}$ particularly since addition of iodide ion to the oxidized solution led to the isolation of $[Rh_2I_2(CNBu^n)_4(DPM)_2](PF_6)_2$ (ref. 200). Photolysis of $[Rh_2br_4]^{2+}$ in acetonitrile containing n-butyliodide at wavelengths longer than 550 nm occurs by a radical chain process to produce $[Rh_2br_4(Bu)(I)]^{2+}$ as the major product as depicted in Scheme XIV (ref 201).

$$[Rh_2br_4]^{2+} + BuI \xrightarrow{h\nu} [\cdot Rh_2br_4I]^{2+} + Bu\cdot$$

$$[Rh_2br_4]^{2+} + Bu\cdot \longrightarrow [\cdot Rh_2br_4(Bu)]^{2+}$$

$$[\cdot Rh_2br_4(Bu)]^{2+} + BuI \longrightarrow [Rh_2br_4(Bu)(I)]^{2+} + Bu\cdot$$

$$2[\cdot Rh_2br_4(Bu)]^{2+} \longrightarrow 2[Rh_2br_4]^{2+} + Bu\text{-}Bu$$

$$2[\cdot Rh_2br_4I]^{2+} \longrightarrow [Rh_4br_8I_2]^{4+}$$

Scheme XIV

The salts $[Rh(CNR)_4]^+(ATCNQ)^-$ (R = Ph, m-xylyl, mesityl) have been prepared by combination of salts of the corresponding ions. Some mixed ATCNQ/TCNQ salts were also made (ref. 202). The adsorption of methylisocyanide on Rh(1,1,1) at 120 K has been studied. The initial monolayer appears to consist mainly of {Rh(μ-CNMe)Rh} moieties with terminal coordination increasing as the coverage increases. This is in contrast to the behavior of carbon monoxide which favors initial terminal coordination. Also in contrast to experiments with carbon monoxide, heating of the isocyanide monolayer produces fragmentation before desorption occurs. It is thought that the initial process is cleavage of the carbon-nitrogen bond (ref. 203).

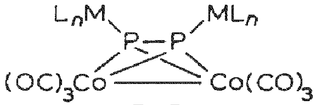
Metal Carbonyl Complexes and Related Compounds

a) Homonuclear Carbonyl Compounds

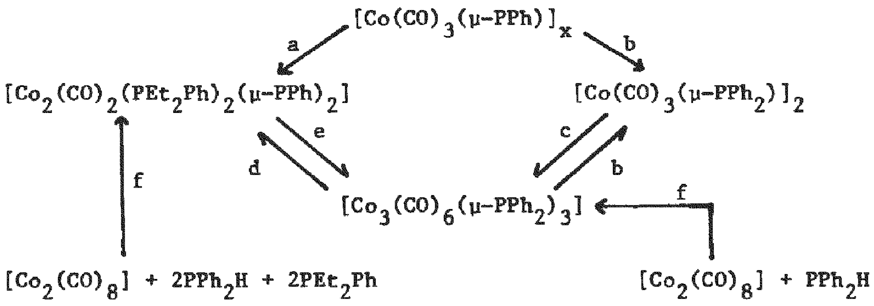
Low yields of $[HCo(CO)_4]$ and $[HCo(CO)_3PBu^n{}_3]$ are obtained from syngas (CO/H_2) and basic cobalt carbonate and Co_3O_4 plus tributylphosphine respectively in toluene but on addition of butyric acid the yields are markedly increased (ref. 204). A large scale, high yield synthesis of cobalt carbonyls is reported to use the reaction of syngas with cobalt(II) carbonate in isobutanol at elevated temperature and pressure (ref. 205). The reaction of $[HCo(CO)_4]$ plus carbon monoxide with styrene, α-methylstyrene and 1,1-diphenylethylene has been studied in n-octane and nujol. In the latter medium the rate is only slightly slower than in the former but carbonylation is significantly enhanced at the expense of hydrogenation which is taken as support for the intermediacy of a geminate radical pair (ref. 206).

Gamma irradiation of $[XCo(CO)_4]$ (X = H, D) in a krypton matrix at 77 K produces $[XCo(CO)_4]^{\pm}$ and some $[\cdot Co(CO)_4]$. Annealing the matrix at 100 K causes conversion to the unbridged form of $[Co_2(CO)_8]^{\pm}$ together with some $[\cdot Co_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}H)]$. Ultraviolet irradiation of $[HCo(CO)_4]$ at 77 K generates $[\cdot Co(CO)_4]$ and $[\cdot H_2Co(CO)_3]$ (refs. 207, 208). Infrared studies of $[HCo(CO)_4]$ and related complexes in frozen matrices suggests that in the absence of polarizing influences the hydrogen bears a partial negative charge. The ability of the molecule to act as a Brönsted acid despite the apparent hydridic character of the hydrogen is attributed to a weak cobalt-hydrogen bond; much as is the case with hydrogen iodide (ref. 209).

Reaction of $Na[Co(CO)_4]$ with $[L_nM(PCl_3)]$ affords [81] (ML_n = $Cr(CO)_5$, $W(CO)_5$, $cpMn(CO)_2$) in which there is effectively in situ generation and use of P_2 as an eight-electron ligand (ref. 210). Addition of chlorodiphenylphosphine to a THF solution of $Na[Co(CO)_4]$ at -60°C yields a species thought to be $[Co(CO)_4(PPh_2)]$ which on warming polymerizes to $[Co(CO)_3(\mu\text{-}PPh_2)]_x$, originally formulated by Hayter as a dimer. Workup of the supernatant in the dark does furnish a small amount of $[Co(CO)_3(\mu\text{-}PPh_2)]_2$ however. The polymer can also be formed from $[Co_2(CO)_8]$ and diphenylphosphine in toluene at room temperature. Further reactions of the polymer are depicted in Scheme XV. Also diethylphenylphosphine converts $[Co_3(CO)_6(\mu\text{-}PPh_2)_3]$ to



[81]



a) PEt_2Ph, Δ, THF. b) CO(1000 psi), Δ, toluene. c) hν, toluene.
d) PEt_2Ph, 140°C, toluene. e) CO, 25°C, toluene. f) Δ, toluene.

Scheme XV

$[Co_3(CO)_5(PEt_2Ph)(\mu\text{-}PPh_2)]_3$. The polymer, $[Co(CO)_3(\mu\text{-}PPh_2)]_x$ catalyzes the hydroformylation of hex-1-ene with a product ratio of straight-to-branched chain aldehydes that is greater than observed when $[Co_2(CO)_8]$ alone is the catalyst precursor. This would suggest that the active species is not that derived from $[Co_2(CO)_8]$ but the fact that $[Co_2(CO)_6(P(n\text{-hexyl})Ph_2)_2]$ was identified in the reaction solution also indicates that the diphenylphosphido bridge is not resistant to cleavage (ref. 211). Electrochemical oxidation of $[Co(CO)_4]^-$ generates $[\cdot Co(CO)_4]$ which then dimerizes to $[Co_2(CO)_8]$. When done in the presence of dimethylphenylphosphine, however, the product is $[Co(CO)_3(PMe_2Ph)_2]^+$. It is not certain whether this arises from initial formation of $[Co_2(CO)_8]$ followed by substitution and disproportionation, by disproportionation of $[\cdot Co(CO)_4]$ to $[Co(CO)_4]^-$ and $[Co(CO)_4]^+$ followed by substitution into the latter or by direct substitution into $[\cdot Co(CO)_4]$ followed by disproportionation. The same product could also be formed by electrochemical reduction of $[Co_2(CO)_6(PMe_2Ph)_2]$ to $[Co(CO)_3(PMe_2Ph)]^-$ and subsequent oxidation in the presence of ligand (ref. 212).

The conproportionation of $[Co_2(CO)_8]$ and $[Co_2(CO)_6L_2]$ to $[Co_2(CO)_7L]$ occurs thermally for L = PBu^n_3, PBu^t_3 and PMe_2Ph and photochemically for these plus those where L = $PMePh_2$, PPh_3 and $P(OPh)_3$. The thermal reaction is slow except for L = PBu^t_3 and Scheme XVI is suggested with either the

$$[Co_2(CO)_6L_2] \rightleftharpoons 2[\cdot Co(CO)_3L]$$

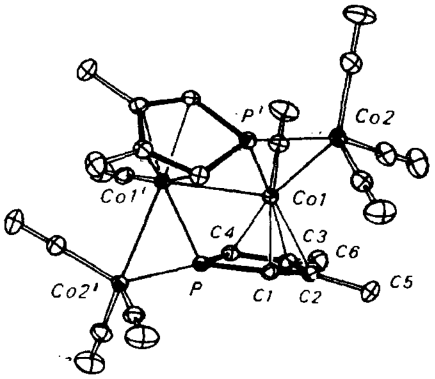
$$[\cdot Co(CO)_3L] + [Co_2(CO)_8] \longrightarrow [Co_2(CO)_8]^{\dot{-}} + [Co(CO)_3L]^+$$

$$[Co_2(CO)_8]^{\dot{-}} \longrightarrow [\cdot Co(CO)_4] + [Co(CO)_4]^-$$

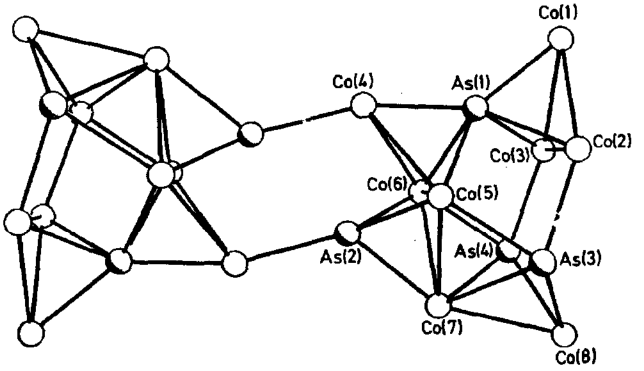
$$[Co(CO)_4]^- + [Co(CO)_3L]^+ \longrightarrow [Co_2(CO)_7L]$$

Scheme XVI

first or the second step being rate-determining. In the photochemical systems a photostationary state is reached which contains all three species but with the conproportionation product favored. The mechanism here is proposed to be the homolysis of both reactant species followed by recombination and cross-coupling. Once the product is formed, it also participates in this process (ref. 213). Several new phosphorus and arsenic ligands have been reacted with $[Co_2(CO)_8]$. The bulky ligand bis(bis(trimethylsilyl)-methyl)phosphine (L) forms $[LCo(CO)_3Co(CO)_4]$ (ref. 214) while 3,3',4,4'-tetramethyl-1,1'-biphospholyl fragments with the formation of [82]. Attempts to generate $[(\eta^5\text{-}Me_2C_4H_2P)Co(CO)_2]$ from [82] were unsuccessful (ref. 215). Extended reaction of $[Co_2(CO)_8]$ with cyclo-hexaphenylhexaarsenic in hot toluene yielded $[Co_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})(CO)_{16}]_2$ whose heavy-atom skeleton is shown in [83]. In this centrosymmetric complex As(3) and As(4) bear the phenyl groups, Co(1) and Co(8) each bear three carbonyl groups, Co(5) and Co(6) bear one carbonyl group each and the rest bear two each (ref. 216). The ferrocenylphosphine oligomers and polymers $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$ (x = 1-4), $Ph_2P[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$ (x = 1, 2) and $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xOH$ (mol. wgt. 8,900-161,000) react with $[Co_2(CO)_8]$ to give a variety of products. Those studied most were ones where the cobalt moieties were of the type shown in [84]. The oligomeric



[82]



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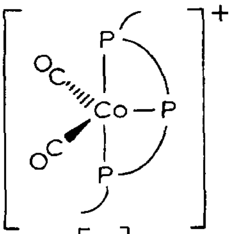
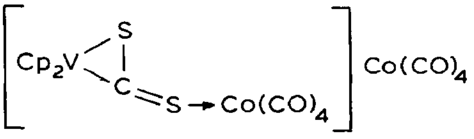


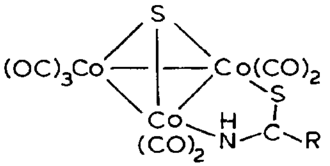
[84]

complexes catalyzed olefin hydroformylation with a product distribution very similar to analogous triphenylphosphine systems while the polymeric ones showed a lower selectivity to alcohol. This was suggested to be the result of inhibition of the aldehyde reduction step because of a greater tendency for the ligand to coordinate in a rigid tridentate fashion (ref. 217). Reaction of $[cp_2V(\eta^2-CS_2)]$ with $[Co_2(CO)_8]$ yields [85] (ref. 218) while

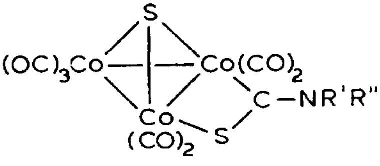


[85]

carbon disulfide itself reacts with $[Co_2(CO)_8]$ to give $[(OC)_9Co_3CC(O)SCCo_3(CO)_9]$ among other products. This complex was originally considered to be $[((OC)_9Co_3C)_2(CS)_2]$ because of disorder problems in the original structure determination (see J. Chem. Soc., Chem. Commun., (1978)841) (ref. 219). As with the previous reaction a variety of products results from reaction of $[Co_2(CO)_8]$ with carbon diselenide but these are not all analogs of those found in the carbon disulfide reaction. Products so far identified are $[Co_3(CO)_9(\mu_3-Se)]$, $[Co_4(CO)_{12}]$, $[Co_4(CO)_{10}Se_2]$, $[Co_6C_2(CO)_{14}Se_2]$ and $[Co_6C(CO)_{12}Se_2]$. The structure of the last consists of a trigonal prism of cobalt atoms centered by the carbide and capped by selenium on the triangular faces (ref. 220). Reaction of thioamides (RC(S)NR'R") with $[Co_2(CO)_8]$ in THF gives [86] (R = Me, Ph, p-anisyl; R' = R" = H) or [87] (R = H, Cl; R'



[86]



[87]

= R" = Me) (ref. 221). An attempt to prepare an alkoxycarbene complex of cobalt by reaction of $[Co_2(CO)_8]$ with phenyllithium followed by triethyloxonium tetrafluoroborate was unsuccessful and instead produced $[EtOCCo_3(CO)_9]$ (ref. 222).

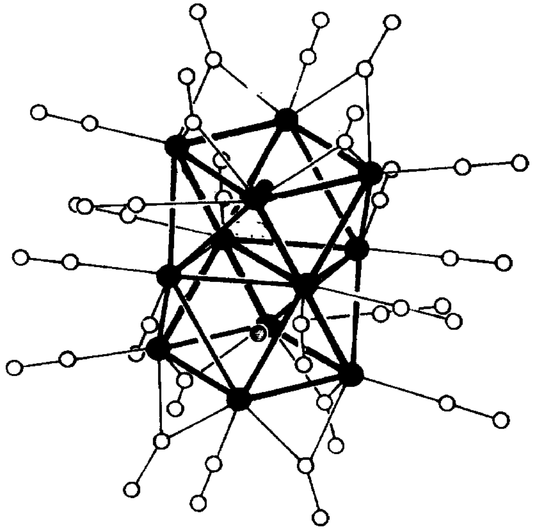
Dicobalt octacarbonyl mediates the conversion of alkyl peroxides or hydroperoxides to the corresponding alcohols and aldehydes or ketones. Both give similar product distributions but the hydroperoxides react much more rapidly (ref. 223). Thermal decomposition of $[Co_2(CO)_8]$ in toluene containing ethyl(2-hexyl) sodium sulfosuccinate forms a ferrofluid with a very narrow size distribution for the cobalt particles. This is thought to be the result of a diffusion-controlled growth from the decomposition of $[Co_4(CO)_{12}]$ which is formed as an intermediate (refs. 224, 225). A bottleneck in hydroformylation systems using $[Co_2(CO)_8]$ as the catalyst precursor is the slow rate of hydrogenation to $[HCo(CO)_4]$. Rate enhancements of up to three hundred-fold can be realized by the addition of bases such as pyridine and nitrogen-containing heterocycles (ref. 226). An infrared spectroscopic study of the reaction showed that under carbon monoxide the major product is $[Copy_6][Co(CO)_4]_2$ and that when dihydrogen is added this is reduced to $pyH[Co(CO)_4]$ more rapidly than is $[Co_2(CO)_8]$. Presumably this is in equilibrium with $[HCo(CO)_4]$ (ref. 227). Molecular electrostatic potentials have been used to map out the coordination sphere of a metal using $[HCo(CO)_4]$ as an example. The predicted bond angles and distances are in good agreement with experiment (ref. 228). A study of the vibronic activation of the carbonyl ligands in clusters, including $[Co_2(CO)_8]$ and $[Rh_6(CO)_{16}]$, suggests that bridging carbonyls are more destabilized than terminal ones (ref. 229). Charge density maps obtained from a low temperature determination of the crystal structure of $[Co_2(CO)_8]$ support a bonding model where the primary metal-metal interaction occurs through the bridging carbonyl ligands (ref. 230). The gas phase, multiphoton dissociation/ionization of $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ generates Co_2^+ ions (ref. 231).

Several papers report on the chemistry of alkylidynenonacarbonyltricobalt complexes. Reaction of $[BrCCo_3(CO)_9]$ with 2-hydroxyethyl α-methylacrylate yields $[CH_2{=}C(Me)C(O)OCH_2CH_2OC(O)CCo_3(CO)_9]$ which was polymerized to form a supported cluster. The related vinyl monomers $[\underline{p}\text{-}RC_6H_4CCo_3(CO)_9]$ (R = $CH{=}CH_2$, $CH_2{=}C(Me)C(O)$) were also prepared. Hydroformylation of hex-1-ene in the presence of $[PhCCo_3(CO)_9]$ at 100°C was studied but in contrast to claims by Pittman (J. Am. Chem. Soc., 99(1977)1986) no more than a 60% recovery of the cluster could be achieved. Further work suggested that some conversion of the cluster to $[Co_2(CO)_8]$ had occurred so that the actual catalysis may very well be carried out by species derived from this rather than by the cluster (ref. 232). Another heterogenized system, [Ⓟ-$C(O)CCo_3(CO)_9$] (Ⓟ = polystyrene-divinylbenzene copolymer) has been reported to catalyze the hydroformylation of hept-1-ene but again incomplete recovery occurred so that catalysis by the intact cluster is also doubtful (ref. 233). Heating $[HCCo_3(CO)_9]$ with FcHgCl in benzene yields $[FcCCo_3(CO)_9]$ as the major product. The substitution products $[FcCCo_3(CO)_8L]$ (L = PPh_3, Pcy_3, $P(OMe)_3$) and $[FcCCo_3(CO)_{9-n}L_n]$ (n = 2, 3; L = $P(OMe)_3$, $P(OPh)_3$) were prepared using appropriate quantities of the ligands in refluxing hexane. Cyclic voltammetric studies showed that $[FcCCo_3(CO)_9]$ underwent reversible one-electron oxidation (at iron) and reduction (at cobalt) steps. For the substituted derivatives the reduction step becomes irreversible but now the iron-oxidized species can be further oxidized at cobalt in a reversible, one-electron step. The data indicate the presence of largely localized valence sites with only weak interaction between them. The oxidation of $[FcCCo_3(CO)_9]$ can also be carried out chemically by silver perchlorate and $[FcCCo_3(CO)_9]ClO_4$ is isolated. Reaction of methylferrocene with the acylium ion $[C(O)CCo_3(CO)_9]^+$ gave a mixture of 1,2-, 1,3- and 1,1'-$[MeFcC(O)CCo_3(CO)_9]$ (refs. 234, 235). The radical anions $[YCCo_3(CO)_9]^{\cdot -}$, $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}F_3CC_2CF_3)]^{\cdot -}$, $[Co_2(CO_4)(C_6(CF_3)_6)]^{\cdot -}$ and $[Co_2Fe(CO)_9(\mu_3\text{-}S)]^{\cdot -}$ react with methyl iodide to give the neutral clusters, methyl radicals and iodide ion. The decrease in rate which occurs when the counterion is PPN or a crown ether-complexed sodium ion in place of the sodium ion itself is interpreted to indicate that the reaction proceeds most readily from a tight ion pair (ref. 236). A combination of photoelectron spectroscopic measurements and Fenske-Hall molecular orbital calculations on $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}RC_2R')]$ (R = H, Ph; R' = H, Ph), $[RCCo_3(CO)_9]$ (R = H, Ph) and $[Co_4(CO)_{10}(\mu_4\text{-}\eta^4\text{-}RC_2R')]$ (R = H, Ph; R' = Ph) have been used to probe the perturbation of carbyne fragments by attachment to metal atoms. The results indicate that there is increasing donation of charge to the carbyne carbon as the number of attached metal atoms increases. This is in contrast to previous work on the adsorption of alkynes on metal surfaces in which ligand-to-metal charge transfer was proposed to occur. The present authors conclude that either the complexes studied are not good models for the interaction of alkynes with metal surfaces or that the data in the earlier work were incorrectly interpreted (ref. 237). A second theoretical paper on alkylidynenonacarbonyltricobalt clusters and related species also concluded that the primary interaction of the alkylidyne moiety with the tricobalt unit involves metal-to-carbon backbonding using π-symmetry orbitals. The large energy difference calculated between the sp lone pair on the alkylidyne carbon and metal acceptor orbitals suggested that interaction between them should not be significant (ref. 238).

The complexes prepared from $[(\eta^3\text{-}2\text{-}MeC_3H_4)Co(CO)_2L]$ (L = PPh_3, $PBu^n{}_3$) and originally formulated as $[Co_3(CO)_6L_3]$ (J. Chem. Soc., Chem. Commun., (1969) 590. J. Organometal. Chem., 33(1971)73.) are now proposed to be $[Co_3(CO)_3L_3(\mu\text{-}CO)_3(\mu\text{-}H)_3]$ on the basis of a structure determination and reactions with carbon monoxide and deuterium which generate H_2 and HD respectively (ref. 239). Electrochemical studies on $[Co_4(CO)_{12-2n}(DPM)_n]$ (n = 0-2) show the existence of a reversible, one-electron reduction step while the last also undergoes a reversible, one-electron oxidation and a second, irreversible, one electron reduction (ref. 240). The temperature programmed thermal decomposition of $[Co_4(CO)_{12}]$ in flowing dihydrogen appears to be a complex process (ref. 241).

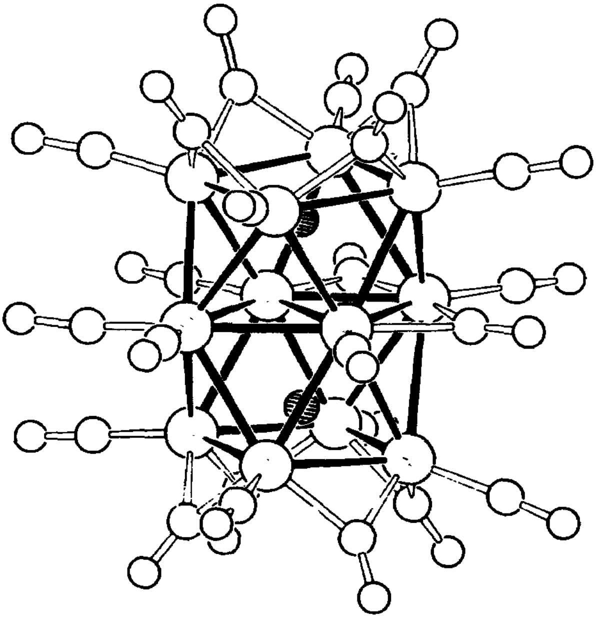
Reaction of $[M_4(CO)_9(TPM)]$ (M = Rh, Ir) with other phosphine ligands yields $[M_4(CO)_8L(TPM)]$ (L = PPh_3, $PPh_2(CH_2)_2Si(OEt)_3$) where substitution occurs at the vertex not coordinated to TPM. The complexes containing the siloxyphosphine could be attached to a silica surface. Supported $\{M_4(CO)_8(TPM)\}$ moieties could also be got by reaction of $[M_4(CO)_9(TPM)]$ with phosphinated silica or styrene-divinylbenzene copolymer (ref. 242). A low yield of $[Rh_6(CO)_{13}(L_3)]$ (L_3 = $MeSi(PBu^n{}_2)_3$) is obtained from the room temperature reaction of $[Rh_6(CO)_{16}]$ and the tripod ligand. In a similar fashion $[M_4(CO)_{12}]$ gives $[M_4(CO)_9(L_3)]$ (M = Co, Rh; L_3 = $MeSi(PR_2)_3$ (R = Et, Pr^n, Bu^n)). The rhodium complex (R = Et) readily decomposed. To obtain $[Ir_4(CO)_9(MeSi(PEt_2)_3)]$ from $[Ir_4(CO)_{12}]$, it was necessary to carry out the reaction in the presence of trimethylamine N-oxide. The yield was very low (ref. 243).

Brief heating of $K_2[Rh_6C(CO)_{15}]$ in isopropanol yields $K_2[Rh_{12}(C)_2(CO)_{24}]$ ([88]) which is isoelectronic with $[Rh_{12}(C_2)(CO)_{25}]$ but not isostructural since the latter has the two carbon atoms bonded together. Complex [88] reacts with methanolic sodium hydroxide under dinitrogen or dihydrogen to give a mixture of clusters including the paramagnetic and rather unstable

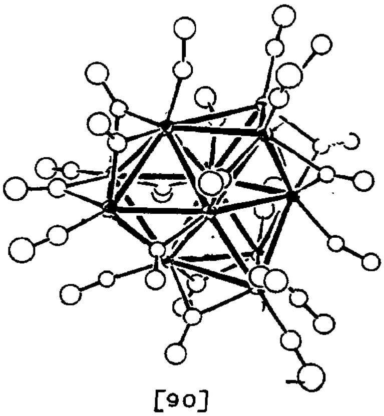


[88]

$[Rh_{12}(C)_2(CO)_{23}]^{3-}$ ([89]). In methanol containing a large excess of potassium hydroxide [88] forms $[Rh_{12}(C)_2(CO)_{23}]^{4-}$ which can also be got directly from $K_2[Rh_6C(CO)_{15}]$ in refluxing isopropanol. It is proposed that a regular metal-atom polyhedron is more demanding than an irregular one with respect to the number and distribution of ligands which can be attached. Thus ligands can be accommodated on the surface as long as a regular arrangement is possible. If further electron pairs are required to fill the cluster orbitals then the cluster will be an anion (refs. 244, 245). The anionic cluster, $[Rh_{11}(CO)_{23}]^{3-}$ ([90]) can be synthesized by a variety of

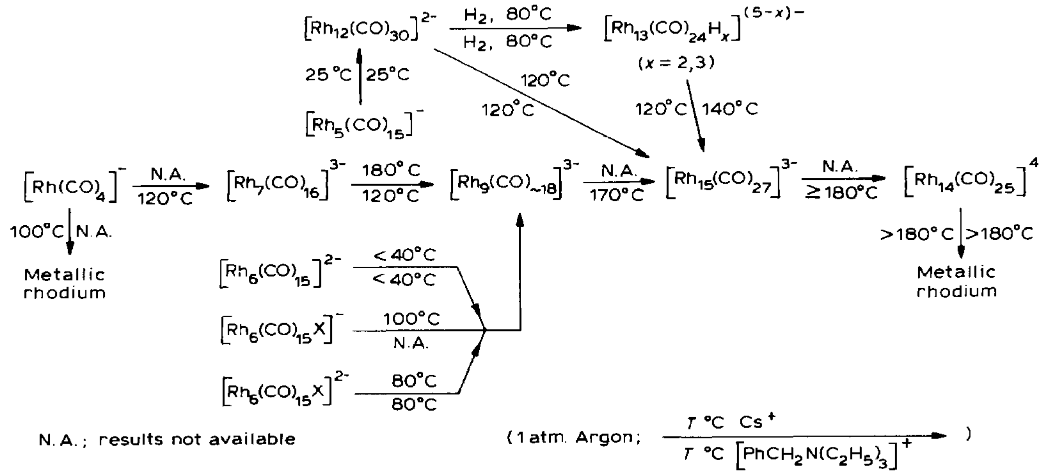


[89]



[90]

routes including reaction of $[Rh_7(CO)_{16}]^{3-}$ with iron(III) chloride in acetonitrile or with $[Rh_4(CO)_{12}]$, of $[Rh_5(CO)_{15}]^-$ with $[Rh_6(CO)_{15}]^{2-}$ and of $[Rh_4(CO)_{12}]$ with $[Rh(CO)_4]^-$ in a 2:3 ratio. On heating, [90] forms $[Rh_{14}(CO)_{25}]^{4-}$ among other products. Complex [90] is also seen initially in the reaction of $[Rh_4(CO)_{12}]$ or $[Rh_{12}(CO)_{30}]^{2-}$ with base at elevated temperature and therefore appears to be an important intermediate in the various reactions of rhodium carbonyls which produce high nuclearity clusters (ref. 246). Another study of the growth and decomposition of rhodium carbonyl clusters at elevated temperatures concludes that the course of the reaction depends on the identity of the cation which is used. The higher nuclearity clusters are more favored when benzyltrimethylammonium salts are present than when cesium salts are used. Also the identification of bibenzyl and triethylamine in systems using the former cation suggests it becomes involved in redox reactions with the rhodium carbonyls. Thus the growth of clusters could occur by the combination of metal carbonyl fragments generated by reduction of the starting complexes by the counterion although when clusters are the reactant it is uncertain whether this reduction precedes or parallels the thermal fragmentation of the starting cluster. In some instances it is likely that $[Rh(CO)_4]^-$ reacts with the counterion. An outline of the transformations studied is given in Scheme XVII (ref. 247).

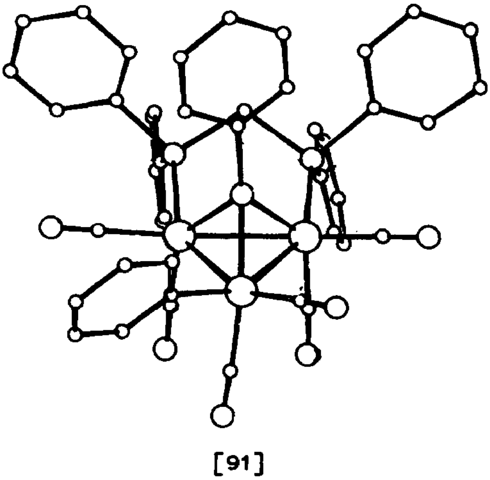


N.A.; results not available (1 atm. Argon; $\xrightarrow[T\ ^\circ C\ [PhCH_2N(C_2H_5)_3]^+]{T\ ^\circ C\ Cs^+}$)

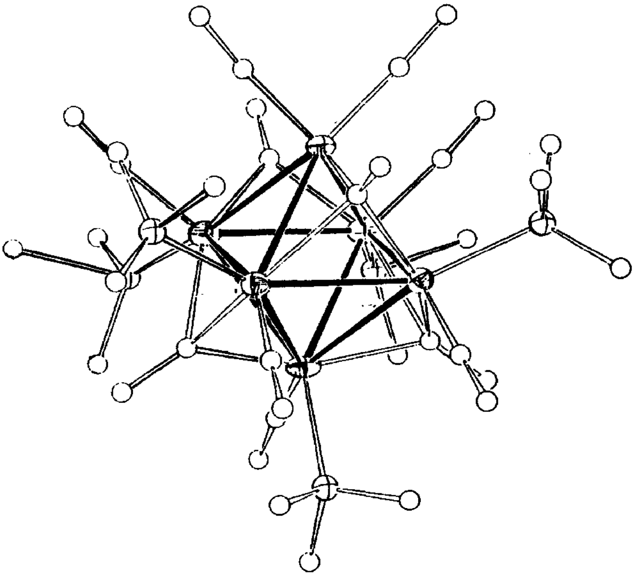
Scheme XVII

A reinvestigation of the interconversion of $[Rh_4(CO)_{12}]$ and $[Rh_2(CO)_8]$ under high pressures of carbon monoxide has been reported. The use of hexane rather than mineral oil as solvent permitted a higher concentration of the dimer to be achieved at low temperature. The thermodynamic parameters for the equilibrium were obtained and it was found that the initial rate of reaction of carbon monoxide with $[Rh_4(CO)_{12}]$ was much faster than with $[Co_4(CO)_{12}]$ (ref. 248). The ^{103}Rh and $^{13}C\{^{103}Rh\}$ NMR spectra of $[Rh_4(CO)_{12-n}(P(OPh)_3)_n]$ (n = 1-4) have been obtained. The apical rhodium atom resonates at lowest frequency and the mean of the ^{13}C chemical shifts for the carbonyl ligands shifts to lower field as the extent of substitution increases (ref. 249). The same group has also obtained variable-temperature ^{13}C, $^{13}C\{^{103}Rh\}$, $^{13}C\{^{31}P\}$ and ^{31}P NMR spectra for $[Rh_9E(CO)_{21}]^{2-}$ and $[Rh_{10}E(CO)_{22}]^{3-}$ (E = P, As) as well as for $[Rh_{12}Sb(CO)_{27}]^{3-}$. At elevated temperature complete fluxionality of the carbonyl groups and the metal atoms occurs in all clusters. At room temperature all are static except for the last which remains fluxional even at -97°C (ref. 250).

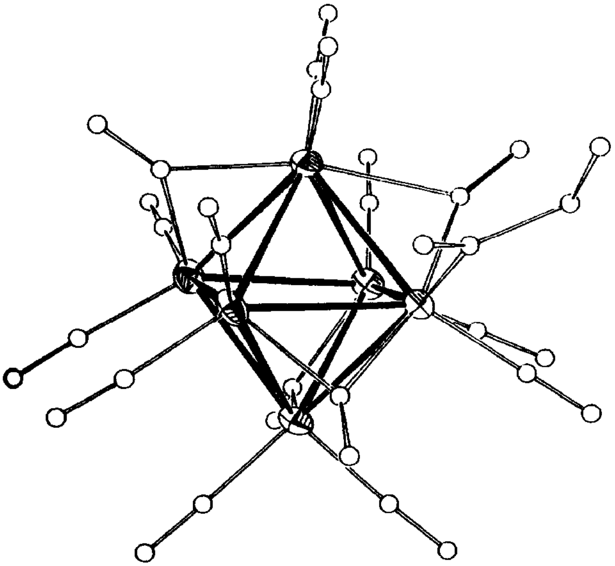
Only a low yield of the desired $[Ir_4(CO)_9(TPM)]$ was obtained from the reduction of $[IrCl(CO)_2(p\text{-toluidine})]$ with zinc and carbon monoxide in aqueous 2-methoxyethanol in the presence of TPM. Two other products were isolated, one of which is [91] in which the TPM ligand has fragmented (ref. 251). Two reactions of $[Ir_6(CO)_{16}]$ are those with trimethylphosphite in refluxing toluene which gives [92] (ref. 252) and with a 1:1:2 mixture of carbon monoxide, dihydrogen and ethylene in aqueous THF which forms $Ph_4P[Ir_6(CO)_{15}(COEt)]$ ([93]). Reaction of [93] with iodine in methanol generates methyl propionate (ref. 253). The low temperature ^{13}C and ^{31}P NMR spectra of $[Ir_4(CO)_{11}(PEt_3)]$ show that the complex contains three bridging carbonyl ligands in the basal plane and exists as a 7:1 mixture of axial and radial isomers ([94] and [95]). The complex is fluxional and the carbonyl scrambling process as determined from magnetization transfer experiments is proposed to involve the exchange $CO_b \rightarrow CO_d \rightarrow CO_a \rightarrow CO_f$ by a merry-go-round mechanism



[91]

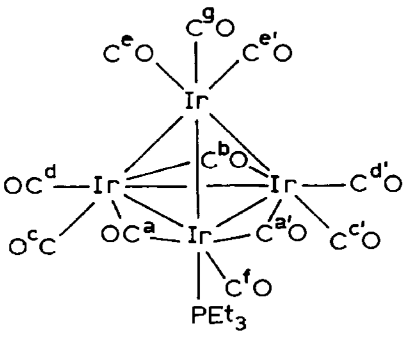


[92]

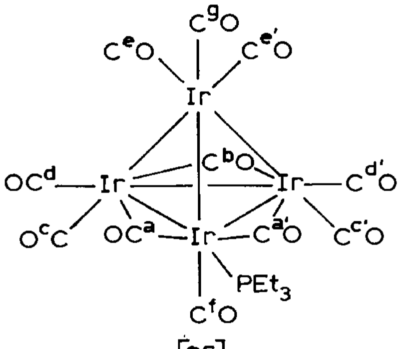


[93]

involving an all-terminal intermediate accompanied by a second process which also equilibrates these carbonyl groups with the axial CO_c and CO_e ligands. This is proposed to involve interconversions of [94] and [95] <u>via</u> the unbridged intermediate (ref. 254).



[94]



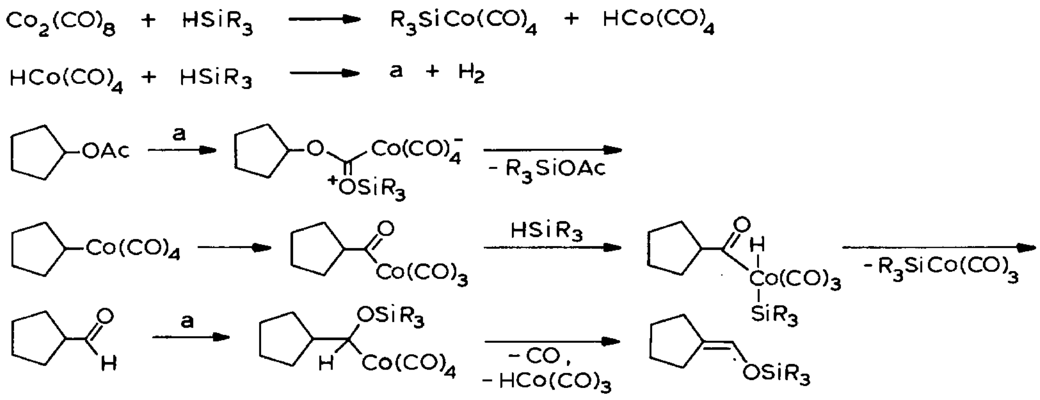
[95]

Two discussions of the electronic structures of metal carbonyl clusters, including those of the cobalt group have used the fragment molecular orbital (Extended Hückel) approach. In $[Rh_4(CO)_{12}]$ the π-backbonding to the bridging carbonyl ligands appears to be greater than to the terminal ligands (ref. 255). The existence of a greater number of bridging carbonyl ligands in clusters of the lighter elements is attributed to a lower ability of those metal t_{2g} orbitals to participate in π-backbonding to terminal carbonyl ligands thereby making them more available for forming pd hybrids appropriate for the formation of σ-bonds to bridging carbonyl ligands (ref. 256). A simple electron-counting rule for close-packed, high nuclearity clusters based on the extended Hume-Rothery rule has been applied to rhodium carbonyl clusters containing thirteen to twenty two metal atoms (ref. 257). Also reported is a generalized method for predicting the number of cluster valence molecular orbitals in condensed metal clusters (ref. 258).

A sizeable number of papers report the use of $[Co_2(CO)_8]$ and derivatives as catalyst precursors for a variety of organic transformations. For example 3,3-disubstituted penta-1,4-dienes are converted into the corresponding 3,3-disubstituted 2-methylcyclopentan-1-ones by syngas or under water-gas-shift conditions in the presence of $[Co_2(CO)_8]$ (ref. 259). A photochemical hydroformylation of olefins in methanol uses cobalt(II) acetate, $[Co_2(CO)_8]$ or $[Co_2(CO)_6(PBu^n{}_3)_2]$ as the catalyst precursor and a high selectivity to the linear aldehyde is found. The photolysis enhances the rate when internal olefins are used irrespective of the catalyst precursor but with terminal olefins it has no effect except to reduce the induction period when cobalt(II) acetate is the catalyst source (ref. 260). Butenes can be hydroformylated in the presence of $[HM(CO)_4]$ (M = Co, Rh) either alone or in the presence of monodentate phosphines (ref. 261) but when DPPE or $Bu^n{}_2P(CH_2)_4PBu^n{}_2$ is added, chelate complexes are formed which are inactive for propene hydroformylation. However at elevated temperature the complex of the latter ligand evidently undergoes ring opening to give a species with an activity comparable to that formed with tributylphosphine (ref. 262). Hydroformylation of ethylene with 1:1 mixtures of H_2 and D_2 in the presence of $[Co_2(CO)_8]$ or $[Rh_4(CO)_{12}]$ yields approximately 50% d_1 aldehyde implying that the formation of $\{MH_2\}$ or $\{MH_2(olefin)\}$ species does not occur. Rather it is proposed that activation of dihydrogen occurs on a metal alkyl or, more probably, a metal acyl complex. In light of the results reported in reference 87, however, it may be that hydridocarbonyl metal species are responsible for the hydrogenolysis step (ref. 263). A mixture of $[Co_2(CO)_8]$ and tri-*n*-dodecylphosphine is reported to catalyze the hydroformylation of propylene trimers with a selectivity to the alcohol of up to 80% (ref. 264).

The hydroformylation of acrylonitrile in methanol containing $[Co_2(CO)_8]$ has been investigated. At moderate temperature the product is the dimethylacetal but with increasing temperature, the yield drops and a greater percentage of products resulting from hydrogenation and hydrodimerization is seen. The thermal stability of the catalyst is improved and these side reactions are minimized by the addition of di(cyanomethyl)amine but with more basic amines, hydrogenation and hydrodimerization again predominate. Addition of phosphines to the catalyst system causes the major product to be 2-cyanoethylmethyl ether *via* a phosphine-catalyzed Michael addition of acrylonitrile and solvent (ref. 265). The carbonylation and hydrogenation of olefins or conjugated diolefins bearing electron-withdrawing groups occurs in the presence of $[HCo(CO)_4]$ with the latter process predominating at high temperature (ref. 266). A radical mechanism is proposed in the hydrogen-transfer from 9,10-dihydroanthracene or 9-fluorenol to 1,1-diphenylethylene mediated by $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$ (ref. 267). Attempts to effect the asymmetric hydrogenation of α,β-unsaturated ketones using $[Co_2(CO)_6L_2]$ (L = neomenthyldiphenylphosphine) gave only low optical yields (ref. 268). The hydrocarboxylation of hex-1-ene can be effected by treatment with carbon monoxide in aqueous dioxane in the presence of $[HCo(CO)_4]$ however if the water concentration is too high the system is inactivated (ref. 269). Condensation of amides with formaldehyde and carbon monoxide occurs in the presence of $[Co_2(CO)_8]$ to give N-acylaminodiacetic acids (ref. 270).

Reactions involving silicon include the conversion of phenylisocyanate to diphenylurea by bis(trimethylsilyl)amine in the presence of $[Rh_6(CO)_{16}]$ or $[Co_2(CO)_8]$ in which oxidative addition of a silicon-nitrogen bond to the metal is proposed (ref. 271) and the addition of trialkylsilanes to various species catalyzed by $[Co_2(CO)_8]$. For example, trialkylsilanes and alkyl acetates form [(trialkylsiloxy)methylene]alkanes in the presence of carbon monoxide and [$Co_2(CO)_8$] in benzene. Scheme XVIII illustrates the proposed mechanism for a typical reaction (ref. 272). The same workers also report a



a) $R_3SiCo(CO)_4$

Scheme XVIII

convenient synthesis of (E)-3-silylacrylates from the reaction of methylacrylate and $HSiR_3$ (R_3 = Et_2Me, Me_3, Me_2Ph) and the formation of 1,5-disiloxypentanes from the same silanes and THF, both in the presence of [$Co_2(CO)_8$] alone (refs. 273, 274). In the hydrosilylation of olefins catalyzed by [$Co_2(CO)_8$] or [$Rh_4(CO)_{12}$] instances of high selectivity and stereospecificity were attributed to an associative reaction of the olefin with a metal carbonyl hydride (ref. 275).

Continuing interest in C_1 chemistry is evidenced by several reports on studies of the mechanisms of carbon monoxide hydrogenation and methanol homologation. For the former process, a mechanism based on successive formation of formyl and formaldehyde complexes derived from [$HCo(CO)_4$] has been proposed with the nature of the products (methanol, methyl formate or ethylene glycol) depending on the mode of rearrangement of [$(H_2CO)Co(CO)_3$] which is considered to be a key intermediate (ref. 276). In methanol homologation using cobalt carbonyl systems the merits of various iodine sources as promoters as well as other additives have been discussed. Hydrated trichlorides of rhodium and iridium promote acetaldehyde formation in the presence of lithium iodide and [$Co(CO)_4$]$^-$. The function of the added metal is thought to facilitate the formation of [$CH_3Co(CO)_4$] according to Scheme XIX (ref. 277). A second paper reports that methyl iodide is better

$$MCl_3 + H_2O + CO \xrightarrow{I^-} [M(CO)_2I_2{}^-] + H^+$$

$$H^+ + I^- \longrightarrow HI$$

$$HI + CH_3OH \longrightarrow CH_3I + H_2O$$

$$CH_3I + [Co(CO)_4]^- \longrightarrow [CH_3Co(CO)_4] + I^-$$

Scheme XIX

than ionic iodides for the promotion of [$Co_2(CO)_8$] as a catalyst while a combination of the two exhibits a synergistic effect (ref. 278). A kinetic study of methanol homologation in a catalytic system prepared from [$Co_2(CO)_8$], iodine and tributylphosphine proposes the rate-determining step to be the reaction of methanol with a cobalt carbonyl complex. This is surprising since it is usually considered that in iodide-promoted systems the activation of methanol proceeds as outlined in the final three steps of Scheme XIX (ref. 279). A final paper on this subject reports on the optimum conditions for the conversion of methanol to acetaldehyde using a catalyst derived from cobalt(II) acetate and iodine under high pressure (ref. 280).

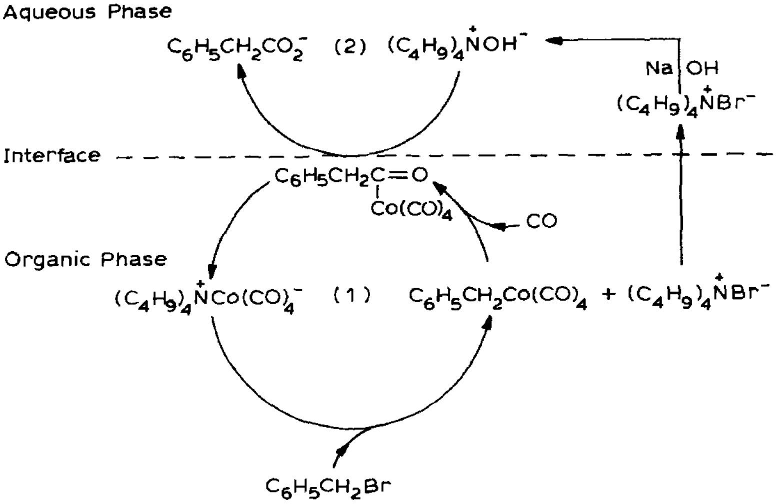
Several papers report on the carbonylation of alkyl halides to the corresponding carboxylic acid derivatives both in homogeneous systems and in two-phase systems under phase-transfer conditions. In methanol or isobutanol containing catalytic quantities of [$Co_2(CO)_8$] esters are formed according to Scheme XX (R = Bu^n, $HOCH_2$, MeC(O), MeO_2C, CN; R' = Me. R = Ph; R' =

$$RCH_2Cl + CO + [Co(CO)_4]^- \longrightarrow [RCH_2C(O)Co(CO)_4]$$

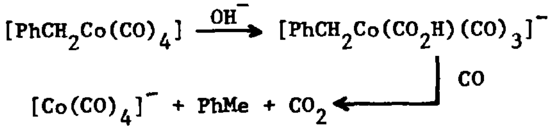
$$[RCH_2C(O)Co(CO)_4] + R'OH \xrightarrow{base} RCH_2CO_2R' + [Co(CO)_4]^-$$

Scheme XX

Me, Bu^i) (refs. 281, 282). In phase-transfer systems the results seem to be rather variable. Using benzyl bromide and H_2O/C_6H_6 or $CH_2Cl_2/NaOH/Bu^n{}_4NBr/CO/[Co(CO)_4]^-$ the product is phenyl acetate and the rate is strongly dependent on the stirring rate. Scheme XXI is proposed and the rate-determining step is thought to be the cleavage of [$PhCH_2C(O)Co(CO)_4$] by tetrabutylammonium hydroxide at the interface. Toluene is formed as a by-product possibly via Scheme XXII (ref. 283). With optically active α-phenethyl halides in $H_2O/S/PhMe_3NBr/NaOH/CO/[Co_2(CO)_8]$ (S = Bu^nOH, Am^tOH, Bu^tOMe) carbonylation also occurs but the product has the opposite configuration and considerable racemization occurs. The results are interpreted in terms of the processes



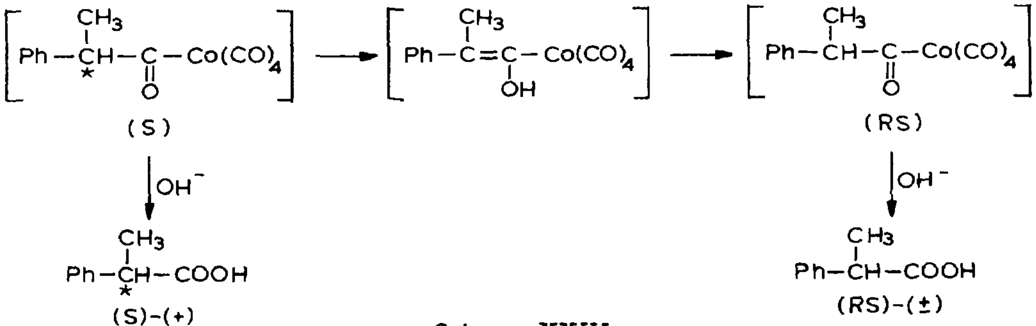
Scheme XXI



$$[PhCH_2Co(CO)_4] \xrightarrow{OH^-} [PhCH_2Co(CO_2H)(CO)_3]^- \xrightarrow{CO} [Co(CO)_4]^- + PhMe + CO_2$$

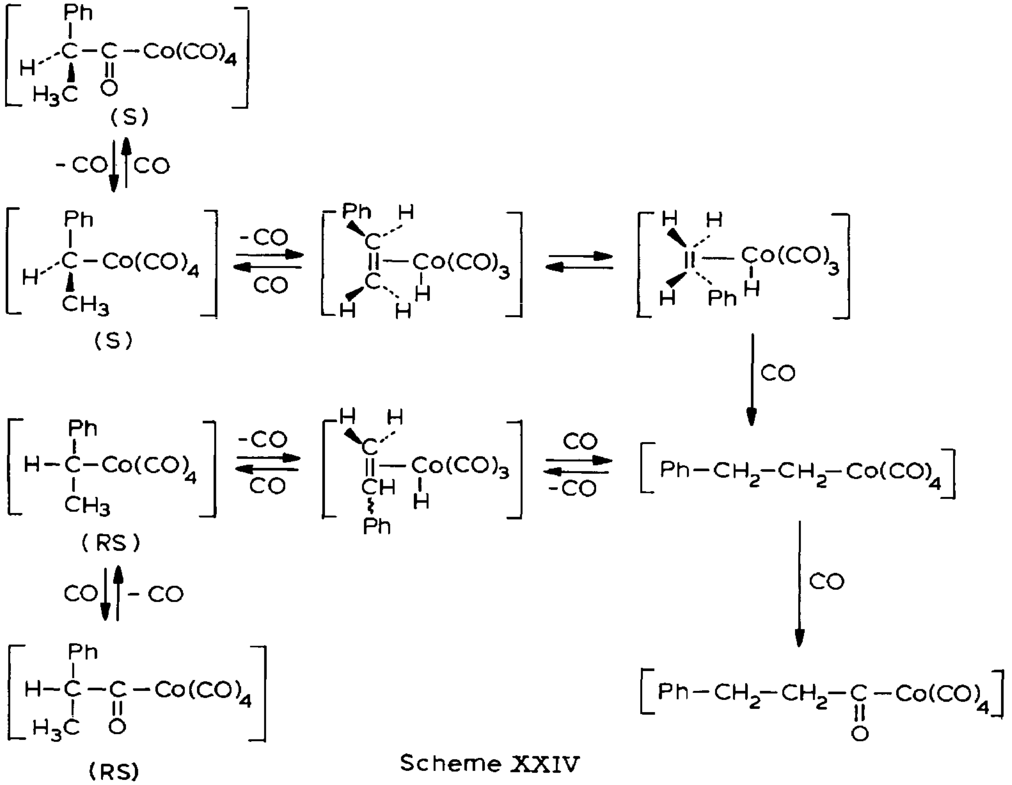
Scheme XXII

of Schemes XXIII and XXIV. The significant inhibition of the double carbonylation of α-phenethylbromide which is noted when the benzylic hydrogen is



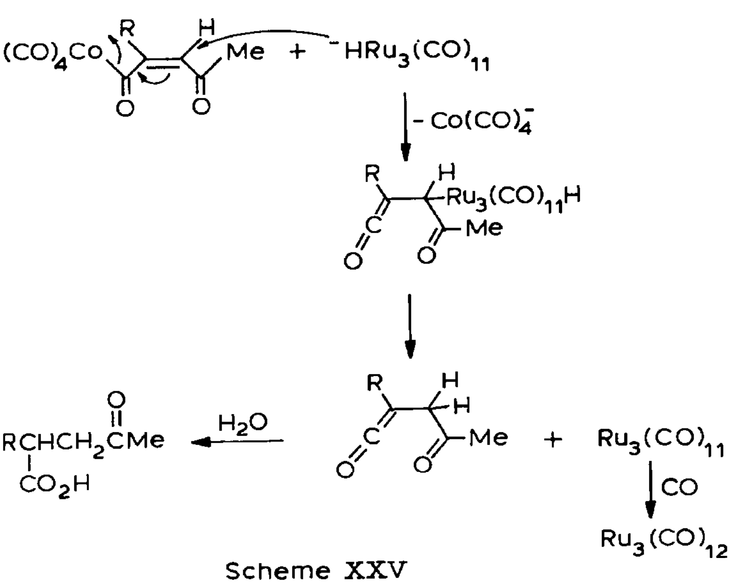
Scheme XXIII

replaced by deuterium is taken to support the enolic intermediate of Scheme XXIII (ref. 284). By contrast, the reaction of α-phenethylbromide in toluene containing $[Co_2(CO)_8]/CO/NaOH/H_2O/bzEt_3NCl$ forms 2,3-diphenylbutane (rac:meso = 1.13:1.00) rather than carbonylation products. Evidently a radical mechanism operates and it is proposed that either $[PhCHMeCo(CO)_4]$ forms and undergoes homolysis of the cobalt-carbon bond or radicals are generated directly by electron-transfer from $[Co(CO)_4]^-$ to the α-phenethylbromide (ref. 285). The phase-transfer-catalyzed carbonylation of aryl and vinyl halides to the corresponding acids has been reported to occur under photolytic conditions (refs. 286, 287).



Scheme XXIV

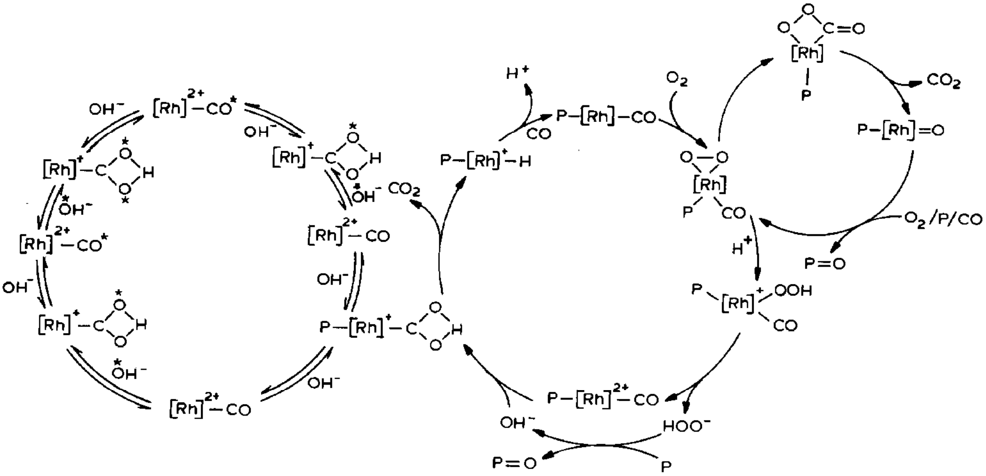
Under acidic conditions ($H_2O/HBF_4/C_6H_6/NaX/[Co_2(CO)_6L_2]$ (X = 4-dodecylbenzenesulfonate; L = CO, PBu^n_3)) 1,1-diarylethylenes can be hydrogenated to the corresponding ethanes in high yield. It is presumed that $[HCo(CO)_3L]$ is formed initially (ref. 288). The azadienes RHC=CR'CH=NR" are converted by the phase transfer system $H_2O/C_6H_6/bzMe_3NCl/CO/MeI/[Co_2(CO)_8]$ to a mixture of the amides RCH=CR'CH(NHR")C(O)Me and R"NHC(O)Me (R = Ph; R' = H; R" = p-tolyl. R = Ph; R' = Me; R" = p-ClC_6H_4) (ref. 289). Carbonylation of the mixture $[Co_2(CO)_8]/C_6H_6/H_2O/NaOH/(dodecyl)Me_3NCl$ followed by addition of methyl iodide and subsequent addition of $[Ru_3(CO)_{12}]$ and 1-alkynes affords the γ-keto acids $RCH(CO_2H)CH_2C(O)Me$ (R = Ph, p-tolyl, p-anisyl, cy). The proposed function of the $[Ru_3(CO)_{12}]$ is indicated in Scheme XXV. In the absence of $[Ru_3(CO)_{12}]$ the products are but-2-enolides (ref 290). The aminoalkynes $R_2NCH_2C{\equiv}CH$ (R_2N = Et_2N, morpholino) are carbonylated to $R_2NC(O)C(Me){=}CHC(O)NR_2$ in the presence of $[Co_2(CO)_8]$ (ref. 291) while in the presence of rhodium carbonyls plus tertiary phosphines cycloheptatriene is converted to diformylcycloheptanes. In the absence of phosphine, rhodium or



Scheme XXV

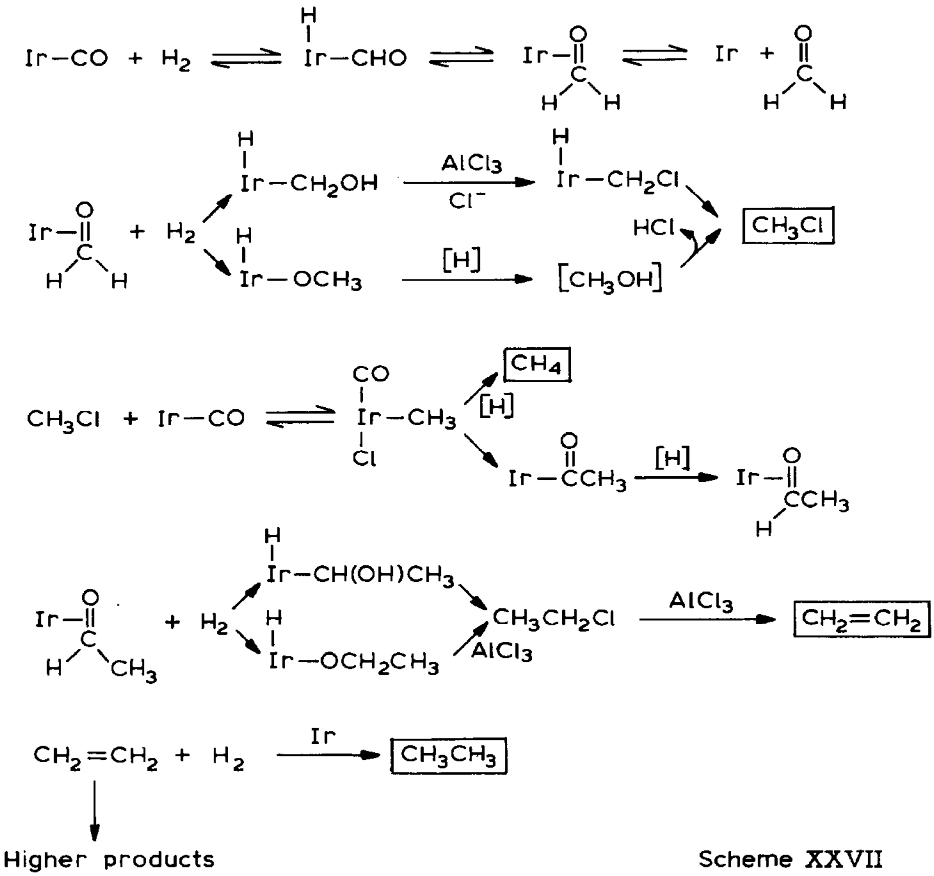
cobalt carbonyls give more active catalysts but only one formyl group is introduced (ref. 292).

Under water-gas-shift conditions $[Rh_6(CO)_{16}]$ serves as a catalyst precursor for the synthesis of butan-1,4-diol from allyl alcohol. Up to 65% yield can be realized when N,N,N',N'-tetramethyl-1,3-propanediamine is added presumably because it can coordinate to the metal and prevent cyclization of an intermediate metal acyl complex. Use of 4-dimethylaminopyridine in place of the diamine channels the reaction to reasonable yields of γ-butyrolactone (ref. 293). The addition of sodium carbonate to $[Rh_4(CO)_{12}]$ generates a better catalyst than is the carbonyl itself for the carbonylation of diphenylacetylene in ethanol to high yields of 5-ethoxy-3,4-diphenyl-2(5H)-furanone. Diethyl-2,3-diphenylsuccinate and 3-(ethoxycarbonyl)-2-phenylindanone are also formed in small quantities. Related species are obtained from other acetylenes and alcohols and an ethoxycarbonylrhodium complex of unknown nuclearity is proposed as an intermediate (ref. 294). Reaction of $[Rh_6(CO)_{16}]$ with (-)-DIOP in refluxing benzene yields $[Rh_6(CO)_{10}((-)\text{-DIOP})_3]$ which has been used to catalyze the hydrogenation of prochiral olefins. Optical yields were generally less than 50% (ref. 295). Other rhodium carbonyls have been reported to catalyze the homologation of methanol to ethanol when amines are present (ref. 296) and the reduction of nitrobenzene under water-gas-shift conditions in the presence of phenanthroline derivatives (ref. 297). The hydrodenitrogenation and other reactions catalyzed by cobalt-molybdenum oxide catalysts have been modeled using homogeneous systems based on $[Rh_6(CO)_{16}]$. Hydrogen exchange and transalkylation reactions of tertiary amines appear to proceed in similar fashion with both catalysts but in the hydrodenitrogenation of pyridine in the presence of carbon monoxide and water the rhodium complex yields $H_2C(CH_2CH_2R)_2$ (R = piperidinyl) while the heterogeneous catalyst yields $R(CH_2)_4Me$ (ref. 298). The addition of carbon-hydrogen bonds of benzene, furan, thiophene, and N-methylpyrrole to diphenylacetylene is catalyzed by species derived from $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ giving the appropriately trisubstituted olefins. The catalytic addition of benzene to diphenylketene and various isocyanates was also effected. Oxidative addition of the carbon-hydrogen bond to a metal carbonyl species is proposed to occur initially. This is said to be followed by coupling of the aryl fragment with the acetylene or other unsaturated molecule with subsequent reductive elimination (ref. 299). Under carbon monoxide $[Rh_6(CO)_{16}]$ forms a catalyst for the oxidation of triphenylphosphine to its oxide by dioxygen at elevated temperature. In benzene solution infrared spectroscopic evidence was found for the formation of $[Rh_2(CO)_2(PPh_3)_2(C_6H_6)_2]$ and its conversion to $[Rh_2(CO)_6(PPh_3)_2]$ and then $[Rh_4(CO)_{10}(PPh_3)_2]$. These transformations occur at room temperature but to regenerate $[Rh_6(CO)_{16}]$ requires raising the temperature. In the presence of water, the yield of carbon dioxide is increased relative to triphenylphosphine oxide which suggests that attack of water or hydroxide ion on a coordinated carbonyl group occurs at some point in the cycle. On the basis of labelling studies the catalysis is thought to occur according to Scheme XXVI (O* = ^{18}O label; [Rh] = rhodium cluster of possibly variable



Scheme XXVI

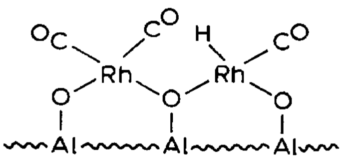
nuclearity) (ref. 300). The hydrogenation of carbon monoxide catalyzed by $[Ir_4(CO)_{12}]$ in an aluminum chloride/sodium chloride melt has been reinvestigated using both recycle and single-pass flow systems. The major products are methane, ethane and methyl chloride. Also when the iridium complex is introduced into the melt a burst of methane production occurs suggesting that the active catalyst is generated by the initial reduction of one carbonyl group per cluster. Scheme XXVII presents the proposed mechanism.



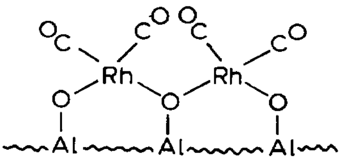
Scheme XXVII

Although the results of the new study are reasonably similar to those originally reported by Muetterties, several notable differences are seen including the presence of methyl chloride and the absence of a high initial activity and hydrocarbon products containing more than three carbon atoms. Evidently the active species in the present work is different from that in the earlier study but the data are insufficient to indicate what the difference may be (ref. 301).

Studies of supported metal carbonyl catalysts include those of $[Co(CO)_4]^-$ on anion exchange resins for the carbonylation of organic halides (ref. 302) and those on cobalt carbonyl moieties attached to phosphinated polymers or silica for olefin hydroformylation (refs. 303, 304). Three more studies report on the use of $[Co_2(CO)_8]$ to form alumina-supported catalysts for the homologation of methanol to paraffins (C_1-C_{12}) (ref. 305), the dehalogenation of α-bromo sulfoxides (ref. 306) and the Fischer-Tropsch synthesis of hydrocarbons (ref. 307). On silica $[MeCCo_3(CO)_9]$ physisorbs and undergoes a slow reaction with dioxygen to give decarbonylated products. On alumina it initially physisorbs and then reacts to give species readily converted to carbonate, bicarbonate and Co(II) by dioxygen. The complex adsorbs inside the super cages of Na-Y zeolites but otherwise behaves as on alumina (ref. 308). Polystyrene-supported $[Co_4(CO)_8(\mu\text{-}CO)(\mu_4\text{-}PPh)_2]$ is more active than the unsupported species for hex-1-ene hydroformylation but less thermally stable (ref. 309). No reaction appears to occur when $[Rh_4(CO)_{12}]$ is supported on zinc oxide but on heating in a hydrogen atmosphere both metallic rhodium and metallic zinc (possibly an alloy) are formed. By contrast, heating in a syngas atmosphere produces various supported rhodium carbonyls but the support remains unchanged (ref. 310). The interaction of rhodium cluster carbonyls with alumina surfaces appears to involve initial reaction with surface hydroxyl groups to give [96] which on treatment with carbon monoxide liberates dihydrogen to form [97]. The exchange of carbon monoxide with these and related supported carbonyl species have been studied and in some instances the observation of both slow and fast exchange rates was interpreted to indicate that some of the rhodium exists in pores of the support. Treatment of [97] with a carbon monoxide/water vapor stream generates carbon dioxide and reduces the rhodium to Rh(0) carbonyl species presumably physisorbed on the support. At low temperature and a high CO/H_2O ratio $[Rh_6(CO)_{16}]$ is regenerated but under more strenuous conditions agglomeration of metallic rhodium particles occur (refs. 311-314). Deposition of $[Ir_4(CO)_{12}]$ on alumina by a soxhlet extraction technique provides a widely dispersed layer of iridium carbonyl species probably similar to those described above for rhodium (ref. 315). Decomposition of such samples by heating in vacuo ultimately yields a deposition of iridium metal which has been used to catalyze hydrogen-deuterium exchange. The maximum activity is seen when no carbonyl ligands remain (ref. 316).



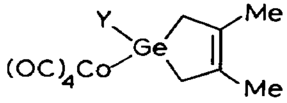
[96]



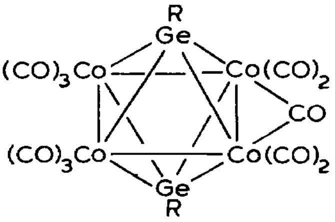
[97]

b) Heteronuclear Metal-Metal Bonded Compounds

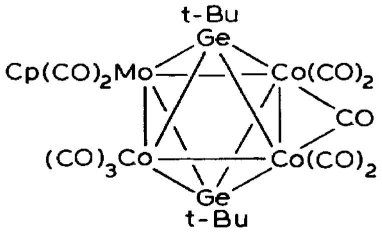
Displacement of chloride in $[O(SiMe_2CH_2)_2SnCl_2]$ by $M[Co(CO)_4]$ (M = Li, Na) yields $[O(SiMe_2CH_2)_2SnCl_m(Co(CO)_4)_n]$ (m = n = 1; m = 0, n = 2). Related complexes can be got from $[Me_2Si(OSiMe_2CH_2)_2SnCl_2]$ while with $[Cl_2Sn(CH_2SiMe_2OSiMe_2CH_2)_2SnCl_2]$ is obtained $[((OC)_4Co)_2Sn(CH_2SiMe_2OSiMe_2CH_2)_2Sn(Co(CO)_4)_2]$ (ref. 317). Dicobalt octacarbonyl reacts photolytically with neat $(CF_3)_3GeH$ to give $[(CF_3)_3GeCo(CO)_4]$ (ref. 318) while with GeF_2 in ether the product is $[F_2Ge(Co(CO)_4)_2]$. In refluxing THF the reaction of GeF_2 with $[Co_2(CO)_6L_2]$ (L = PPh_3, $P(OPh)_3$) gives the analogous $[F_2Ge(Co(CO)_3L)_2]$ while with one equivalent of $[Ph_3SiCo(CO)_4]$ the unstable $[Ph_3SiGe(F)_2Co(CO)_4]$ is formed which subsequently decomposes to Ph_3SiF and $[FGeCo(CO)_4]$ which is the first example of a germylene containing a germanium-transition metal bond. The last reaction using two equivalents of the cobalt complex yields $[:Ge(Co(CO)_4)_2]$. These germylenes add to 2,3-dimethylbuta-1,3-diene to give the germacycle [98] (Y = F, $Co(CO)_4$). Complex [98] (Y = $Co(CO)_4$) can also be synthesized from $[I_2GeCH_2C(Me)=C(Me)CH_2]$ and $Na[Co(CO)_4]$ and on thermolysis regenerates the diene and $[:Ge(Co(CO)_4)_2]$ (ref. 319). Trihalogermanes react with $K[Co(CO)_4]$ in refluxing cyclohexane to yield mixtures of $[RGeCo_3(CO)_9]$ and [99] (R = Me, Bu^t, Ph). Heating [99] (R = Bu^t) with $[cpMo(CO)_3]_2$ in benzene forms [100] (ref. 320). The He(I) and He(II) photoelectron spectra of $[L_3MCo(CO)_4]$ (M = Si, Ge, Sn, Pb; L = Cl, Br, Me) have been measured and bands involving the Co–M bond identified (ref. 321).



[98]



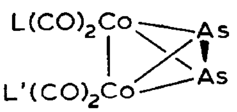
[99]



[100]

In benzene, $[Zn(Co(CO)_4)_2]$ reacts with $[ZnN(Me)_2(CH_2)_2CH_2]$ to give $[CH_2(CH_2)_2(Me)_2NZnCo(CO)_4]$ (ref. 322). A full report of the reduction of the complexes $[CoCl(L_4)]BPh_4$ ($L_4 = E(CH_2CH_2PPh_2)_3$ (E = N,P)) by sodium amalgam has appeared. The initial product is $[(Co(L_4))_2(\mu\text{-}Hg_2)]$ which reacts with carbon monoxide and sodium tetraphenylborate to give $[Co(CO)(L_4)]BPh_4$ and with carbon dioxide under the same conditions to yield the carbonyl complex plus unidentified, carbonate-containing species (ref. 323). Sodium amalgam reduction of $Hg[Co(CO)_4]_2$ followed by successive additions of tetramethylammonium chloride and more of the mercury-cobalt carbonyl complex yields $Me_4N[Hg(Co(CO)_4)_3]$ which on further reaction with triphenylphosphine and $[Ni(ophen)_3]^{2+}$ gives $Hg[Co(CO)_3(PPh_3)]_2$ and $[Ni(ophen)_3][Co(CO)_4]_2$. Cadmium and zinc analogs were prepared in similar fashion as were the complexes $PPN[Hg(Co(CO)_4)_2ML_n]$ (ML_n = $cpFe(CO)_2$, $cpW(CO)_3$), $PPN[M'(Co(CO)_4)(ML_n)_2]$ (ML_n = $cpCr(CO)_3$, $cpW(CO)_3$; M' = Zn, Cd) and $Bu^n{}_4N[M(Co(CO)_4)(cpW(CO)_3)]$ (M = Zn, Cd, Hg). The formation of the mixed anions appears to be reversible (ref. 324). The vibrations ν_{Co-C} and δ_{Co-CO} have been assigned in $[Co_2(CO)_8]$, $[HgCl(Co(CO)_4)]$, $Hg[Co(CO)_4]_2$ and some of their axially substituted derivatives (ref. 325). Rare-earth derivatives of $[Co(CO)_4]^-$ can be got from anhydrous trihalides and $Na[Co(CO)_4]$ or $Hg[Co(CO)_4]_2$. These are formulated as $[Cl_2MCo(CO)_4]$ (M = Ho, Dy, Yb, Sm). The holmium complex reacts with triphenylphosphine to give $[Cl_2HoCo(CO)_3(PPh_3)]$ (ref. 326). Related species, formulated as $[M(Co(CO)_4)_3]\cdot nTHF$ (n = 1-4; M = Sm, Tm, Yb), are prepared from $[Co_2(CO)_8]$ and a mercury amalgam of the appropriate metal (ref. 327). In toluene the reaction of $[cpMH_2]$ (M = Mo, W) with $[Co_2(CO)_8]$ yields $[cpMH(CO)][Co(CO)_4]$ plus $[Co_4(CO)_{12}]$ (ref. 328) while $Na[Co(CO)_4]$ simply displaces chloride from the carbyne complex $[ClW(CPh)(CO)_4]$ to give $[(OC)_4CoW(CPh)(CO)_4]$ in which the $\{Co(CO)_4\}$ moiety appears to have approximately C_{3v} symmetry (ref. 329).

Complex [101] (L = L' = CO) forms the unstable adducts [102] in low yield



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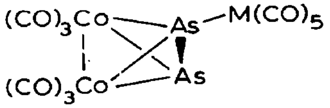
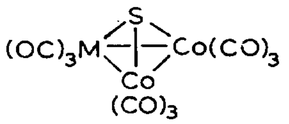


[102]

on reaction with $[M(CO)_5(THF)]$ (M = Cr, Mo, W). From [101] (L = L' = CO) the derivatives having L = PMe_3, $P(OMe)_3$; L' = CO and L = L' = PMe_3, $P(OMe)_3$; L = PMe_3, L' = $P(OMe)_3$ can be prepared on reaction with the appropriate ligands. Several of these add $\{M(CO)_5\}$ moieties to either one or both arsenic atoms but no heteronuclear metal-metal bonded species could be generated (ref. 330). The same workers found however that $[Me_2AsM'cp(CO)_3]$ (M' = Mo, W) would replace a carbonyl group on cobalt in [103] (M = Fe, Ru) and the product on refluxing in benzene rearranged to [104].



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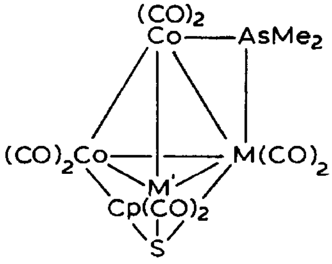
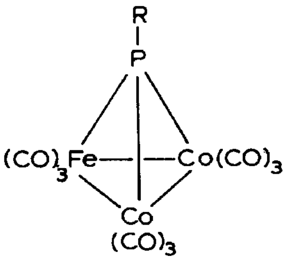


[104]

An analogous reaction with [105] (R = Me, Bu^t, Ph) initially gave [106] (R = Bu^t; M = Mo, W) and then [107]. With the others the observed product was



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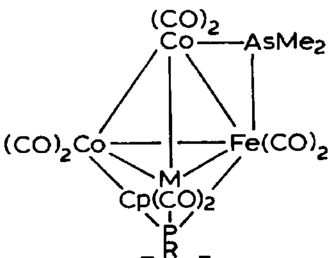

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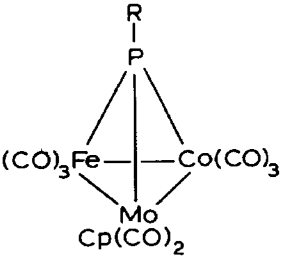
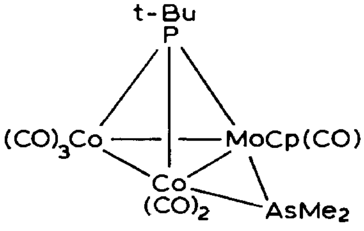


[107]

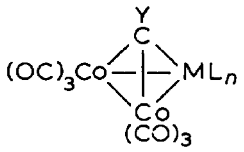
[107]. Reaction of [$Bu^tPCo_3(CO)_9$] with [$cpMo(CO)_3AsMe_2$] however gave [108]



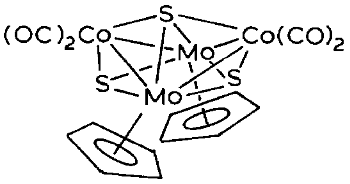
[108]

(refs. 331, 332). An alternative to the tedious and sometimes unpredictable thermal syntheses of similar mixed-metal clusters is the electron-transfer catalyzed formation of [109] (Y = Me, Ph, H; ML_n = cpFe(CO), cpM'(CO)$_2$ (M' = Cr, Mo, W)) from [$YCCo_3(CO)_9$] and [$ML_n(CO)$]$_2$ in the presence of catalytic amounts of sodium benzophenone ketyl. Complex [109] (Y = Ph; ML_n = cpMo(CO)$_2$) can also be generated by controlled potential electrolysis of [$PhCCo_3(CO)_9$] in the presence of [$cpMo(CO)_3$]$_2$ (ref. 333). Reduction of the polymeric species [$cp_2Mo_2S_x$]$_n$ with lithium triethylborohydride yields [$cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$] which on reaction with [$Co_2(CO)_8$] gives the butterfly-type cluster [110] (ref. 334). On the other hand direct reaction of [$cp'_2Cr_2S_5$]

or $[\mathrm{cp'_2Mo_2S_4}]$ with $[\mathrm{Co_2(CO)_8}]$ yields $[\mathrm{cp'_2M_2Co_2(\mu_3\text{-}S)_4(CO)_2}]$ (M = Cr, Mo)



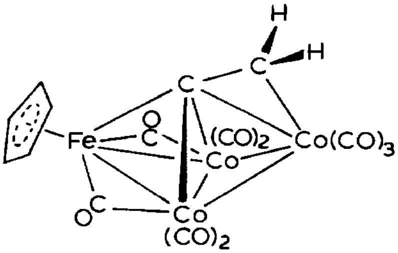
[109]



[110]

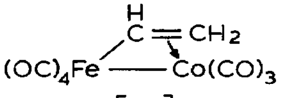
which contains a cubane-type $\{\mathrm{M_2Co_2S_4}\}$ core (ref. 335).

The vinylidene-bridged dimer trans-$[\mathrm{cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)}]$ reacts with $[\mathrm{Co_2(CO)_8}]$ in diethyl ether at room temperature to give a variety of products including $[\mathrm{Co_4(CO)_{12}}]$, $[\mathrm{cpFeCo(CO)_4(\mu\text{-}CO)_2}]$, $[\mathrm{cp_2Fe_2(CO)_2(\mu\text{-}CO)_2}]$ and [111] (ref. 336). By contrast, the vinyl-bridged dimer $[\mathrm{PPh_4}][\mathrm{Fe_2(CO)_6}$-

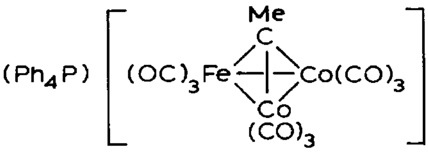


[111]

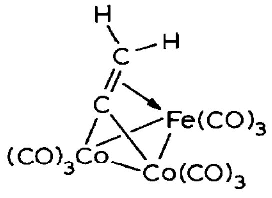
$(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{CH{=}CH_2})]$ and $[\mathrm{Co_2(CO)_8}]$ in dichloromethane yield [112], [113] and $[\mathrm{PPh_4}][\mathrm{Co(CO)_4}]$. Complex [112] converts to [113] on reaction with $[\mathrm{PPh_4}]$-$[\mathrm{Co(CO)_4}]$ while protonation of [113] with trifluoroacetic acid yields $[\mathrm{MeCFeCo_2(CO)_9H}]$. In refluxing hexane [112] forms $[\mathrm{MeCCo_3(CO)_9}]$, [114] and [115] (ref. 337).



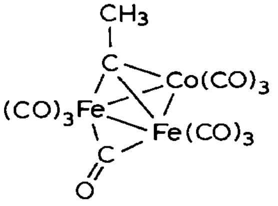
[112]



[113]

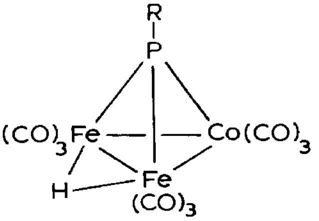


[114]

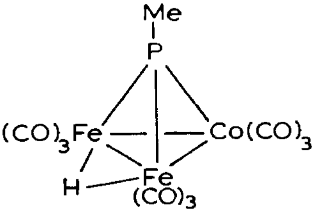


[115]

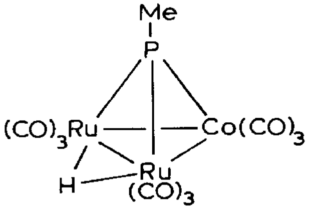
Several other cobalt-iron and -ruthenium clusters have been obtained from $[(OC)_4Fe(\mu\text{-}PHR)Co(CO)_3]$ (R = Me, Bu^t, Ph) which can be prepared from $[Co_2(CO)_8]$ and $[Fe(CO)_4(PRH_2)]$ or, in one instance, from $K[Co(CO)_4]$ and $[Fe(CO)_4(PHMeCl)]$. Its reaction with $[(\eta^3\text{-}C_3H_5)Co(CO)_3]$ yields [105] while in refluxing benzene with $[M_3(CO)_{12}]$ (M = Fe, Ru) the products are [116] (R = Me, Bu^t) and a mixture of [117] and [118] respectively. Heating $[(OC)_4Fe(\mu\text{-}PHR)Co(CO)_3]$ in tetrahalomethanes yields $[(OC)_4Fe(\mu\text{-}PRX)Co(CO)_3]$ (R = Me; X = Cl, Br. R = Bu^t; X = Br) which on reaction with $K[ML_n]$ (ML_n = $Mn(CO)_5$, $cpFe(CO)_2$) affords [119] (R = Me, Bu^t). In refluxing toluene complexes [119] convert to [120] (R = Me, Bu^t) and [121] (R = Bu^t) respectively (refs. 338, 339). In related work, $[Fe_2(CO)_6(\mu\text{-}PHR)_2]$ (R = Me, Ph) reacts with $[Co_2(CO)_8]$ to form a mixture of [122], [123] and $[Co_4(CO)_{12}]$. The two mixed-metal clusters evidently are formed by separate pathways since [122] is not a precursor to [123] (ref. 340).



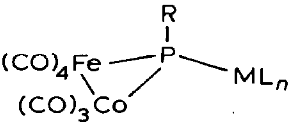
[116]



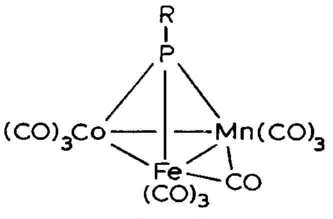
[117]



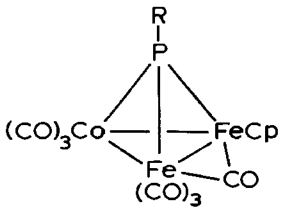
[118]



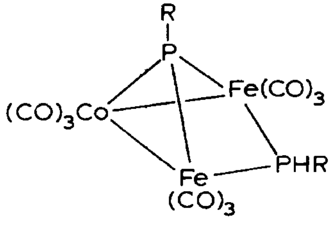
[119]



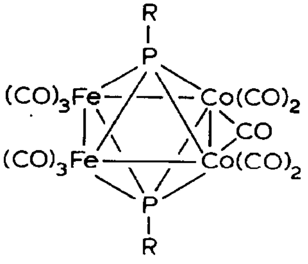
[120]



[121]

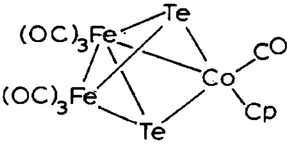


[122]

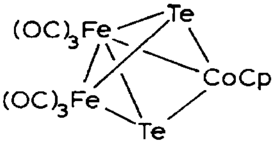


[123]

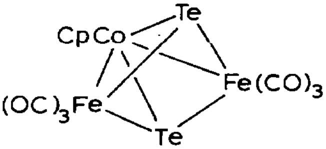
The reactions of nitrosyl hexafluorophosphate with iron-cobalt and ruthenium-cobalt clusters are complex and only infrequently were nitrosyl ligands observed in the products. More frequently reduction of the nitrosyl cation appeared to occur. Thus with PPN$[Fe_3Co(CO)_{13}]$ in dichloromethane the products were $[Fe_3(CO)_{12}]$, $[Fe_4N(CO)_{11}(NO)]$ and $[FeCo_2(CO)_9(\mu_3\text{-}NH)]$ while with $Et_4N[FeCo_3(CO)_{12}]$, the μ_3-imido cluster and $[Co_4(CO)_{12}]$ formed. The only product identified from reaction with PPN$[CoRu_3(CO)_{13}]$ was $[CoRu_3N(CO)_{12}]$ while conversion of the PPN salt to PPN$[H_2CoRu_3(CO)_{12}]$ by reaction with dihydrogen and subsequent treatment with nitrosyl hexafluorophosphate afforded $[HRu_3(CO)_{10}(NO)]$, $[H_4Ru_4(CO)_{12}]$, $[Ru_3(CO)_{12}]$, $[H_3CoRu_3(CO)_{12}]$, $[H_2Ru_4(CO)_{13}]$ and $[H_2Ru_3(CO)_9(\mu_3\text{-}NH)]$ (ref. 341). Reaction of $[Fe_3Te_2(CO)_9]$ with $[cpCo(CO)_2]$ in refluxing acetonitrile yields [124] which is further converted to a mixture of [125] and [126] on decarbonylation with trimethylamine N-oxide. Regeneration of [124] is difficult, requiring carbonylation



[124]

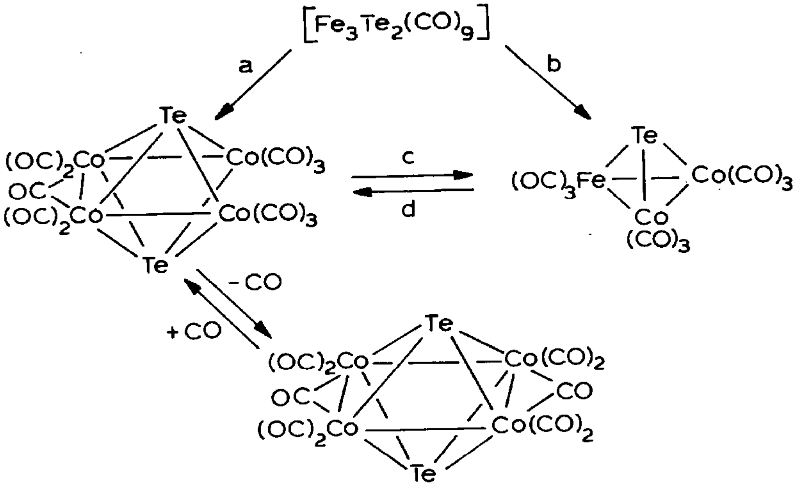


[125]



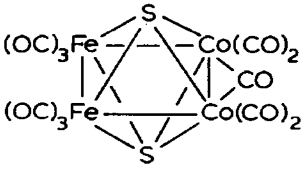
[126]

at 2000 psi. Other chemistry of $[Fe_3Te_2(CO)_9]$ is outlined in Scheme XXVIII. The reactions of [127] with $[Co_2(CO)_8]$ and $[cpMo(CO)_3]_2$ were also described. In the first the product was [103] (M = Fe) while the second gave a species analogous to [107] but capped by a sulfur atom rather than by a phosphido group (ref. 342).



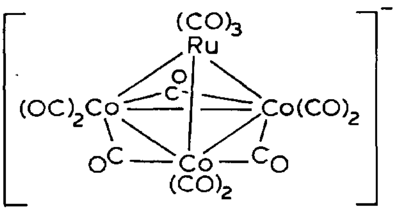
a) $2[Co_2(CO)_8]$, 150°C, CO(2000 psi), CH_2Cl_2, 24 h. b) $2[Co_2(CO)_8]$, 180°C, CO(1700 psi), hexane, 4 h. c) $[Fe(CO)_5]$, 180°C, CO(1300 psi), hexane, 4 h. d) $[Co_2(CO)_8]$, 140° C, CO(1900 psi), hexane, 48 h.

Scheme XXVIII



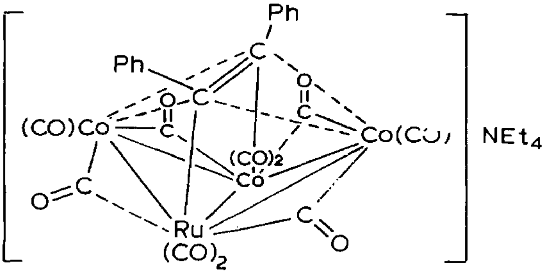
[127]

Several preparations of the monoanionic cluster [128] have appeared with the best (90% yield) being the reaction of $[Co_2(CO)_8]$ with $Et_4N[RuCl_4(MeCN)_2]$ in refluxing THF. The yields of the PPN and sodium salts from $M[Co(CO)_4]$ (M = PPN, Na) and hydrated ruthenium(III) chloride in refluxing THF decrease in that order and in all three syntheses other clusters are formed as well. In the second synthesis some of these have been identified as $[Ru_3(CO)_{12}]$, $PPN[Ru_3Co(CO)_{13}]$ and $PPN[Ru_4Cl_4(CO)_{10}]$. Protonation of $Na[RuCo_3(\mu\text{-}CO)_3(CO)_9]$ with phosphoric acid yields $[HRuCo_3(CO)_{12}]$ while

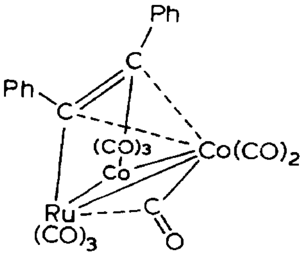


[128]

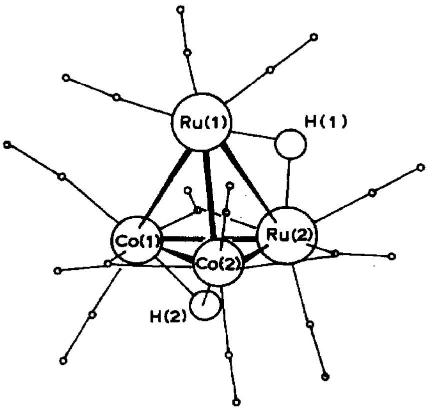
reaction with [AuCl(PPh$_3$)] gives [(PPh$_3$)AuRuCo$_3$(CO)$_{12}$]. By contrast PPN[RuCo$_3$(μ-CO)$_3$(CO)$_9$] does not react with the gold complex but in refluxing acetone it does react with diphenylacetylene to give the butterfly cluster [129] from which a {Co(CO)} fragment can be removed by reaction with hydrogen chloride to give [130]. The sodium salt of [128] provides a catalyst for the homologation of methanol with syngas to form ethanol and dimethylether as the major products. Other catalyst precursors studied were [Co$_2$(CO)$_8$], [M$_4$(CO)$_{12}$] (M = Co, Rh), [M$_3$Co(CO)$_{13}$]$^-$ (M = Fe, Ru), [FeCo$_3$(CO)$_{12}$]$^-$, [RhCo$_3$(CO)$_{12}$] and [Rh$_2$Co$_2$(CO)$_{12}$] (refs. 343-345). Hydrogenation of [Ru$_2$Co$_2$(CO)$_{13}$] in hot hexane yields [131] while under comparable conditions diphenylacetylene gives [132] suggesting that hydrogen prefers the ruthenium



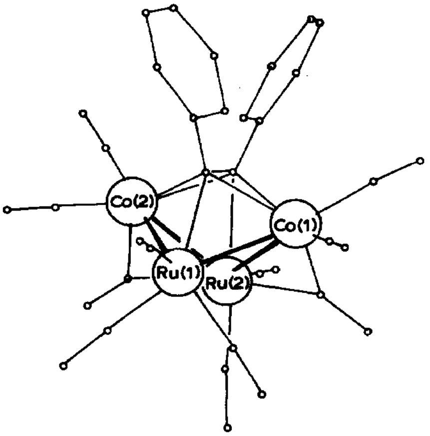
[129]



[130]

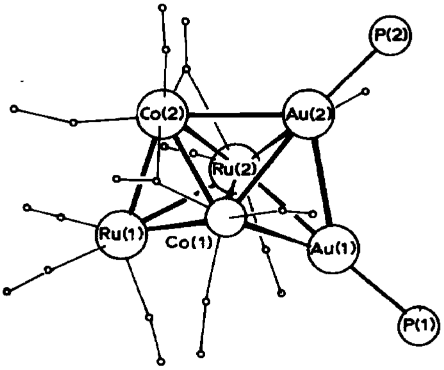


[131]



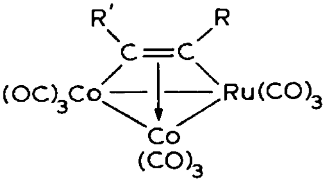
[132]

sites while the acetylene attacks at cobalt. Deprotonation of [131] with potassium hydride yields $[Ru_2Co_2(CO)_{12}]^{2-}$ which then reacts with [AuCl-(PPh_3)] to afford [133] which is postulated to form in a stepwise fashion

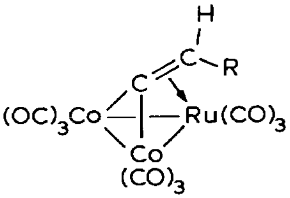


[133]

(refs. 346, 347). Complex [103] (M = Ru) can be synthesized by reaction of $[(OC)_4RuCo_2(CO)_6(\mu\text{-}CO)]$ with hydrogen sulfide or diethyl sulfide. Analogs capped by methylphosphide or -arsenide moieties were got using methylphosphine or -arsine. Reaction of $[(OC)_4RuCo_2(CO)_6(\mu\text{-}CO)]$ with acetylenes gives [134] (R = R' = H, Ph. R = H; R' = Ph), which rearranges to [135] (R' = H;

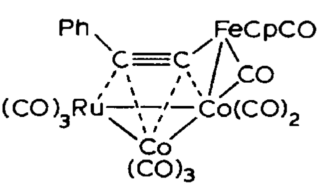


[134]

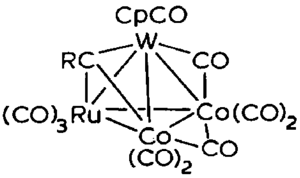


[135]

R = H, Ph) in refluxing hexane. The same cluster also reacts with [cpFe-$(CO)_2(C{\equiv}CPh)$] and $[cpW(CR)(CO)_2]$ (R = p-tolyl) to give [136] and [137]



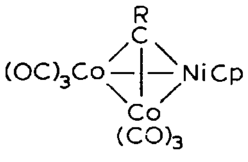
[136]

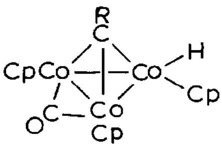


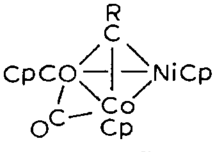
[137]

respectively while with $K[Co(CO)_4]$ followed by acidification with phosphoric acid $[HRuCo_3(CO)_{12}]$ is formed (refs. 348, 349). Chloride displacement from $[cpRuCl(PPh_3)_2]$ by $Tl[Co(CO)_4]$ forms $[cpRu(Co(CO)_4)(PPh_3)_2]$ which provides a catalyst for the homologation of methanol with a high selectivity to ethanol. Similar results were obtained using a mixture of $[cpRuCl(PPh_3)_2]$ and $[Co_2(CO)_8]$ (ref. 350).

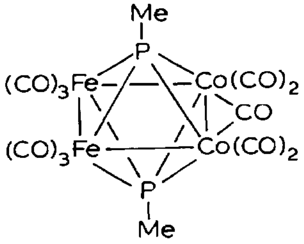
Extended reaction of $[RCCo_3(CO)_9]$ ($R = CO_2Pr^i$) with $[cp_2Ni]$ at room temperature in THF yields [138] while at reflux the products are [139] plus [140] (ref. 351). The reaction of [105] (R = Me) with $[cpNi(CO)]_2$ for short

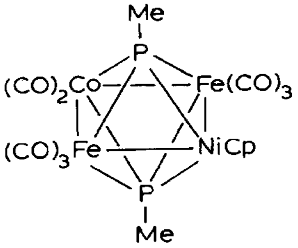

[138]


[139]

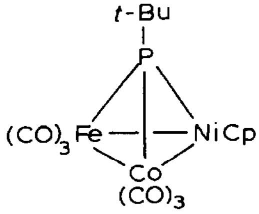

[140]

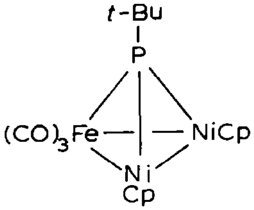
times in refluxing benzene yields a metal mirror, $[cpCo(CO)_2]$ and [141] plus [142] while when $R = Bu^t$ the products after longer reflux are [143], [144]

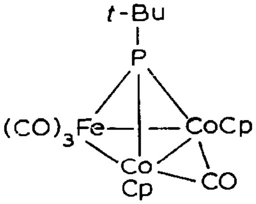

[141]


[142]

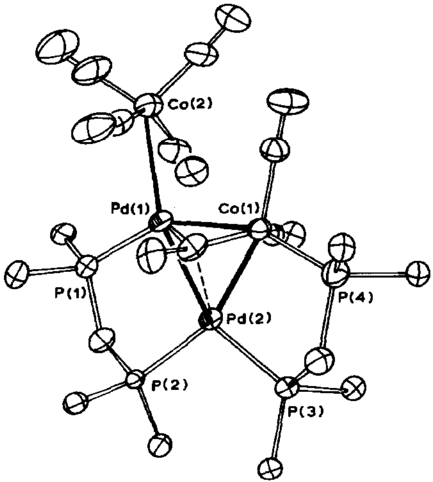
and [145] plus a metal mirror and $[cpCo(CO)_2]$ (ref. 352). From $[ClCCo_3(CO)_9]$ and $[Ni_6(CO)_{12}]^{2-}$ are obtained the clusters $[Co_3Ni_9(C)(CO)_{20}]^{3-}$,


[143]


[144]

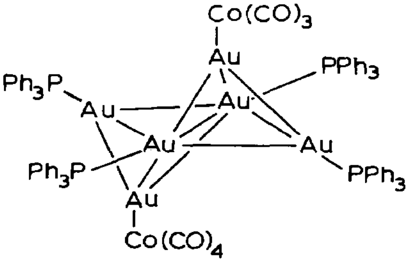

[145]

$[Co_3Ni_7(C_2)(CO)_{15}]^{3-}$ and $[Co_6Ni_2(C_2)(CO)_{16}]^{2-}$. The first is found to have a core consisting of a carbide-centered tetracapped square antiprism of metals apparently randomly distributed. The other two have cores approximating two trigonal prisms of metals sharing an edge and a square face respectively. Carbon-carbon distances for the carbide moieties are 1.43Å for the second and 1.49Å for the last. While $[Co_3Ni_9(C)(CO)_{20}]^{3-}$ reacts with carbon monoxide to give $[Co(CO)_4]^-$ and $[Ni(CO)_4]$ (no carbide derived species identified) its reaction with syngas generates ethane implicating the intermediate formation of $[Co_3Ni_7(C_2)(CO)_{15}]^{3-}$ (refs. 353, 354). Attempts to generate cobalt-nickel clusters from mononuclear precursors such as $[NiCl_2(DPPE)_2]$ and $Na[Co(CO)_4]$ were unsuccessful. Among the products identified were $[Ni(CO)_2(DPPE)]$, $[Co_2(CO)_6(DPPE)]$ and $[(OC)_3Co(\mu-CO)_2Co(CO)-(DPPE)]$ (ref. 355). The tetrametallic cluster $[Pd_2Co_2(CO)_7(DPM)_2)]$ ([146])



[146]

is synthesized by the low temperature reaction of $[Co(CO)_4]^-$ with $[PdCl-(DPM)]_2$ and provides another example of ligand mobility in DPM-bridged dimeric complexes (ref. 356). Clusters formulated as $[Pt_2Co_2(\mu-CO)_3(CO)_5-(PPh_3)_2]$, $[Pt_3Co_2(\mu-CO)_5(CO)_4(PPh_3)_3]$ and $[Pt_5(\mu-CO)_5(CO)(PPh_3)_4]$ are reported to be formed on reaction of $[Co_2(CO)_8]$ with a species given as $[PtCl(PPh_3)_2]$. What this latter species really is is uncertain. Evidently there is a typographical error in the original paper or in the abstract. The first cluster provides an active catalyst for the hydroformylation of hex-1-ene but its integrity in the catalyst system was not established (ref. 357). Reaction of $[Au_8(PPh_3)_7](NO_3)_2$ with $Li[Co(CO)_4]$ forms [147] (ref. 358).



[147]

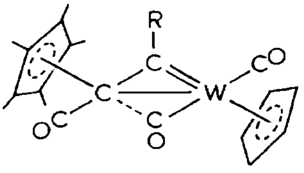
A 65% yield of $[cp_2Rh_2(CO)_2(\mu\text{-}CO)]$ results when concentrated pentane solutions of $[cpRh(CO)_2]$ are photolyzed. Some reactions of this dimer are outlined in Scheme XXIX (ref. 359). An effectively heterobimetallic oxidative addition of methyl iodide occurs regiospecifically with $[cp'Rh(\mu\text{-}PMe_2)_2Mo(CO)_4]$ forming $[cp'Rh(Me)(\mu\text{-}PMe_2)Mo(CO)_3I]$ which is proposed to contain a rhodium-to-molybdenum donor bond. The iodide ligand occupies an equatorial site on molybdenum and readily dissociates in polar solvents (ref. 360).

$$\begin{tikzcd}
 & {[cpRh(CO)_2] + [cpRh(CO)(TCNE)]} & \\
{[cpRh(\mu\text{-}CO)]_3} & {[cp_2Rh_2(CO)_2(\mu\text{-}CO)]} \arrow[l, "c"'] \arrow[r, "b"] \arrow[u, "a"'] \arrow[d, "d"'] & {[cpRh(CO)(\mu\text{-}SnCl_2)]_3} \\
 & {[cp_2Rh_2(CO)_2(HgCl_2)(\mu\text{-}CO)]} &
\end{tikzcd}$$

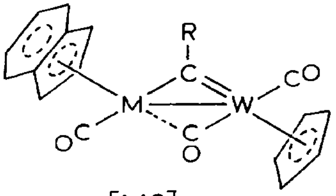
a) TCNE, benzene. b) $SnCl_2$. c) MCl_2 (M = Pd, Pt). d) $HgCl_2$, acetone.

Scheme XXIX

The carbyne complexes $[cpW(CR)(CO)_2]$ (R = Me, p-tolyl) react with $[cp'Co(CO)_2]$ in refluxing toluene or with $[(\eta^5\text{-}C_9H_7)M(C_2H_4)_2]$ (M = Rh, Ir) following carbonylation in petroleum ether to yield [148] (R = p-tolyl) and [149] (R = p-tolyl; M = Rh, Ir. R = Me; M = Rh) respectively. Analogous species,

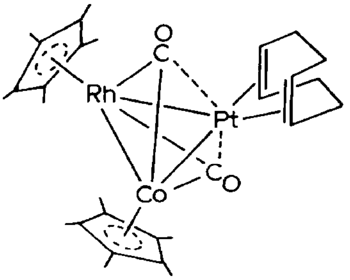


[148]

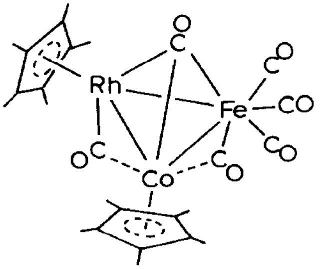


[149]

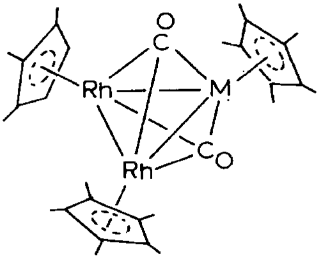
$[M(acac)(CO)(\mu\text{-}CR)(\mu\text{-}CO)M'cp(CO)]$ (M = Ir; R = p-tolyl; M' = W. M = Rh; R = Me; M' = Mo) were prepared similarly from $[M(acac)(CO)_2]$ (M = Rh, Ir) (ref. 361). Addition of $[cp'Co(C_2H_4)_2]$ to $[cp'Rh(CO)_2]$ affords $[cp'_2RhCo(\mu\text{-}CO)_2]$ which reacts as do its homometallic analogs with $[Pt(COD)_2]$, $[Fe_2(CO)_9]$ and diazomethane in THF to afford [150], [151] and $[cp'_2RhCo(CO)_2(\mu\text{-}CH_2)]$ respectively. The last on refluxing in toluene converts to $[cp'_2RhCo(\mu\text{-}CO)(\mu\text{-}CH_2)]$. Similarly $[cpCo(C_2H_4)_2]$ adds to $[cp'Ir(CO)_2]$ forming $[cp'Ir(\mu\text{-}CO)_2Cocp]$ which reacts further with $[cpCo(C_2H_4)_2]$ to give $[cp'Ircp_2Co_2(\mu\text{-}CO)_3]$. The iridium-rhodium analogs with all combinations of cp and cp' ligands were also prepared. The cobalt ethylene complex and its rhodium analog also add to $[cp'_2Rh_2(\mu\text{-}CO)_2]$ to give [152] (M = Co, Rh) while $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ and $[cp'_2RhCo(\mu\text{-}CO)_2]$ form [153] (refs. 362, 363). The complexes $[cp'_2RhM(\mu\text{-}CO)_2]$ (M = Co, Rh) have been considered isolobal with ethylene and indeed are found to coordinate an $\{Mo(CO)_5\}$ fragment (from $[Mo(CO)_5(THF)]$) as would an olefin. The crystal structure of the dirhodium complex shows the Rh-Rh axis to be staggered with respect to the equatorial carbonyl groups on the molybdenum (see [390]) while NMR studies show that in the cobalt-rhodium complex the $\{Mo(CO)_5\}$ undergoes a hindered rotation about an axis joining it to the midpoint of the cobalt-rhodium vector (ref. 364).



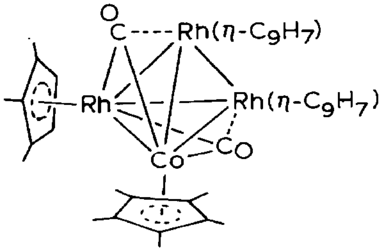
[150]



[151]

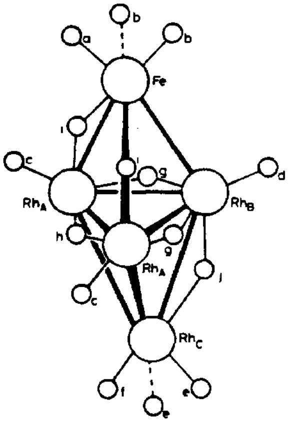


[152]



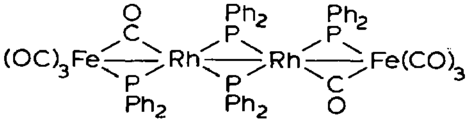
[153]

A full paper has now appeared on the syntheses of mixed iron-rhodium carbonyl cluster anions. These are formed from $[RhCl(CO)_2]_2$ and $[HFe(CO)_4]^-$, $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$ or $[Fe_4(CO)_{13}]^{2-}$, from hydrated rhodium(III) chloride and $[Fe_3(CO)_{11}]^{2-}$ or from $[Rh_7(CO)_{16}]^{3-}$ and an excess of $[Fe(CO)_5]$. From infrared studies, the initial species formed in all reactions is $[Fe_2Rh(CO)_{10\ \mathrm{or}\ 11}]^-$ for which the formulation $[Fe_2Rh(CO)_{10}]^-$ (all terminal carbonyls) is favored. Attempts to isolate this species under nitrogen led instead to the recovery of $[Fe_2Rh_4(CO)_{16}]^{2-}$ plus $[Fe_4(CO)_{13}]^{2-}$ and $[Fe(CO)_5]$ while under carbon monoxide was obtained $[FeRh_4(CO)_{15}]^{2-}$ among other products. The best yields could be realized by slow addition of solutions of $[RhCl(CO)_2]_2$ in THF to a solution of $Na[HFe(CO)_4]$ in THF from which salts of $[Fe_2Rh_4(CO)_{16}]^{2-}$ could be crystallized under nitrogen. In the presence of carbon monoxide salts of $[FeRh_4(CO)_{15}]^{2-}$ could be obtained. Other satisfactory routes to the latter cluster include the addition of solid $[Rh_4(CO)_{12}]$ to a THF suspension of $Na_2[Fe(CO)_4]$ and the reaction of $[Fe(CO)_5]$ with $[Rh_4(CO)_{11}]^{2-}$. If the reaction of $[Rh_4(CO)_{12}]$ with $[Fe(CO)_4]^{2-}$ is carried out by combining solutions of the reagents, however, one obtains only $[Rh_{12}(CO)_{30}]^{2-}$ and $[Fe(CO)_5]$. Reaction of either $[FeRh_4(CO)_{15}]^{2-}$ or $[Fe_3(CO)_{11}]^{2-}$ with $[RhCl(CO)_2]_2$ affords $[FeRh_5(CO)_{16}]^-$ which can also be got from $[Rh_{12}(CO)_{30}]^{2-}$ and $[Fe(CO)_4]^{2-}$. In the latter two reactions a coproduct is $[Rh_7(CO)_{16}]^{3-}$. The structure of $[FeRh_4(CO)_{15}]^{2-}$ is shown schematically as [154] while both $[FeRh_5(CO)_{16}]^-$ and $[Fe_2Rh_4(CO)_{16}]^{2-}$ have structures like that of $[Rh_6(CO)_{16}]$ with the last existing as a 1:3 mixture of cis- and trans- isomers.



[154]

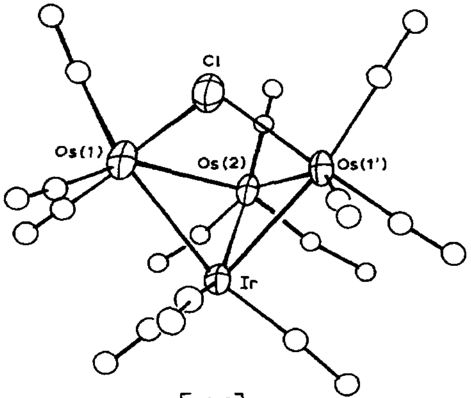
Complex [154] is fluxional and initially shows exchange of the apical terminal ligands with the axial-equatorial bridging ligands. At higher temperatures these bridging ligands exchange with the terminal ligands in the equatorial plane. The metal skeleton is non-fluxional (ref. 365). Another full report of results previously mentioned in the 1982 Annual Survey is of the reaction of $Li[Fe(CO)_4(PPh_2)]$ with $[MCl(CO)L_2]$ to give $[L(OC)_3Fe(\mu\text{-}PPh_2)M(CO)_xL]$ ($M = Ir$; $L = PPh_3$; $x = 2$. $M = Rh$; $L = PPh_3$, PEt_3; $x = 1$) which also contains a metal-metal bond. The authors consider that formulation as an Fe(0)-M(I) complex with a donor bond from iron is the most appropriate. The transfer of the phosphine to the iron which occurs in the course of the reaction probably occurs intermolecularly. The iron-rhodium complex reversibly adds one carbonyl ligand to rhodium while the iron-iridium complex can be induced to lose one carbonyl group from iridium on heating or photolysis. Reaction of $[(PPh_3)(OC)_3Fe(\mu\text{-}PPh_2)Ir(CO)_2(PPh_3)]$ with carbon monoxide or hydrogen yields $[(PPh_3)(OC)_3Fe(\mu\text{-}PPh_2)Ir(CO)_3(PPh_3)]$ and $[(PPh_3)(OC)_3Fe(\mu\text{-}PPh_2)IrH_2(CO)(PPh_3)]$ respectively in which the metal-metal bond has been cleaved. By contrast, hydrogen adds to $[(PPh_3)(OC)_3Fe(\mu\text{-}PPh_2)Ir(CO)(PPh_3)]$ to yield $[(PPh_3)(OC)_2H_2Fe(\mu\text{-}PPh_2)IrH_2(CO)(PPh_3)]$ while addition of hydrogen chloride (introduced as its adduct with N,N-dimethylacetamide) gives $[(PPh_3)(OC)_4Fe(\mu\text{-}PPh_2)IrH(Cl)(CO)(PPh_3)]$ both of which retain the metal-metal bond. The latter complex decomposes on heating to give $[Fe(CO)_3(PPh_3)_2]$, $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-}PPh_2)_2]$, $[IrCl(CO)(PPh_3)_2]$ and other unidentified products (ref. 366). Carbonylation of a mixture of $[Fe(CO)_4(PPh_2H)]$ and $[(\eta^3\text{-}C_3H_5)_2RhCl]_2$ in ethanol affords the linear tetranuclear complex [155] (ref. 367). The complex $[Fe_3(\mu_3\text{-}Te)_2(CO)_9]$ on refluxing with $[cpRh(CO)_2]$ in acetonitrile gives the rhodium



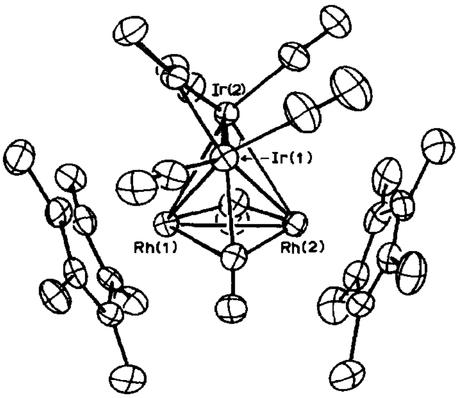
[155]

analog of [124] which on decarbonylation using trimethylamine N-oxide gives an inseparable mixture of isomers which slowly interconvert. These were identified as the rhodium counterparts of [125] and [126] by reaction with triphenylphosphine which gave monoligated derivatives which no longer interconverted and could be separated. The ^{125}Te NMR spectra of these and related complexes were measured from which it appears that the tellurium chemical shifts are primarily dependent upon the number of metal-metal bonds with which the tellurium atom is associated rather than on the electron count of the cluster (ref. 368). Syntheses of the known clusters $Et_4N[Fe_5Rh(C)(\mu\text{-}CO)_4(CO)_{12}]$ and $Et_4N[Fe_4M(C)(CO)_{14}]$ (M = Co, Rh) have been reported. The latter complexes react further with $[(\eta^3\text{-}C_3H_5)PdCl]_2$ to give $Et_4N[Fe_4MPd(C)(CO)_{15}]$ (refs. 369, 370).

The fragment $\{MCl(CO)_2\}$(M = Rh, Ir) which presumably could be generated in situ from $[MCl(CO)_2$ (p-toluidine)] is proposed to be isolobal with $\{PtL_2\}$ and methylene and should give analogous products with $[H_2Os_3(CO)_{10}]$. The reaction occurs but not to give the anticipated products. The iridium complex is formulated as $[IrOs_3(\mu\text{-}H)_2(\mu\text{-}Cl)(CO)_{10}]$ with a structure shown to be [156]. The hydride ligands were not located crystallographically but are thought to bridge the osmium-osmium bonds. The rhodium analog is thought to have the same structure. With $[cp'_2Rh_2(\mu\text{-}CO)_2]$, $[Ir(CO)_2Cl$(p-toluidine)] again behaves unexpectedly to form $[cp'_2Rh_2Ir_2(\mu\text{-}CO)(\mu_3\text{-}CO)_2(CO)_4]$ ([157]) (ref. 371). In related work, reaction of $[H_2Os_3(CO)_{10}]$ with $[cpRh(CO)_2]$ and hydrogen in aromatic solvents at 90°C yields the arene complex [158] (R = H, Me) while using $[cp'Rh(CO)_2]$ in heptane under the same conditions afforded

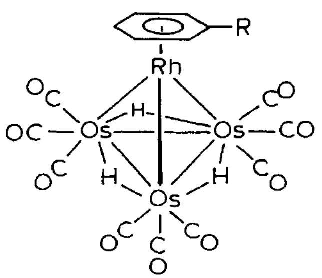


[156]

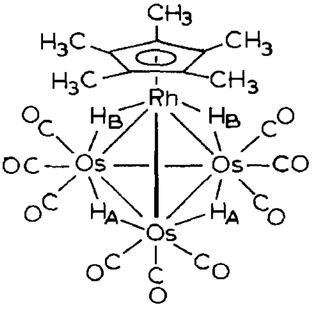


[157]

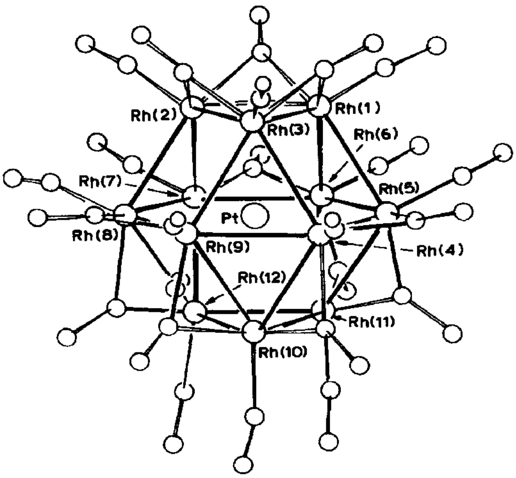
[159] (ref. 372). The controlled pyrolysis of Na[PtRh$_5$(CO)$_{15}$] in methanol containing sodium bicarbonate yields a mixture of anionic clusters from which salts of [Pt$_2$Rh$_{11}$(CO)$_{24}$]$^{3-}$, [PtRh$_{12}$(CO)$_{24}$]$^{4-}$ and [Pt$_2$Rh$_9$(CO)$_{22}$]$^{3-}$ were isolated by fractional crystallization. The structure of the second was found to be [160] while that of the first is similar but with the second platinum atom disordered over the surface of the cluster. Reaction of [Pt$_2$Rh$_{11}$(CO)$_{24}$]$^{3-}$ with [Rh(CO)$_2$(MeCN)$_2$]$^+$ and with acid yields [Pt$_2$Rh$_{12}$(CO)$_{26}$]$^{2-}$ and [PtRh$_{13}$(CO)$_{25}$]$^{3-}$ respectively (refs. 373, 374). Several



[158]

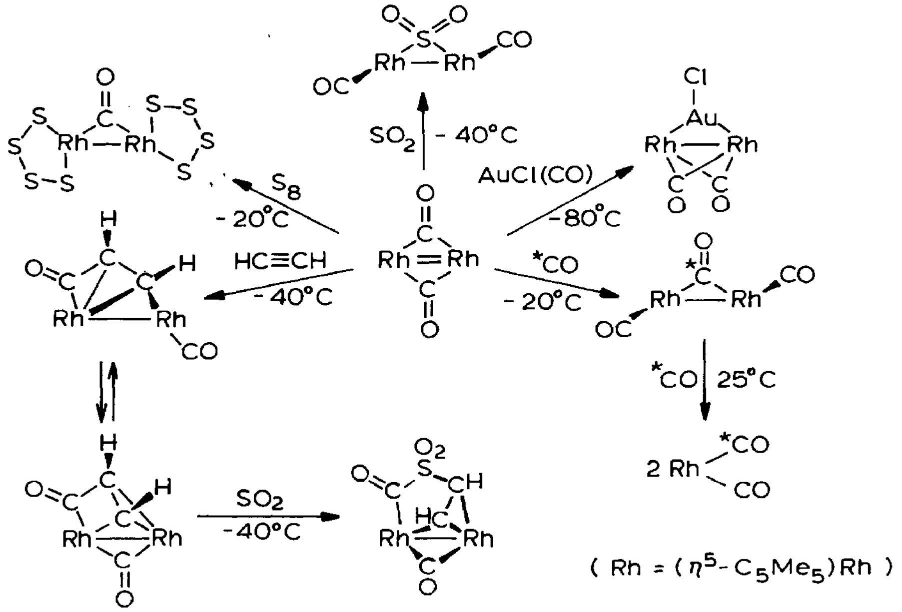


[159]



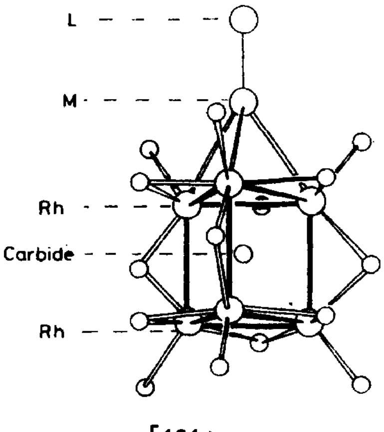
[160]

reactions of [cp'$_2$Rh$_2$(μ-CO)$_2$] are detailed in Scheme XXX. In contrast to

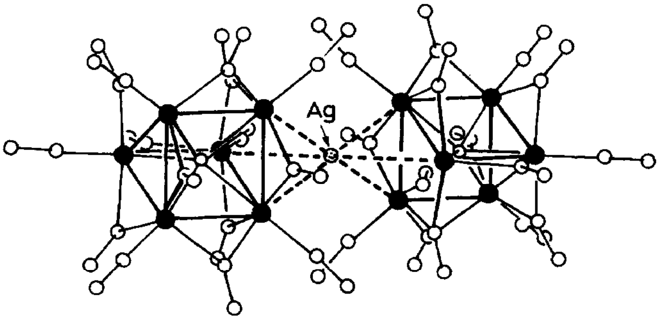


Scheme XXX

the reaction with cyclooctasulfur, those with selenium or tellurium give [cp'$_2$Rh$_2$(CO)$_2$(μ-E)] (E = Se, Te) while with phenylacetylene only one isomer is found corresponding to the acetylene adduct shown in the lower left of Scheme XXX with the phenyl group attached to the carbon atom which bridges the metal-metal bond (ref. 375). Addition of [AuCl(PPh$_3$)] to (bzMe$_3$N)[Rh$_6$C-(CO)$_{15}$] yields [161] (M = Au; L = PPh$_3$). Analogs with M = Cu; L = MeCN and M = Ag; L = PEt$_3$ were also prepared. Treatment of the rhodium cluster anion with silver tetrafluoroborate in acetone successively yields the mixed-metal clusters $[(Rh_6C(CO)_{16})_2(\mu\text{-}Ag)]^{3-}$, $[Rh_6C(CO)_{16}(\mu\text{-}Ag)Rh_6C(CO)_{16}(\mu\text{-}Ag)Rh_6C(CO)_{16}]^{4-}$, $[Rh_6C(CO)_{16}(\mu\text{-}Ag)]_n^{n-}$, $[AgRh_6C(CO)_{16}(\mu\text{-}Ag)Rh_6C(CO)_{16}(\mu\text{-}Ag)Rh_6C(CO)_{16}Ag]^{2-}$, $[(AgRh_6C(CO)_{16})_2(\mu\text{-}Ag)]^-$ and $[Ag_2Rh_6C(CO)_{16}]$ as the silver/cluster reactant ratio varies from 1:2 to 3:1. The structure of the first cluster is [162]. In all instances the silver ions cap triangular faces of the rhodium cluster and so long as the silver/cluster ratio is less than one they bridge adjacent clusters. Above this ratio the opposite faces also become capped (ref. 376).



[161]



[162]

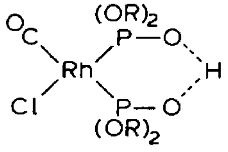
The deuterium NMR spectrum of $[DFeCo_3(CO)_{12}]$ has been obtained and its chemical shift is in the range associated with edge-bridging hydride ligands. With this parameter available a reexamination of the proton NMR spectrum of the corresponding hydride complex located the previously unobserved hydride resonance which is broadened by quadrupolar coupling to a width of ca 500 Hz (ref. 377). The same hydride together with $[FeCo_3(CO)_{12}]^-$ have been studied by variable temperature ^{13}C NMR. The spectra at the low temperature limit are consistent with the established structures. On warming, the nine carbonyl ligands on the Co_3 unit exchange first followed at higher temperatures by exchange of all twelve (ref. 378). The gas-phase ultraviolet photoelectron spectra of $[Co_3(CO)_9(\mu_3\text{-}S)]$ and $[H_{n-1}Fe_nCo_{3-n}(CO)_9\text{-}(\mu_3\text{-}S)]$ (n = 1-3) have been measured and correlated with Fenske-Hall molecular orbital calculations. These show that, although the metal-metal bonding appears to be delocalized in the neutral complexes, on photoionization a localization of the cobalt and iron *d* electrons occurs (refs. 379, 380).

Intense interest continues in the area of bimetallic catalyst systems for the conversion of syngas into organic chemicals. Many of these involve combinations of cobalt and ruthenium but combinations of cobalt with iron, rhodium, palladium or platinum have also been studied. A mixture of cobalt (II) acetate and $[Rh(acac)_3]$ serves as a catalyst precursor for the homologation of methyl acetate to ethyl acetate by syngas and carbonyl complexes are thought to be formed but no more details are available (ref. 381). Other workers found that catalysis of the same reaction could be effected by addition of $[RuCo_3(CO)_{12}]^-$ or $[Rh_3Co(CO)_{13}]^-$ under carbon monoxide alone but no evidence for the integrity of the clusters under reaction conditions was presented (ref. 382). Conversion of syngas to ethylene glycol and its monomethyl ether is catalyzed by a mixture of $[Ru(acac)_3]$ and $[Rh(acac)_3]$ in molten tetrabutylphosphonium iodide. Some methanol and ethanol were also formed and although several ruthenium carbonyl clusters and one of empirical formula $[RhRu_2(CO)_{12}]$ could be isolated at the end of the reaction, no rhodium carbonyls were found. Although it was not determined if a bimetallic species were the active catalyst, the very low yield of glycol in the absence of ruthenium indicates that catalysis does not occur exclusively on rhodium species (ref. 383). A final homogeneous ruthenium-cobalt system was shown to catalyze the syngas conversion of dimethyl ether to ethyl acetate (ref. 384). A number of studies are also reported on the use of clusters supported on various surfaces for syngas conversion. Reaction of $[HFeCo_3\text{-}(CO)_{12}]$ with silica gel functionalized with 3-aminopropyl groups provides a means of supporting $[FeCo_3(CO)_{12}]^-$ moieties. Following hydrogen activation at 200°C a catalyst is generated which provides a narrower range of hydrocarbons (maximum at C_5-C_6) from syngas than other Fischer-Tropsch catalysts. A higher olefin content is also obtained and the methane yield is low. Ethylene is proposed to be the primary product and at low pressure, much of this is incorporated into the growing hydrocarbon chain on the surface (ref. 385). On the other hand, when $[Co_2(CO)_8]$ or $[HCo_3Fe(CO)_{12}]$ is supported on silica together with tetrabenzyltitanium or -zirconium and activated by hydrogenation, the yield of alcohols is increased compared to what is observed when the Group IV metal is absent. Supported titanium or zirconium hydrides are thought to be present (ref. 386). Fair yields of methane are formed from syngas using a catalyst prepared from PPN[$CoRu_3(CO)_{13}$] on alumina (ref. 387) while [(DPPE)$PdCo_2(CO)_7$] is better than [$Co_2(CO)_8$] as a catalyst for methanol homologation. The platinum analog is also active but gives a different product distribution (ref. 388). The cluster [$Pt_2Co_2(CO)_8$-$(PPh_3)_2$] is a poor catalyst for the hydrogenation of olefins and internal alkynes but functions reasonably well with terminal alkynes. However it is unlikely that cluster catalysis occurs since the original complex is not recoverable (ref. 389). Finally, {$RhCo_3(CO)_{10}$} moieties supported on phosphinated silica are better catalysts for the hydroformylation of hex-1-ene than the analogous unsupported cluster (ref. 390).

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

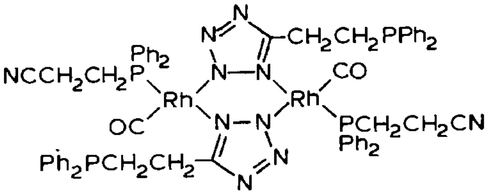
Addition of two equivalents of lithium di(*tert*-butyl)phosphide to [$CoCl_2$-$(PMe_3)_2$] in THF at -78°C yields the mixed-valence dimer [$CoCl(PMe_3)$-$(\mu\text{-}PBu^t{}_2)_2Co(PMe_3)$] while an excess of the phosphide causes further reduction to *trans*-[$(Me_3P)(N_2)Co(\mu\text{-}PBu^t{}_2)_2Co(N_2)(PMe_3)$]. Carbonylation of the dinitrogen complex occurs with some difficulty to give *cis*-[$(Me_3P)(CO)Co$-$(\mu\text{-}PBu^t{}_2)_2Co(CO)(PMe_3)$]. The all-carbonyl analog, [$(OC)_2Co(\mu\text{-}PBu^t{}_2)_2Co$-$(CO)_2$] is synthesized by treating [$Co_2(CO)_8$] with iodine followed by reaction with the phosphide as before. The last three complexes are proposed to contain cobalt-cobalt double bonds (ref. 391). In refluxing toluene, one carbonyl group in [$Co_4(\mu_4\text{-}PPh)_2(CO)_{10}$] can be replaced by a triphenylphosphine ligand while in refluxing acetonitrile the product is [$Co_4(\mu_4\text{-}PPh)_2$-$(CO)_9(MeCN)$]. The acetonitrile ligand can be replaced by trimethylphosphite and if the reaction in acetonitrile is carried out for longer times followed by replacement of this solvent by toluene and addition of trimethylphosphite [$Co_4(\mu_4\text{-}PPh)_2(CO)_8(P(OMe)_3)_2$] can be obtained (ref. 392).

A common source of rhodium(I) carbonyl complexes is [$RhCl(CO)_2]_2$. Its reaction with trialkyl and triarylphosphites in ethanol gives the expected [$RhCl(CO)(P(OR)_3)_2$] complexes plus the hydrolysis products [$RhCl(CO)(P(OR)_2$-$OH)_2$] and ones formulated as [$RhCl(CO)(P(O)(OR)_2)_2$]. The last are more likely to be [163] (ref. 393). With triphenylphosphine sulfide it gives [$RhCl(CO)_2(SPPh_3)$]. Also [$RhCl(PPh_3)_3$] reacts with carbonyl sulfide to give

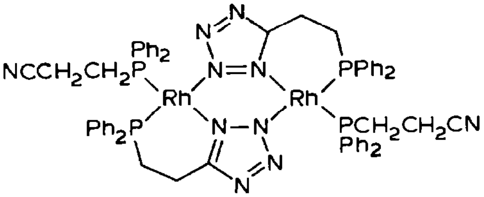


[163]

$[RhCl(CO)(PPh_3)_2]$ plus $[RhCl(SPPh_3)_3]$ (ref. 394). Complexes of the type $[RhCl(CO)(PPh_2R)_2]$ (R = vinyl, 3-propenyl, etc.) are also prepared from $[RhCl(CO)_2]_2$ and the olefinic moieties on the ligands are not coordinated to the metal. As the complexes are insensitive to γ-irradiation it is proposed that they might be able to be grafted onto polymers by this process to give supported complexes for catalytic applications (ref. 395). A 1,3-cycloaddition of organic nitriles to the azide ligand in $[Rh(N_3)(CO)(PPh_3)_2]$ occurs readily to afford 5-substituted tetrazolato complexes. With 2-cyanoethyldiphenylphosphine a mixture of [164] and [165] is obtained while with

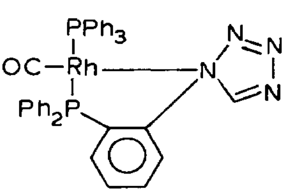


[164]



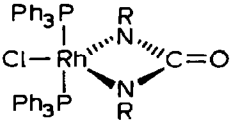
[165]

2-cyanophenyldiphenylphosphine the product is [166] (ref. 396). Extended



[166]

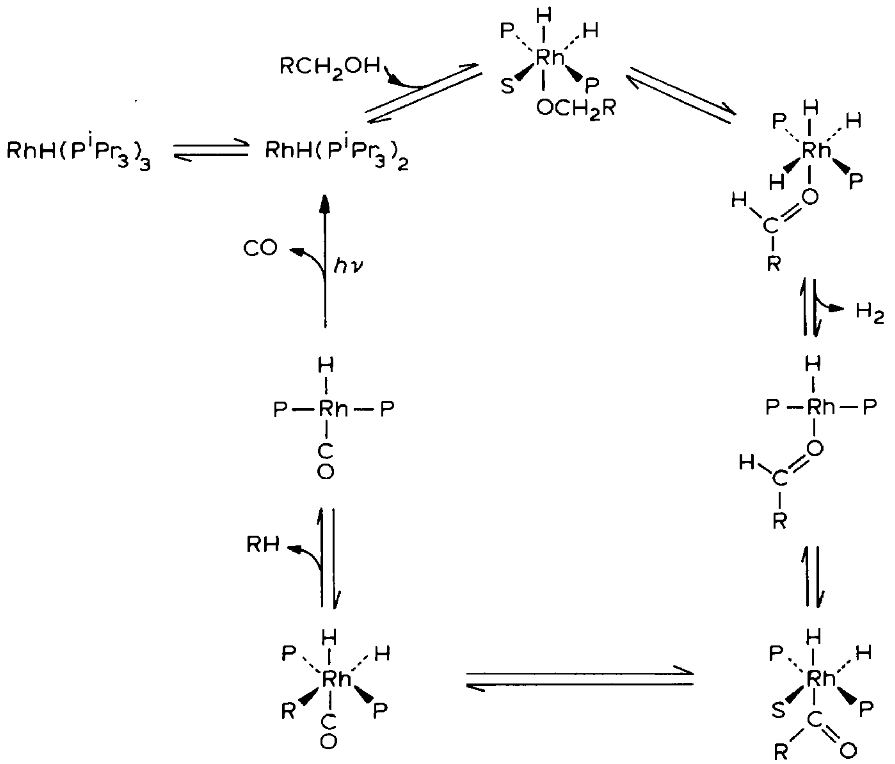
reaction of $[RhCl(CO)(PPh_3)_2]$ with diphenylphosphorylazide gives the urylene complex [167] (R = $P(O)(OPh)_2$) but with short reaction times the only



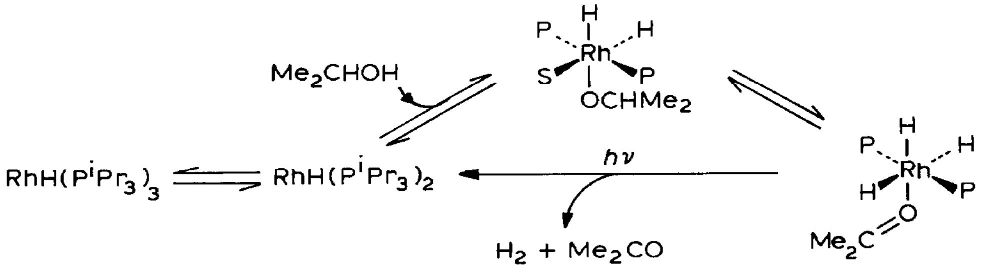
[167]

product is $[RhCl(PPh_3)_2]_2$ (ref. 397). The cationic complex cis-$[Rh(CO)_2(L_2)]BPh_4$ (L_2 = 2-(2-phenylaminoethyl)pyridine) has been studied as a catalyst for the carbonylation of methanol (ref. 398) while addition of acetyl chloride to $[RhCl(CO)_2A]$ (A = NH_3, $MeNH_2$) at elevated temperature leads to amide complexes via acylation of the amine ligand (ref. 399). Thermal decomposition of these amine complexes in air in the solid state leads to oxidation of the carbonyl group. In toluene solution the methylamine complex appears to catalyze the oxidation of carbon monoxide to carbon dioxide (ref. 400). Refluxing hydrated rhodium(III) chloride in DMF containing anthranilic acid (HA) yields [Rh(CO)$_2$(A)] in which one carbonyl group can be substituted by triphenylphosphine (ref. 401).

The rhodium complexes [RhH(PPr$^i_3$)$_3$] or [RhH(CO)(PPr$^i_3$)$_2$] form catalysts for the photochemical decomposition of alcohols. In methanol and ethanol the products are dihydrogen and carbon monoxide with methane also being formed from the latter alcohol while in isopropanol the products are dihydrogen and acetone. The proposed mechanisms are given in Schemes XXXI and XXXII respectively (ref. 402). The interaction of the {Rh(CO)(PPh$_3$)$_2$$^+$}

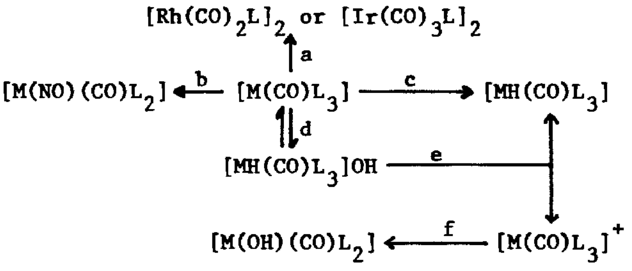


Scheme XXXI



Scheme XXXII

moiety with purine-pyrimidine base pairs and of $[RhCl(CO)_2]_2$ with nucleobases and nucleosides has been studied (refs. 403-405). Metathesis of $[RhCl(CO)L_2]$ (L = PPh_3, $P(\underline{p}\text{-}EtC_6H_4)_3$) with bromide readily gives the analogous bromo complexes but it proved much more difficult to get the iodide derivatives by this route. In the absence of dioxygen and using excess ligand the products are either $[RhI(P(\underline{p}\text{-}EtC_6H_4)_3)_2]_2$ or cis- plus trans-$[RhI(CO)(PPh_3)_2]$ while in its presence, polymeric dioxygen adducts form (ref. 406). The yellow quasiracemates $[Rh(CO)_2((1S)\text{-}3\text{-trifluoroacetylcamphorate})]$ and $[Ir(CO)_2((1R)\text{-}3\text{-trifluoroacetylcamphorate})]$ react in a 1:1 ratio to give a black-violet dichroic product with a highly ordered chain structure containing alternating pairs of rhodium and iridium complexes (ref. 407). Two reversible, one-electron reduction processes are seen for $[M(CO)(PPh_3)_3]^+$ (M = Rh, Ir) in DME. In the absence of excess phosphine the rhodium complex forms $[Rh(CO)(PPh_3)_2(DME)]_2$. Further chemistry of the electrogenerated $[M(CO)(PPh_3)_3]$ complexes is shown in Scheme XXXIII (L = PPh_3). In acetonitrile no clean electrochemical behavior is seen unless

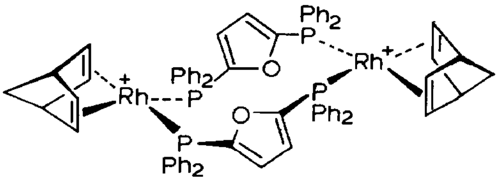


a) CO. b) NO. c) H_2. d) H_2O. e) $[M(CO)L_3]$. f) OH^-.

Scheme XXXIII

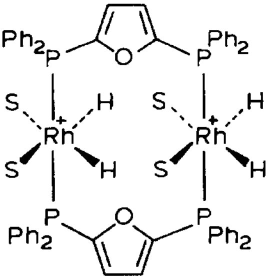
excess ligand is present (ref. 408). Oxidative addition of methyl iodide to $[RhCl(CO)L_2]$ (L = 2,4-dimethoxyphenyldimethylphosphine) occurs much more rapidly than to the corresponding dimethylphenylphosphine complex but halogen scrambling occurs. Cleaner results are obtained with $[RhBr(CO)L_2]$ and methyl bromide and a neighboring-group participation by the o-methoxy group is proposed to explain the rate enhancement (ref. 409). In a recent study of $[RhCl_2(Pcy_3)_2]$ the low magnetic moments found were attributed to the presence of $[RhHCl_2(Pcy_3)_2]$ as an impurity. The solid material is unreactive towards dihydrogen and dioxygen but with carbon monoxide a mixture of $[RhCl(CO)(Pcy_3)_2]$ and paramagnetic $[RhCl_2(CO)(Pcy_3)_2]$ are obtained together with $[RhHCl_2(CO)(Pcy_3)_2]$ from the impurity. The rhodium(II) carbonyl is unstable and disproportionates to $[RhCl(CO)(Pcy_3)_2]$ and $[RhCl_3(CO)(Pcy_3)_2]$ (ref. 410).

Binuclear complexes containing bridging phosphine ligands continue to attract much interest. Addition of 2,5-bis(diphenylphosphino)furan to dichloromethane solutions of $[Rh(NBD)_2]BF_4$ forms the dication [168] which on

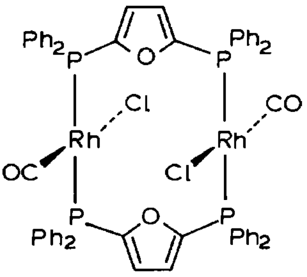


[168]

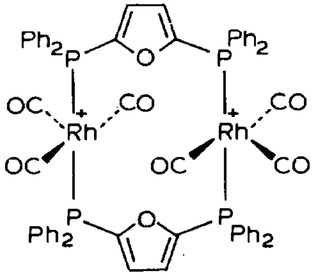
hydrogenation in the cold eliminated norbornane with the formation of a methanol solvate. Further hydrogenation in warm solutions forms [169] (S = MeOH) which can be reconverted to [168] on reaction with NBD. Reaction of the same ligand with $[RhCl(CO)_2]_2$ yields [170] which on treatment with two equivalents of silver tetrafluoroborate gives [171]. Complex [171] reversibly loses carbon monoxide with the formation of [172] while reaction of $[RhCl(CO)_2]_2$ with the ligand in the presence of one equivalent of silver



[169]

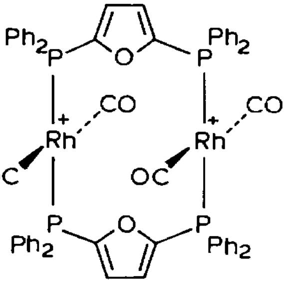


[170]



[171]

tetrafluoroborate affords [173] (ref. 411). In the absence of carbon monoxide, no mixed metal dimers can be obtained from $[RhCl(CO)_2]_2$ and



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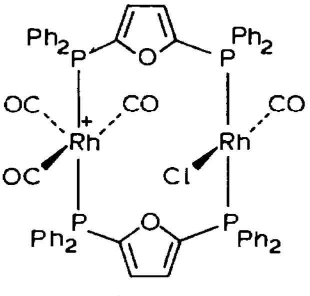
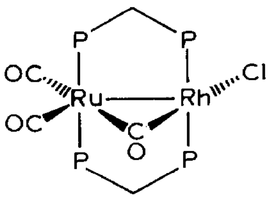
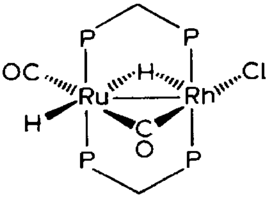


[173]

$[Ru(COD)(DPM)_2]$; only $[Ru(CO)(COD)(DPM)]$ and either $[Rh_2Cl_2(CO)_2(DPM)_2]$ or $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ form. However at 80°C in toluene under carbon monoxide the major product is [174]. This reacts with sodium borohydride to give [175] although a better yield is obtained from $[RuH_2(DPM)_2]$ and $[RhCl(CO)_2]_2$. Complex [174] is an effective catalyst precursor for olefin

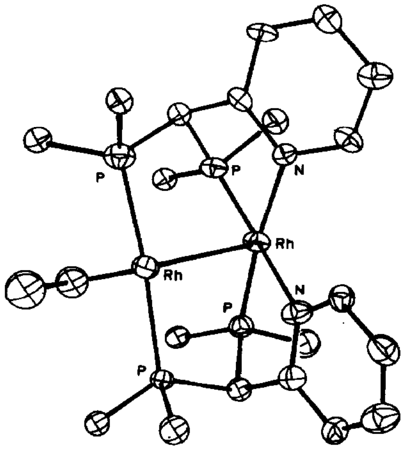


[174]

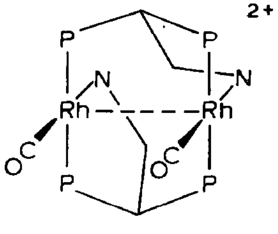


[175]

hydroformylation (ref. 412). Under nitrogen DADPM reacts with $[RhCl_2(CO)_2]^-$ to form $[Rh_2Cl_2(CO)_2(DADPM)_2]$ while under carbon monoxide the A-frame complex $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DADPM)_2]^+$ forms which reversibly decarbonylates giving $[Rh_2(CO)_2(\mu\text{-}Cl)(DADPM)_2]^+$. The last complex reacts with successive aliquots of <u>tert</u>-butylisocyanide to give $[Rh_2(CO)_2Cl(CNBu^t)(DADPM)_2]^+$, $[Rh_2(CNBu^t)_2(CO)Cl(DADPM)_2]^+$ and finally $[Rh_2(CNBu^t)_4(DADPM)_2]^{2+}$. Although originally formulated as containing head-to-tail arrangements of the DADPM ligands, subsequent work has shown that 15-25% of the head-to-head isomer is also present. The isomer ratio varies depending on the mode of preparation (refs. 413, 414). Reaction of $Li[RhCl_2(CO)_2]$ with PNP in ethanol-dichloromethane followed by addition of sodium tetraphenylborate yields $[Rh_2(CO)(PNP)_2](BPh_4)_2$ ([176] with phenyl rings omitted for clarity) which adds carbon monoxide to give $[Rh_2(CO)_2(PNP)_2](BPh_4)_2$ (schematically shown as [177]). Complex [177] as its tetrafluoroborate or

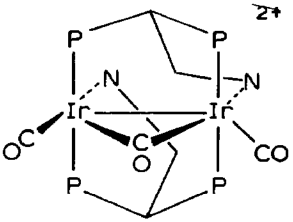


[176]

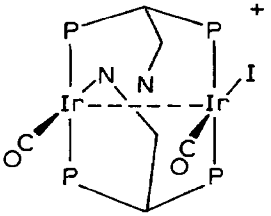


[177]

hexafluorophosphate salt can also be prepared by treating $[RhCl(NBD)]_2$ with the appropriate silver salt and PNP to form $[Rh(NBD)(PNP)]^+$ followed by reaction with carbon monoxide. In an analogous sequence $[IrCl(COD)]_2$ can be converted to $[Ir(COD)(PNP)]BF_4$ and then to $[Ir_2(CO)_2(\mu\text{-}CO)(PNP)_2](BF_4)_2$ ([178]). This on purging with dinitrogen gives the iridium analog of [177] which then reacts with tetrabutylammonium iodide to form [179]. By contrast

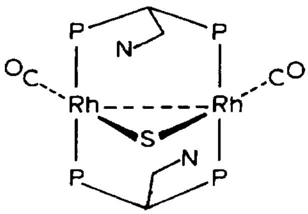


[178]



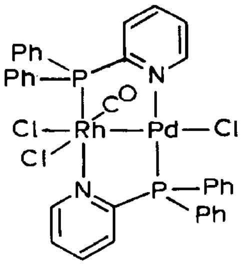
[179]

[177] is converted to monomeric [RhCl(CO)(PNP)] in which one phosphine group is uncoordinated by tetramethylammonium chloride but with sodium sulfide the product is [180] (refs. 415-417). In related work, [181] can be synthesized

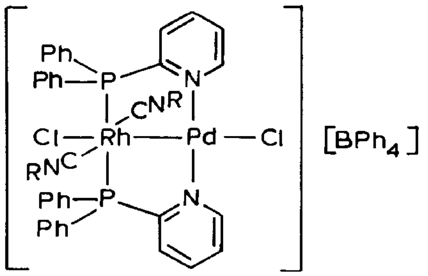


[180]

from either $[PdCl_2(PPh_2py)_2]$ and $[RhCl(CO)_2]_2$ or $[RhCl(CO)(PPh_2py)_2]$ and $[PdCl_2(COD)]$. The platinum analog can be prepared <u>via</u> the first route with

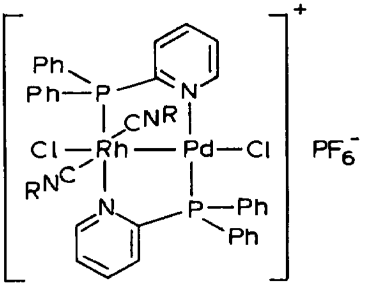


[181]

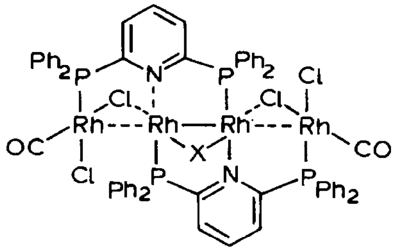


[182]

an intermediate formulated as $[PtCl(PPh_2py)_2][RhCl_2(CO)_2]$ being detected. Reaction of $[Rh(CNMe)_4]^+$ with 2-pyridyldiphenylphosphine yields <u>trans</u>-$[Rh(CNMe)_2(PPh_2py)_2]^+$ which reacts with $[PdCl_2(NCPh)_2]$ or $[PdCl_2(COD)]$ to give [182] and [183] (R = Me) respectively. Heating [182] converts it to

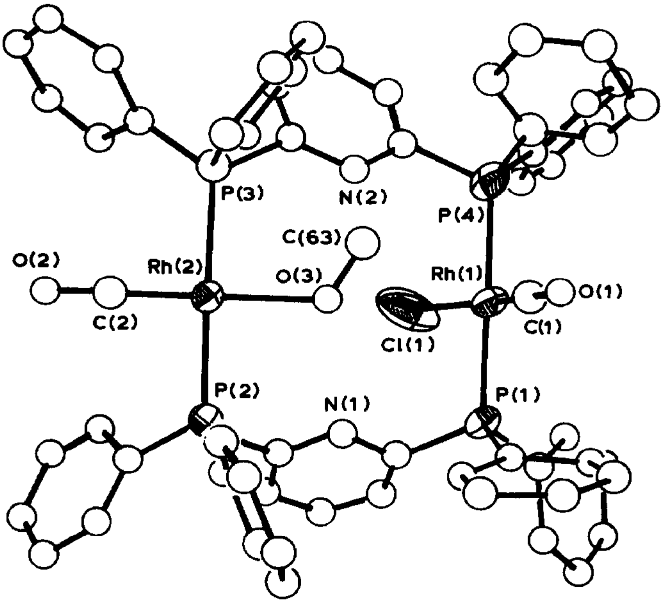


[183]



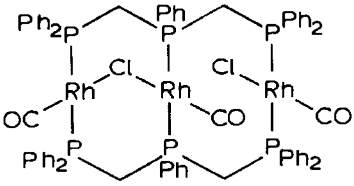
[184]

[183] together with other species as yet unidentified. The platinum analog of [181] undergoes oxidative addition of halogens at platinum (refs. 418, 419). Linear tetranuclear complexes can be prepared from $[RhCl(CO)_2]_2$ and 2,6-bis(diphenylphosphino)pyridine (L_2). The product is [184] (X = CO) which readily reacts with sulfur dioxide to form the analog with X = SO_2. Regeneration of [184] occurs on carbonylation and if methanolic ammonium hexafluorophosphate is then added the complex loses two rhodium atoms as a mixture of $[RhCl(CO)_2]_2$ and $[RhCl_2(CO)_2]^-$ to give $[Rh(CO)(MeOH)(\mu\text{-}L_2)_2Rh(CO)Cl]PF_6$ ([185]). Complex [185] reverts to [184] on reaction with $[RhCl(CO)_2]_2$ (refs. 420, 421). Whereas the phosphinopyridine ligand just



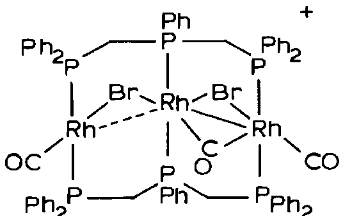
[185]

discussed gives tetranuclear complexes, the tridentate phosphine DPMP gives only linear trimers ([186]) with $[RhCl(CO)_2]_2$. The molecule is fluxional

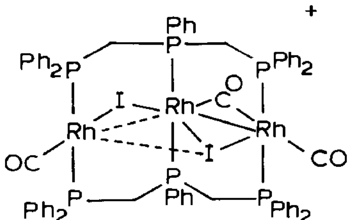


[186]

via a bridge-terminal exchange of the chloride ligands and while it adds sulfur dioxide and activated acetylenes it is unreactive towards carbon monoxide. Reaction with bromide or iodide ions yields [187] and [188]



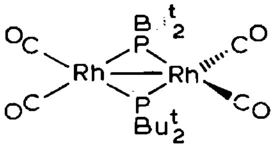
[187]



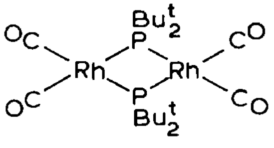
[188]

respectively. The former is fluxional, possibly via exchange of carbonyl ligands across the front of the molecule while the latter adopts a static structure. The latter does add carbon monoxide, however, to yield $[Rh_3I_2(CO)_4(DPMP)_2]^+$ (refs. 422, 423).

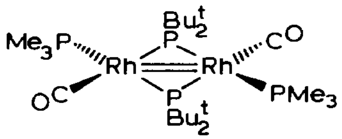
The "yellow dimer" obtained from hydroformylation systems using $[RhH(CO)(PPh_3)_3]$ and originally formulated as $[Rh(CO)_2(PPh_3)_2]_2$ has now been shown to be $[(PPh_3)_2(OC)Rh(\mu\text{-}CO)_2Rh(CO)_2(PPh_3)]$. It can also be prepared by reducing $[RhCl(CO)(PPh_3)_2]$ with sodium amalgam under 60 psi of carbon monoxide at 60°C to form $[Rh(CO)_4]^-$, venting the reactor and adding methanol to crystallize the product. It is thought that the complex forms via the reaction of methanol with species such as $[Rh(CO)_x(PPh_3)_{4-x}]^-$ to give $[RhH(CO)_x(PPh_3)_{4-x}]$ which then loses dihydrogen and dimerizes (ref. 424). In a related system, toluene solutions of $[RhH(L_2)_2]$ (L_2 = DPPP, DPPB, DIOP) react with carbon monoxide to eliminate dihydrogen and form $[(OC)(L_2)Rh(\mu\text{-}CO)_2Rh(CO)(L_2)]$ (ref. 425). The low temperature reaction of $[RhCl(CO)_2]_2$ with lithium di-tert-butylphosphide gives $[Rh_2(CO)_4(\mu\text{-}PBu^t{}_2)_2]$ and $[Rh_3(CO)_3(\mu\text{-}PBu^t{}_2)_3]$. In the trimer the $\{Rh_3P_3\}$ core is virtually planar and all three metals are coordinatively unsaturated. The dimer exists in conformation [189a] at low temperature and [189b] at room temperature. Because of the reversible metal-metal bond cleavage accompanying this isomerization, the complex is thermochroic. Reaction of [189a,b] with trimethylphosphine yields [190] which is proposed to contain a metal-metal double bond (refs. 426-428).



[189a]

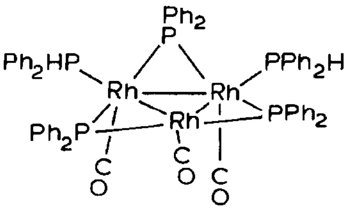


[189b]



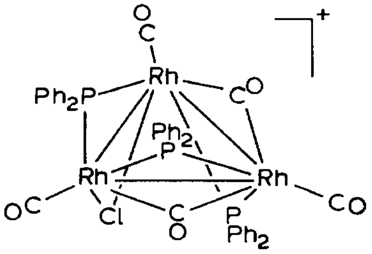
[190]

Reaction of $[RhCl(CO)_2]_2$ with four equivalents of diphenylphosphine in benzene yields $[RhCl(CO)(PPh_2H)_2]$ which can be deprotonated with diethylamine to give an unstable green complex proposed to be [191]. With only two equivalents of the phosphine the product is $[Rh_3(CO)_3(\mu-Cl)_2(\mu-PPh_2)_3(\mu-CO)]$ which reacts with silver hexafluoroantimonate and carbon



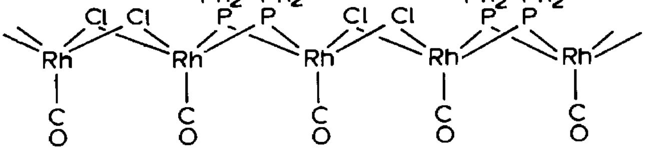
[191]

monoxide to give [192], with diethylamine to give $[Rh_3(\mu-PPh_2)_3(CO)_5]$ plus other unidentified products and slowly converts in solution to the



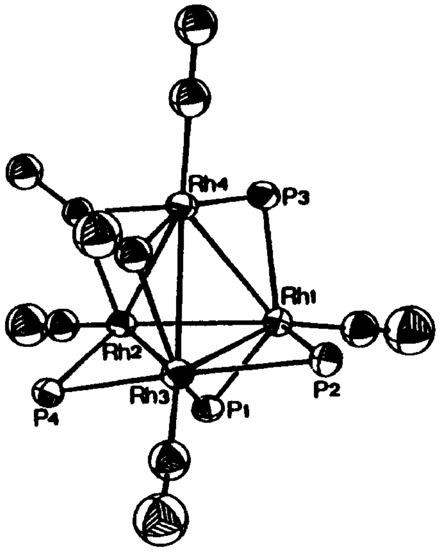
[192]

apparently polymeric [193]. It is proposed that [193] is the species patented previously as $[Rh_4(CO)_4(PPh_2H)_2(\mu-Cl)_4(\mu-PPh_2)_2]$. In alcohols, $[Rh_3(CO)_5(\mu-PPh_2)_3]$ adds carbon monoxide and one product so far identified

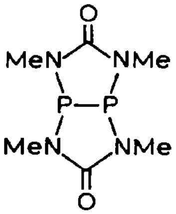


[193]

is $[Rh_3(CO)_7(\mu-PPh_2)_3]$ (refs. 429, 430). The slow addition of lithium diphenylphosphide to a THF solution of $[RhCl(CO)_2]_2$ so as to give a final reagent ratio of 4:3 yields [194]. If the ratio used is 2:1 (See J. Organometal. Chem., 188(1980) C27.) the product is $[Rh_4(CO)_5(\mu-PPh_2)_5]$ instead (ref. 431).

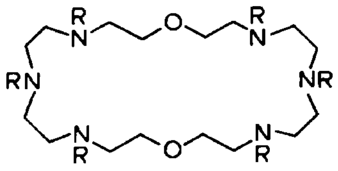


[194]

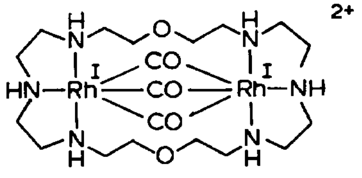


[195]

The central phosphorus atom of DPMP remains uncoordinated in the complexes $[L_nM(DPMP)]$ (L_nM = Cl_2Pt, Cl_2Pd, $(OC)_4Mo$) and can then coordinate to rhodium to form $[RhCl(CO)(L_nM(DPMP))_2]$ (ref. 432). An analogous species has been reported in which the ligand is $[Mo(L)(NO)I(NH(CH_2)_3PPh_2)]$ (L = tris-(3,5-dimethylpyrazolyl)borate) (ref. 433). The phosphorus-phosphorus bond in [195] (P-P) remains intact upon reaction with $[RhCl(CO)_2]_2$ in hot toluene and the product isolated is $[Rh_2Cl_2(CO)_2(\mu\text{-P-P})_2]$ (ref. 434). The ditopic macrocycle [196] (R = H) reacts with $[RhCl(CO)_2]_2$ to give [197] which contains a short rhodium-rhodium bond (2.58Å) and is fluxional at room temperature presumably via the interconversion of two dissymmetric conformers. With [196] (R = Me) a similar binuclear species but containing only terminal carbonyl ligands is formed (ref. 435). A monodentate DPM complex, [cpRh(CO)(DPM)], is formed from this ligand and $[cpRh(CO)_2]$ in



[196]

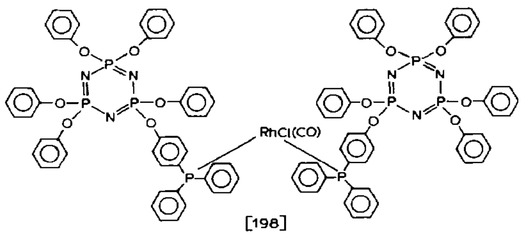


[197]

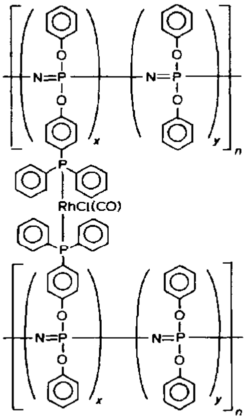
refluxing heptane presumably because dimer formation is sterically unfavorable. Chelated complexes, [cpRh(L_2)], are formed when L_2 is DPPE or DPPP while with DPPB the dimer [(cpRh(CO))$_2$(μ-DPPB)] is obtained. Protonation of [cpRh(DPPE)] with tetrafluoroboric acid in dichloromethane gives [cpRhH-(DPPE)]BF_4 and while the DPPP and DPPB complexes also appear to react, the desired hydrides appear to be unstable as no such species could be detected. With hydrogen chloride [(cpRh(CO))$_2$(μ-DPPB)] forms [Rh_2(CO)$_2$(μ-Cl)$_2$(μ-DPPB)] while [cpRh(L_2)] (L_2 = DPPE, DPPP) gives [Rh_2(L_2)$_2$(μ-Cl)$_2$]. The DPPE complex can also be got from [cpRhH(DPPE)]$^+$ on addition of chloride ion. It is thought that all these reactions may involve migration of a hydride from the metal to the cyclopentadienyl ring. With methyl iodide [cpRh(L_2)] (L_2 = DPPE, DPPP) affords the unstable [cpRhMe(L_2)]I while [cpRh(CO)(DPM)] yields [cpRh(C(O)Me)I]I (ref. 436). Addition of triphenylphosphine to [cp_2Rh_2(CO)$_2$-(μ-CO)] in pentane yields [cp_2Rh_2(PPh_3)(μ-CO)$_2$] which is proposed to contain a polar metal-metal bond. When performed in benzene solution the product is [cpRh(CO)(PPh_3)] suggesting that the former complex is an intermediate in the formation of the latter. No reaction occurred with P(o-tolyl)$_3$ (ref. 437).

The complexes [M(MNT)LL']$^-$ (M = Rh, Ir; L = L' = CO, P(OPh)$_3$; L = CO, L' = PPh_3. M = Ir; L = CO; L' = CN^-) have been synthesized and their emission spectra studied. Both the emission and the excitation spectra are highly structured and these features are attributed to vibrations of the {M(MNT)} moiety. The excitations are proposed to involve metal-to-ligand(MNT) charge transfer ($d \to \pi^*$) and the emission bands appear not to be split by spin-orbit coupling in contrast to other square planar rhodium and iridium complexes studied recently (ref. 438). The ^{17}O NMR spectra of [RhCl(CO)$_2$]$_2$ and other carbonyl complexes have been measured. The spin-lattice relaxation times for this nucleus are quite small at room temperature and are dominated by the electric quadrupole term. When corrected for correlation times, the derived quadrupole coupling constants show a dependence on the stereochemistry of the carbonyl groups involved (ref. 439). The anion [$RhBr_2$(CO)$_2$]$^-$ is an electrocatalyst for the oxidation of carbon monoxide to carbon dioxide in a carbon monoxide-dioxygen fuel cell. A current efficiency of 90% over fifteen cycles was observed (ref. 440). Detailed mass spectral studies have been published on [RhCl(CO)$_2$(L)] and [Rh_2(CO)$_2$L'$_2$-(μ-A)$_2$] (L = 3,5-dimethylpyrazole, 3,5-bis(trifluoromethyl)pyrazole. L' = CO, PPh_3, A = 3,5-dimethylpyrazolate, 3,5-bis(trifluoromethyl)pyrazolate) (ref. 441).

A number of cyclic and linear phosphazines containing pendant diphenylphosphino groups have been studied as supports for heterogenizing metal complexes. With [RhCl(CO)$_2$]$_2$ two such species can be bridged by {RhCl(CO)}



[198]



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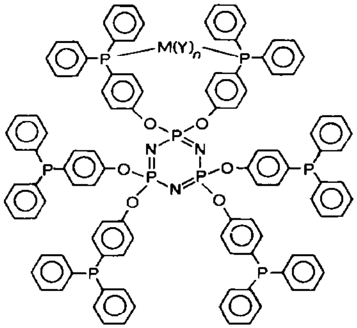
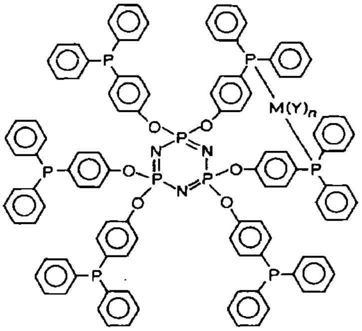


[200]



[201]

moieties giving [198] and [199] (x = 0.3; y = 1.7. x = 0.6; y = 1.4; n ∿ 7000) respectively. If the cyclic phosphazine contains several pendant diphenylphosphino groups the reaction gives a mixture of [200] and [201] ($M(y)_n$ = Rh(CO)Cl) which interconvert in an intramolecular fashion (ref. 442). By the same route the complexes [$RhCl(CO)L_2$] (L = $P(OEt)_3$, 3,5,6 bicyclophosphite of 1,2-O-isopropylidene-α-D-glucofuranose) were prepared and used as catalysts for the hydrogenation of dec-1-ene and methylenesuccinic acid (ref. 443). The hydrogenation of acrylonitrile to propionitrile can be catalyzed by [$RhCl(CO)(PPh_3)_2$] but the catalyst is short-lived. Its life and activity can be enhanced by the addition of formaldehyde and the formation of {$RhCl(PPh_3)_2$} is proposed as the initial step (ref. 444). A number of studies have appeared which use [$RhH(CO)(PPh_3)_3$] to catalyze the hydroformylation of various substrates. With octa-1,6-diene, only the terminal double bond reacts while with 4,4-diacetylhepta-1,6-diene both mono- and diformyl products are obtained. Methylenecyclopentane gives β-cyclopentylacetaldehyde but methylene cyclobutane isomerizes to 1-methylcyclobutene (ref. 445). The stability and recycle characteristics of [$RhH(CO)(PPh_3)_3$] in the catalyzed hydroformylation of dodec-1-ene are improved by the addition of phosphinous acids and the formation of

$[Rh_2(CO)_2(PPh_3)_2(R_2PO)_2]$ (R = n-octyl, Ph) is proposed (ref. 446). The highest selectivity to linear aldehydes from hex-1-ene are found when the system contains a 1.5 mol quantity of DIOP or trans-1,2-bis(diphenylphosphino)cyclobutane and again a binuclear species is proposed as the active catalyst (ref. 447). Other systems include one effecting hydroformylation of allyl alcohol (ref. 448) and one using ultraviolet irradiation to enhance activity. In the latter study a catalyst prepared from hydrated rhodium (III) chloride and NBD was found to be most active under photochemical conditions (ref. 449).

A 4:1 mol ratio of triphenylphosphine and $[RhCl(CO)_2]_2$ produced a catalyst system for the hydroformylation of (+)(R)-1-phenylethylvinyl ether and (R)(S)-4-phenyl-1-pentene. These substrates were used to investigate the influence of the presence of an oxygen atom on the regio- and diastereoselectivity of the process. The ether showed a preference for attachment of the formyl group to the carbon α to the oxygen while in the other substrate preferential attachment to the terminal carbon of the double bond was observed. A greater diastereoselectivity was observed for the ether (ref. 450). The dimeric complexes $[Rh_2(P(OMe)_3)_2L_2(\mu\text{-}SBu^t)_2]$ (L = $P(OMe)_3$, CO) catalyze the hydroformylation of the hex-1-ene but only the latter shows significant activity. It is however much more active than $[RhH(CO)(PPh_3)_3]$ although the selectivity to linear aldehyde is moderate. It is suggested from control experiments that the active catalyst is dimeric (ref. 451). In situ infrared monitoring of the hydroformylation of propene in the presence of $[Rh(acac)(CO)(PPh_3)]$ suggests the presence of $[RhH(CO)(PPh_3)_3]$ which converts to $[RhH(CO)_2(PPh_3)_2]$ at carbon monoxide pressures above 17 atm (ref. 452). A 1:10 mixture of $[Rh(CO)_2(acac)]$ and $[Ru(acac)_3]$ in acetic acid containing triethylamine generates a catalyst for the conversion of syngas to methyl and ethyl acetates together with significant quantities of ethylene glycol acetate. The catalyst is described as a synergic system with the rhodium apparently governing the selectivity but no heterobimetallic species were detected (ref. 453).

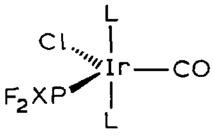
In the hydrosilylation of styrene by $HSiR_3$ (R = Et, Pr^i, Ph, OEt, Cl) in the presence of $[RhCl(PPh_3)_3]$ or $[RhH(CO)(PPh_3)_3]$ the best selectivity is found when the ratio Rh/Si is approximately 10^{-4}. However when this ratio is greater than 10^{-3} hydrogenation of the styrene becomes a competitive process (ref. 454). A variety of rhodium(I) and iridium(I) complexes catalyze the redistribution reactions of siloxanes bearing hydrogen substituents on silicon (ref. 455).

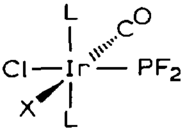
In alcohol solvents $[RhCl(CO)_2]_2$ is a catalyst precursor for the oxidation of hex-1-ene to hexan-2-one by molecular oxygen. Although the presence of a hydroperoxo complex, $[RhCl_2(CO)(O_2H)]^{2-}$, was detected and although it decomposed on attempted isolation it was shown to be relatively inactive for oxidation of the olefin. Rather, it appeared that a rhodium(III) chloro complex was the active catalyst since the activity of the system was enhanced by the addition of chloride ion (ref. 456). A combination of $[RhCl(CO)(PPh_3)_2]$ and benzoyl peroxide initiates the polymerization of vinyl monomers with a rate which appears dependent on the concentration of the rhodium complex. A radical mechanism seems certain but the initiation step is unclear (ref. 457). Various β-trimethylsilylallyl alcohols are catalytically isomerized in a regiospecific fashion to the corresponding trimethylsilyl enol ethers by $[RhH(CO)(PPh_3)_3]$ (ref. 458) while $[RhCl(CO)_2]_2$ catalyzes the isomerization of trans-bicyclo[4.1.0]hept-3-ene to the cis isomer in 65% yield. Using $[RhCl(COD)]_2$ however gives only 51% yield of the cis-isomer with the major portion of the remaining product being 1-methylcyclohexa-1,3-diene. The mechanism has not yet been elucidated (ref. 459).

The complexes $[Rh(L_2)_2]Cl$ (L_2 = DPPE, DPPP), $[RhCl(CO)(DPPP)_2]_2$ and $[RhCl(CO)(PPh_3)_2]$ have been studied as catalysts for the carbonylation of aryl azides to arylisocyanates. The last complex when supported on phosphinated polymers is approximately as active as in homogeneous media and shows good recycle characteristics (ref. 460). Other supported catalysts include one derived from $[RhH(CO)(PPh_3)_3]$ supported on an NaX zeolite which is about as active and more selective for the homologation of methanol to methyl acetate and dimethyl ether than those prepared similarly from rhodium (III) chloride or $[RhCl(NH_3)_5]Cl_2$ (ref. 461). The nature of the surface species obtained by reaction of $[RhCl(CO)_2]_2$ with phosphinated polymers and silica surfaces depends on the concentration of ligand sites and, in the case of the polymers, on the extent of crosslinking. The activity for catalysis of hydrosilylation is maximized when the support is rigid and the concentration of ligand sites is low as this presumably favors the formation of coordinatively unsaturated metal species (ref. 462). A polystyrene-divinylbenzene copolymer has been functionalized with acetylacetonato, ethyldithiocarbamato and ethylamino groups. Reaction of these with $[RhCl(CO)_2]_2$ provides supported cis-$\{Rh(CO)_2\}$ moieties on the first two and cis-$\{RhCl(CO)_2\}$ with the third. The first two are decarbonylated on photolysis or reaction with dihydrogen while the last is unaffected (ref. 463).

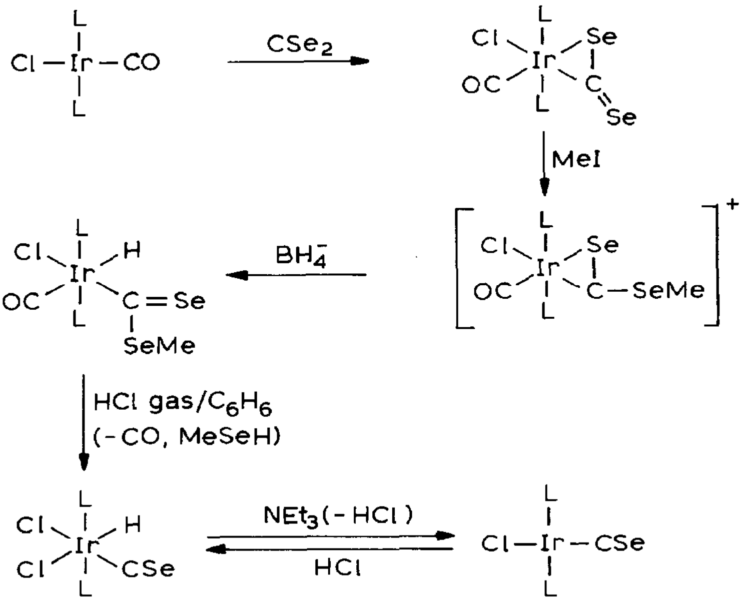
At low temperature the fluorophosphines PF_2X (X = F, H) add to $[IrCl(CO)(PEt_3)_2]$ giving [202] which on warming rearranges to [203] ($L = PEt_3$). Bromo and iodo analogs were also synthesized. Addition of diborane to [203] (X = Cl) gives $[IrX_2(CO)(PEt_3)_2(PF_2BH_3)]$ while reaction of the same complex with dioxygen, cyclooctasulfur or selenium forms $[IrCl_2(CO)(PEt_3)_2(P(E)F_2)]$ (E = O, S, Se). Complex [203] (X = Cl) also reacts with $[(arene)MCl_2]_2$ (M = Ru;

arene = C_6H_6, p-cymene. M = Os; arene = p-cymene) to give $[IrCl_2(CO)(PEt_3)_2(\mu\text{-}PF_2)((arene)MCl_2)]$ while with $[M'Cl_2(COD)]$ (M' = Pd, Pt) the


[202]

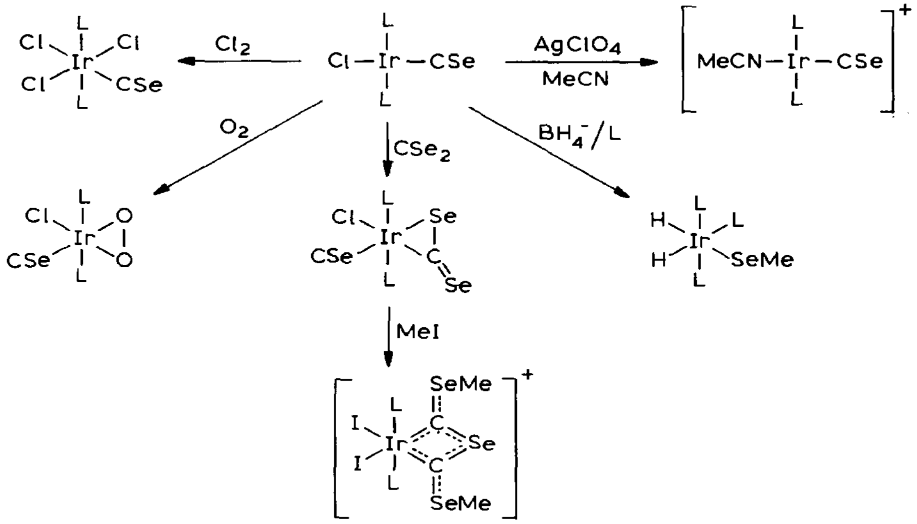

[203]

product is $[MCl_2((\mu\text{-}PF_2)IrCl_2(CO)(PEt_3)_2)_2]$ (ref. 464). The conversion of $[IrCl(CO)(PPh_3)_2]$ to $[IrCl(CSe)(PPh_3)_3]$ is outlined in Scheme XXXIV (L =

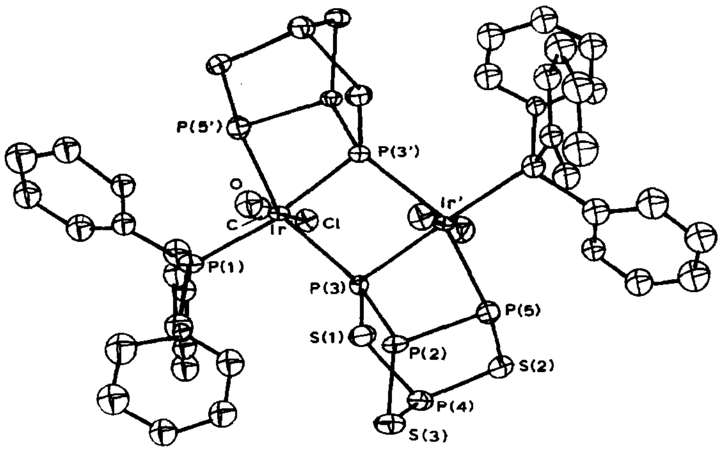


Scheme XXXIV

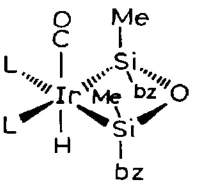
PPh_3) while further chemistry of the selenocarbonyl complex is shown in Scheme XXXV (ref. 465). Other reactions of $[IrCl(CO)(PPh_3)_2]$ include those with RHgCl (R = 2,5-$Cl_2C_6H_3$, 2,3,4-$Cl_3C_6H_2$, 2,4,6-$Cl_3C_6H_2$, C_6Cl_5, $CCl{=}CCl_2$) to form $[IrCl_2(HgR)(CO)(PPh_3)_2]$ (ref. 466), with tin(II) and mercury(II) chloride added successively in either order to give trans-$[IrCl(CO)(SnCl_3)(HgCl)(PPh_3)_2]$ (ref. 467) and with P_4S_3 wherein oxidative addition of a phosphorus-phosphorus bond occurs to yield [204] (ref. 468). Reaction of $[IrCl(CO)(PPh_3)_2]$ with $(H(bz)MeSi)_2O$ gives primarily [205] plus some [206] (L = PPh_3) which are unstable in solution in the absence of the disiloxane and which are catalyst precursors for the redistribution of substituents on silicon (refs. 469, 470). More details of the conversion of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene to tricyclo[3.2.1.$0^{2,7}$]oct-3-ene catalyzed by



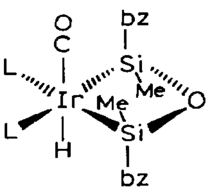
Scheme XXXV



[204]

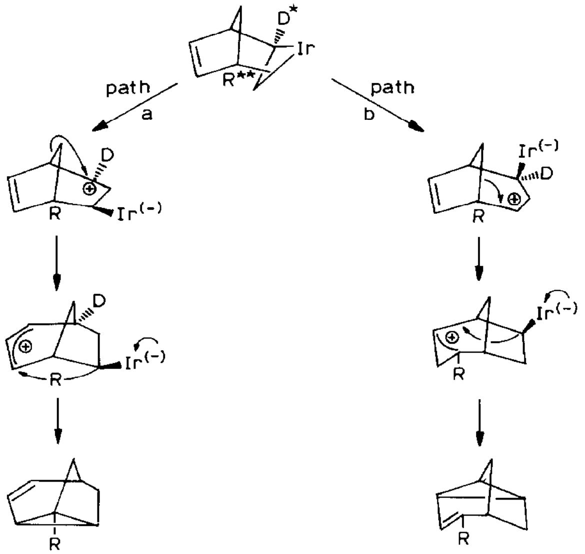


[205]



[206]

[IrCl(CO)$(PPh_3)_2$] have appeared. Labelling experiments indicate initial formation of the iridacycle shown at the top of Scheme XXXVI followed by conversion to products by a two-path process (R = H, or when R = Me, the



Scheme XXXVI

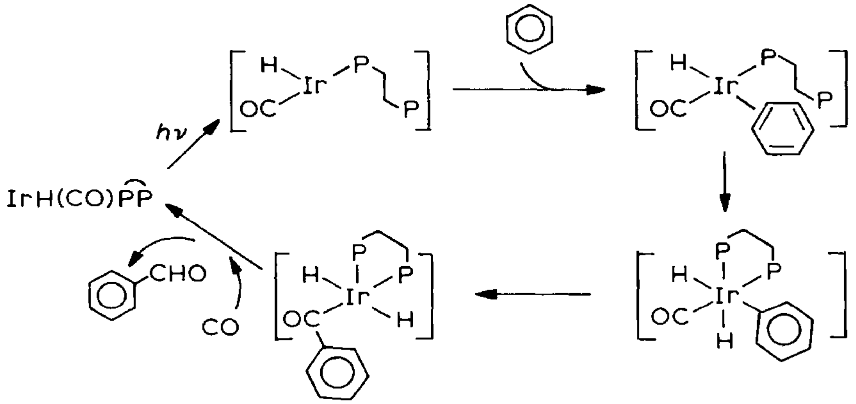
deuterium label is absent) (ref. 471). Reaction of DPPE with $[IrI_2(CO)_2]^-$ in hot THF yields [IrI(CO)(DPPE)] some of whose subsequent chemistry is detailed in Scheme XXXVII. These experiments suggest the formation of

$$\begin{tikzcd}
{[IrI(CO)(DPPE)]} \arrow[dr, "a"] \arrow[dd, "b"] & & \underline{fac}\text{-}[IrHD_2(CO)(DPPE)] \arrow[dd, "d"] \\
& \underline{fac}\text{-}[IrH_3(CO)(DPPE)] \arrow[dl, "c"] \arrow[ur, "d"] & \\
{[IrH(CO)_2(DPPE)]} & & \underline{fac}\text{-}[IrD_3(CO)(DPPE)] \arrow[ul, "e"]
\end{tikzcd}$$

a) $NaBH_4$, H_2, $EtOH/CH_2Cl_2$. b) $NaBH_4$, CO. c) Δ or hν, CO, C_6H_6.
d) Δ or hν, D_2/CO, C_6D_6. e) hν or Δ, H_2/CO, C_6H_6 or C_6D_6.

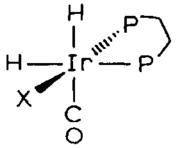
Scheme XXXVII

[IrH(CO)(DPPE)] as in intermediate in many of these reactions. The additional observations that photolysis of $[IrH_3(CO)(DPPE)]$ in deuterobenzene in vacuo forms $[IrH_2D(CO)(DPPE)]$ and that prolonged photolysis of the same solution under carbon monoxide or syngas atmospheres generates $[IrH(CO)_2$-(DPPE)] plus benzaldehyde suggest this intermediate is able to activate carbon-hydrogen bonds, possibly as depicted in Scheme XXXVIII (ref. 472). Further study of [IrI(CO)(DPPE)] and its chloro and bromo analogs shows that reversible activation of dihydrogen occurs to give [207] which slowly

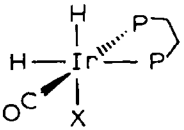


Scheme XXXVIII

equilibrates with [208] (X = Cl, Br, I). Conversion of [IrBr(CO)(DPPE)] to [Ir(CN)(CO)(DPPE)] occurs on reaction with PPN[CN] and reaction of the cyano complex with dihydrogen gives an equilibrium mixture of three isomeric dihydrides. The major one is [207] (X = CN) but [208] (X = CN) and a third one

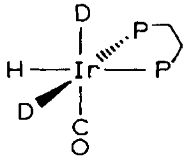


[207]



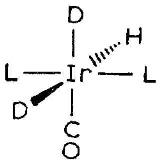
[208]

with the hydride ligands both trans to phosphorus are also seen. Dehydrobromination of [208] (X = Br) with DBU yields [IrH(CO)(DPPE)] which gives [209] as the initial product on reaction with deuterium. Other isotopomers

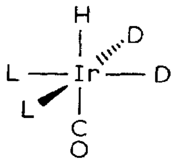


[209]

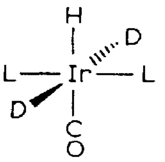
are formed subsequently as the system equilibrates. The stereochemical results are interpreted to indicate that the approach of the dihydrogen molecule to [IrH(CO)(DPPE)] occurs parallel to the OC-Ir-P axis with the π* orbital of the carbonyl group assisting the oxidative addition by increasing the overlap of a filled metal orbital with the σ* orbital of the dihydrogen molecule (ref. 473). Other workers have continued their work on the stereochemistry of oxidative addition of dihydrogen to iridium(I) centers with particular attention to the origin of products having trans-hydride ligands. Addition of $[IrH_3(CO)(PPh_3)_2]$ to liquid styrene yields the styrene complex $[IrH(CO)(CH_2{=}CHPh)(PPh_3)_2]$ which is unstable above -20°C. Addition of deuterium to this complex at -30°C forms a mixture of [210] and [211] (L = PPh_3) which on warming to room temperature rapidly forms a mixture of [212] and [213] (L = PPh_3). Intermolecular H/D exchange occurs on allowing the solution to remain at room temperature. When deuterium is added to $[IrH(CO)(PPh_3)_3]$ at room temperature [210] and [211] form but [213] is never seen. The H/D scrambling in the products is suggested to occur via an intermolecular process such as depicted in Scheme XXXIX (L = PPh_3) and this same process is now proposed for the formation of [212] rather than a direct trans-oxidative addition (note however that an intramolecular process has been claimed to lead to [212]: J. Chem. Soc., Chem. Commun., (1984)281) (ref. 474). Conversion of $[IrHCl_2(CO)(PPh_3)_2]$ to $[IrH(P(OMe)_3)_5](BPh_4)_2$ occurs on reaction with the phosphite and sodium tetraphenylborate in a methanol-butane-2-one mixture. The triethylphosphite analog is similarly formed in ethanol-butan-2-one (ref. 475). Refluxing either $[IrH_3(PPh_3)_3]$ or



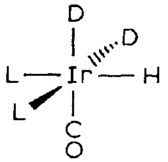
[210]



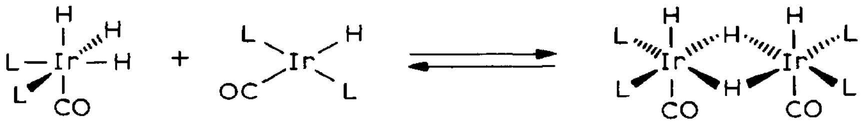
[211]



[212]



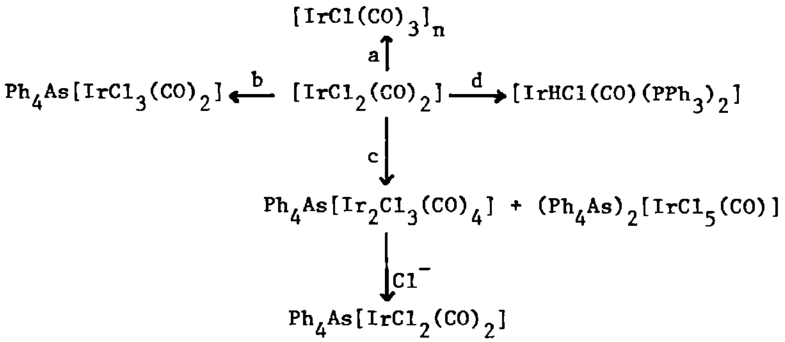
[213]



Scheme XXXIX

$[IrH(CO)(PPh_3)_3]$ in DMF yields a mixture of $[IrH(O_2CMe)_2(PPh_3)_2]$ and $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-}PPh_2)_2]$. The same reaction with $[IrH_3(PPh_2(\underline{p}\text{-tolyl}))_3]$ yields only $[Ir_2(CO)_2(PPh_2(\underline{p}\text{-tolyl}))_2(\mu\text{-}PPh_2)(\mu\text{-}PPh(\underline{p}\text{-tolyl}))]$. Since $[IrH(O_2CMe)_2(PPh_3)_2]$ contains one bidentate acetate ligand it will react with carbon monoxide giving trans-$[IrH(CO)(O_2CMe)_2(PPh_3)_2]$ (ref. 476). That $[IrH_2Cl(CO)(PPh_3)_2]$ reacts stoichiometrically with acrylonitrile to give propionitrile is taken to indicate that the $[IrCl(CO)(PPh_3)_2]$-catalyzed hydrogenation of acrylonitrile involves initial oxidative addition of dihydrogen to iridium. Observation of inhibition by chloride suggests that the hydride complex loses chloride to provide a site for coordination of the olefin (ref. 477). Chlorination of $[IrCl_2(CO)(PEt_3)_2(PCl_2)]$ yields the five coordinate phosphorus complex $[IrCl_2(CO)(PEt_3)_2(PCl_4)]$. Reaction with $[IrCl(CO)(PEt_3)_2]$ or triethylphosphine regenerates the starting complex and forms $[IrCl_3(CO)(PEt_3)_2]$ or dichlorotriethylphosphorane respectively (ref. 478).

As discussed earlier for some rhodium complexes, $[Ir(N_3)(CO)(PPh_3)_2]$ undergoes a 1,3-cycloaddition with nitriles to yield the tetrazolato complexes trans-$[Ir(N_4CR)(CO)(PPh_3)_2]$ (R = Me, CF_3) (ref. 479). Reduction of ammonium hexachloroiridate(IV) with hydrogen at 400°C yields an active form of iridium metal which can be converted to $[IrCl_2(CO)_2]$ using a 2:1 mixture of chlorine and carbon monoxide at 300°C while at 200°C in the additional presence of hydrogen chloride the product is "$HIrCl_4(CO)$". This is readily converted to $M[IrCl_4(CO)]$ (M = Cs, PPN). If the active iridium metal is treated with chlorine and carbon monoxide at 180°C, the product is $[Ir_2Cl_6(CO)_4]$ from which $Ph_4As[IrCl_4(CO)_2]$ can be obtained on reaction with hydrogen chloride and tetraphenylarsonium chloride. Further chemistry of $[IrCl_2(CO)_2]$ is outlined in Scheme XL (ref. 480). The hydride chemical shifts plus ν_{Ir-H} and $\nu_{C\equiv O}$ in the all-trans-$[IrH(X)Cl(CO)(PPh_3)_2]$ (X = $SeCN^-$, $NCSe^-$, $CF_3O_2SO^-$, $C_4F_9O_2SO^-$, FBF_3^-) and the all-trans-$[IrHCl(CO)L(PPh_3)_2]BF_4$ (L = PPh_3, cyNC, MeCN, H_2O, acetone, THF) have been measured to assess the trans-influence of neutral and anionic ligands. It is found that the hydride chemical shift correlates well with ν_{Ir-H} and each parameter correlates with the electronegativity of the ligand (X or L) but neither



a) CO in toluene. b) Ph_4AsCl, HCl in chloroform. c) Ph_4AsCl in ethanol. d) PPh_3, HCl in chloroform.

Scheme XL

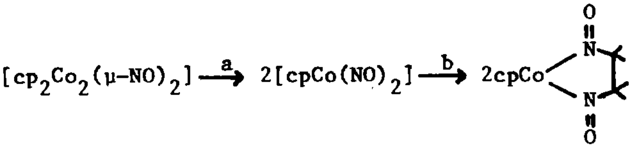
correlates with $\nu_{C\equiv O}$ (carbonyl cis to hydride). The variation in the other two parameters is attributed to changes in the σ-donor strength of X or L (ref. 481).

Extended-Hückel molecular orbital calculations on the band structure of $[IrCl(CO)_3]_n$ suggest that bound states are not possible without a partial oxidation of the metal. This indicates that the repeat unit in the polymer is nonstoichiometric (ref. 482). The mechanism of the reduction and homologation of formaldehyde in the presence of iridium complexes has been discussed (ref. 483). Finally, $[IrCl(CO)(PPh_3)_2]$ has been supported on a phosphinated styrene-divinylbenzene copolymer and found to be an efficient catalyst for the hydrogen-transfer from formic acid to the olefinic bond in α,β-unsaturated ketones (ref. 484).

Metal Nitrosyl and Aryldiazo Complexes

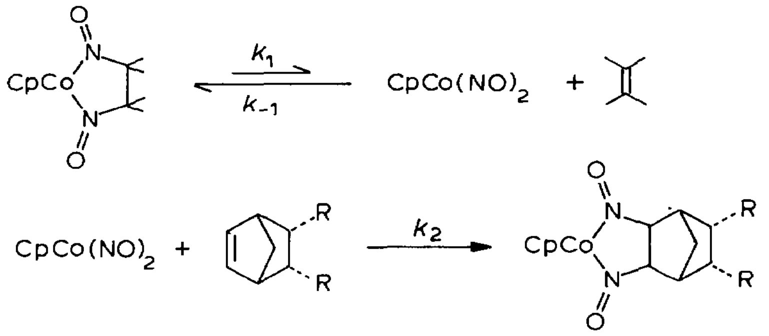
The complex $[cp_2Co_2(\mu\text{-}NO)_2]PF_6$ can be synthesized from $[cpCo(CO)_2]$ and nitrosyl hexafluorophosphate in refluxing dichloromethane or from $[cp_2Co_2(\mu\text{-}NO)_2]$ on oxidation with ferricinium hexafluorophosphate. The cation shows a reversible, one-electron reduction and an irreversible one-electron oxidation in cyclic voltammetric experiments. It also reacts with triphenylphosphine to form $[cp_2Co_2(\mu\text{-}NO)_2]$ plus $[cpCo(NO)(PPh_3)]PF_6$ and with silver hexafluorophosphate in the presence of cyclooctene to yield $[cpCo(cyoct)(NO)]PF_6$. Finally, the dimeric cation reacts with o-xylylisocyanide to form

$[Co(NO)(CNR)_3]$ plus $[cp_2Co_2(CNR)_2(\mu\text{-}NO)]PF_6$. The behavior of the pentamethylcyclopentadienyl analogs is somewhat different. At room temperature $[cp'Co(CO)_2]$ and nitrosyl hexafluorophosphate yield $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}NO)]PF_6$ which can only be converted to $[cp'_2Co_2(\mu\text{-}NO)_2]$ by reaction with nitric oxide; the original reaction with excess nitrosyl hexafluorophosphate gives $[cp'_2Co_2(\mu\text{-}O_2PF_2)_3]PF_6$ instead. Reduction of $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}NO)]PF_6$ with sodium borohydride gives the neutral dimer which shows reversible, one-electron oxidation and reduction processes in dichloromethane. A previously reported irreversibility of the oxidation step when performed in acetonitrile must therefore reflect a problem with the solvent. Unlike the cyclopentadienyl analog, reduction of $[cp'_2Co_2(\mu\text{-}NO)_2]PF_6$ with lithium triisobutylborohydride affords only a low yield of air-sensitive $[cp'_2Co_2\text{-}(\mu\text{-}NO)_2]$ (ref. 485). A full report has now appeared on the reaction of $[cp_2Co_2(\mu\text{-}NO)_2]$ with olefins in the presence of nitric oxide. The mechanism of Scheme XLI is proposed on the basis of kinetic studies. The intermediacy of $[cpCo(NO)_2]$ was demonstrated by its identification in dilute solutions and its subsequent bimolecular reaction with olefins to give the same products. The intermediate is unstable, particularly in concentrated solution and decomposes to unidentified products. The stability of the dinitrosoalkane complexes increases with the bulk of the olefin from which they are formed and significant nitrogen-to-cobalt π-backbonding is proposed since displacement of the dinitrosoalkane by triphenylphosphine could not be accomplished. Despite this, reaction of the dinitrosoalkane complexes with olefins occurs readily and stereospecifically under thermal or photochemical conditions as depicted for one example in Scheme XLII. With NBD the bis adduct [214] can be formed (refs. 486, 487). Also appearing in full are the details of the insertion of nitric oxide into cobalt-carbon bonds. Reduction of $[cp_2Co_2(\mu\text{-}NO)_2]$ with sodium amalgam yields $Na[cpCo(NO)]$ which reacts with alkyl iodides to form $[cpCo(NO)R]$ (R = Me, Et, Pr^i, p-tolylCH_2) which is only stable at low temperature. Addition of a phosphine yields $[cpCo\text{-}(N(O)R)L]$ (L = PPh_3, PEt_3). Insight into the mechanism was obtained from an experiment where methyl iodide was added to a mixture of $Na[cpCo(NO)]$ and

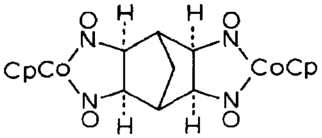


a) NO. b) olefin

Scheme XLI

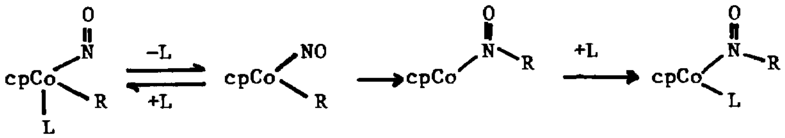


Scheme XLII

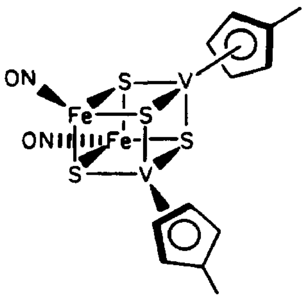


[214]

triethylphosphine at -60°C whereupon [cpCo(NO)Me(PEt$_3$)], containing a bent nitrosyl ligand was detected. On warming, [cpCo(N(O)Me)(PEt$_3$)] formed at a rate which decreased as the concentration of the phosphine in the original solution increased which suggests the process of Scheme XLIII (ref. 488).



Scheme XLIII



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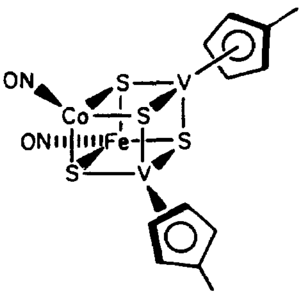

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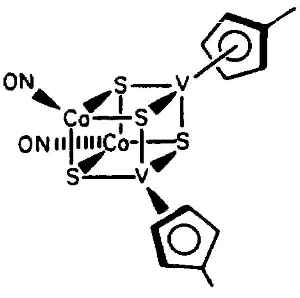
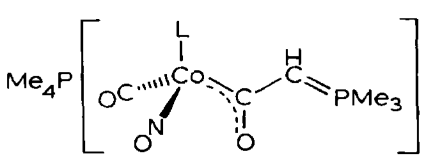


[217]

A mixture of $[Co(NO)(CO)_3]$, [215] and trimethylamine N-oxide yields [216] on briefly refluxing in THF while under more forcing conditions further transmetalation occurs to form [217] (ref. 489). Attempts to effect a nucleophilic nitrosylation of $[Co(CO)_3(NO)]$ and $[Co_2(CO)_8]$ with $PPN[NO_2]$ in THF yields $PPN[Co(NO_2)(CO)_2(NO)]$ and $[Co(NO)(CO)_3]$ plus $PPN[Co(CO)_4]$ respectively. The results here were not very encouraging but the process works well with other metals (ref. 490). On the other hand the same reaction with $[Co(CO)_3L_2]A$ ($L = PPh_3$; $A = PF_6^-$. $L = PBu^n{}_3$; $A = [Co(CO)_4]^-$) readily affords $[Co(NO)(CO)_2(L)]$. With $[cpCo(C_3F_7)(CO)(PPh_3)]PF_6$, $PPN[NO_2]$ produces an air-sensitive oil which was thought to be $[cpCo(C_3F_7)(NO)]$ but could not be satisfactorily characterized (ref. 491). A reversible reaction occurs between $[Co(CO)_2(NO)L]$ ($L = CO$, PMe_3) and trimethylphosphinemethylene to form [218] which on heating forms [219] (ref. 492). An improved preparation of $[CoI(NO)_2(L)]$ ($L = PPh_3$, PPh_2Et) from $[CoI(NO)_2]$ and the ligand in refluxing acetone has appeared. The structure of the triphenylphosphine complex shows both nitrosyl ligands to be essentially linear (ref. 493). Exchange of ^{15}NO with $[Co(NO)_2(PPh_3)_2]^+$ has been studied and the initial product found to be that in which only one nitrosyl ligand has exchanged (ref. 494). Reaction of anhydrous cobalt(II) thiocyanate with phosphite ligands gives $[Co(NCS)L_4]^+$ ($L = P(OEt)_3$, $PPh(OEt)_2$) which is sometimes contaminated with $[Co(NCS)_2L_3]$. The former complex reacts with nitric oxide to give initially $[Co(NCS)L_3(NO)]^+$ which disproportionates to $[Co(L)_2(NO)_2]^+$ and $[Co(NCS)_2L_4]^+$ and reacts further with nitric oxide to form $[Co(NO)_2L_2]^+$ (ref. 495). Ion/molecule reactions of the fragment ions produced from $[Co(NO)(CO)_3]$ by electron impact with 2-chloroethanol, 1-chloroethylacetate and $CH_2{=}CHCH_2R$ ($R = NH_2$, Cl, Br, OH, $OCH_2CH{=}CH_2$) have been studied. The number of different reaction paths observed increases as the number of ligands remaining on the cobalt ion increases (ref. 496).



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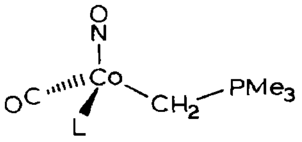


[219]

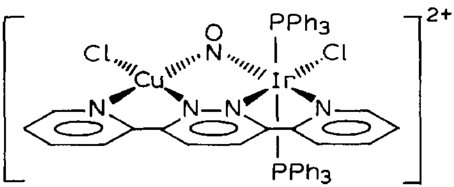
Chloro-, dichloro- and trifluoroacetic acids react with $[M(NO)(PPh_3)_3]$ ($M = Rh$, Ir) in benzene to give $[M(O_2CR)(NO)(PPh_3)_2]$ ($R = CF_3$, CH_2Cl, $CHCl_2$) while with trichloro- or tribromoacetic acid decarboxylation occurs to yield $[MX_2(NO)(PPh_3)_2]$ ($X = Cl$, Br). With very short reaction times, however, $[Rh(O_2CCX_3)(NO)(PPh_3)_2]$ could be isolated. A stoichiometric quantity of trihaloacetic acid reacts with $[RhH(CO)(PPh_3)_3]$ in hot benzene to give $[RhX(CO)(PPh_3)]$ ($X = Cl$, Br) while excess acid affords $[RhX_3(CO)(PPh_3)_2]$.

With the iridium analog, the reaction proceeds through $[IrH_2(CO)(PPh_3)_3]^+$ to $[IrH_2(CO)(O_2CCX_3)(PPh_3)_2]$ which can be decomposed to $[IrH(CO)(PPh_3)_3]$, trihalomethane and carbon dioxide. Unfortunately this does not provide a catalytic cycle for decarboxylation of these acids since in the presence of excess acid one forms $[IrH_2(CO)(PPh_3)_3]^+$ but on heating the product is now $[IrX_3(CO)(PPh_3)_2]$ (X = Cl, Br) (ref. 497).

In acetonitrile solution nitrosyl hexafluorophosphate converts either $[Rh(COD)(bipy)]PF_6$ or $[Rh(CO)_2(bipy)]PF_6$ to $[Rh(NO)(bipy)(MeCN)_3](PF_6)_2$ which on treatment with dioxygen forms $[Rh(NO_2)(bipy)(MeCN)_2](PF_6)_2$. Oxidation of a coordinated nitrosyl ligand occurs similarly in $[Rh(NO)(MeCN)_4](BF_4)_2$ to give $[Rh(NO_2)(MeCN)_4](BF_4)_2$ which reacts with olefins to give aldehydes or ketones. By contrast, $[RhCl_2(NO)(MeCN)_2]$ is inert to dioxygen (ref. 498).

Nitrogen-15 NMR chemical shifts have been determined for a large number of nitrosyl complexes including $[Co(NO)(CO)_2L]$ (L = CO, PPh_3), $[RhCl(NO)(PPr^i_3)_2]ClO_4$ and $[RhCl(CO)(NO)(PPr^i_3)_2]ClO_4$. Bent nitrosyl ligands appear 350-700 ppm downfield from what is observed for their linear counterparts (refs. 499-501).

Addition of 3,6-bis(2'-pyridyl)pyridazine (dppn) to $[Ir(NO)(MeCN)_3(PPh_3)_2](PF_6)_2$ yields $[Ir(NO)(dppn)(PPh_3)_2](PF_6)_2$ which reacts further with copper(II) chloride to give [220] and with $[PdCl_2(NCPh)_2]$ or $[PtI_2(COD)]$ to give $[Ir(NO)(dppn)(PPh_3)(PdCl_2)]^{2+}$ and $[Ir(NO)(dppn)(PPh_3)(PtI_3)]^+$ respectively (refs. 502, 503). In a related study the di-imine of 9,10-phenanthrenequinone also reacts with $[Ir(NO)(MeCN)_3(PPh_3)_2](PF_6)_2$ to give [221] which on treatment with weak bases rearranges to [222] (ref. 504).



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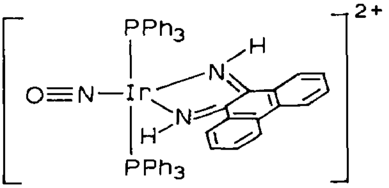

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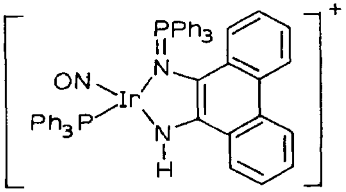
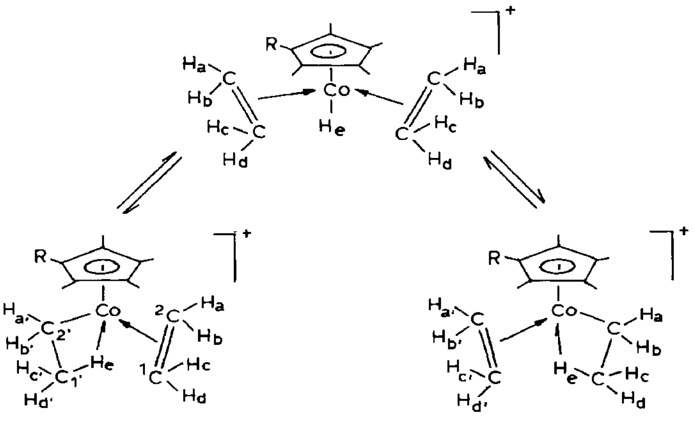


[222]

An EPR study on $[Ir(NO)Br_3(PPh_3)_2]$ in the solid state is interpreted to indicate that the unpaired electron density resides largely in the π^* orbital of the nitrosyl ligand. On this basis the complex is suggested to be the best formulated as an iridium(III) complex of neutral nitric oxide (ref. 505).

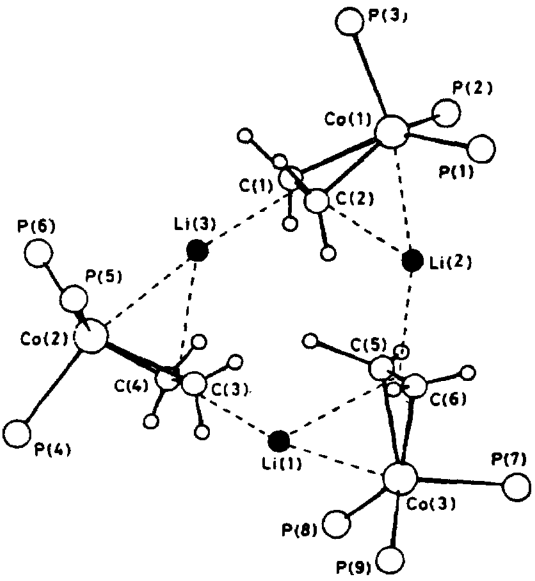
Metal Alkene Complexes

Reaction of a mixture of cycloocta-1,5-diene, cyclopentadiene and $[Co(acac)_3]$ with an "organically solvated" magnesium powder formed by reaction of powdered magnesium in THF with anthracene yields [cpCo(COD)]. The same reducing agent is also useful for the synthesis of $[cp_2Co]$ and η^3-allyl complexes of cobalt (ref. 506). The versatile synthon, $[cpCo(C_2H_4)_2]$, is prepared by the potassium reduction of $[cp_2Co]$ at -20°C in diethyl ether under an ethylene atmosphere. Its use in forming mixed-metal complexes has been described earlier (see refs. 362, 363) and at -10°C it reacts with but-2-yne forming $[cpCo(\eta^6-C_6Me_6)]$. At room temperature it catalyzes the cyclotrimerization of unsymmetrical internal alkynes and the co-cyclotrimerization of alkynes with nitriles (ref. 507). The analog, $[cp'Co(C_2H_4)_2]$ on prolonged refluxing in n-octane yields the carbyne complex $[cp'_3Co_3(\mu_3-CMe)_2]$ which appears to be the first example of the generation of a μ_3-carbyne moiety from ethylene in the absence of pre-formed metal-hydride or -carbene species. Under an ethylene atmosphere more strenuous conditions are required to get the product and substantial amounts of ethane are formed together with smaller amounts of C_4, C_6, C_8 and C_{10} mono-olefins (ref. 508). Protonation of $[(\eta^5-C_5H_4R)Co(C_2H_4)_2]$ (R = Me, Et) with tetrafluoroboric acid yields the ethyl complex $[(\eta^5-C_5H_4R)CoEt(C_2H_4)]BF_4$ rather than the expected hydride. The low temperature proton NMR spectrum provides evidence for formulation of the complexes with an agostic ethyl group as shown at the bottom of Scheme XLIV. This spectrum shows that the equilibration of H_e is

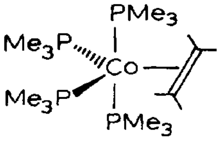


Scheme XLIV

still rapid at -90°C and the process of Scheme XLIV is proposed. Rotation of the ethylene ligand coupled with this process provides an explanation for the observed equilibration of all of the hydrogen atoms of the ethyl and ethylene ligands that is observed at higher temperatures (ref. 509). Alkali metal reduction of [Co(L)(PMe$_3$)$_3$] (L = C_2H_4, cyclopentene) in pentane affords [M(Co(L)(PMe$_3$)$_3$)]$_3$ (M = Li, K, Rb, Cs). The structure of the lithium compound is [223]. The complexes function as carriers of the alkali metal in hydrocarbon media for the formation of intercalation compounds (refs. 510, 511). At low temperature olefins add to [CoX(PMe$_3$)$_3$] (X = Cl, Br) to form [CoX(olefin)(PMe$_3$)$_3$] (olefin = C_2H_4, C_3H_6, cyclopentene) which dissociate on warming. Reaction of the adducts with organolithium reagents at -78°C yields [224] (R = Me, Ph) which do not show any tendency for the olefin to insert into the cobalt-carbon bond (ref. 512). In refluxing hexane [cp'Co(CO)$_2$] and octafluorocyclooctatetraene yield a mixture of [225] (R = Me) and [226] which on standing in solution equilibrate to give primarily the latter complex. With [cpCo(CO)$_2$] only [225] (R = H) formed in



[223]



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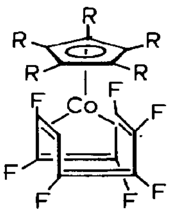

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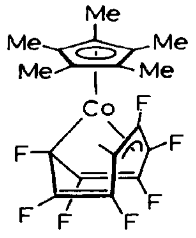
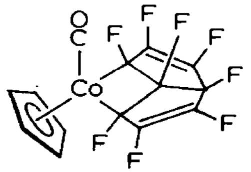


[226]

low yield and no isomerization to the analog of [226] was observed. The equilibration of [225] and [226] is formally an intramolecular redox reaction and its observation only when R = Me is attributed to the greater electron-denoting ability of the pentamethylcyclopentadienyl ligand. In neat OFCOT at 80°C $[cpCo(CO)_2]$ also forms [227] in very low yield (ref. 513). Reaction of $[Co(H)(N_2)(PPh_3)_3]$ with diallyl ether forms propene, allyl alcohol and a η^3-η^2-bonded diallyl ether complex as depicted in Scheme XLV (L = PPh_3) (ref. 514). The diethyl fumarate complex $[Co(MeCN)_3(L)_2]$ (L = diethyl fumarate) reacts with trimethylphosphite and maleic anhydride in toluene to form the pseudo-tetrahedral species $[Co(P(OMe)_3)_3(MA)]$ (ref. 515) and, in the presence of zinc metal, catalyzes the addition of <u>gem</u>-dihaloalkanes to dimethylfumarate to form <u>trans</u>-bis(carboxymethyl)cyclopropanes. The function of the zinc is to reduce the cobalt(II) bromide formed to regenerate a cobalt(0) olefin complex (ref. 516). With $[Co_2(CO)_8]$, 1,1-dimethylsilole reacts as a diene to form a mixture of [228] and [229]. Complex [229] converts to [228] in refluxing toluene on or chromatography on



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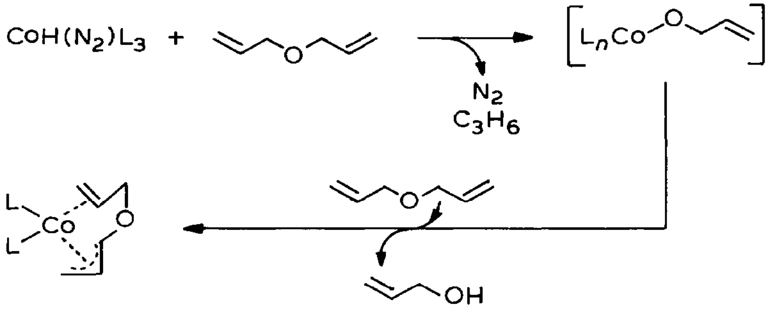
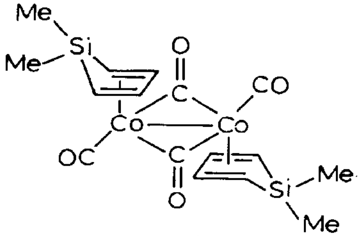


Scheme XLV

alumina. Reduction of the mixture of isomers with sodium amalgam forms $[(\eta^4\text{-}C_4H_4SiMe_2)Co(CO)_2]^-$ which reacts with iodine and triphenyltin chloride



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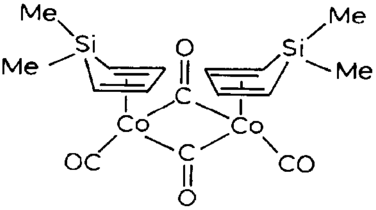
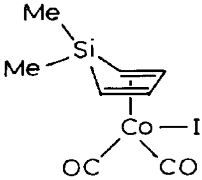


[229]

to yield [230] and [231] respectively. No η^5-coordination of the silole ligand could be achieved (ref. 517).



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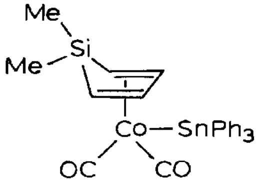
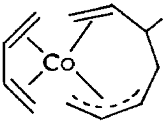
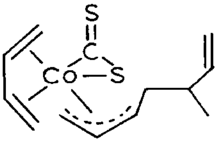


[231]

Reduction of $[Co(acac)_2]_4$ with ethoxydiethylaluminum provides a species able to catalyze the linear dimerization of buta-1,3-diene. Linear trimers and cyclodimers are also formed. The catalysis is inhibited by the addition of phosphines and the involvement of Co(0)-butadiene complexes which undergo oxidative addition of carbon-hydrogen bonds is proposed (ref. 518). In a related system, the reduction of $[Co(acac)_3]$ by triethylaluminum in the presence of buta-1,3-diene yields [232] which is converted to [233] on



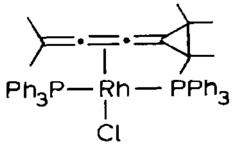
[232]



[233]

reaction with carbon disulfide. Complex [233] catalyzes the formation of syndiotactic poly-1,2-butadiene (ref. 519). Reduction of $[Co(acac)_3]$ with diethylaluminum hydride in the presence of COD forms $[Co(H)(COD)_2]$ which catalyzes the dimerization of propylene. The same reduction in the presence of triphenylphosphine gives $[Co(H)(PPh_3)_3]$ which is a more active catalyst and affords a greater selectivity to 2-methylpent-1-ene (ref. 520). Butadiene polymers functionalized with phosphonate and phosphinate groups have been used to support cobalt complexes which have been studied as catalysts for the hydrogenation and isomerization of allyl benzene. Unfortunately the activity was found to be very low (ref. 521).

The cumulene complexes [234]-[236] are formed from the appropriate cumulene and $[RhCl(PPh_3)_3]$. The analog with $Ph_2C{=}C{=}C{=}CPh_2$ was also synthesized while with $R_2C{=}C{=}C{=}C(H)MEt_3$ (M = Si, Ge; R = Me, Ph. M = Si; R = Ph) a mixture of E and Z isomers of the corresponding $[RhCl(PPh_3)(cumulene)]$ species were formed. In an attempt to prepare a bimetallic cumulene complex, $[Pt(PPh_3)_2(Ph_2C{=}C{=}C{=}C(H)EEt_3)]$ (E = Si, Ge) was reacted with $[RhCl(PPh_3)_3]$ but the only product was $[RhCl(PPh_3)_2(Ph_2C{=}C{=}C{=}C(H)EEt_3)]$ (refs. 522-524). Chloride abstraction from $[RhCl(CO)(PPh_3)_2]$ by silver perchlorate in acrylonitrile yields $[Rh(CH_2{=}CHCN)(CO)(PPh_3)_2]ClO_4$. This reacts with dihydrogen in chloroform to give $[Rh(CH_3CH_2CN)(CO)(PPh_3)_2]ClO_4$ which can also be prepared directly by reaction of the acrylonitrile complex with propionitrile. If the hydrogenation is carried out in acrylonitrile solution the products are propionitrile and polymerized acrylonitrile (ref. 525). Acetylene adds to $[RhCl(PPr^i_3)_2]$ to give $[Rh(C_2H_2)Cl(PPr^i_3)_2]$ which reacts successively with sodium cyclopentadienide and chalcogens to form [237] and then [238] (E = S, Se, Te) (ref. 526). The ethylene complex



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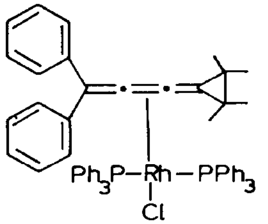

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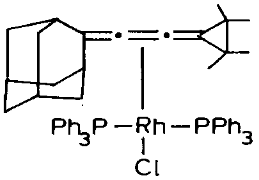

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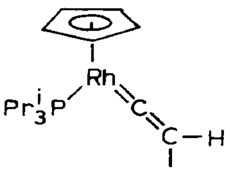

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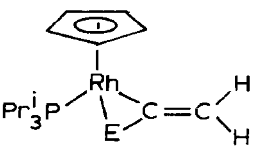
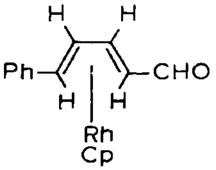


[238]

$[RhH(C_2H_4)(PPr^i_3)_2]$ is formed from ethylene and $[RhH(N_2)(PPr^i_3)_2]$ at low temperature. A variable temperature NMR study showed the original trans-olefin hydride complex to isomerize to the cis isomer and at temperatures above 0°C to undergo rapid and reversible conversion to [RhEt(PPr$^i_3$)$_2$] (ref. 527). Addition of 5-phenylpenta-2,4-dien-1-al to [RhCl(cyoct)$_2$]$_2$ forms [RhCl(Ph(CH=CH)$_2$CHO)]$_2$ which reacts successively with thallium cyclopentadienide, acetophenone in the presence of hydroxide ion and hexafluorophosphoric acid etherate to form [239], [240] and [241] in that order. The same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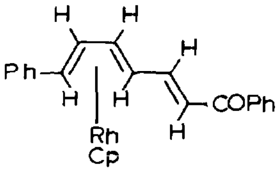
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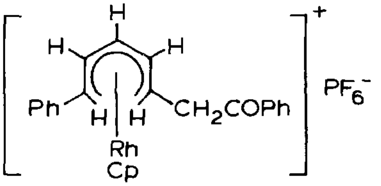
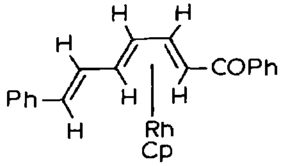

[241]

reaction with 1,7-diphenylhepta-2,4,6-trien-1-one and then thallium cyclopentadienide proceeds analogously to give [242] which is protonated by tetrafluoroboric acid etherate to give [243] and by hydrohalic acids to form [244] (X = Cl, Br) (ref. 528). Reaction of [RhCl(C$_2$H$_4$)$_2$]$_2$ with four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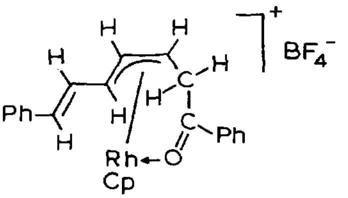
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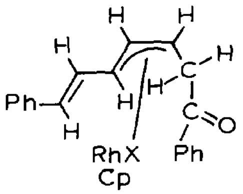
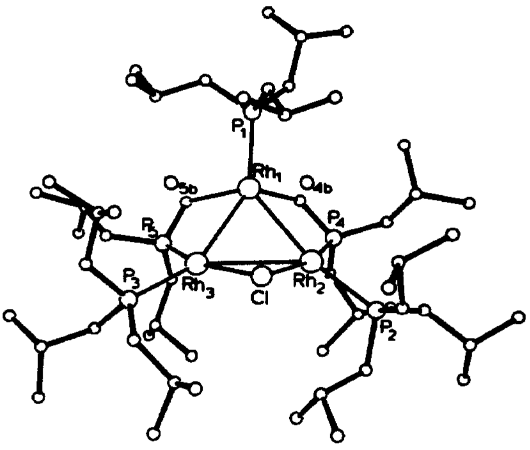
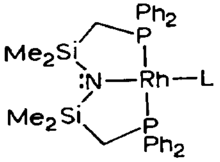

[244]

equivalents of triisopropylphosphite followed by reduction with potassium triisopropoxyborohydride under dihydrogen yields [Rh(μ-H)(P(OPr^i)$_3$)$_2$]$_2$ plus the alkane-soluble salt K[H$_3$Rh$_3$(μ-Cl)(μ-OP(OPr^i)$_2$)$_2$(P(OPr^i)$_3$)$_3$]. The heavy atom skeleton of the latter is shown as [245]. The hydride ligands were not located in the structure but one is thought to cap the face of the metal triangle while the others bridge the Rh$_1$-Rh$_2$ and Rh$_1$-Rh$_3$ edges. The alkane solubility is attributed to a tight encapsulation of the potassium counterion by the oxygen atoms of the phosphite ligands (ref. 529). The rhodium(I) amido complexes [246] (L = CO, cyoct, C$_2$H$_4$, PMe$_3$, PPh$_3$) are prepared from Li[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] and [RhCl(L)$_2$]$_2$ (L = CO, cyoct, C$_2$H$_4$), [Rh(PMe$_3$)$_4$]Cl and [RhCl(PPh$_3$)$_3$] respectively. The iridium analog of [246] (L = cyoct) is prepared similarly from [IrCl(cyoct)$_2$]$_2$ and the other derivatives can be prepared from this by displacement of cyclooctene with the appropriate ligands. Similarly, reaction of [MCl(COD)]$_2$ (M = Rh, Ir) with Li[PhCH$_2$NSiMe$_2$CH$_2$PPh$_2$] gives [247]. Complexes [246] (L = cyoct, PPh$_3$) catalyze the



[245]



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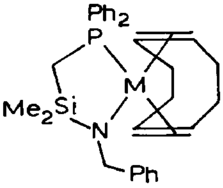
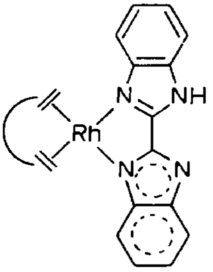


[247]

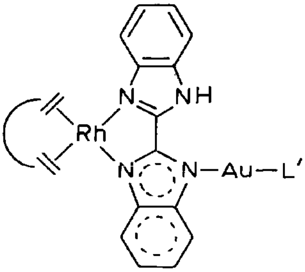
hydrogenation of hex-1-ene and are even more effective for isomerization of the olefin under dihydrogen. The iridium analog of [246] (L = cyoct) also catalyzes the hydrogenation of hex-1-ene but no isomerization is observed (ref. 530).

Standard methods have been used to synthesize $[Rh(Me_3TFB)L_2]PF_6$ (L = O-, N-, P-, As-, Sb-donor ligands), $[Rh(\eta^6\text{-arene})(Me_3TFB)]PF_6$ (arene = C_6Me_6, mesitylene, C_6H_6) and $[Rh(Me_3TFB)(PPh_3)(S)]PF_6$ (S = acetone, DMSO). In several of these, the Me_3TFB ligand could be replaced by two carbonyl ligands (ref. 531). Two groups have reported on the reaction of $[MCl(COD)]_2$ (M = Rh, Ir) with various bifunctional nitrogen-donor ligands (N-N), such as pyrazine, quinoxaline, 4,4'-bipyridine and phenazine and its oxide. The first reports initial formation of $[RhCl(COD)(\mu\text{-N-N})RhCl(COD)]$ which reacts with carbon monoxide to give $[RhCl(CO)_2(\mu\text{-N-N})RhCl(CO)_2]$ and with bipy to give $[Rh(COD)(bipy)][RhCl_2(COD)]$ (ref. 532) while the second reports the initial product is $[MCl(COD)(N\text{-}N)]$ (ref. 533). Reaction of $[MCl(diolef)]_2$ with indole and silver salts yields $[(\eta^6\text{-indole})M(diolef)]X$ (M = Rh, Ir; diolef = COD; X = ClO_4^-, BF_4^-. M = Rh; diolef = TFB, Me_3TFB. X = ClO_4^-)

while the same reaction using [LAuIn] (L = PPh_3, P(o-tolyl)$_3$, P(p-tolyl)$_3$; In = indolate anion) yields [(η^6-InAuCl)M(diolef)]X (ref. 534). Deprotonation of 2,2'-bibenzimidazole (H_2L_2) occurs on reaction with [Rh(acac)-(diolef)] (diolef = COD, NBD) to yield [248] which converts to [249] on reaction with silver perchlorate and [AuClL'] (L' = PPh_3, $P(OMe)_3$).

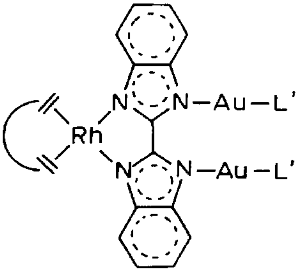


[248]



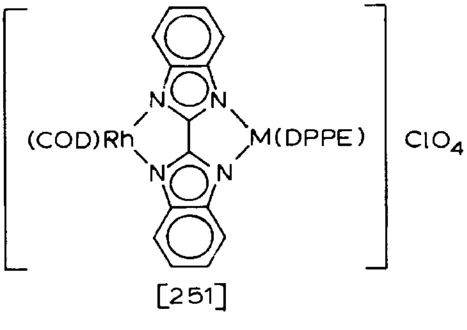
[249]

The reaction of [Rh(COD)(acetone)$_x$]ClO_4 with [$L'_2Au_2(L_2)$] (L'_2 = $(PPh_3)_2$, $(P(OMe)_3)_2$, DPM, DPPE) yields [250]. All of the above complexes react with



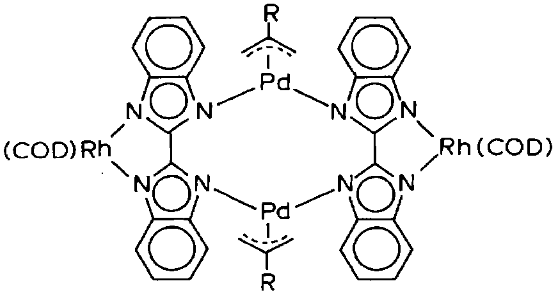
[250]

carbon monoxide to replace the diolefin ligands with two carbonyl groups and these in turn react with triphenylphosphine and trimethylphosphite to replace one carbonyl group with the phosphorus ligand (ref. 535). In further work on bibenzimidazolate complexes, [Rh(COD)(acetone)$_x$]ClO_4 reacts with [M(L_2)(DPPE)] to give [251] (M = Pd, Pt). As before the COD ligand is

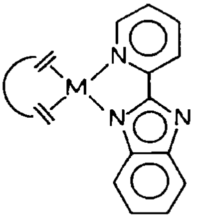


[251]

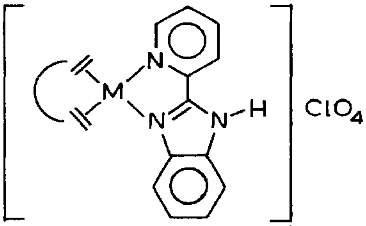
replaced by two carbonyl ligands and one of these in turn can be replaced by triphenylphosphine (ref. 536). Using [248] and $[(\eta^3\text{-2-RC}_3H_4)Pd(acac)]$ (R = H, Me) the product is [252]. This can also be formed from [Rh(acac)(COD)] and $[(\eta^3\text{-2-RC}_3H_4)Pd(HL_2)]$ and the analogs with 2,2'-biimidazole were also prepared. The latter on reaction with carbon monoxide yielded tetracarbonyl derivatives by displacement of the COD ligands while [252] gave instead $[(\eta^3\text{-2-RC}_3H_4)_4Pd_4(\mu\text{-}L_2)_2]$ and $[Rh_4(CO)_8(\mu\text{-}L_2)_2]$ (ref. 537). In related work, [M(acac)(COD)] (M = Rh, Ir) reacts with 2-(2'-pyridyl)benzimidazole to form [253] which can be reversibly protonated to give [254]. Complex [254] (M = Rh) can be generated directly from reaction of $[RhCl(NBD)]_2$, silver perchlorate and the ligand. As before displacement of the diolefin by carbon monoxide occurs. Further reaction of [253] with silver perchlorate and triphenylphosphine yields [255] while [256] (L = PPh_3, $P(OMe)_3$) results on



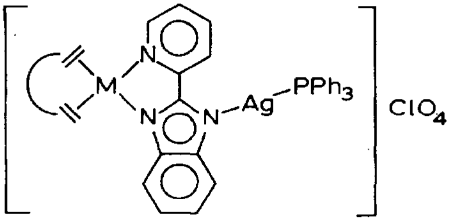
[252]



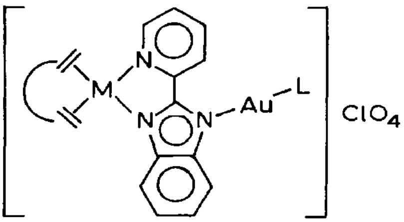
[253]



[254]

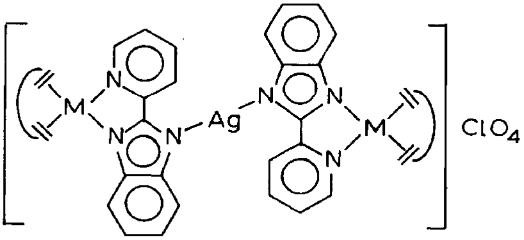


[255]



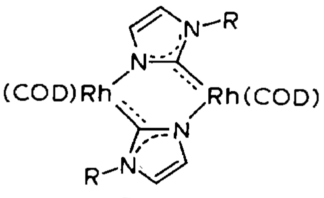
[256]

reaction of [253] with silver perchlorate and [AuCl(L)]. Use of an excess of the rhodium or iridium complex in the former reaction yields [257] (ref. 538).



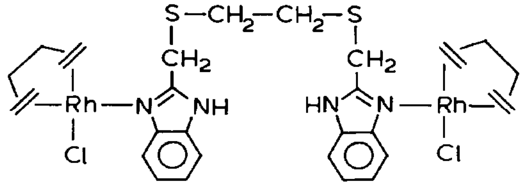
[257]

The complexes [RhCl(COD)L] (L = pyrazole, dimethylpyrazole) and [Rh(COD)-L_2] (L = pyrazole) show dynamic behavior in solution. The structures of the first two complexes have been determined and the pyrazole complex is found to have the plane of the pyrazole ligand nearly parallel to the coordination plane thereby permitting it to stack in the solid state with a relatively short metal-metal distance (3.452Å) (ref. 539). Treatment of $[RhCl(NBD)]_2$ with 2-pyridine carboxylic acid in the presence of sodium carbonate yields $[Rh(NBD)(C_5H_4NCOO)]$ containing a chelating pyridine carboxylate ligand. This reacts with carbon monoxide to form $[Rh(CO)_2(C_5H_4NCOO)]$ which is converted to $[Rh(CO)L(C_5H_4NCOO)]$ (L = $P(\underline{p}\text{-}XC_6H_4)_3$(X = Me, Cl, F, OMe)) on reaction with phosphines. The last complexes undergo oxidative addition with halogens and methyl iodide (ref. 540). The chloride bridge in $[RhCl(COD)]_2$ is cleaved by N-substituted imidazoles to yield $[RhCl(COD)(C_3H_3N_2R)]$ (R = Me, vy) which on reaction with methyllithium form [258] (ref. 541). The ligand 1,6-bis(2'-benzimidazolyl)-2,5-dithiahexane reacts with $[RhCl(diolef)]_2$ (diolef = COD, TFB) to yield [259] while with $[Rh(diolef)_2]ClO_4$,



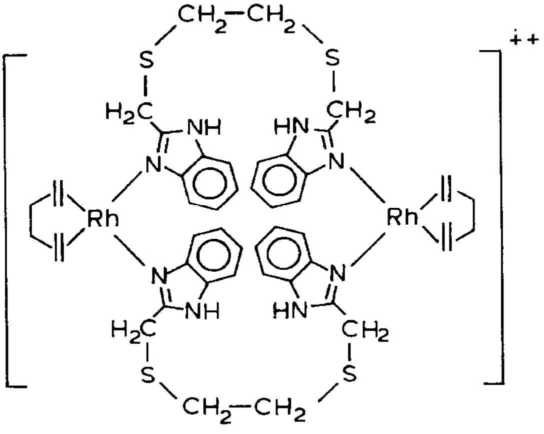
[258]

the product is [260]. Deprotonation of [259] (diolef = TFB) yields a species which may be a dimer. This reacts with silver perchlorate and



[259]

$[AuCl(PPh_3)]$ to yield a product containing two $\{Au(PPh_3)\}$ moieties for every two rhodium atoms. These are thought to be bound to the sulfur atoms (ref.

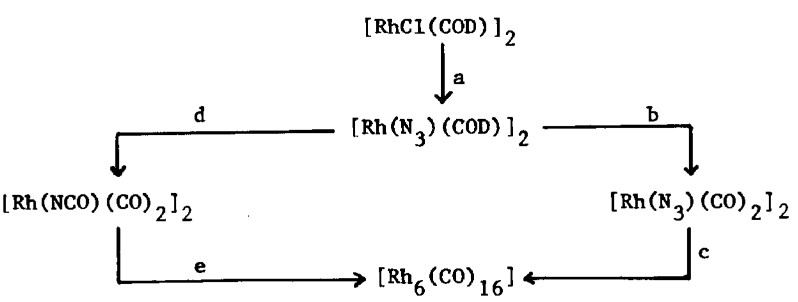


[260]

542). Other sulfur-ligand complexes reported are of the formula $[Rh(diolef)L_2]ClO_4$ (diolef = NBD, COD; L = THT, $\overline{CH_2CH_2CH_2S}$, SMe_2, SEt_2; L_2 = 1,4-dithiacyclohexane, $MeS(CH_2)_3SMe$, $Bu^tS(CH_2)_2SBu^t$). These can be prepared from $[RhCl(diolef)]_2$, silver perchlorate and the monodentate ligands or from $[Rh(diolef)_2]ClO_4$ and stoichiometric quantities of the ligands (except SEt_2). With one equivalent of dimethyl- or diethylsulfide the latter reaction yields $[Rh(NBD)_2L]ClO_4$ (ref. 543). In a related reaction, treatment of $[RhCl(COD)]_2$ with two equivalents of silver hexafluorophosphate and then the hexathia crown ether 1,4,7,11,14,17-hexathiacycloeicosane ([20]ane S_6) yields $[Rh_2(COD)_2([20]aneS_6)](PF_6)_2$. Each metal is coordinated to three adjacent sulfur atoms and the complex is unreactive towards dihydrogen and triphenylphosphine (ref. 544).

Reaction of $[MCl(diolef)]_2$ (M = Rh, Ir; diolef = NBD, COD, DCP) with tin(II) chloride and PPN[Cl] in acetone/dichloromethane yields $(PPN)_2[M(SnCl_3)_3(diolef)]$ which for M = Rh and diolef = NBD reacts with Lewis base ligands to form $(PPN)_2[Rh(SnCl_3)_3L_2]$ (L = CO, CNcy). Using [MCl(COD)L] (M = Rh, Ir; L = $P(\underline{p}\text{-}XC_6H_4)_3$ (X = Cl, F, H, OMe)) and stoichiometric quantities of tin(II) chloride and PPN[$SnCl_3$] permits the synthesis of PPN[M(COD)-($SnCl_3$)$_2$L] while with [IrCl(COD)]$_2$ and two equivalents of tin(II) chloride in the presence of excess diolefin [Ir($SnCl_3$)(COD)(diolef)] (diolef = COD, NBD) is formed. The ^{119}Sn NMR spectra of all the products have been measured and while the $^2J_{^{119}Sn-^{117}Sn}$ values are sensitive to structural changes, there is no correlation between these values and either $^1J_{Rh-^{119}Sn}$ or $^1J_{Rh-P}$ (refs. 545, 546). The neutral complexes [Rh($SnCl_3$)(NBD)L_2] (L = $P(OMe)_nPh_{3-n}$, $P(OEt)_nPh_{3-n}$ (n = 0-3), $P(OPr^i)_3$) have also been reported (ref. 547).

A new synthesis of [$Rh_6(CO)_{16}$] is shown in Scheme XLVI and the same

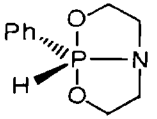


a) NaN_3, benzene. b) CO, benzene, 10 min. c) CO, ethanol, 24 h.

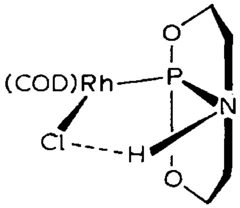
d) CO, benzene, 10 h. e) CO, ethanol, 15 h.

Scheme XLVI

authors report synthesizing [$Ir_4(CO)_{12}$] from [IrCl(COD)]$_2$ by treatment with carbon monoxide in aqueous ethanol followed by addition of an aqueous solution of disodium citrate (ref. 548). The dimer, [RhCl(COD)(μ-P(X)N-(Bu^t)P(X)NBu^t)RhCl(COD)], (X = F, Cl) results when equimolar quantities of [RhCl(COD)]$_2$ and the aminocyclodiphosphazines (P(X)N(Bu^t))$_2$ are combined but if a 1:2 ratio is used, the monomer [RhCl(COD)(P(X)N(Bu^t)P(X)NBu^t)] forms (ref. 549). Reaction of 2-diphenylphosphinoethyltrimethylammonium nitrate (L^+[NO_3]) with [RhCl(NBD)]$_2$ in methanol yields [RhCl(NBD)(L^+)]NO_3 which reacts with carbon monoxide to form *cis*-[RhCl(CO)$_2$(L^+)]NO_3, with dihydrogen to give norbornane and metallic rhodium and with a second equivalent of L^+[NO_3] to yield [Rh(NBD)(L^+)$_2$]$^{3+}$ which was identified in solution. This last complex can also be got by reaction of [RhCl(NBD)]$_2$ with silver nitrate in ethanol followed by addition of L^+[NO_3]. In methanol or water solution [Rh(NBD)(L^+)$_2$]$^{3+}$ reacts with dihydrogen to ultimately give norbornane and [Rh(L^+)$_2S_2$]$^{3+}$ (S = MeOH, H_2O). In methanol the intermediate hydride complex [RhH_2(L^+)$_2$(MeOH)$_2$]$^{3+}$ was detected. These systems are active catalysts for the hydrogenation of maleic and crotonic acids and, when a non-polar phase is also present, for hex-1-ene and styrene. In the latter case almost no leaching of the rhodium complex occurs from the aqueous phase. Adsorption of the cationic rhodium complex on a cation exchange resin affords a heterogenized catalyst active for olefin hydrogenation and hydroformylation (ref. 550). Reaction of [Rh(acac)(COD)] with trityl tetrafluoroborate in dichloromethane followed by addition of the ligands $Ph_2PCH_2CH_2SR$ (PSR: R = Me, Et, Ph) yields $[Rh(PSR)_2]BF_4$. The tetraphenylborate analogs (R = Et, Ph) can be got from $[RhCl(COD)]_2$ and stoichiometric quantities of the ligands in alcohols followed by addition of sodium tetraphenylborate. The corresponding iridium complexes were prepared in a similar fashion. Reaction of $[Rh(PSR)_2]BPh_4$ with carbon monoxide or dioxygen yields $[Rh(CO)(PSR)_2]BPh_4$ (R = Ph) and $[Rh(O_2)(PSR)_2]BPh_4$ (R = Et, Ph) respectively. Two equivalents of $Ph_2PCH_2CH_2SPh$ react with $[RhCl(COD)]_2$ in dichloromethane under carbon monoxide to give the chelate complex [RhCl(CO)(PSR)] (R = Ph) while with four equivalents of the ligand the product is trans-$[RhCl(CO)(PSR)_2]$ (R = Ph) where the ligand binds only through phosphorus (refs. 551, 552). The bicyclic phosphorane [261] undergoes a tautomerization on reaction with $[RhCl(COD)]_2$ to give [262] which then converts to $[Rh(PNH)_2][RhCl_2(COD)]$

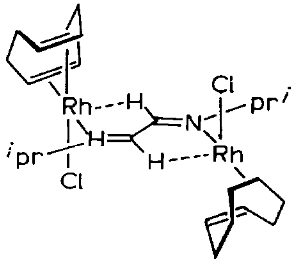


[261]



[262]

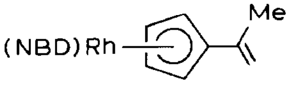
(PNH = tautomer of [261] with the hydrogen bound to nitrogen). Reaction of this complex with more [261] in the presence of suitable anions gives $[Rh(PNH)_2]A$ (A = Cl^-, BPh_4^-, ClO_4^-, PF_6^-, BF_4^-) (ref. 553). The structure of the diazadiene complex [263], prepared from $[RhCl(COD)]_2$, suggests the



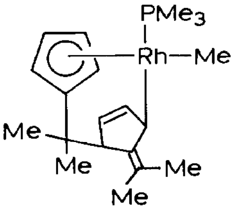
[263]

presence of a weak rhodium-hydrogen interaction which appears to persist in solution (ref. 554).

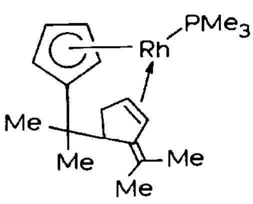
Treatment of $[RhCl(NBD)]_2$ with methyllithium at -78°C in the presence of dimethylfulvene yields [264] while the same reaction with $[RhCl(PMe_3)(COD)]$ gives [265]. Use of isopropylmagnesium bromide in place of methyllithium in the latter reaction affords [266] instead (ref. 555). Reaction of



[264]

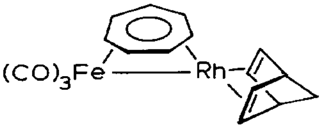


[265]

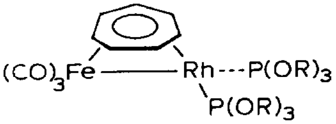


[266]

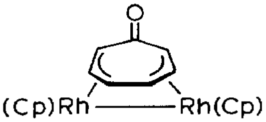
$Li[(\eta^3-C_7H_7)Fe(CO)_3]$ with $[RhCl(NBD)]_2$ yields [267] which reacts with phosphites to form [268] (R = Me, Ph). Analogs of [267] containing {M(COD)} (M = Rh, Ir) moieties were also prepared. From $[(\eta^3-C_7H_7)Co(CO)_3]$ and $[Rh(NBD)_2]BF_4$ was obtained $[(OC)_3Co(\mu-C_7H_7)Rh(NBD)]BF_4$ which is assigned a structure like that for [267] while successive treatments of $[RhCl(C_2H_4)_2]_2$ with tropone and thallium cyclopentadienide yielded [269] (ref. 556). The



[267]



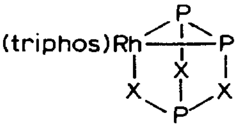
[268]



[269]

complexes $[(\eta^6-C_6H_5PMePh)MoL_2L']$ (L = $PMePh_2$; L' = $P(OMe)_3$), $CNBu^t$. L_2 = DPPE; L' = $PMePh_2$, CO) function as monodentate ligands and on reaction with

$[RhCl(COD)]_2$ form $[(COD)RhCl((\eta^6\text{-}C_6H_5PMePh)MoL_2L')]$ (ref. 557). In a mixture of benzene, THF and n-butanol, $[RhCl(COD)]_2$ reacts with triphos and P_4X_3 (X = S, Se) to yield [270] (ref. 558). At low temperature $[RhCl(COD)]_2$ reacts with one equivalent of dilithium tert-butylphosphide and then trimethylphosphine to form $[Rh_2(PMe_3)_4(\mu\text{-}PHBu^t)_2]$ (ref. 559) while with one equivalent of lithium diphenylphosphide the product is $[Rh_2(COD)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)]$ which on reduction with lithium triethylborohydride forms [271]. It is suggested that [271] forms via the initial formation of $[Rh_2(COD)_2(\mu\text{-}H)(\mu\text{-}PPh_2)]$ which eliminates benzene to give $[Rh_2(COD)_2(\mu\text{-}PPh)]$ followed by dimerization of this coordinatively unsaturated species (ref. 560).



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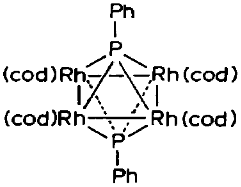
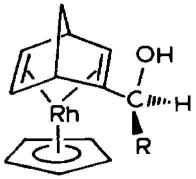


[271]

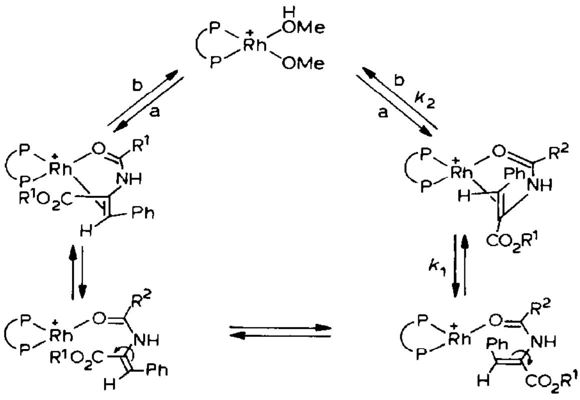
Dioxygen complexes of rhodium containing olefinic ligands are reported to be formed by the reaction of superoxide salts with rhodium(I) olefin complexes, for example $[RhCl(COD)]_2$. In this instance the product on heating undergoes a migration of the dioxygen moiety to the COD ligand (ref. 561). The redistribution reaction of $[RhCl(CO)_2]_2$ with $[RhCl(CO)(cyoct)]_2$ has been studied. Also the latter complex was found to react further with cyclooctene to form $[RhCl(cyoct)_4]$ plus $[RhCl(CO)_2(cyoct)_2]$ (ref. 562). The proton NMR and mass spectra of a variety of rhodium(I) and iridium(I) olefin complexes, for example $[cpRh(C_2H_4)_2]$ and $[Rh(acac)(C_2H_4)_2]$, have been obtained. From the NMR spectra, free energies of activation for the olefin rotation processes have been determined (refs. 563, 564). The mass spectra of [272] (R = Me, Fe), its endo-OH isomer and the exo- and endo-isomers of



[272]

the acetylacetonate analog (R = Me) have been determined. The fragmentation patterns differ for the two isomers (ref. 565).

The details of the mechanism of asymmetric hydrogenation of prochiral olefins catalyzed by rhodium complexes are now reasonably well established so that the majority of the papers in this area are concerned with optimizing conditions in previously established systems or with the investigation of new ligands. Two papers have appeared, however, that are primarily concerned with mechanistic details. In the first, the hydrogenation of (Z)-methyl-α-acetamidocinnamate in the presence of $[Rh(NBD)(L_2)]^+$ (L_2 = $Ph_2P(CH_2)_nPPh_2$ (n = 3-5)) as catalyst precursors has been explored. The first two on hydrogenation form $[Rh(L_2)S_2]^+$ (S = solvent) which then bind the olefin. The binding constant for the complex with n = 3 is greater than when n = 4 and this turn is greater than when L_2 = DIOP but the rates of oxidative addition of dihydrogen and of the transfer of the second hydride to the alkyl group in the hydridoalkyl intermediate increase significantly in the same order possibly because the increasing flexibility of the ligand makes the conformational changes required for the formation of the various transition states more favorable. At room temperature hydrogenation of $[Rh(NBD)(Ph_2P(CH_2)_5PPh_2)]^+$ yields the internally metallated complex $[\overline{RhH-(Ph_2P(CH_2)_2C}H(CH_2)_2PPh_2]S_2]^+$ which only slowly reacts further with dihydrogen. The same reaction when run at -80°C does yield $[Rh(L_2)S_2]^+$ which slowly undergoes the metallation. If this solution is briefly warmed and then recooled, $[Rh(L_2)(norbornene)]^+$ is detected indicating that here, and presumably in the other systems, the hydrogenation of the NBD ligand in the catalyst precursor occurs in a stepwise fashion (ref. 566). In the second paper, the two diastereoisomeric enamide adducts shown in Scheme XLVII (R^1 =

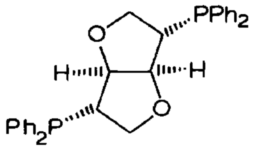


a) + $R^2C(O)NHC(CO_2R^1)CHPh$. b) - $R^2C(O)NHC(CO_2R^1)CHPh$.

Scheme XLVII

Me; R^2 = Ph; P-P = DIPAMP) have been studied by ^{31}P and ^{13}C NMR spectroscopy using the spin excitation transfer technique. The results indicate that the interconversion of the diastereoisomeric adducts occurs intramolecularly via dissociation of only the olefinic moiety as shown in the lower portion of Scheme XLVII (ref. 567).

Good rates and high optical yields are observed in asymmetric hydrogenations of acylaminocinnamic acids and esters catalyzed by $[Rh(NBD)(cycphos)]^+$. The catalyst precursor is found to exist in two polymorphic forms with three different conformations in the solid state indicating considerable flexibility in the ligand. The high optical yields suggest that the ligand can maintain a fixed conformation of the chelate ring but is sufficiently flexible to readily accommodate the geometrical changes required in the coordination sphere as the reaction proceeds (ref. 568). The easily prepared chiral ligands (S)-PROLOPHOS and (S)-BUTAPHOS (L_2) form the complexes $[Rh(COD)(L_2)]ClO_4$ which are catalyst precursors in ethanol solution for the asymmetric hydrogenation of α,β-unsaturated acids and esters. The higher optical yields obtained using the former ligand are attributed to the greater rigidity of the ligand backbone (ref. 569). It might be noted as an aside that there is not necessarily any conflict between the conclusions reached in the previous two papers regarding the effects of the degree of flexibility in the ligand backbone. Thus if this flexibility does not hinder the ligand's ability to direct substrate coordination preferentially to one face and/or to preferentially enhance the rate of hydrogenation of one diastereoisomeric catalyst-substrate complex then good optical yields should result. The cholesterol-derived ligands (+)-DICOL and (-)-DIOCOL give rhodium complexes with $[RhCl(COD)]_2$ which are inactive as catalysts for the hydrogenation of α,β-unsaturated acids and esters under mild conditions but at 70 atm pressure of dihydrogen high conversions are observed. The optical yields however were very low except with the DIOCOL complex and (Z)-α-acetamidocinnamic acid (ref. 570). Other phosphine ligands used to generate analogous catalysts are DBu^tPF (ref. 571), DIOXOP (ref. 572), MABP (ref. 573) and (S,S)-dpcp (ref. 574). The first showed no enantioselectivity in the hydrogenation of prochiral olefins while the others showed increasing optical yields with the last being the best. Two further ligands studied are [273] and [274] (Ar = Ph, p-anisyl; R = $(CH_2)_2CHMe_2$, $(CH_2)_2NMe_2$. Ar = Ph; R = $(CH_2)_3NMe_2$). The former gives modest optical yields with acylaminocinnamic acids while the latter gives a wider range with various dehydrodipeptides (refs. 575, 576). Generally high optical yields were observed in the asymmetric hydrogenation of dehydrodi- and tripeptides catalyzed by rhodium complexes of PhCAPP and BPPM (refs. 577, 578) while only modest optical yields resulted when cinnamic acid derivatives were hydrogenated using rhodium complexes of ethylene-di-N,N'-diphenylphosphino-d-N,N'-dehydroabietylamine (ref. 579) or $Ph_2PCH_2CH_2NRR'$



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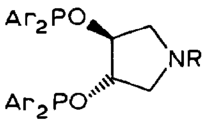
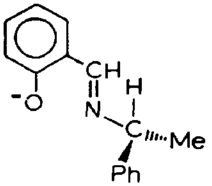


[274]

(R = R' = Me. R = H, R' = CHMePh) (ref. 580). Also neutral and cationic rhodium complexes of DIOP have been used to catalytically hydrogenate (Z)-dehydrotryptophans (ref. 581) while an analysis of the results obtained from the hydrogenation of cinnamic and acrylic acid derivatives using rhodium complexes of (-)-NORPHOS, (+)-PROPHOS, (+)-DIOP and (-)-BPPFA when compared with the Ruch/Ugi theory demonstrated that the observed enantioselectivity could not be calculated (ref. 582).

Complexes derived from $[RhCl(COD)]_2$ having the formula $[Rh(COD)(L_2)]$ (L_2 = [275], [276]) were used to catalyze the hydrogenation of N-acetylamidocinnamic acid and the hydrosilylation of acetophenone by diphenylsilane.



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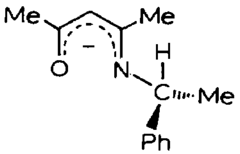
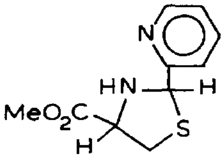


[276]

The low optical yields were attributed to an opening of the chelate ring during the reaction (ref. 583). By contrast the hydrosilylation reaction proceeds with substantial optical yields when a similar complex formed from [277] is used as the catalyst (ref. 584) while the hydrosilylation of



[277]

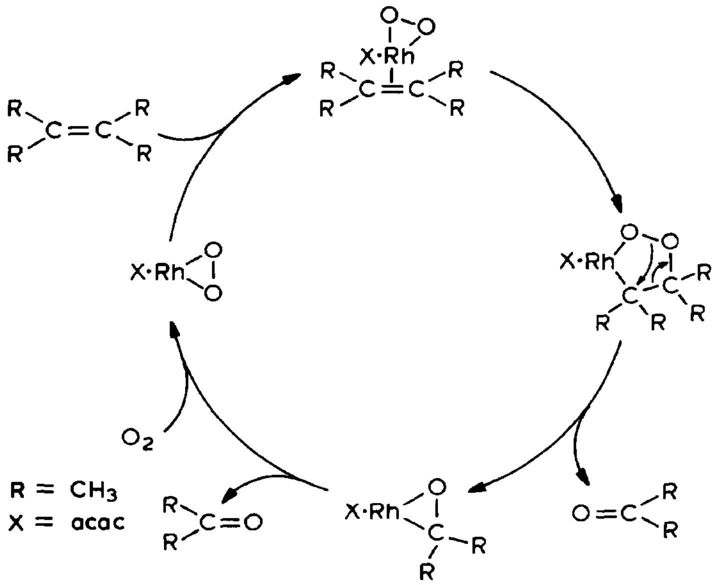
estrone methyl ether catalyzed by a rhodium -(-)-DIOP catalyst followed by hydrolysis affords a greater yield of the 17-α alcohol than do other reduction methods (ref. 585).

A sector rule has been developed to predict the configuration (R or S) of the products formed by the asymmetric hydrogenation of acylaminocinnamic acids catalyzed by rhodium complexes of DIOP, DIPAMP and related ligands (ref. 586).

A catalyst prepared in situ from $[RhCl(hexa\text{-}1,5\text{-}diene)]_2$, (-)-2-pyridinalphenylethylamine and potassium hydroxide in isopropanol provides modest optical yields in the conversion of ketones to alcohols (ref. 587). A stereoselective hydrogenation of cyclic ketones such as 4-tert-butylcyclohexanone to the corresponding alcohols can be achieved in the presence of catalysts derived from $[RhCl(NBD)]_2$ and phosphines. With a phosphine/rhodium ratio of 1:1 or 1.5:1 a 90% yield of the trans-alcohol is formed with tributylphosphine while with triphenylphosphine the yield is 71%. Addition of triethylamine to the former system has no effect but in the latter the product is now predominantly (73%) the cis-alcohol. The change is attributed to the extent to which the presumed $[RhH_2L_xCl]$ (L = phosphine) intermediate is converted to $[RhHL_x]$ by the added base. With the more basic phosphine the former predominates and favors coordination of the ketone to the metal via the oxygen atom while with the less basic phosphine the latter complex is favored which, being softer, can coordinate the ketone via the carbon-oxygen double bond (ref. 588). At 160°C $[Rh(CHIRAPHOS)_2]Cl$ in the absence of solvent catalyzes the asymmetric cyclization of pent-4-enols to cyclopentanones in 40-50% chemical and ca 50% optical yields (ref. 589).

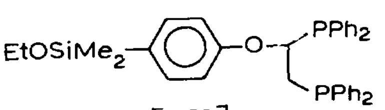
A comparison has been made of the hydrogenation and hydroformylation reactions of styrene as catalyzed by $[RhCl(CO)_2]_2$ and $[RhCl(PPh_3)_3]$ with those catalyzed by $[HCo(CO)_4]$, a system where radicals appear to be involved. The rhodium systems appear not to involve radical processes (ref. 590). Complexes formed from $[Rh(O_2CMe)(COD)]_2$ and various phosphorus ligands have been found to be active hydroformylation catalysts for hindered olefins. The best ligand tested was tri(o-tert-butylphenyl)phosphite (ref. 591). Cocondensation of rhodium atoms with cyclic dienes followed by warming to room temperature produced a red solution which catalyzed the hydroformylation of a variety of cyclic dienes (ref. 592).

The water-gas-shift reaction (WGSR) is catalyzed by the complexes $[Rh(COD)L_2]^+$ (L = PPh_3, PPh_2Me, $PPh_2(p\text{-}C_6H_4SO_3^-)$; L_2 = DPPE, DPPP, vdiphos) in aqueous dioxane with the most active being that with the sulfonated phosphine at pH 2-3. The system has been used as a source of dihydrogen for the hydrogenation of benzalacetone (ref. 593). A phase-transfer system based on $[RhCl(hexa\text{-}1,5\text{-}diene)]_2$, benzene and aqueous cetyltrimethylammonium bromide buffered to pH 7.6 is effective for the hydrogenation of arenes and unsaturated heterocycles and of aryl ketones to cyclohexylketones plus the corresponding alcohols (ref. 594). Phenylacetylene is converted to high molecular weight (ca 10,000) polymers in the presence of catalytic amounts of [Rh(COD)(L_2)]PF_6 (L_2 = bipy, ophen) and sodium hydroxide. No cyclotrimers were observed. Using [$Co_2(CO)_6$(PhC≡CH)] as the catalyst however, an 80% yield of 1,2,4-triphenylbenzene can be obtained in refluxing benzene (ref. 595). A variety of rhodium(I) olefin complexes including [RhClL_2]$_2$ (L = C_2H_4; L_2 = COD, divinylcyclobutane), [cpRh(L_2)] (L_2 = COD, divinylcyclobutane) and [Rh(acac)$(C_2H_4)_2$] as well as [$(\eta^3\text{-}C_3H_5)_2$RhCl]$_2$, [$(\eta^3\text{-}C_3H_5)_3$Rh] and [RhCl$(PPh_3)_3$] are catalysts for the oxidation of olefins to ketones via cleavage of the carbon-carbon double bond. Scheme XLVIII is proposed (ref. 596).



Scheme XLVIII

The ligand [278] when attached to silica reacts with [M(COD)$(MeCN)_2$]BF_4 (M = Rh, Ir) to provide a mixture of the supported complexes [279] and [280]. The relative amounts of the two complexes depends on the distribution of the ligands on the surface. Reaction of the free ligand (L_2) with [Rh(acac)(NBD)] and trityl tetrafluoroborate forms [Rh(NBD)(L_2)]BF_4 which can be converted into $[(\eta^3\text{-}C_3H_5)Rh(L_2)]$ by reaction with allylmagnesium bromide. Both complexes are catalyst precursors for the hydroformylation of styrene in homogeneous systems. Supporting $[Rh(NBD)(L_2)]BF_4$ on silica provides a heterogenized catalyst for the same reaction whose activity decreases linearly with the increase in the calculated percentage of isolated metal complexes on the surface. This result was interpreted to indicate that aldehyde formation occurs <u>via</u> a binuclear elimination process as indicated in Scheme XLIX (ref. 597). Intercalation of $[Rh(COD)(PPh_3)_2]^+$ into hectorite yields a heterogenized catalyst for the hydroformylation of hex-1-ene. However with a loading of 5%, significant desorption of the metal was observed so that most of the catalysis probably occurs in solution. Treatment of $[RhCl(COD)]_2$ and the quaternized phosphine $[Ph_2P(CH_2)_2\text{-}PPh_2bz]^+$ $(P\text{-}P^+)$ with syngas followed by sodium tetrafluoroborate yields $[RhCl(CO)(P\text{-}P^+)_2]BF_4$ which on intercalation in hectorite gave a catalyst much more resistant to leaching and which afforded a selectivity to the inear aldehyde about twice that for the unsupported catalyst (ref. 598). inally, support of $\{Rh(NBD)^+\}$ moieties on polystyrene functionalized with iphenylphosphino, imidazole or tetramethylbiimidazole groups forms a catalyst for the hydrogen-transfer hydrogenation of hex-1-ene and acetophenone by isopropanol (ref. 599).



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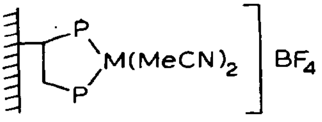

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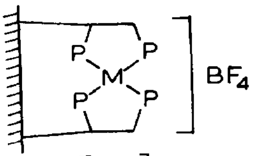
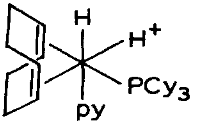


[280]

$$L_nM\text{-}H + RC(O)ML_m \rightarrow L_nM\text{-}ML_n + RC(O)H$$

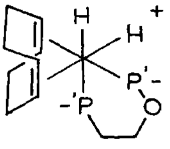
Scheme XLIX

The formation of only [281] when dihydrogen undergoes oxidative addition



[281]

to [Ir(COD)(py)(Pcy$_3$)]PF$_6$ has been attributed to electronic factors. This was deduced from the observation that oxidative addition of dihydrogen to [Ir(COD)(POP)]BF$_4$ yielded only the isomer [282] and it was considered that this indicated preferential formation of [283] as an intermediate or transition state because the more electronegative diphenylphosphinoxy group should



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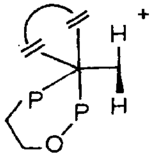
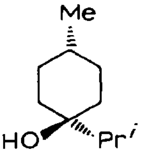


[283]

prefer to occupy an axial site (ref. 600). The same group has also found that [Ir(COD)(py)(Pcy$_3$)]PF$_6$ catalyzes the stereospecific hydrogenation terpinen-4-ol to [284] which contrasts dramatically with the results using Pd/C where a 20:80 mixture of [284] and the isomer having the opposite configuration at C-1 is formed. The stereospecificity is attributed to the directing effect of the hydroxyl group which can coordinate to the metal to form the intermediate [285]. This proposed intermediate is supported by the



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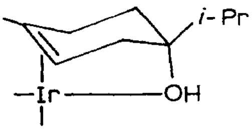
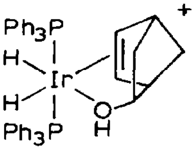


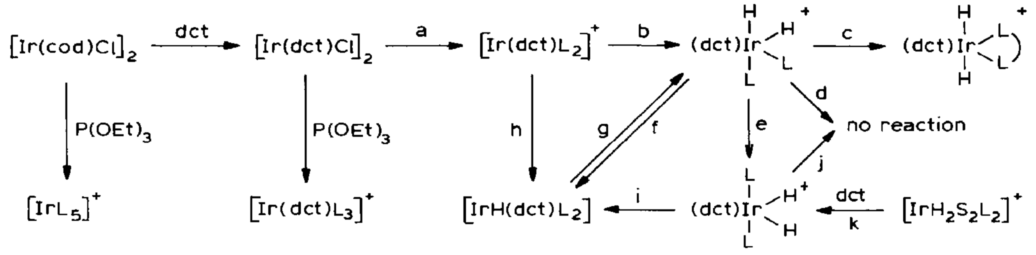
[285]

isolation of [286] from the reaction of [IrH$_2$(PPh$_3$)$_2$(acetone)$_2$]$^+$ and



[286]

endo-5-norbornen-2-ol (ref. 601). The chemistry of iridium complexes of dibenzocyclooctatetraene (dct) is shown in Scheme L. A brief investigation of related rhodium systems showed that [RhH$_2$(PPh$_3$)$_2$(EtOH)$_2$]$^+$ reacted with dct at -80°C to give [RhH$_2$(PPh$_3$)$_2$(dct)]$^+$ which eliminated dihydrogen at temperatures above -20°C and the [Rh(PPh$_3$)$_2$(dct)]$^+$ thus formed was unreactive towards dihydrogen. The dct ligand is thus more electron-withdrawing

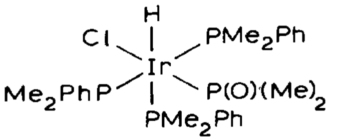


a) $AgBF_4$, L (= PPh_3, $PMePh_2$, 0.5 DPPE, 0.5 DPPP). b) H_2, -30°C. c) MeOH, -30°C, L_2 = DPPP. d) 65°C, L = 0.5 DPPP. e) MeOH, L = PPh_3, $PMePh_2$. f) py, L = 0.5 DPPP. g) H^+, L = PPh_3, 0.5 DPPP. h) $LiHBEt_3$, L = PPh_3. i) $KOBu^t$, L = PPh_3. j) 180°C, L = PPh_3. k) S = acetone, L = PPh_3, $PMePh_2$.

Scheme L

than is COD as well as being more resistant to metallation (ref. 602). In further work this group has found that dct reacts with homogeneous rhodium and iridium complexes which show catalytic activity to completely inactivate them but has little if any effect on the activity of heterogeneous catalysts such as metal surfaces and colloidal suspension. It is thus proposed as a test for the homogeneity of catalyst solutions which is superior to previous methods such as filtration, centrifugation and the the ability to reduce nitrobenzene. Using this test, $[RhCl(PPh_3)_3]$, $[Rh(NBD)(PPh_3)_2]^+$ and $[Ir(COD)(PMePh_2)_2]^+$ when used as hydrogenation catalyst precursors appear to give homogeneous catalysts but the system generated from $[RhCl_3py_3]$ and sodium borohydride in DMF which had previously been thought to be homogeneous appears instead to be heterogeneous (ref. 603).

The oxidative addition of phosphorus-hydrogen bonds of secondary phosphites to iridium occurs when these ligands react with $[IrCl(cyoct)_2]_2$ and triphenylphosphine or dimethylphenylphosphine in refluxing benzene. Isolated products include [287] and [288] (R = OMe; R_2 = $OCH_2CMe_2CH_2O$, $OCMe_2CMe_2O$). A triphenylarsine analog of [288] (R = OMe) and a rhodium analog of [287] were also prepared. Reaction of $[IrCl(cyoct)_2]_2$ with dimethylphosphite in refluxing benzene followed by addition of two equivalents of triphenylphosphine gave $[IrHCl(PPh_3)_2(P(O)(OMe)_2)]$ which added pyridine to give a mixture of [289] and [290] and reacted with thallium acetylacetonate



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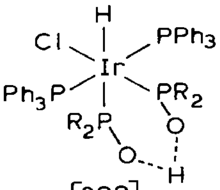

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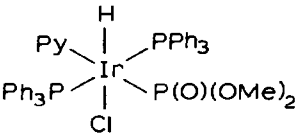

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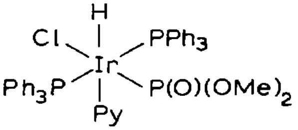
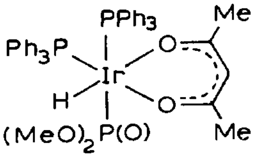


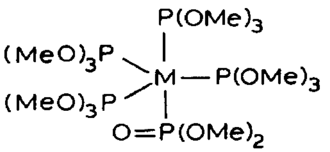
[290]

to form [291]. Successive addition of triphenylarsine and phosphorus acid to $[IrCl(cyoct)_2]_2$ gave a species analyzing as $[IrHCl(AsPh_3)(H_2PO_3)(H_3PO_3)]$ but the spectroscopic data were inconsistent with this formulation so the product may be a mixture (ref. 604). Addition of DIPHOL to $[IrCl(COD)]_2$ forms [IrCl(COD)(DIPHOL)] whose structure shows the molecule to adopt a distorted trigonal bipyramidal geometry with the conformation of the ligand considerably different from that found for DIOP in the analogous complex of the latter ligand (ref. 605). Complex [292] (M = Ir) which can be prepared from $[(\eta^5\text{-}C_9H_7)Ir(C_2H_4)_2]$ and excess trimethylphosphite or from $[IrCl(P(OMe)_3)_5]$ on reduction with sodium or its amalgam is fluxional and reacts

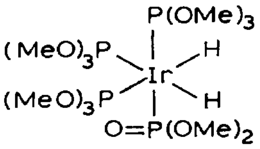


[291]

with dihydrogen to yield [293]. The product of the reaction of trimethylphosphite with $[cpRh(C_2H_4)_2]$ was shown to be [292] (M = Rh) and not $[Rh_2(P(OMe)_3)_8]$ as reported previously (J. Chem. Soc., Chem. Commun., (1974) 147). It reacts with dihydrogen to form $[RhH(P(OMe)_3)_4]$ and dimethylphosphite.

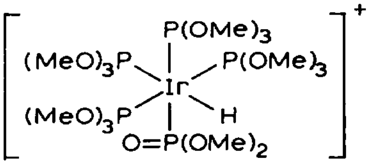


[292]

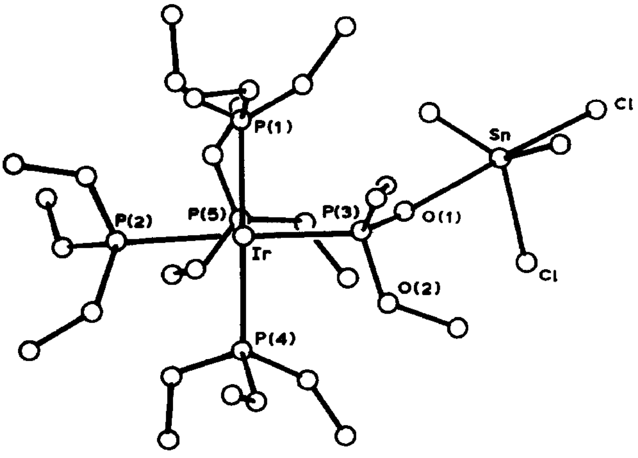


[293]

The complex $[Rh_2(P(OMe)_3)_8]$ can be prepared however by the reduction of $[RhCl(C_2H_4)_2]_2$ with sodium amalgam in the presence of trimethylphosphite. Complex [292] (M = Rh, Ir) reacts with methyl iodide to give $[M(P(OMe)_3)_5]I$ and with tetrafluoroboric or *p*-toluenesulfonic acids (M = Ir) to yield [294]. When M = Rh the latter reactions instead give $[RhX(P(OMe)_3)_4]$ (X = BF_4, tosylate) and dimethylphosphite. Finally, [292] (M = Ir) reacts with dimethyltin dichloride in THF to form [295] (ref. 606). Addition of

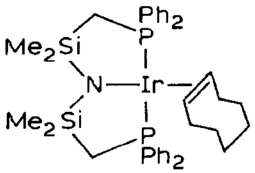


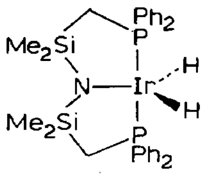
[294]



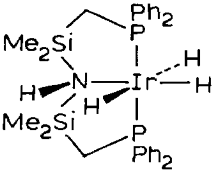
[295]

dihydrogen to [296] in toluene solution yields [297] after removal of the solvent in vacuo. Monitoring the reaction by NMR shows that in deuterobenzene the initial product is [298] while if it is run in pentane [299] precipitates. It was also observed that [299] isomerizes to [298] under dihydrogen and under dinitrogen forms a mixture of [298] and [297]


[296]


[297]

suggesting that the conversion of [297] to [298] and/or [299] involves a ligand-assisted heterolytic splitting of dihydrogen. Complex [297] adds Lewis bases ligands to form [300] (L = CO, PMe_3) while [296] reacts with formaldehyde to yield [301] possibly <u>via</u> an intermediate formyl hydride complex.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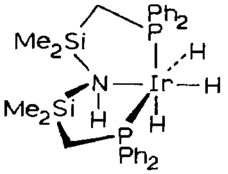
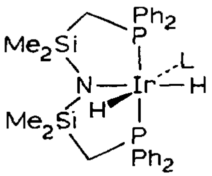
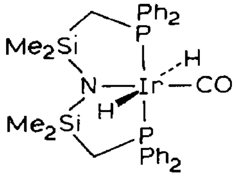
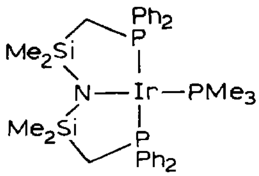
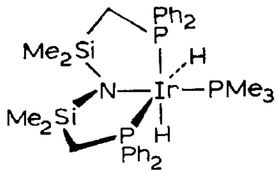

[299]


[300]

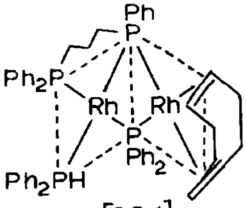

[301]

Also, [302] adds dihydrogen to give [303] (ref. 607).


[302]

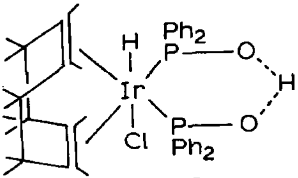

[303]

The metal-metal bonded dimers $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-}PPh_2)_2]$ and $[Ir_2(COD)_2(\mu\text{-}PPh_2)_2]$ are formed from lithium diphenylphosphide and $[IrCl(CO)(PPh_3)_2]$ and $[IrCl(COD)]_2$ respectively. The latter complex is unreactive towards carbon monoxide and phosphines. By contrast, $[Rh_2(COD)_2(\mu\text{-}PPh_2)_2]$ appears not to contain a metal-metal bond and reversibly undergoes successive replacement of the COD ligands with ditertiary phosphines (DPPE, vdiphos, DPPP, $Ph_2PCH_2CH_2PPhEt$). The same reaction with $Ph_2P(CH_2)_3PHPh$ yields [304] while with triphenylphosphine the only product formed is $[(COD)Rh(\mu\text{-}PPh_2)_2\text{-}Rh(PPh_3)_2]$ which appears to contain a metal-metal bond. Similar results were observed with triethylphosphine, tricyclohexylphosphine and methyldiphenylphosphine. Most of the complexes form olefin hydrogenation

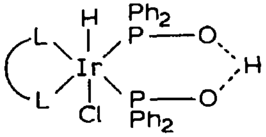


[304]

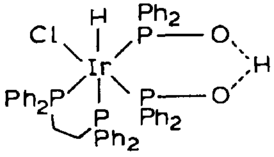
catalysts (ref. 608). Reaction of $[IrCl(COD)]_2$ with chlorodiphenylphosphine in aqueous methanol yields [305] which slowly loses COD in solution and reacts with bidentate ligands to form [306] (L-L = DPPE, DPAE, ARPHOS, $PhS(CH_2)_2SPh$). The isomer [307] is also formed with DPPE. Complex [305]



[305]

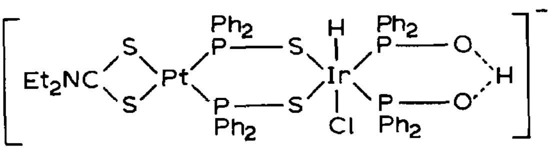


[306]



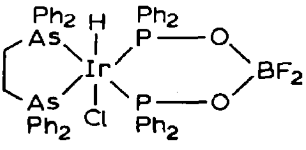
[307]

reacts with $[Pt(S_2CNEt_2)(PSPh_2)_2]$ to form [308] while [306] (L-L = DPAE)

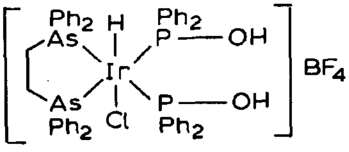


[308]

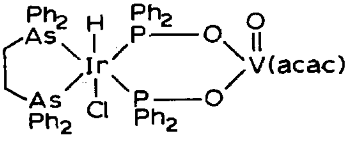
reacts with boron trifluoride etherate, tetrafluoroboric acid and $[V(O)-(acac)_2]$ to form [309], [310] and [311] respectively. Performing the last



[309]

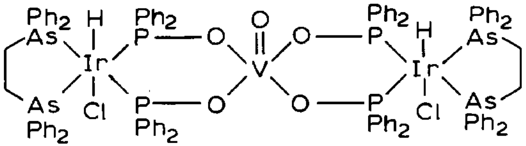


[310]

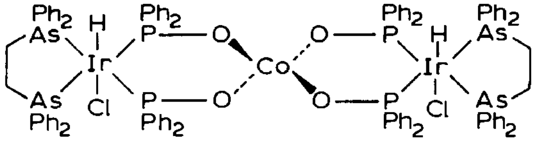


[311]

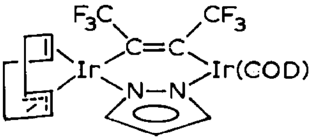
reaction at reflux yields [312] and under the same conditions $[Co(acac)_2]_4$ forms [313] (ref. 609). Reaction of $[IrCl(COD)]_2$ with fpzH yields $[Ir(COD)(\mu\text{-}fpz)]_2$ which is unreactive towards hexafluorobut-2-yne, dimethylacetylene dicarboxylate, iodine and methyl iodide at room temperature. The same reaction but with pyrazole also present forms a mixture of $[Ir(COD)(\mu\text{-}pz)]_2$, $[Ir(COD)(\mu\text{-}fpz)]_2$ and $[Ir_2(COD)_2(\mu\text{-}pz)(\mu\text{-}fpz)]$ which were separated by fractional crystallization. The last does react with hexafluorobut-2-yne to form [314] apparently via an iridium-mediated transfer of a proton from COD to the fpz moiety. It is thought that [314] may be a mixed valence Ir(I)-Ir(III) complex, but the data presently available do not strongly support this proposal (ref. 610).



[312]

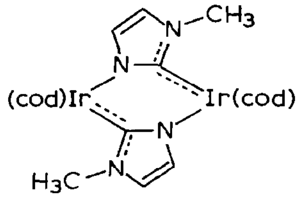


[313]

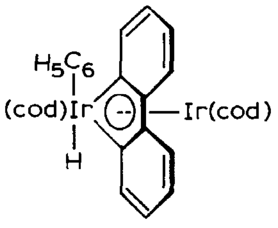


[314]

The complex [Ir(COD)(ophen)(acac)] in which the acetylacetonate ligand is bound to the metal via the γ-carbon atom can be prepared either from [IrCl(COD)(ophen)] and thallium acetylacetonate or from [Ir(COD)(acac)] and ophen (ref. 611). Chloride abstraction from $[IrCl(COD)]_2$ by silver salts in the presence of a variety of nitrogen and sulfur ligands yields $[Ir(COD)L_2]BF_4$ (L = RCN (R = Me, Ph, bz, p-tolyl, p-anisyl)), $[Ir_2(COD)_2(\mu\text{-}L)_2](ClO_4)_2$ (L = THT, Me_2S, Et_2S, $\overline{CH_2CH_2CH_2S}$) or $[Ir_2(COD)_2(\mu\text{-}L_2)_2](ClO_4)_2$ (L_2 = $RS(CH_2)_2SR$ (R = Me, Bu^t), Me_2S_2). Addition of other ligands to $[Ir(COD)(MeCN)_2]^+$ affords the derivatives $[Ir(COD)L_2]^+$ (L = 2-Mepy, 2-Etpz, 5-nitro-6-methylquinoline; L_2 = succinonitrile, 8-aminoquinoline, en, TMEDA, $PhHNCH_2CH_2NHPh$). Triphenylphosphine adds to $[Ir_2(COD)_2(\mu\text{-}L)_2]^{2+}$ (L = Me_2S, Et_2S) forming $[Ir_2(COD)_2(PPh_3)_2(\mu\text{-}L)_2]^{2+}$ (refs. 612, 613). Metathesis of $[Ir(diolef)_2]Cl$ (diolef = 2,3-dimethylbuta-1,3-diene) with silver tetrafluoroborate forms $[Ir(diolef)_2]BF_4$ which adds DMSO giving $[Ir(diolef)_2(DMSO)]BF_4$ (ref. 614). Reaction of methyllithium with [IrCl(COD)L] (L = N-methylimidazole) yields [315]. The same reaction using phenyllithium also gives [315] together with [316] (ref. 615).

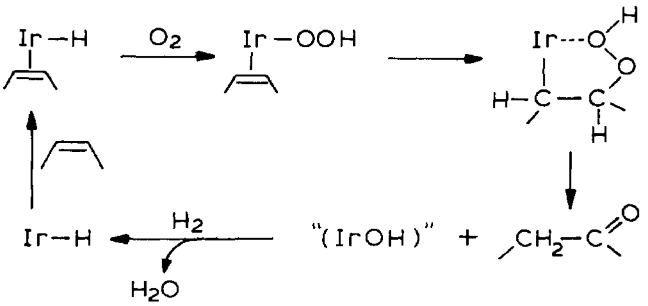


[315]



[316]

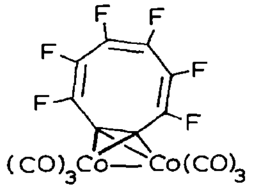
The complex $[Ir(COD)(py)(Pcy_3)]ClO_4$ is a catalyst precursor for the hydrogenation of $Me_2C{=}C(CO_2Me)NHC(O)R$ (R = Me, Ph) but no enantiospecificity was observed. The neomenthyldiphenylphosphine analog was inactive but with $[Ir(COD)(NCPh)L]ClO_4$ (L = Pcy_3, PPh_2neomenthyl) modest optical yields were obtained (ref. 616). In the presence of an equimolar quantity of potassium hydroxide, $[IrR(chel)]ClO_4$ and [Ir(R)(X)(chel)] (R = hexa-1,5-diene; chel = bipy, ophen; X = Cl, Br, I) are catalyst precursors for the selective reduction of unhindered cyclohexanones to the corresponding alcohols (hydroxyl group equatorial) by isopropanol (ref. 617). In DMA $[IrHCl_2(COD)]_2$ is a slow but selective catalyst for the conversion of cyclooctene to cyclooctanone and water under a mixture of dihydrogen and dioxygen. Scheme LI is proposed (ref. 618). The complexes [M(acac)(COD)] (M = Rh, Ir) appear comparable in activity to cis-$[PtCl_2(NH_3)_2]$ in inhibiting Lewis lung carcinoma in mice (ref. 619).



Scheme LI

Metal Alkyne Complexes

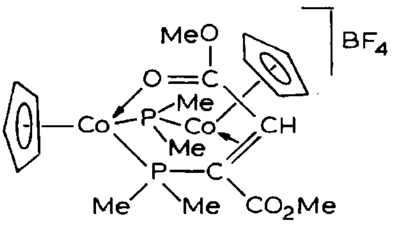
Diphenylacetylene adds to $[CoX(PMe_3)_3]$ (X = Br, I) in toluene at -80°C to form $[CoX(PMe_3)_3(Ph_2C_2)]$ which is only stable in solution at low temperature. The same complex together with $[Co(PMe_3)_4(Ph_2C_2)]^+$ result when the reaction is performed in acetone but on addition of sodium tetraphenylborate in methanol the product isolated is $[Co(PMe_3)_3(Ph_2C_2)]BPh_4$ in which the acetylene is considered to be a four-electron donor. Addition of acetonitrile to a toluene solution of $[CoX(PMe_3)(Ph_2C_2)]$ causes partial conversion to a mixture of $[Co(PMe_3)_3(MeCN)_2]^+$, $[Co(PMe_3)_4(Ph_2C_2)]^+$ and $[Co(PMe_3)_3(MeCN)(Ph_2C_2)]^+$. The last was isolated as its tetraphenylborate salt and found to have a trigonal bipyramidal structure with axial phosphine ligands (ref. 620). The acetylenes $RC{\equiv}CH$ (R = $SiMe_3$, $SnEt_3$, $B(NEt_2)_2$) and $RC{\equiv}CR'$ (R = R' = $SiMe_3$, $SnMe_3$, $BNEt_2$. R = $SiMe_3$; R' = Ph. R = $B(NEt_2)_2$; R' = Me) form normal $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-acetylene})]$ complexes with $[Co_2(CO)_8]$. One triple bond of the bis(alkynes), $RC{\equiv}C\text{-}E\text{-}C{\equiv}CR'$ (E = CH_2; R = H; R' = Ph. E = $SiMe_2$, $SnMe_2$, $SnPh_2$; R = R' = H. E = $BNEt_2$; R = R' = Me, Bu^t), can similarly bind a $\{Co_2(CO)_6\}$ moiety and with an excess of $[Co_2(CO)_8]$, another can be attached to the second triple bond. Three $\{Co_2(CO)_6\}$ moieties can be bound to $Ph_2Sn(C{\equiv}CH)C{\equiv}CSn(C{\equiv}CH)Ph_2$. The proton, ^{13}C, ^{59}Co, ^{11}B, ^{29}Si and ^{119}Sn NMR spectra of the various complexes have been measured (ref. 621). After five days, a 2% yield of [317] could be obtained from OFCOT and $[Co(CO)_4]^-$



[317]

(ref. 622). The addition of acetylenes to [cpCo(PPh$_3$)(acetylene)] to form cobaltacyclopentadienes has been investigated. The reaction is inhibited by excess phosphine which suggests it proceeds via dissociation of phosphine from the starting complex followed by addition of the second acetylene molecule to the metal prior to metallacycle formation. From molecular orbital calculations the most favorable conformation of the proposed bis-(acetylene) intermediate is that with the two acetylene molecules in an "upright" orientation (ref. 623).

In refluxing methanol, dimethylacetylene dicarboxylate reacts with [cp$_2$Co$_2$(μ-PMe$_2$)(μ-H)]BF$_4$ to yield a mixture of [318] and [319]. An alternative synthesis of the latter is from [cp$_2$Co$_2$(μ-PMe$_2$)$_2$] and the acetylene (ref. 624). At room temperature in an open system [Co$_2$(CO)$_8$] reacts with [cpMCl(HFB)$_2$] (M = Mo, W) to form [320] (R = CF$_3$) and a species considered to be either [321a] or [321b]. Reaction of [320] (M = Mo) with triethylphosphine replaces the carbonyl group on molybdenum while with the tungsten analog one carbonyl group on cobalt is also replaced. If the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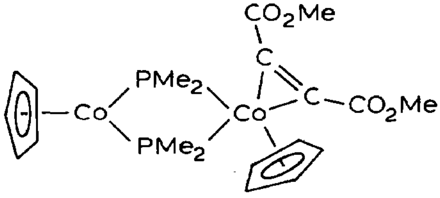
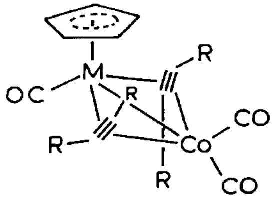

[319]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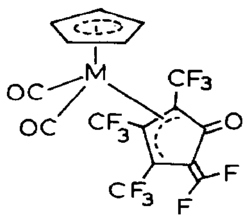
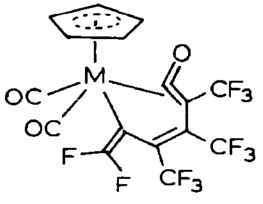
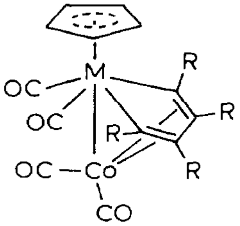

[321a]


[321b]

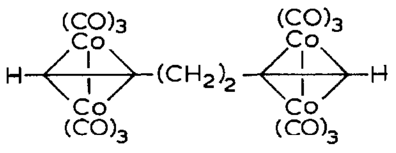
original reaction is run in a closed system a third product formulated as



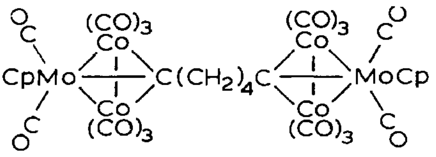
[322]

[322] (R = CF_3) also forms (ref. 625). The dimetallated olefin complex $K_6[(NO)_5Co(\mu\text{-}MeO_2CC{=}CCO_2Me)Co(CN)_5]\cdot 6H_2O$ is formed when $[Co(H_2O)_6]Cl_2$, potassium cyanide and dimethylacetylene dicarboxylate are reacted in aqueous methanol. The stereochemistry about the double bond is trans. All attempts to isolate salts of other cations failed and the double bond is unreactive towards Diels-Alder dienes (ref. 626).

The product of the reaction of $[Co_2(CO)_8]$ with $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HC_2Bu^t)]$ under dihydrogen in hot benzene is the alkylidyne complex $[Bu^tCCo_3(CO)_9]$. Hydrogenolysis at 60°C yields $Bu^tCH{=}CH_2$, $Bu^tCH_2CH_3$ and $Bu^tCH_2CH_2CHO$ and the process is accompanied by the observation of CIDNP in the vinyl hydrogen resonances of the product alkene. The process is proposed to involve dissociation of carbon monoxide from the cluster followed by oxidative addition of dihydrogen and cluster fragmentation with the formation of vinyl radicals. This was supported by the observation that the analogous species $[RCCo_3(CO)_9]$ (R = cyclopropyl) gave no cyclopropyl-containing products on hydrogenolysis. This is consistent with the formation of a cyclopropylmethyl radical since it rapidly undergoes ring-opening. Also studied was the reaction of [323] with $[cpMoH(CO)_3]$ which gave [324] (ref. 627). The



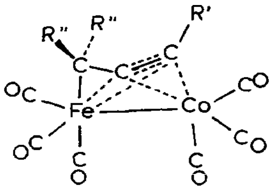
[323]



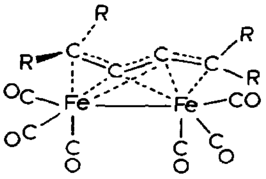
[324]

course of the reaction of $[HFeCo_3(CO)_{12}]$ with hex-3-yne is solvent-dependent as shown in Scheme LII (ref. 628). In related work, the reaction of

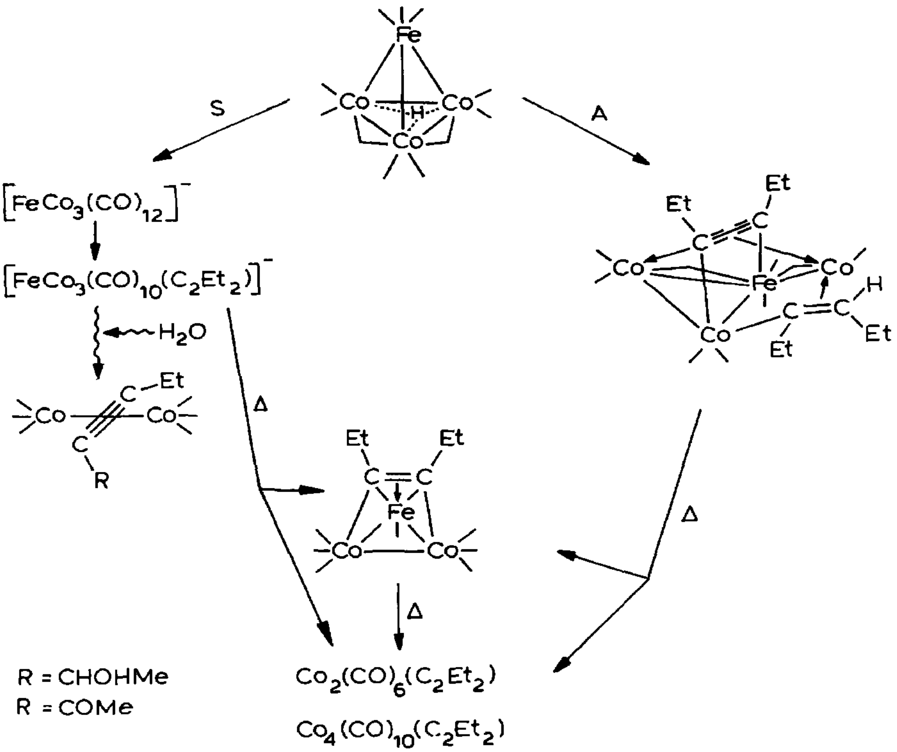
$[Co_2(CO)_6(\mu-\eta^2-RC_2CR'_2OH)]$ (R = Me; R' = H. R = Et; R'_2 = (H)(Me). R = CH_2OH; R' = H. R = CMe_2OH; R' = Me) with $[Fe(CO)_5]$ in refluxing acetone forms [325] (R' = Et; R" = H, Me. R' = Me; R" = H. R' = CH_2OH; R" = H. R' = CMe_2OH; R" = Me) which in the case of the last two react further to form [326] (R = H, Me) (ref. 629).



[325]



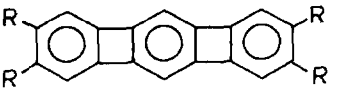
[326]



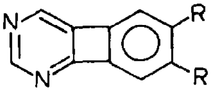
S) EtC≡CEt, Lewis base solvent. A) EtC≡CEt, aprotic, water-free solvent.

Scheme LII

The use of cobalt complexes, particularly $[cpCo(CO)_2]$ to mediate reactions of alkynes in organic synthesis continues to be the subject of numerous papers. For example $[Co_2(CO)_8]$ assists the intramolecular cyclization of suitable enynes to form functionalized cyclopentanones (ref. 630) while the biphenylene derivatives [327] and [328] (R = $SiMe_3$) are obtained by the

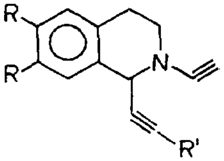


[327]

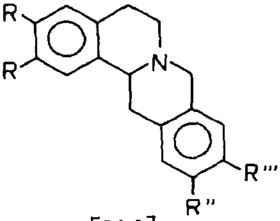


[328]

cocyclization of BTMSA with 1,2,4-5-tetra(ethynyl)benzene and 4-methoxy-5,6-diethynylpyrimidine respectively in the presence of [cpCo(CO)$_2$] (refs. 631, 632). Similarly cocyclization of [329] (R = H, MeO; R' = H) with acetylene or BTMSA in the presence of [cpCo(CO)$_2$] occurs regiospecifically to give [330] (R = H, MeO; R" = R'" = SiMe$_3$. R = MeO, R" = R'" = H) while

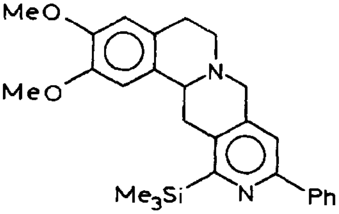


[329]



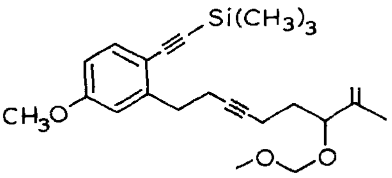
[330]

under similar conditions [329] (R = MeO; R' = SiMe$_3$) and benzonitrile yields [331] (ref. 633). Photolysis of a mixture of [332] and [cpCo(CO)$_2$] in



[331]

refluxing m-xylene provides a 72% yield of [333] as the only detectable



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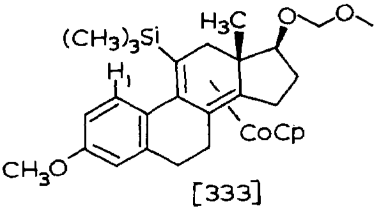
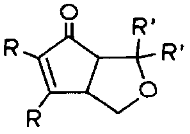


[333]

diastereoisomer which could be oxidatively demetallated to give the free steroid (ref. 634) while similar conditions were used to afford a regiospecific synthesis of 5-indolizinones by the cocyclization of acetylenes with isocyanatoalkynes (ref. 635). The regioselective formation of [334] (R

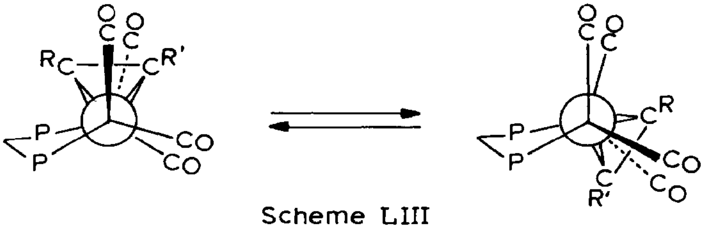


[334]

= H, Me; R' = H. R = H; R' = Me) occurs when $[Co_2(CO)_6(\mu-\eta^2-RC_2R)]$ is reacted with the appropriate dihydrofuran (ref. 636).

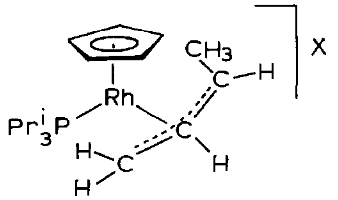
Protection of the carbon-carbon triple bond in conjugated enynes by coordination to a $\{Co_2(CO)_6\}$ moiety permits selective acylation of the olefinic portion. Thus, for example $HC\equiv C-C(Me)=CH_2$ can be converted into $HC\equiv C-CMe(OMe)CH_2R$ (R = Bu^t, $Bu^tC(O)$, MeC(O)) (refs. 637, 638). Similarly, the use of $\{Co_2(CO)_6\}$-stabilized propargyl cations provides a ready synthesis of 1,4-diynes on reaction with trialkynylaluminums (ref. 639).

Reduction of $[Co_2(CO)_6(HFB)]$ electrochemically or with sodium benzophenone ketyl followed by addition of ligands provides high yields of $[Co_2(CO)_5L(HFB)]$ (L = MeCN, PPh_3, Pcy_3, $P(OMe)_3$, $P(OPh)_3$). With larger quantities of ligand up to four carbonyl groups can be replaced. The success of this process results from the lability of the carbonyl ligands in the radical anion produced on reduction. Depending of the lifetime of the radical anion the reaction may be either electron-transfer-catalyzed or simply electron-induced (ref. 640). The complexes $[Co_2(CO)_4(DPM)(\mu-\eta^2-RC_2R')]$ (R = R' = H, Ph. R = H; R' = Ph) are fluxional according to their proton and ^{13}C NMR spectra. The fluxional process is proposed to be a rocking of the alkyne about the cobalt-cobalt axis as shown in Scheme LIII (ref. 641).

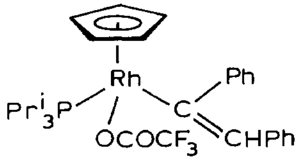


Scheme LIII

The acetylene complexes <u>trans</u>-$[RhCl(RC_2R')(PPr^i_3)_2]$ (R = R' = Me, Ph. R = Ph; R' = H) are formed by the reaction of $[RhCl(cyoct)_2]_2$, triisopropylphosphine and the acetylene. The phenylacetylene complex is in equilibrium with the acetylide species $[\mathrm{RhHCl(C_2Ph)(PPr^i{}_3)_2}]$ which can be trapped as $[\mathrm{RhHCl(C_2Ph)(py)(PPr^i{}_3)_2}]$ on addition of pyridine to the equilibrium mixture. At low temperature the pyridine adduct reacts with sodium cyclopentadienide to generate $[\mathrm{Rh(C_2Ph)(py)(PPr^i{}_3)_2}]$ plus cyclopentadiene. Warming the mixture leads to the formation of the vinylidene complex $[\mathrm{cpRh({=}C{=}CHPh)(PPr^i{}_3)}]$. On the other hand, reaction of trans-$[\mathrm{RhCl(RC_2R')(PPr^i{}_3)_2}]$ directly with sodium cyclopentadienide yields $[\mathrm{cpRh(RC_2R')(PPr^i{}_3)}]$ for all three acetylenes. Protonation of the but-2-yne complex with tetrafluoroboric or hexafluorophosphoric acids forms [335] ($X = BF_4$, PF_6) at low temperature and on warming the hexafluorophosphate salt converts to the syn-isomer. Protonation of the diphenylacetylene adduct with trifluoroacetic acid in diethyl ether forms [336] which on acidification in methanol converts to [337] (refs. 642, 643). Reaction of $[\mathrm{Rh(tmhd)(C_2H_4)(HFB)}]$ with propylene or cyclopropane in ether at 60°C yields [338] while at room temperature its reaction with tetramethylallene forms [339]. Both products



[335]



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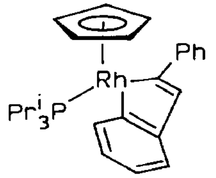

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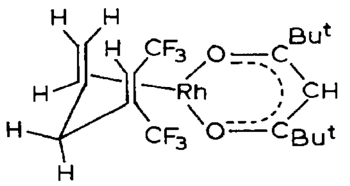

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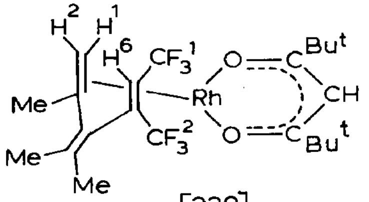
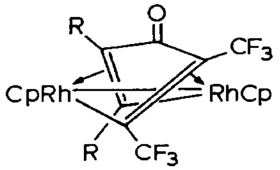


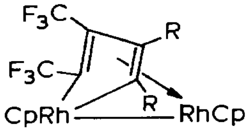
[339]

react with carbon monoxide to form [Rh(tmhd)$(CO)_2$]. Replacement of ethylene in [Rh(tmhd)(C_2H_4)(HFB)] by Group V ligands occurs in ether solution to form [Rh(tmhd)(L)(HFB)] (L = PPh_3, Pcy_3, $AsPh_3$, $PMePh_2$, $PEtPh_2$) and for all but tricyclohexylphosphine a second ligand adds to yield [Rh(tmhd)L_2(HFB)]. The latter complex (L = $SbPh_3$; L_2 = DPPE) forms directly from the ethylene complex. Only the ethylene ligand in [Rh(tmhd)$(C_2H_4)(C_2F_3X)$] is replaced by group V ligands with the formation of [Rh(tmhd)L(C_2F_3X)] (L = PPh_3, $AsPh_3$, $SbPh_3$; X = F, Cl, Br, CF_3) (refs. 644, 645).

In studies to elucidate the mechanism of formation of cyclopentadienone complexes of rhodium from [cpRh$(CO)_2$] and acetylenes [$cp_2Rh_2(CO)_2(\mu\text{-}CO)$] was reacted with HFB and di-*tert*-butylacetylene. The first gave the dimetallated olefin complex [$cp_2Rh_2(CO)_2(\mu\text{-}F_3CC{=}CCF_3)$] while the latter gave [$cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}C_2Bu^t{}_2)$]. Reaction of either [cpRh$(CO)_2$] or [$cp_2Rh_2(CO)_2(\mu\text{-}CO)$] with BTMSA gave [$cp_3Rh_3(CO)_3$] and [$cp_3Rh_3$(CO)(BTMSA)] as the major products while [$cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}$HFB)] and internal alkynes yielded [$cp_2Rh_2(CO)_2(\mu\text{-}F_3CC{=}CCF_3)$] plus [340] and [341] (R = Me, Bu^t, Ph) as the

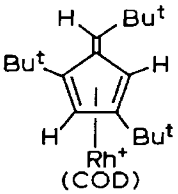


[340]

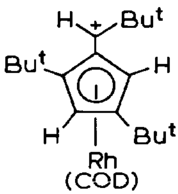


[341]

major products suggesting that binuclear species may be intermediates in the formation of the cyclopentadienone complexes (ref. 646). Chloride abstraction from $[RhCl(COD)]_2$ with silver hexafluorophosphate followed by addition of *tert*-butylacetylene forms a cationic complex which is considered to be best described by the canonical forms [342a] and [342b]. This is supported



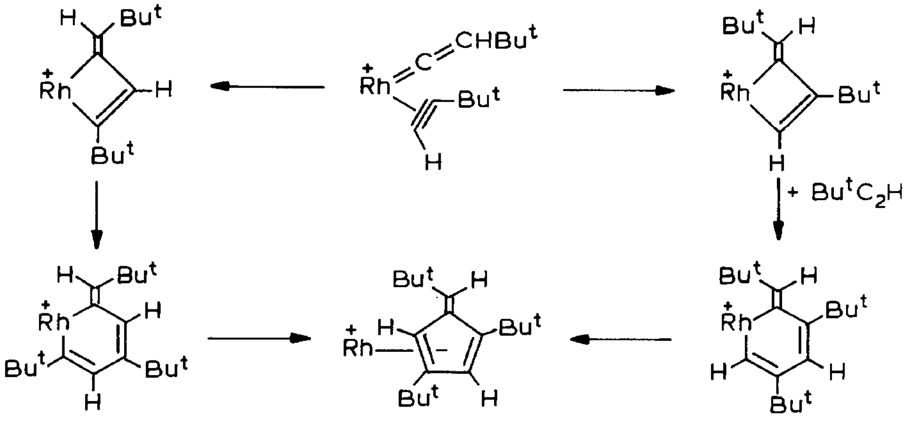
[342a]



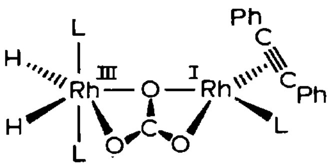
[342b]

by the selective addition of hydride ion to the exocyclic carbon atom when [342] reacts with potassium tri-*sec*-butylborohydride at -78°C. The mechanism of formation of [342] is thought to involve oxidative addition of the acetylene to $[Rh(COD)]^+$ to form $[(COD)Rh(H)(C{\equiv}CBu^t)]^+$, addition of a second acetylene molecule to give $[(COD)Rh(=C=CHBu^t)(HC{\equiv}CBu^t)]^+$ and further reaction of this species as shown in Scheme LIV (COD ligand omitted for clarity) (ref. 647).

The bicarbonate complex $[RhH_2(\eta^2-O_2COH)(PPr^i_3)_2]$ reacts with three equivalents of diphenylacetylene to yield [343], ($L = PPr^i_3$) carbon dioxide and trans-stilbene. With smaller quantities of the acetylene both [343] and the stilbene are seen together with unreacted starting material but no dihydrogen evolution is seen. The same reaction with dimethylacetylene dicarboxylate yields dimethylfumarate and dihydrogen is evolved while with HFB only dihydrogen evolution occurs. Evidently the ease of dihydrogen evolution from $[RhH_2(\eta^2-O_2COH)(PPr^i_3)_2]$ increases with an increase in the π-acidity of the acetylene in the initial adduct. The formation of [343] is thought to occur as depicted in Scheme LV ($L = PPr^i_3$) (ref. 648). Phenyl- and diphenylacetylene add to $[cp'_2Rh_2(\mu-CO)_2]$ to form [344] (R = H, Ph; R' = Ph) while acetylene itself gives a reversibly interconverting mixture of [344] (R = R' = H) and [345]. These react further with sulfur dioxide to form [346] (R = H, Ph). Cobalt analogs of [344] (R = R' = H) and [346] (R =



Scheme LIV

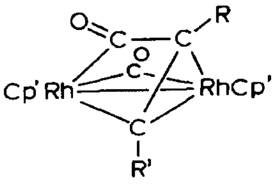


[343]

$$\begin{tikzcd}
{[RhH_2(O_2COH)L_2]} \arrow[r, "a"] & {[Rh(O_2COH)L_2] + PhCHCHPh} \arrow[d, "a"'] \\
{[Rh_2H_2L_3(\mu\text{-}O_2CO)(Ph_2C_2)]} & {[Rh(Ph_2C_2)(OC(O)OH)L_2]} \arrow[l, "b"']
\end{tikzcd}$$

a) Ph_2C_2. b) $[RhH_2(O_2COH)L_2]$

Scheme LV



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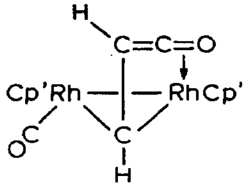
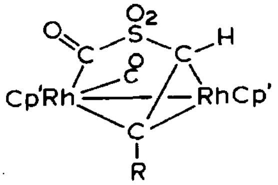
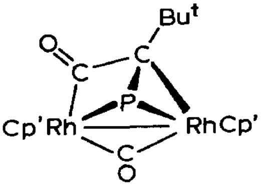


[345]



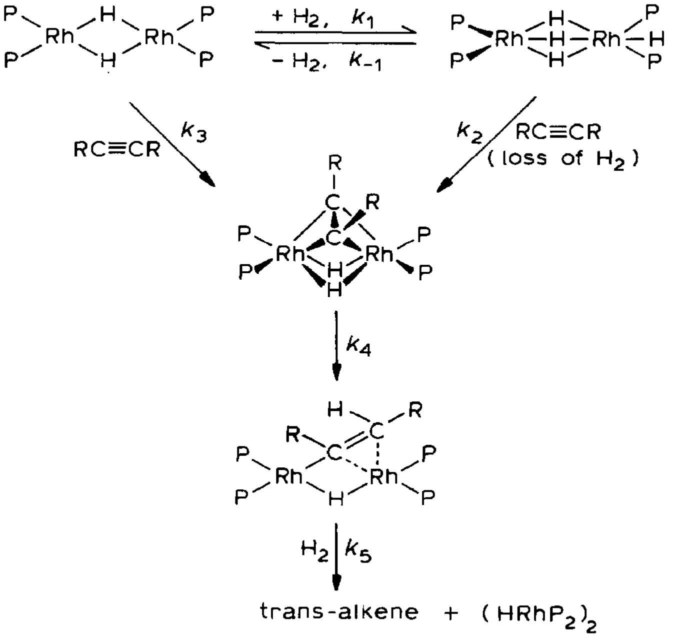
[346]

H) were also prepared. The related complex [347] was formed from the phosphaalkyne $Bu^tC{\equiv}P$ (refs. 649, 650).



[347]

A stereoselective catalytic hydrogenation of alkynes to trans-olefins has been achieved using [$Rh_2(P(OPr^i)_3)_4(\mu\text{-}H)_2$] as the catalyst precursor. Scheme LVI is proposed with k_5 representing the rate-determining step and

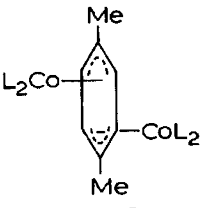


Scheme LVI

the key feature of this system being its ability to form the μ-vinyl complex shown at the bottom of the Scheme. The system rapidly loses its stereoselectivity due to the competitive reaction of this intermediate with alkyne instead of hydrogen to form a species which preferentially catalyzes the formation of the cis-olefin (ref. 651).

Metal π-allyl Complexes

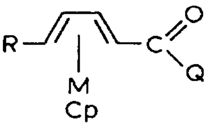
At room temperature in a hexane/p-xylene solution [$(\eta^5\text{-}C_6H_5Me_2)Co(L_2)$] ($L_2$ = $cy_2P(CH_2)_2Pcy_2$) undergoes partial decomposition to yield [348] as an



[348]

example of a $\mu\text{-}\eta^3\text{-}\eta^3$-arene complex (ref. 652). While allyl acetate reacts with [$Me_3SiCo(CO)_4$] to give [$(\eta^3\text{-}C_3H_5)Co(CO)_3$] and trimethylsilylacetate, the same reaction with 2-propenal and 2-vinyloxacyclopropane yields the trimethylsilyloxyallyl cobalt complexes $[(\eta^3\text{-}C_3H_4R)Co(CO)_3]$ (R = $OSiMe_3$, CH_2OSiMe_3) (ref. 653). Photolysis of $[(\eta^3\text{-}C_3H_5)Co(CO)_3]$ in argon or methane matrices at 12 K forms $[(\eta^3\text{-}C_3H_5)Co(CO)_2]$ a result which is consistent with kinetic studies which imply a dissociative process for carbonyl ligand substitution under thermal conditions and with computational results indicating a low bond order for the cobalt-carbon(carbonyl) bond. In a dinitrogen matrix $[(\eta^3\text{-}C_3H_5)Co(CO)_2(N_2)]$ was identified as the photolysis product while in a carbon monoxide matrix, $[(\eta^1\text{-}C_3H_5)Co(CO)_4]$ could be seen which fragmented to form $\{Co(CO)_4\}$ moieties. The last result suggests that reversible formation of an η^1-allyl species could permit a contribution of an associative process to substitution reactions (ref. 654).

The complexes [349] are protonated to [350] (M = Rh, Ir; R = Q = Me; R = Me, Q = OMe. M = Rh; R = Ph; Q = OMe) which indicates that the protonation occurs at the carbon atom adjacent to the acyl or ester substituent rather than at oxygen. Complex [349] (M = Rh; R = Me, Ph, Q = OMe) undergoes a base-catalyzed hydrolysis of the ester and on acidification with trifluoroacetic acid forms the corresponding acid (Q = OH) (ref. 655). Metathesis of $[cpRh(\eta^3\text{-}C_3H_5)Cl]$ with alkali metal salts yields $[cpRh(\eta^3\text{-}C_3H_5)X]$ (X = CN, OCN, SCN, Br, I) while with silver salts the analogs with X = O_2CCH_3, O_2CCF_3, NO_3 are formed. The trifluoroacetate complex was obtained as a mixture of two isomers which did not interconvert at temperatures below 100°C (ref. 656). Di(tertiary phosphites) convert $[(\eta^3\text{-}2\text{-}MeC_3H_4)Rh(COD)]$ to $[(\eta^3\text{-}2\text{-}MeC_3H_5)Rh(L_2)]$ (L_2 = $R_2PCH_2CH_2PR_2$ (R = OMe, OEt, OPr^i)) which on hydrogenation are converted to $[Rh(\mu\text{-}H)(L_2)]_n$ (n = 4; R = OMe, OEt. n = 2; R = OPr^i). Further reaction of these with trimethylphosphine forms $[RhH(PMe_3)_2(L_2)]$ (R = OMe, OPr^i). Dihydrogen oxidatively adds to only one metal in $[Rh_2(\mu\text{-}H)_2(L_2)_2]$ (R = OPr^i) to form the rhodium(III)-rhodium(I) dimer $[(L_2)RhH_2(\mu\text{-}H)_2Rh(L_2)]$. The tetrameric species however do not react with dihydrogen (ref. 657). While bis(bis(trimethylsilyl)methyl)phosphine (L) behaves as a simple phosphine ligand towards $[RhCl(CO)_2]_2$ to form trans-$[RhCl(CO)L_2]$, on heating in hexane with $[(\eta^3\text{-}2\text{-}MeC_3H_4)Rh(COD)]$, [351] forms



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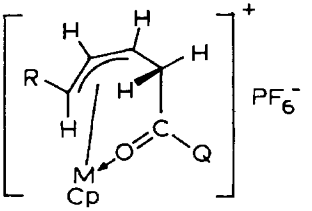

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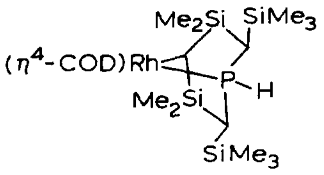

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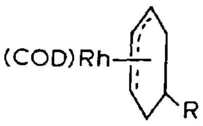

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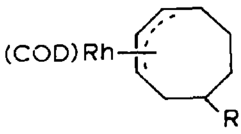
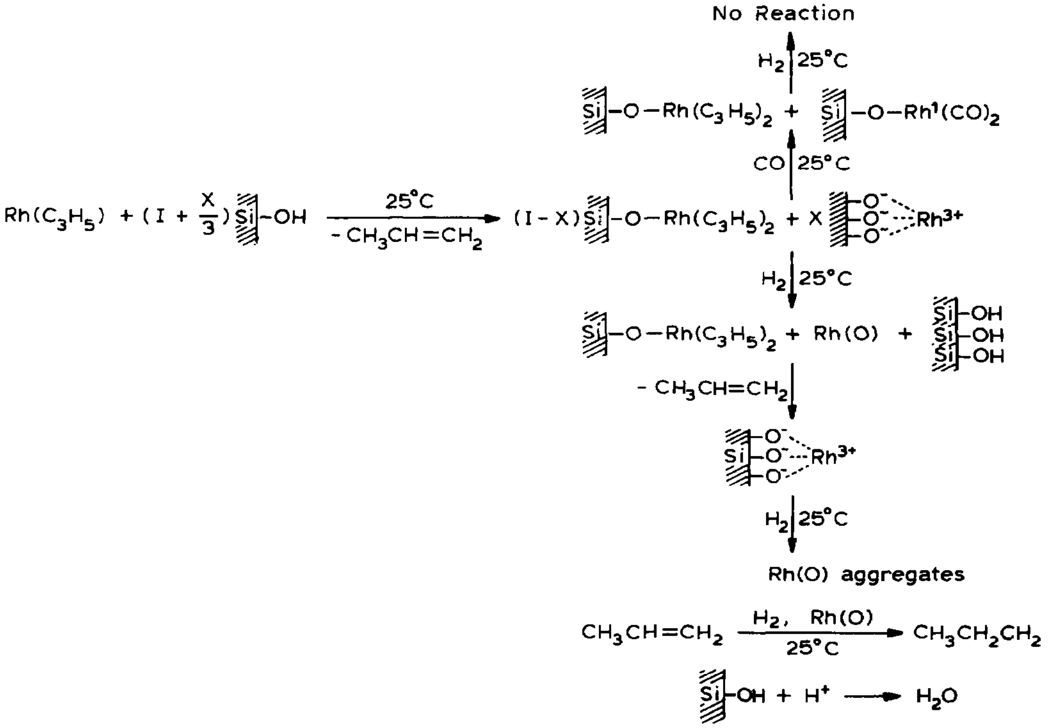


[353]

together with methane and isobutene. It is thought that the reaction may proceed via an η^1-allyl intermediate (ref. 658). Reaction of methyl- or phenyllithium with $[RhCl(COD)]_2$ in the presence of cyclohexa-1,3-diene or COD yields the allylic complexes [352] and [353] (R = Me, Ph). Since the ring substituent is found to occupy an endo equatorial position it is felt that this group transfers from the metal to the ring (ref. 659). The air-sensitive $[(\eta^3-C_8H_{11})Rh(PPh_3)_2]$ is formed by the metal-atom-vapor technique from COD followed by reaction with the phosphine (ref. 660).

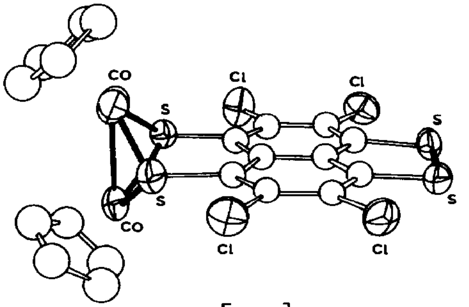
A full report of studies on allylrhodium complexes supported on silica has now appeared. The results are interpreted in terms of the transformations shown in Scheme LVII (ref. 661).



Scheme LVII

Metal Carbocyclic Complexes

Cyclopentadienyldicarbonylcobalt, its pentamethyl analog and derivatives thereof continue to be widely studied. Reaction of [cpCo(CO)$_2$] with phosphines and carbon disulfide in refluxing benzene forms a mixture of [cpCo(L)(CS)], [cpCo(L)(η^2-CS$_2$)], [cp$_3$Co$_3$(μ_3-CS)(μ_3-S)] and [cpCo(L)(CS$_3$)] (L = PEt$_3$, PPr$^n_3$, PBu$^n_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$, CNBu^t) in low yield. The last complex can also be got from [cpCo(L)(CO)] under the same conditions. A low yield of [cpCo(P(OPh)$_3$)(η^2-CS$_2$)] is formed similarly from [cpCo(P(OPh)$_3$)$_2$] while refluxing [cpCo(L)(η^2-CS$_2$)] (L = PMePh$_2$, PPh$_3$) in toluene affords a mixture of [cp$_3$Co$_3$(μ_3-CS)(μ_3-S)], [cpCo(L)(CS)] and [cpCo(L)(CS$_3$)] suggesting that in the initial reaction these three complexes are formed from the η^2-CS$_2$ complex. An electrophilic attack on the uncoordinated sulfur in [cpCo(PPh$_3$)(η^2-CS$_2$)] occurs on reaction with phenylisothiocyanate to form [cpCo(PPh$_3$)(η^2-SC=NPh)] and in the reaction of [cpCo(PPh$_3$)(CS)] with methyl triflate where the product is [cpCo(PPh$_3$)(CSMe)]SO$_3$F. By contrast mercury (II) chloride reacts at the metal in the latter complex to form [cpCo(PPh$_3$)(CS)(HgCl$_2$)] (ref. 662). The major product from [cpCo(CO)I$_2$] and sodium dialkyldithiocarbamates is [cpCo(I)(S$_2$CNR$_2$)] (R = Me, Et. R$_2$ = (Ph)(Me), (CH$_2$)$_5$, ((CH$_2$)$_2$)$_2$O) but some [Co(S$_2$CNR$_2$)$_3$] also forms. In the first complex the iodide ligand can be replaced in metathetical reactions by cyanide, thiocyanate, nitrite, nitrate and SnCl$_2$I ligands while with silver tetrafluoroborate in acetonitrile the product is [cpCo(MeCN)(S$_2$CNMe$_2$)]BF$_4$. With [cpCo(L)I$_2$] (L = PPh$_3$, PcyPh$_2$, PBu$^n_3$, PMe$_2$Ph, P(OPh)$_3$, P(OPr^i)$_3$, SbPh$_3$, CNMe, CNcy) however the product of the reaction with sodium dimethyldithiocarbamate is the ionic species [cpCo(L)(S$_2$CNMe$_2$)]I. Reaction of [cpCo(NO$_2$)(S$_2$CNMe$_2$)] with boron trifluoride etherate in benzyl alcohol yields benzaldehyde and with the corresponding nitrate complex this reaction is catalytic when run in the presence of dioxygen. It is proposed that the boron trifluoride reacts with the nitrate ligand to form nitrosyltetrafluoroborate which is the active oxidizing agent (refs. 663-664). Tetrachlorotetrathionaphthalene reacts with [cpCo(CO)$_2$] in refluxing toluene to form [354] (ref. 665). The antiferromagnetic cluster [355] is reported to be formed when



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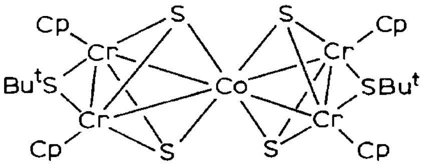
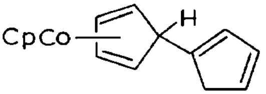


[355]

$[cp_2Cr_2Co(CO)_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2]$ is refluxed in toluene containing 2,2-dimethylpropionic acid (ref. 666). The dithiolate complex $[cpCo(\underline{o}\text{-}S_2C_6H_4)]$ undergoes a reversible dimerization in the solid state with retention of crystallinity (ref. 667).

A number of optically active cobalt Schiff base (SB) complexes of the formula [cpCo(I)(SB)]I have been synthesized from $[cpCo(CO)I_2]$ and the Schiff base ligand (ref. 668). Reaction of $[cp_2Co]$ and cyclopentadiene in air gives a mixture of [356] and [357] (ref. 669). The vinylcyclopentadienide anion can be obtained from 6-methylfulvene and lithium diisopropylamide and on reaction with $[Co_2(CO)_8]/I_2$, $[RhCl(CO)_2]_2$ or $[IrCl(CO)_3]_n$



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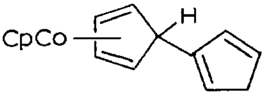
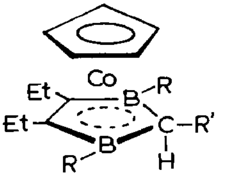


[357]

yields $[(\eta^5\text{-}C_5H_4vy)M(CO)_2]$ (M = Co, Rh, Ir) which have been studied as polymerizeable monomers for the formation of supported catalysts (ref. 670). Oxidative addition of cyanogen halides to $[cp'Co(CO)_2]$ occurs to form [cp'Co(CO)(X)(CN)] (X = Br, I) (ref. 671). The reaction of $[Co_2(CO)_8]$ with two equivalents of either $[(\eta^5\text{-}C_5H_4Bu^t)_2MH_3]$ or $[(\eta^5\text{-}C_5H_4Bu^t)_2M(CO)H]$ (M = Nb, Ta) yields $[Co_4(CO)_{12}]$ and $[(\eta^5\text{-}C_5H_4Bu^t)_2M(CO)Co(CO)_4]$ while with an excess of the cobalt carbonyl, the product is $[(\eta^5\text{-}C_5H_4Bu^t)_2M(CO)(OCCo_3\text{-}(CO)_9)]$ (ref. 672). Oxidation of $[(\eta^4\text{-}C_4H_4)Co_2(CO)_6]$ to $[(\eta^4\text{-}C_4H_4)Co(CO)_3]^+$ occurs on treatment with the trityl cation while iodide ion abstraction from $[(\eta^4\text{-}C_4H_4)Co(CO)_2I]$ by silver ion in the presence of triphenylphosphine yields $[(\eta^4\text{-}C_4H_4)Co(CO)_2(PPh_3)]^+$ (ref. 673). Cocondensation of cobalt atoms with toluene yields a species formulated as $[Co(C_6H_5CH_3)_2]$ on the basis of infrared studies. The complex is stable to -90°C but the mode of attachment of the toluene moieties to the metal was not established (ref. 674).

Insertion of a borane fragment into a metallacycle occurs when [cpCo-(C_4Ph_4)(PPh_3)] ([7], $R^1 = R^2 = R^3 = R^4$ = Ph) is refluxed with BH_3•THF in toluene. In addition to [cpCo(η^5-C_4Ph_4BH)], [cpCo(η^4-C_4Ph_4)] also forms (ref. 675). In refluxing petroleum ether [358] (R = Et; R' = Me. R = Me; R' = H) is formed from [cpCo(C_2H_4)$_2$] and the appropriate 1,3-diborolene. This reacts further with [cpCo(C_2H_4)$_2$] to give [359] and is deprotonated by



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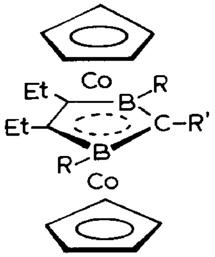
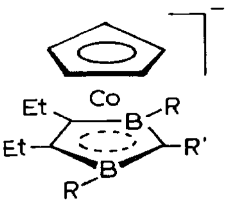


[359]

potassium in THF to form [360] which can be alkylated with alkyl halides to form [361] (R = Et; R' = R" = Me). Attempts to prepare [361] with R" = Me_3Si or Et_2B gave instead that with R" = H presumably via hydrogen-abstraction from the solvent by [360] implying that these substituents are too bulky to become attached to the diborolenyl ring. Complex [361] subsequently decomposes to the analog with R" = H presumably by loss of a methylene



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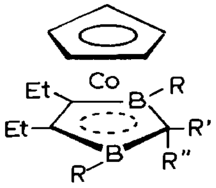
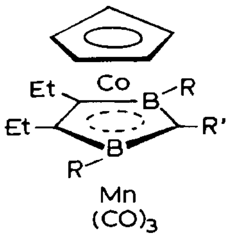


[361]

fragment. The anion [360] reacts with [$Mn_2(CO)_{10}$], [cpFe$(CO)_2$I], MX_2 (M = Cr, Fe, Co, Ni, Cu, Zn) and [Ni$(CO)_4$] to form [362] - [365] respectively.



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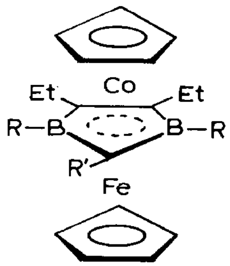
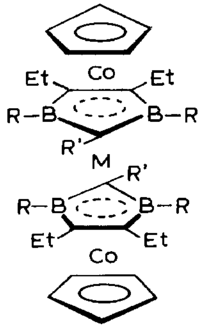


[363]

The observed acidity of the exo-hydrogen in [358] is attributed to the presence of a three-center, two-electron bond involving the cobalt with this



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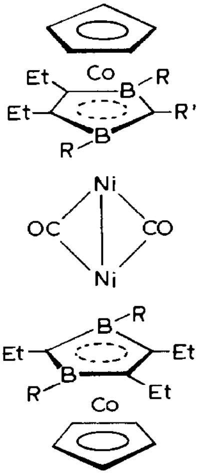
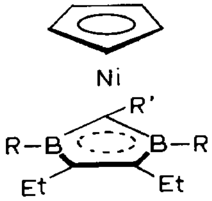


[365]

{CH} moiety leading to the conclusion that [358] should be formulated as a diborolene complex rather than a diborolenyl species (ref. 676). In related work, [366] (R = Et; R' = Me. R = Me, R' = H) reacts with [cpCo(CO)$_2$] in refluxing mesitylene to form [367] with [364] (M = Ni; R = Me; R' = H)



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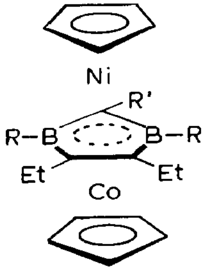
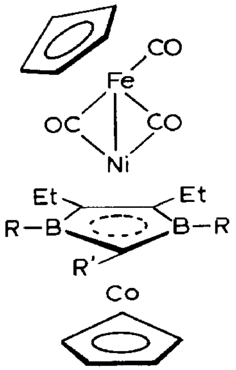


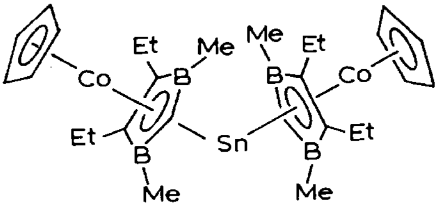
[367]

forming as a byproduct in one instance while on further reaction with [Fe$_2$(CO)$_9$] [367] yields [368]. Complexes [359], [363] and [367] can be



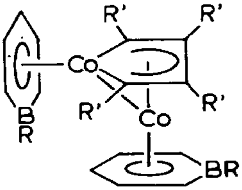
[368]

oxidized to monocations by silver tetrafluoroborate. The electrochemical behavior and the Mössbauer, NMR and EPR spectra of many of these complexes have also been described (ref. 677). The anion [360] (R = Me; R' = H) also reacts with tin(II) chloride to form [369] (ref. 678). Reduction of [(η^6-$C_5H_5BR)_2Co$] (R = Me, Ph) with sodium amalgam followed by addition of COD



[369]

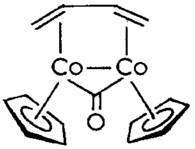
forms [(η^6-$C_5H_5BR)Co(COD)$] which on reaction with acetylenes yields [(η^6-$C_5H_5BR)Co(\eta^4$-$C_4R'_4)$] and [370] (R' = Me, Ph). An alternative synthesis of



[370]

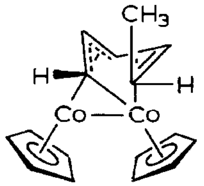
[(η^6-$C_5H_5BR)Co(\eta^4$-$C_4Me_4)$] is the reaction of [(η^4-$C_4Me_4)Co(CO)_2$] with [Tl-(C_5H_5BR)]. The complex [(η^6-$C_5H_5BR)_2Co$] is more reactive than ferrocene towards electrophilic aromatic substitution reactions (ref. 679). Addition of [cpCo($C_2H_4)_2$] to neat 1-R-2-methyl-Δ^3-1,2-azaboroline (R = Bu^t, $SiMe_3$) at -78°C yields [cpCo(η^4-$C_3H_4B(Me)N(R))$] which on warming to room temperature converts to [cpCo(η^5-$C_3H_3B(Me)N(R))$] (ref. 680).

On heating, [cp'Co(CO)$_2$] is converted into [cp'$_2$Co$_2$(μ-CO)$_2$] which on irradiation in petroleum ether solution with di(tertiary phosphines) yields the air-sensitive complexes [cp'Co(L_2)] (L_2 = DPPE, dmpe). The photoelectron spectra of the products indicate that they are quite electron-rich (ref. 681). Photolysis of [cpCo(CO)$_2$] in THF containing an excess of buta-1,3-diene forms [cpCo(η^4-C_4H_6)] which on further photolysis at 5°C in the presence of more [cpCo(CO)$_2$] yields [371]. The bonding of the butadiene ligand in [371] is considered to involve localized η^2-coordination to each metal (ref. 682). Heating [cpCo(η^4-hexa-1,3,5-triene)] in benzene at 60°C



[371]

yields [372] which at temperatures above 80°C undergoes a 1,5-hydrogen shift to form [373]. Complex [373] on photolysis at -96°C forms [374] which



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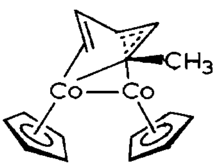
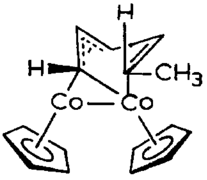
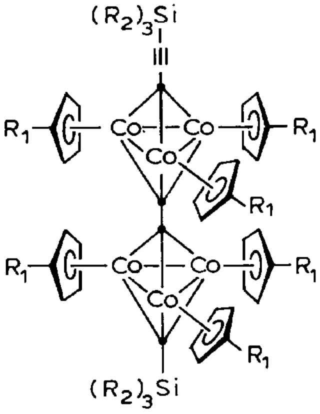


[373]



[374]

reconverts to [373] on warming to room temperature. The hydrogen shift in the conversion of [372] to [373] appears to be endo which suggests that the conversion involves oxidative addition of a carbon-hydrogen bond to one metal followed by reductive elimination at the other (ref. 683). Flash vacuum pyrolysis of [$cp_3Co_3(\mu_3$-CR)(μ_3-CR')] (R = R' = Ph. R = $SiMe_3$; R' = H) gave diphenylacetylene and trimethylsilylacetylene respectively suggesting that alkyne elimination from the bis(carbyne) complex occurs intramolecularly. The process was explored further by studying the interconversions of [375], [376] and [377] (R_1 = H; R_2 = Me. R_1 = R_2 = Me. R_1 = H; R_2 =



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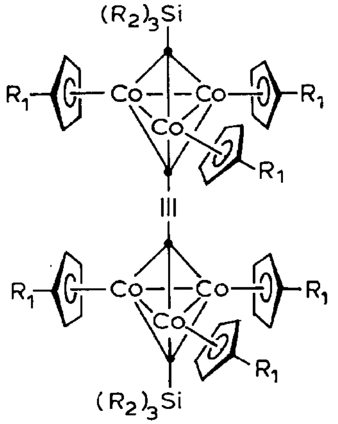
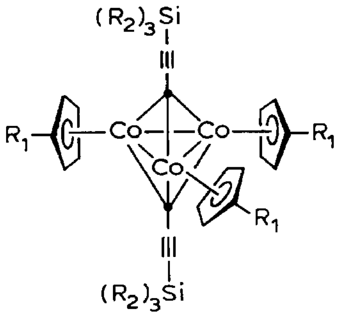
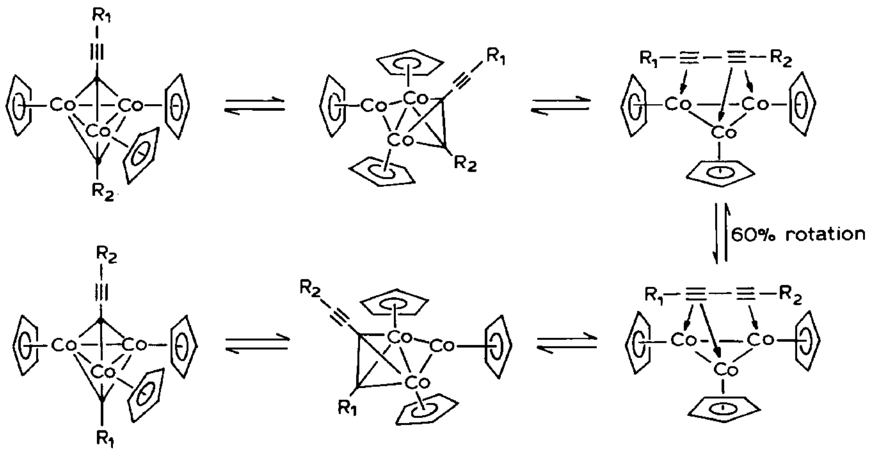


[376]

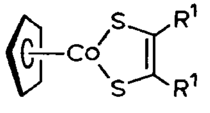


[377]

Et). Flash vacuum pyrolysis of [375] gave [376] and a trace of [377] (R_1 = H; R_2 = Me) while under the same conditions [376] gave [377] and a trace of [375] (R_1 = H; R_2 = Me). Complexes [375] - [377] (R_1 = R_2 = Me) were isolated from the mixture obtained from the reaction of $[(\eta^5\text{-}C_5H_4Me)Co(CO)_2]$ and 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne while the same route using $[cpCo(CO)_2]$ and 1,6-bis(triethylsilyl)hexa-1,3,5-triyne afforded [375] and [377] (R_1 = H; R_2 = Et). Flash vacuum pyrolysis of a mixture of [375] (R_1 = R_2 = Me) and [375] (R_1 = H; R_2 = Et) gave only [376] (R_1 = R_2 = Me or R_1 = H; R_2 = Et) with no crossover. Similarly a mixture of [375] (R_2 = Me) completely deuterated on the cyclopentadienyl rings and [375] (R_1 = H; R_2 = Et) gave completely deuterated [377] (R_2 = Me) and unlabelled [376] (R_1 = H; R_2 = Et) again with no crossover. The rearrangements of these carbyne complexes thus appears to be intramolecular and Scheme LVIII is proposed to explain them (ref. 684). Reduction of $[cp_3Co_3(\mu_3\text{-}CPh)_2]$ with potassium in methyltetrahydrofuran yields a radical anion whose EPR spectrum indicates the unpaired electron to be in an orbital which is a mixture of cobalt $3d_{xy}$ and cyclopentadienyl π orbitals. Electrochemical studies detected a reversible, one-electron oxidation but the EPR spectrum of the radical cation was broad and featureless (ref. 685). Cyclooctasulfur reacts with $[cp_3Co_3(\mu_3\text{-}CR)(\mu_3\text{-}CR')]$ (R = R' = Ph, Bu^n, CO_2Me, $C{\equiv}CSiMe_3$. R = Ph; R' = C_6D_5, Et) to form [378]. The selectivity is again an indication of the intramolecular

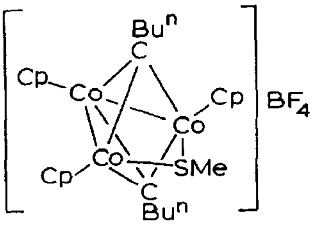


Scheme LVIII



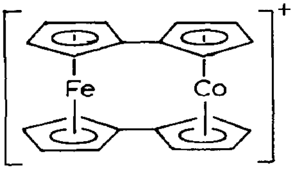
[378]

bis(carbyne) coupling described above. Similar reactions are observed with elemental selenium but they proceed more slowly. Reaction of $[cp_3Co_3(\mu_3\text{-}CBu^n)_2]$ with dimethylmethylthiosulfonium tetrafluoroborate yields [379] which suggests that the reactions of the bis(carbyne) complexes with sulfur may proceed _via_ an initial electrophilic attack on the cluster (ref. 686).



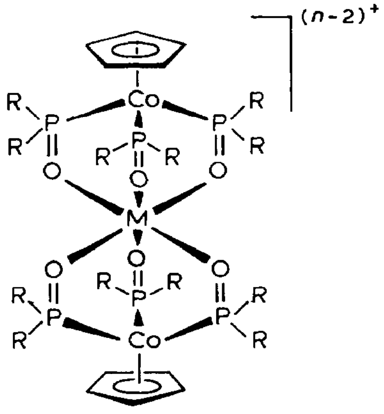
[379]

The fulvalene dianion reacts over two days with a mixture of anhydrous cobalt(II) and iron(II) chlorides in THF to form [380] which was isolated as



[380]

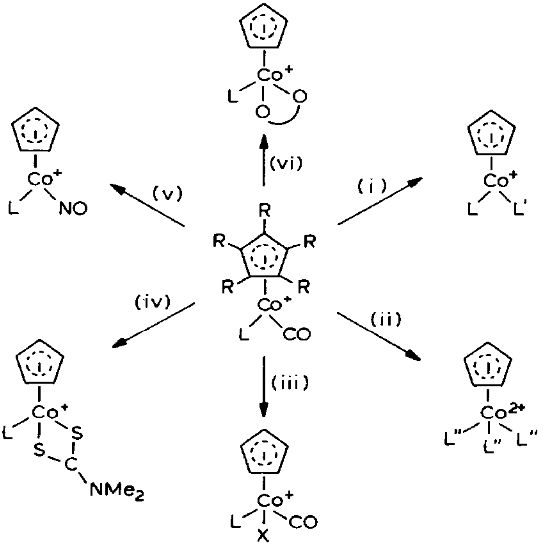
its hexafluorophosphate salt (ref. 687). In refluxing DMF dialkylphosphites react with [cp$_2$Co] to form [381] (M = Co; n = 0; R = Et, bz, Ph, _p_-ClC$_6$H$_4$)



[381]

which can be cleaved to [cpCo(P(O)R$_2$)$_3$]$^-$ by cyanide. From this, [381] (R = Et, bz; M = Al, Pr, Eu, Fe; n = 1. M = Ce; n = 2) can be formed and isolated as hexafluorophosphate salts (ref. 688).

The _cis_ and _trans_ isomers of [cpCo(η^4-C$_4$Ph$_2$Fc$_2$)] show two reversible, one-electron oxidation processes which occur at almost identical potentials. These are therefore attributed to oxidations of the iron centers. Both the unipositive and dipositive ions so produced show intervalence transfer bands in their electronic spectra which are attributed to Co(I)-Fe(III) interactions (ref. 689). Further studies of the reduction of [cpCo(1,5-COT)] by the technique of fast Fourier transform faradaic admittance measurements have enabled it to be characterized as an EC process with the initially formed $[cpCo(1,5\text{-}COT)]^{\dot{-}}$ rapidly isomerizing to $[cpCo(1,3\text{-}COT)]^{\dot{-}}$ (ref. 690). In related work, the complexes $[cpCo(CO)_{2-n}L_n]$ (n = 1; L = PPh_3, Pcy_3. n = 2; L = PPh_3) are reversibly oxidized electrochemically to radical cations in dichloromethane solution. In THF, $[cpCo(CO)(PPh_3)]$ shows a second irreversible oxidation which was thought to be the oxidation of a solvated species. The ferricinium ion oxidizes $[cpCo(CO)(Pcy_3)]$ to the radical cation but the corresponding triphenylphosphine complex gives $[cpCo(PPh_3)_2]^+$ under the same conditions with the yield increasing when excess phosphine is present. No oxidation of $[cpCo(CO)_2]$ by ferricinium ion occurs but when triphenylphosphine is added, $[cpCo(PPh_3)_2]^+$ forms suggesting that $[cpCo(CO)(PPh_3)]$ forms initially and is then oxidized. Further chemistry of these systems is outlined in Scheme LIX (L = Pcy_3; R = H unless otherwise noted). It is



i) L' = PPh_3, py. ii) L" = $P(OMe)_3$. iii) $0.5X_2$ (X = Br, I). iv) $Me_2NC(S)SSC(S)NMe_2$. v) NO(g), L = PPh_3, R = Me. vi) O-O = o-quinone.

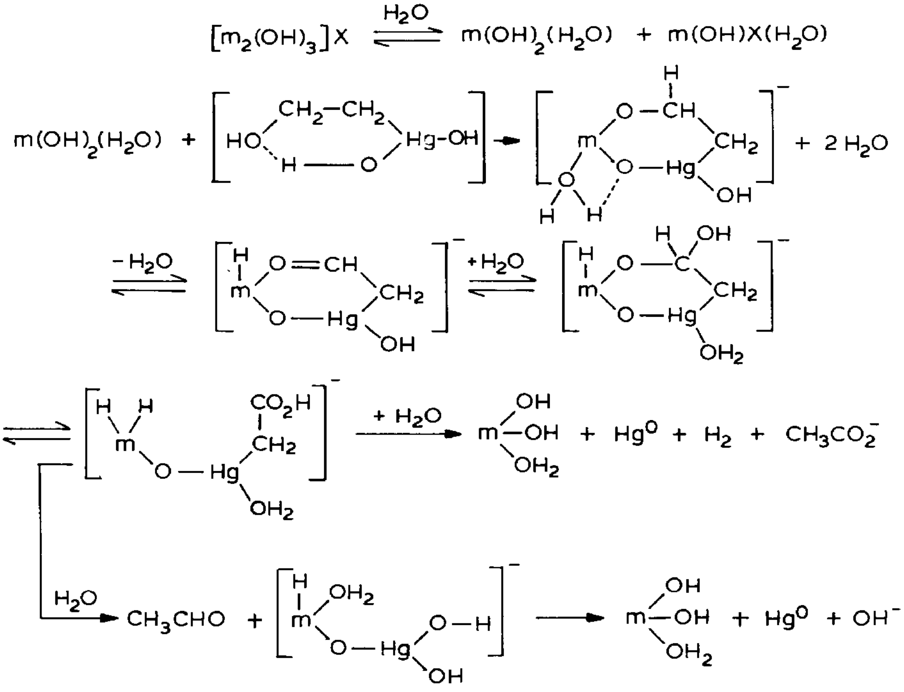
Scheme LIX

thought that a previous statement that $[cpCo(PPh_3)_2]BF_4$ can be oxidized to an air-stable dication by silver tetrafluoroborate (Inorg. Chem., 21(1982) 2056) is incorrect but the present workers have been unable to characterize the yellow product obtained in this reaction (ref. 691). The structures of the 18-electron complex [cpCo(PEt$_3$)$_2$] and the 17-electron complex [cpCo(PEt$_3$)$_2$]$^+$ have been determined in an attempt to determine the origin of their different reactivities. The first easily trimerizes acetylenes while the other does not. Also the first undergoes a slow substitution of triethylphosphine by other ligands while the latter rapidly disproportionates under these conditions. The two complexes show different rotational orientations of the cyclopentadienyl ligand with respect to the CoP$_2$ plane and the neutral species also shows a distortion of the carbon-carbon distances in this ligand which implies a σ+π contribution to the metal-ring binding. The reactivity differences are therefore attributed to differences in the nature of the HOMO between the two complexes (ref. 692). The ^{59}Co NQR spectra of [cpCo(o-bb'C$_6$H$_4$)] (b,b' = various combinations of O, S, NR (R = H, Me, Ph)), [cpCo(S$_2$C$_2$R$_2$)] (R = H, CN, CF$_3$) and [cpCoL$_2$] (L = CO, P(OMe)$_3$, PEt$_3$, PPh$_3$) indicate that the ground state electron distribution on cobalt is primarily controlled by the electronegativity of the attached ligand atoms. No significant π-bonding effects are noted except in the Co-L bonds of the last series of complexes (ref. 693). Molecular orbital calculations have been performed on the cyclopentadienyl(bicyclo[3.2.0]heptatrienyl)cobalt cation and the corresponding anion to determine the minimum energy pathway for migration of the metal from one ring to the other. For the cation the transfer is predicted to proceed relatively directly but for the anion, the {cpCo} moiety is predicted to avoid the area of ring fusion which suggests that a dissociative mechanism may compete (ref. 694).

An extensive series of dicobalt, cobalt-iron and cobalt-nickel dimers among others bridged by two carbonyl groups have been classified according to the metal-metal distances and the angle of intersection of the two MC$_2$ planes in the {M(μ-CO)$_2$M} unit. No correlation was found between steric effects or the interplanar angle and the metal-metal or metal-carbon (of the bridging carbonyl) distances (ref. 695).

The infrared and Raman spectra of [cp$_2$Co]$^+$ intercalated into lamellar solids including ZnPS$_3$ and M$_2$P$_2$S$_6$ (M = Fe, Co, Ni) have been obtained. A weak interaction with the host is observed. An enhancement of the metal-ligand vibrational modes is seen when the frequency of the charge transfer band of the cation is approached in the preresonance Raman spectrum (refs. 696, 697). Using the isolobality principle, the structures of metal clusters with from four to nine metal atoms are considered to be closely analogous to the corresponding boranes. Where such clusters exhibit fluxional behavior and/or high reactivity they correspond by this analogy to nido or arachno polyhedra (ref. 698). Ultraviolet, photoelectron spectra have been measured for [cpM(PMe$_3$)(CX)] (M = Co; X = S, O. M = Rh; X = O) (ref. 699).

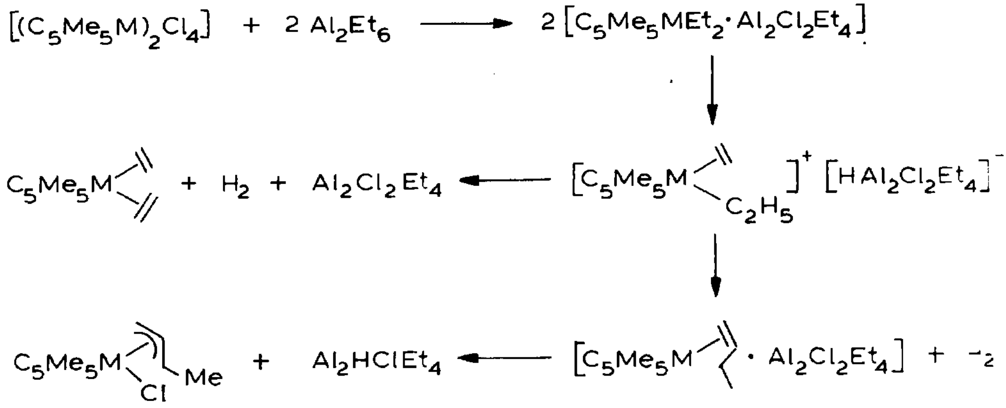
In an attempt to discover a facile route for the hydration of ethylene to ethanol, the reaction of $[cp'_2Rh_2(\mu\text{-}OH)_3]Cl$ with 2-hydroxyethyl derivatives of mercury in aqueous sodium hydroxide was explored. A catalytic decomposition of the mercury compound to metallic mercury was observed and ethanol (14-18%) plus acetate ion (82-86%) formed. The observation of some dihydrogen as a product suggested that water was acting as an oxidizing agent. The ethanol is proposed to arise from the rhodium-catalyzed disproportionation of acetaldehyde (see J. Organometal. Chem., 242(1983)241, Scheme LXXXI) whilst the remainder of the reaction is thought to occur as shown in Scheme LX (ref. 700). An excess of triethylaluminum in benzene provides modest



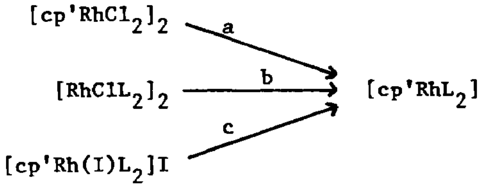
m = cp'Rh

Scheme LX

yields of $[cp'M(C_2H_4)_2]$ and traces of $[cp'M(\eta^3\text{-}1\text{-}MeC_3H_4)Cl]$ when reacted with $[cp'_2M_2Cl_4]$ (M = Rh, Ir) while with $[cp'RhCl_2(PMe_3)]$ and a slight excess of the alkyl aluminum only $[cp'RhEt_2(PMe_3)]$ formed. It is suggested that the presence of the strongly bound phosphine ligand in this instance prevents the elimination reactions depicted in Scheme LXI which could lead to the formation of olefin and allyl complexes (ref. 701). Protonation of $[cp'MMe_2(DMSO)]$ (M = Rh, Ir) with p-toluenesulfonic acid in acetonitrile forms $[cp'MMe(DMSO)(MeCN)]^+$ which can be isolated as the hexafluorophosphate salt. Metathesis with sodium halides forms [cp'MMe(X)(DMSO)] (X = Cl, Br, I). Protonation of the original complex with one equivalent of trifluoroacetic acid in acetone forms [cp'MMe(DMSO)(O_2CCF_3)] while with an excess the product is [cp'M(DMSO)$(O_2CCF_3)_2$] (ref. 702). The synthesis and chemistry of a variety of pentamethylcyclopentadienyl complexes of rhodium are given in

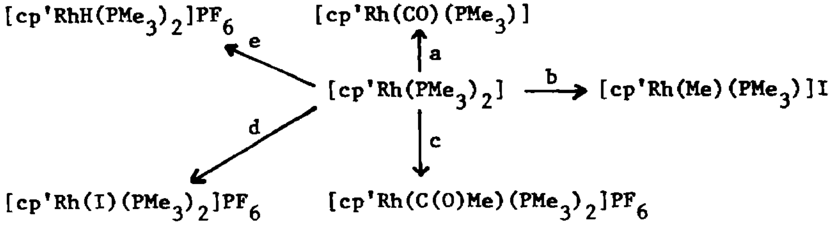


Scheme LXI



a) 4L (L = PMe_3, PMe_2Ph, PMe_2H, $P(OMe)_3$), Na/Hg, Et_2O.
b) Nacp', L = PMe_3. c) Na/Hg, L = PMe_3

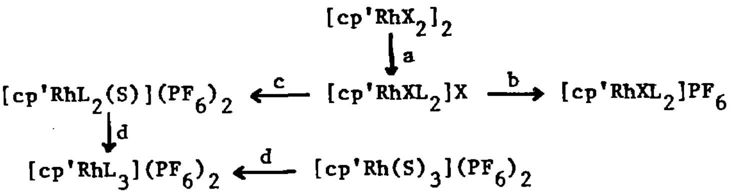
Scheme LXII



a) CO. b) MeI. c) MeC(O)Cl, PF_6^-. d) I_2. e) NH_4PF_6

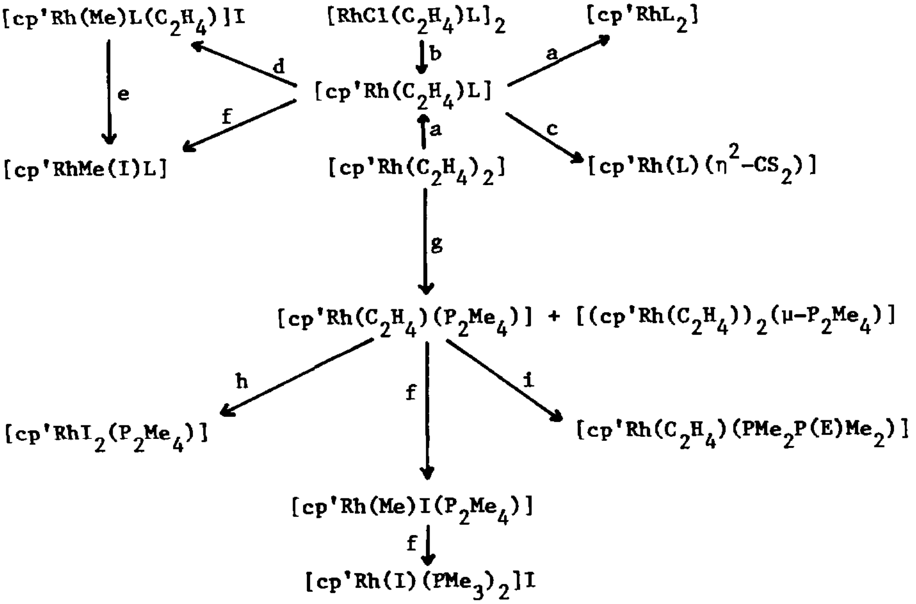
Scheme LXIII

Schemes LXII - LXV. The mechanism of the conversion of [cp'Rh(C_2H_4)(P_2Me_4)] to [cp'Rh(I)(PMe_3)$_2$]I was probed by reacting the ethylene complex with CD_3I to get [cp'Rh(I)(CD_3)(P_2Me_4)] and then reacting this product with CH_3I to



a) 4 PMe_3 (=L), X = Cl, I. b) NH_4PF_6. c) $AgPF_6$, S = acetone. d) PMe_3.

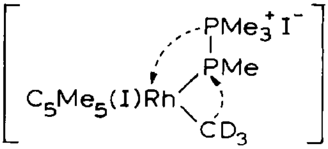
Scheme LXIV



a) L = PMe_3, b) Nacp'. c) CS_2. d) MeI, ether. e) acetone. f) MeI, benzene. g) PMe_2PMe_2. h) I_2. i) E_8 (E = S, Se).

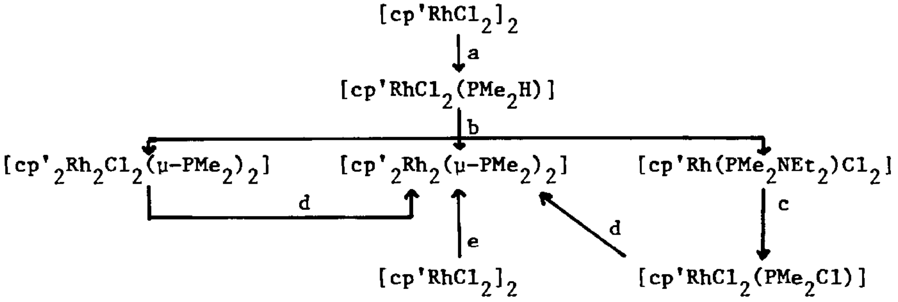
Scheme LXV

form [cp'Rh(I)(PMe_3)(PMe_2CD_3)]I. This suggested that the second equivalent of methyl iodide quaternizes the free phosphorus atom of the monodentate tetramethylbiphosphine ligand to give [382] which rearranges as shown (ref.



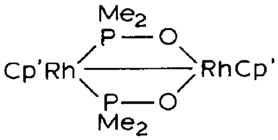
[382]

703). Further chemistry of $[\mathrm{cp'RhCl_2}]$ with dimethylphosphine is outlined in Scheme LXVI. Protonation of $[\mathrm{cp'_2Rh_2(\mu\text{-}PMe_2)_2}]$ with trifluoroacetic acid in benzene yields $[\mathrm{cp'_2Rh_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2}]^+$ while reaction with dioxygen in benzene forms [383]. Complexes [384] (E = S, Se) and [385] (E = Se, Te) are obtained similarly with the heavier chalcogens (ref. 704). The formamimidinato complex $[\mathrm{cp'}\overline{\mathrm{RhNR{=}CH{=}NR}}\mathrm{(Cl)}]$ (R = p-tolyl) is formed on refluxing $[\mathrm{cp'RhCl_2}]_2$ and $\mathrm{K[RN{=}CH{=}NR]}$ in toluene. It reacts with carbon monoxide, phenylisothiocyanate and carbon disulfide to form carbamoyl ([386]) thioureido ([387]) and dithiocarbamate ($[\mathrm{cp'Rh(X_2CN(RO)CH{=}NR)Cl}]$) complexes



a) $\mathrm{PMe_2H}$, acetone. b) $\mathrm{Et_2NH}$, THF. c) HCl, benzene.
d) Na/Hg, $\mathrm{Et_2O}$. e) $[\mathrm{cp'Rh(PMe_2H)_2}]$, MeLi, -78°C.

Scheme LXVI



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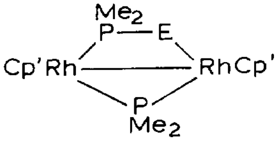

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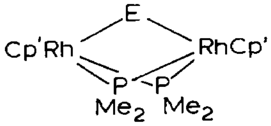

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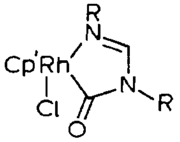
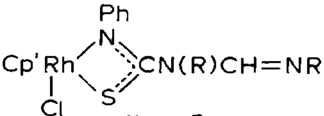


[386]

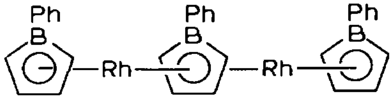


[387]

respectively (ref. 705). Finally, reaction of $[cp'MCl_2]_2$ with arenes in trifluoroacetic acid followed by addition of noncoordinating anions affords $[cp'M(\eta^6\text{-arene})]A_2$ (M = Rh, Ir; arene = C_6Me_6, C_6H_6, mesitylene; A = PF_6, BF_4) (ref. 706).

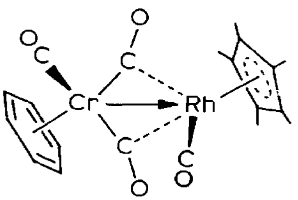
Other arene complexes formulated as $[Rh(DPPE)(arene)]^+$ (arene = C_6H_6, naphthalene, anthracene, 9-methylanthracene, 9-trifluoroacetylanthracene) are obtained by reaction with $[Rh(DPPE)(MeOH)_2]^+$. The anthracene complexes catalyze the hydrogenation of the three anthracenes to the 1,2,3,4-tetrahydro derivatives. The hydrogenation is presumed to occur in a stepwise fashion with the oxidative addition of dihydrogen to the arene complex as the rate-determining step (ref. 707). Alkylation of $[cp'RhCl_2(PMe_3)]$ with methyllithium at -40°C in THF yields $[cp'RhCl(Me)(PMe_3)]$ which is converted to $[cp'RhMe(THF)(PMe_3)]PF_6$ on treatment with silver hexafluorophosphate. This in turn reacts with $[H_2Al(OR)_2]^-$ (R = CH_2CH_2OMe) at -40°C in d_8 THF to form $[cp'RhH(Me)(PMe_3)]$. No further reaction occurs on warming to -17°C unless deuterobenzene is also present in which case reductive elimination occurs and $[cp'Rh(D)(C_6D_5)(PMe_3)]$ forms. Photolysis of $[cp'RhH_2(PMe_3)]$ in liquid propane at -55°C yields $[cp'RhH(Pr^n)(PMe_3)]$ which reductively eliminates propane above -15°. In both these reactions the formation of the 16-electron species $\{cp'Rh(PMe_3)\}$ is proposed which can undergo oxidative addition of carbon-hydrogen or -deuterium bonds (ref. 708). The rhodicinium salts $[(\eta^5\text{-}C_5H_4R)_2Rh]^+$ (R = H, Me) are formed from rhodium(III) chloride and $Tl(C_5H_4R)$ in a mixture of ethanol and DMSO. Oxidation of a mixture of $[cp_2Rh]^+$, $[cpRh(\eta^5\text{-}C_5H_4Me)]^+$ and $[(\eta^5\text{-}C_5H_4Me)_2Rh]^+$ with basic potassium permanganate followed by acidification yields $[cpRh(\eta^5\text{-}C_5H_4CO_2H)]^+$ plus $[(\eta^5\text{-}C_5H_4CO_2H)_2Rh]^+$. The latter on heating in thionyl chloride forms $[(\eta^5\text{-}C_5H_4C(O)Cl)_2Rh]^+$ which is converted to $[(\eta^5\text{-}C_5H_4CO_2Me)_2Rh]^+$ by methanol and to $[(\eta^5\text{-}C_5H_4NH_2)_2Rh]^+$ by sodium azide followed by reaction with hot sulfuric acid (ref. 709).

Addition of 1-phenyl-2,5-dihydroborole to $[RhCl(C_2H_4)_2]_2$ in THF forms [388] (ref. 710). The bimetallic complex [389] is formed on photolysis of



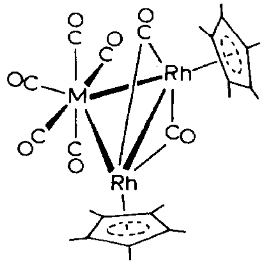
[388]

$[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ and $[cp'Rh(CO)_2]$ in THF. Analogs with mesitylene and hexamethylbenzene substituents on chromium were also prepared. Similarly,

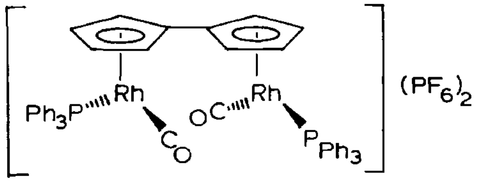


[389]

photolysis of $[cp'_2Rh_2(\mu\text{-}CO)_2]$ and $[M(CO)_6]$ affords [390] (M = Cr, W). The molybdenum analog of [390] was prepared from the rhodium dimer and $[Mo(CO)_5(MeCN)]$ (ref. 711). The initial product of the oxidation of $[cpRh(CO)(PPh_3)]$ electrochemically or with ferricinium hexafluorophosphate is thought to be the radical cation but it then dimerizes to form [391] as the isolated product. This undergoes a reversible, two-electron reduction to [392]. The first step of the dimerization step is thought to be a coupling of the cyclopentadienyl ligands.



[390]



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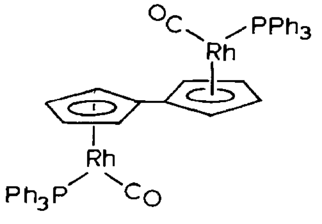
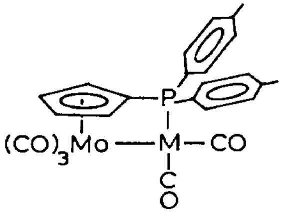


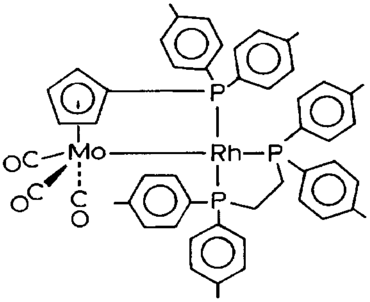
[392]

Treatment of $[cpRh(CO)(PPh_3)]$ with silver hexafluorophosphate however gives $[(cpRh(CO)(PPh_3))_2(\mu\text{-}Ag)]PF_6$ (ref. 712). The arene complex $[(\eta^6\text{-}C_6H_6)Cr(\eta^6\text{-}C_6F_5PPh_2)]$ behaves as a monodentate phosphine ligand (L) on reaction with $[RhCl(CO)_2]_2$ and forms trans-$[RhCl(CO)L_2]$ (ref. 713). By contrast, reaction of $Li[(OC)_3Mo(\eta^5\text{-}C_5H_4P(p\text{-}tolyl)_2)]$ with $[RhCl(CO)_2]_2$ or $[IrCl(CO)_2(p\text{-}toluidine)]$ forms [393] (M = Rh, Ir). One carbonyl



[393]

group can be replaced by a tertiary phosphine (L) (M = Rh; L = PMe_3, P(p-tolyl)$_3$. M = Ir; L = PMe_3, PPh_3). Reaction of $[RhCl(L_2)]_2$ (L_2 = (p-tolyl)$_2$$PCH_2CH_2P$(p-tolyl)$_2$) with the molybdenum complex yields [394]. The rhodium complexes undergo some decomposition when reacted with dihydrogen at elevated temperatures and pressure but no hydride complexes were detected. The iridium complexes however formed [395] (L = CO, PMe_3, PPh_3) although only the trimethylphosphine derivative was sufficiently stable with respect



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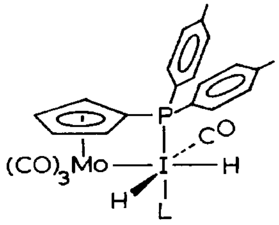
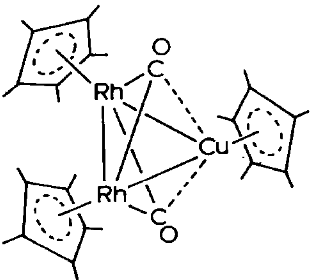


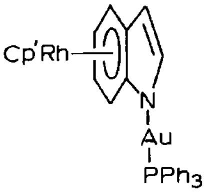
[395]

to reductive elimination of dihydrogen to be isolated in pure form (ref. 714). The {cp'Cu} moiety is considered to be isolobal with a methylene fragment and thus should coordinate to $[cp'_2Rh_2(\mu\text{-}CO)_2]$ to give an analog of the methylene-bridged dimers studied extensively by Herrmann. Indeed the complex [396] could be synthesized by successive treatment of copper(I)



[396]

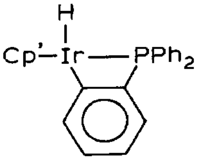
chloride with pentamethylcyclopentadienyllithium and $[cp'_2Rh_2(\mu\text{-}CO)_2]$ (ref. 715). Further details of the reaction of $[cp'Rh(acetone)_3](ClO_4)_2$ with $[Au(In)PR_3]$ (R = Ph, o-tolyl, p-tolyl) have appeared. The structure of the triphenylphosphine complex has been determined which shows it to be [397] (ref. 716).



[397]

The previous proposal that $[cpRh(CO)_2]$ reacts with phosphines, phosphites and isocyanides via an associative process involving a change in the coordination of the cyclopentadienyl ligand from η^5 to η^3 has been further supported by additional studies on $[cp'M(CO)_2]$ (M = Co, Rh) and $[(\eta^5\text{-}C_9H_7)\text{-}Rh(CO)_2]$. The indenyl complex reacts with triphenylphosphine at a rate which is eight orders of magnitude faster than is observed for the cyclopentadienyl analog while the pentamethylcyclopentadienyl rhodium complex reacts significantly more slowly. The latter result is explained by the presence of the electron-donating methyl groups making the "ring slip" less favorable. Although a reasonable linear free energy relationship was seen with the cone angle of the entering ligand, for small ligands, the ligand basicity also affected the rate (refs. 717, 718).

A full report on the activation of carbon-hydrogen bonds by the {cp'IrL} (L = PPh_3, PMe_3) moiety is now available. Here, reaction of $[cp'IrCl_2]_2$ with the phosphine followed by lithium triethylborohydride yields $[cp'IrH_2L]$. Photolysis of the trimethylphosphine complex in hydrocarbon solvents (RH) forms $[cp'IrH(R)(PMe_3)_2]$ (R = cyclo-C_6H_{11}, Bu^tCH_2, Ph) while under the same conditions in benzene $[cp'IrH_2(PPh_3)]$ forms $[cp'IrH(Ph)(PPh_3)]$ plus [398].



[398]

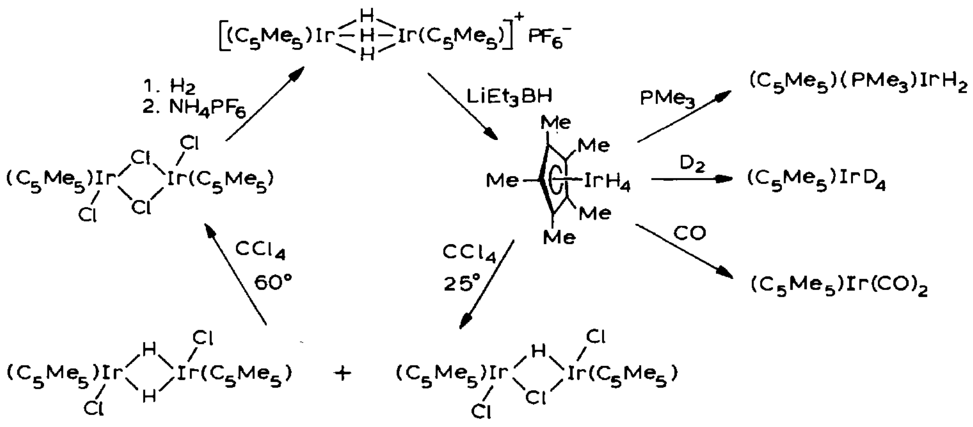
In all instances the presumption is that {cp'IrL} is formed by reductive elimination of dihydrogen and inserts into a carbon-hydrogen bond. The possibility of a free radical process was eliminated by the observation that on photolysis of the dihydride in p-xylene preferential attack on an aromatic carbon-hydrogen bond occurred while in cyclopropane only carbon-hydrogen and not carbon-carbon bond cleavage was seen. This process is thus considered to be a concerted oxidative addition of the carbon-hydrogen bond to the metal and it appears that in saturated hydrocarbons the reactivity of this bond is primary>secondary>tertiary. Photolysis of $[cp'IrH_2(PMe_3)]$ in n-pentane initially yields three isomeric alkyl hydrides which thermally equilibrate to $[cp'IrH(n\text{-}C_5H_{11})(PMe_3)]$. Alkane is eliminated on reaction with oxidizing or electrophilic reagents. Some reactions of $[cp'IrH(CH_2Bu^t)(PMe_3)]$ are shown in Scheme LXVII (L = PMe_3) (ref. 719). Other chemistry of iridium hydrides derived from $[cp'_2Ir_2Cl_4]$ is outlined in Scheme LXVIII (ref. 720). Another reaction of $[cp'_2Ir_2Cl_4]$ is that with triethylsilane in dichloromethane at room temperature which forms $[cp'IrH_2Cl(SiEt_3)]$ via transient formation of $[cp'_2Ir_2Cl_2(\mu\text{-}H)_2]$. Reaction with more silane

$$\begin{tikzcd}
 & {[cp'Ir(CO)L]} \arrow[r, "a"] & {[cp'Ir(CO)_2]} \\
N.\ R. & {[cp'IrH(CH_2Bu^t)L]} \arrow[l, "c"'] \arrow[u, "a"'] \arrow[d, "b"] & \\
 & {[cp'IrBr(CH_2Bu^t)L]} \arrow[r, "d"] \arrow[d, "e"] & CH_2DBu^t \\
Bu^tCH_2Br & Bu^tCH_2HgCl + [cp'IrBr(Cl)L] \arrow[l, "f"'] &
\end{tikzcd}$$

a) CO. b) $CHBr_3$. c) CO_2. d) FSO_3D. e) $HgCl_2$. f) Br_2.

Scheme LXVII

finally forms $[cp'IrH_2(SiEt_3)_2]$ which can be got directly from $[cp'_2Ir_2Cl_4]$ and the silane on refluxing in benzene containing triethylamine (ref. 721).



Scheme LXVIII

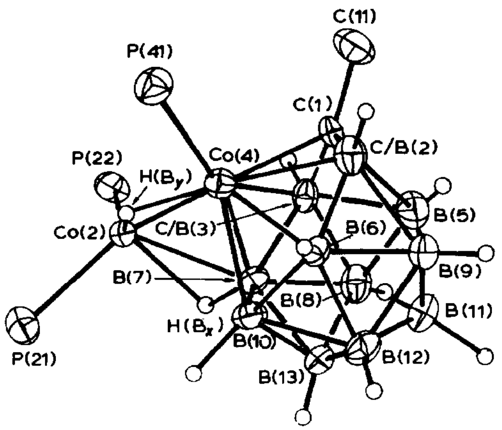
Refluxing hydrated iridium(III) chloride with TFB in ethanol yields $[IrCl(TFB)_2]$ which reacts with silver tetrafluoroborate in acetone containing an arene to form $[(\eta^6\text{-arene})Ir(TFB)]BF_4$ (arene = $C_6H_{6-n}Me_n$ (n = 2-6)). The arene complexes react with dihydrogen to form iridium metal but when done in the presence of a phosphine, arsine or stibine ligand this does not occur and the system can be used to catalyze the hydrogenation of acetophenone (ref. 722).

Extended Hückel molecular orbital calculations have been performed on the {cpML} (M = Co, Rh, Ir; L = CO, phosphine) moiety to probe the orbital structure of these species which have been proposed as reactive intermediates (see ref. 719 for example). A particular aim was to determine whether a non-linear geometry might be preferred so as to maintain a singlet ground state which would avoid problems of spin-forbidden pathways in reactions where these species may be intermediates. The results indicate that strong σ-donor or π-acceptor ligands do indeed favor a non-linear structure and oxidative addition of a carbon-hydrogen bond to the metal in such a species is allowed in the ground state (ref. 723). Deformation density studies on polyenes bound to $\{M(CO)_n\}$ fragments show an intramolecular interruption of the polyene π-system suggesting that differences in the carbon-carbon distances of the bound polyenes should occur. The results also suggest that carbon-carbon bonds of the polyene ligand which are eclipsed by a carbonyl group or similar ligand on the opposite side of the metal should be longer than the others and that an interaction of the π-system of the polyene with the eclipsing ligand should occur in either a through-bond or a through-space fashion. Among the complexes studied were $[cpCo(CO)_2]$ and $[(\eta^5\text{-}C_5H_4Me)Rh(CO)_2]$ (ref. 724). The energies of the low-lying, negative ion states of $[cp_2Co]$ have been obtained by electron-transmission spectroscopy. Using multiple scattering Xα calculations the observed states have been assigned as those resulting from electron capture into metal 3<u>d</u> and cyclopentadienyl π* orbitals (ref. 725).

Metallaborane and -carbaborane Complexes

A systematic nomenclature for polyhedral boranes and their cyclopentadienylcobalt derivatives has been proposed (ref. 726, 727).

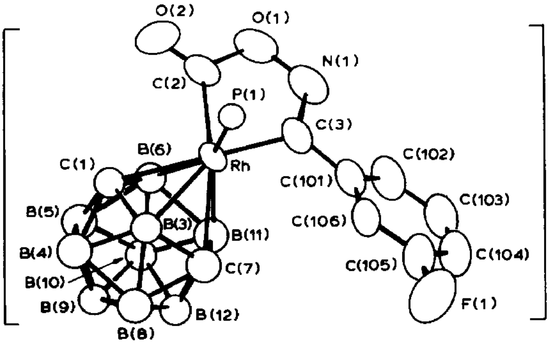
Reaction of <u>closo</u>-$[1\text{-methyl-}1,2\text{-}C_2B_{10}H_{11}]$ with two equivalents of $[Co(PEt_3)_4]$ in toluene yields the thirteen-vertex <u>closo</u>-metallaborane [399]. The nonmethylated carbon atom in the cage was not unequivocally identified (ref. 728). With $[CoCl_2(bipy)]$, $Li[C_2B_{10}H_{11}]$ yields $[Co(C_2B_{10}H_{11})_2(bipy)]$ while with $Li_2[C_2B_{10}H_{10}]$ the product is $[Co(C_2B_{10}H_{10})(bipy)]$. In both instances the carbaborane moieties are proposed to bind to cobalt at the carbon site (ref. 729). A mixture of $[Co(H_2O)_6]Cl_2$, cyclopentadiene and



[399]

4-CB_8H_{14} react in aqueous potassium hydroxide to yield $[cpCoCB_8H_9]^-$ which was isolated as the tetramethylammonium salt (ref. 730). The synthesis of $Cs_n[(B_9C_2H_{11})Co_n(B_8C_2H_{10})_{n-1}]$ (n = 2-4) have been reported together with a determination of their magnetic properties (refs. 731-733).

The rhodacarbaborane complexes $[3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$, $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$ and $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}2,1,12\text{-}RhC_2B_9H_{11}]$ react with bases to remove the hydrogen from the metal as a proton. The starting complexes can be regenerated by treatment of these monoanions with hydrogen halides. The monoanions all coordinate one carbonyl ligand to the metal and the first two also form anionic complexes with ethylene. The anion derived from the first rhodacarbaborane (3,1,2-isomer) has the metal symmetrically bound to the C_2B_3 face of the carbaboranyl moiety but in the 2,1,7-isomer, the face of the carbaboranyl moiety is non-planar and the species is fluxional in solution as predicted by molecular orbital calculations. The carbonyl adducts of the anions derived from the 3,1,2- and 2,1,7-rhodacarbaboranes undergo [3+2] cycloadditions with aryl nitrile N-oxides to form [400] (Ar = Ph, p-FC_6H_4). These adducts on heating release the corresponding nitrile and carbon dioxide. A similar cycloaddition reaction occurs with $[cp'Rh(CO)_2]$ and p-chlorobenzonitrile N-oxide. These results led to the suggestion that the formation of $[IrCl(N_2)(PPh_3)_2]$ from $[IrCl(CO)(PPh_3)_2]$ and aroylazides involves an initial 1,3-dipolar addition of the azide to the {Ir(CO)} moiety (refs. 734, 735) (see also ref. 109). Reaction of $[RhCl(COD)(PEt_3)_2]$ and $Cs_2[7\text{-}(7'\text{-}7',8'\text{-}C_2B_9H_{11})\text{-}7,8\text{-}C_2B_9H_{11}]$ forms [401] which contains a metal-metal bond and two three-center Rh-H-B interactions (ref. 736). In methanol containing three equivalents of potassium hydrox-



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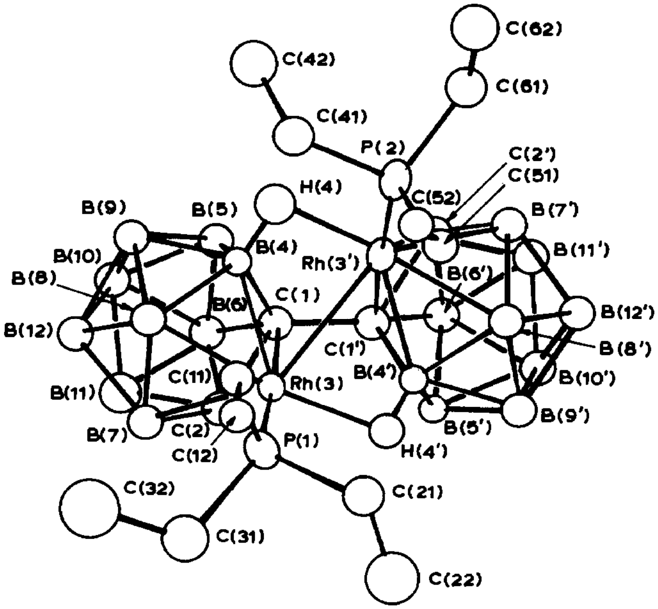
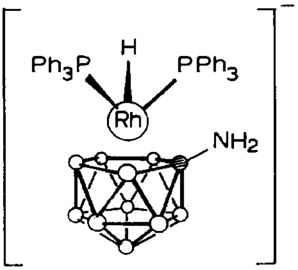
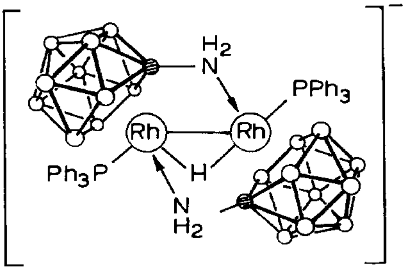


[401]

ide, [RhCl(PPh$_3$)$_3$] and *nido*-[B$_{10}$H$_{12}$CNH$_3$] forms the *closo*-rhodacarbaborane [402] which dimerizes to [403] (shaded circle = C) on refluxing in methanol.



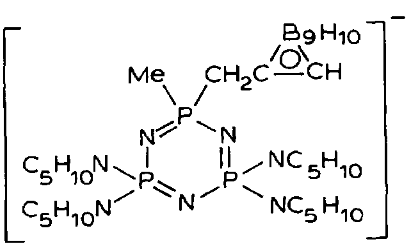
[402]



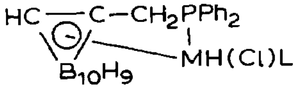
[403]

The dimer can be got directly from the original reactants on refluxing in methanol containing tetrabutylammonium hydroxide (ref. 737). Treatment of closo-[3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] with boron tribromide or bromoform in benzene yields a mixture of species including [$PHPh_3$][closo-3-(PPh_3)-3,3-Br_2-3,1,2-$RhC_2B_9H_{11}$]. Two isomers, presumably reflecting two different rotational orientations of the {$RhBr_2(PPh_3)$} moiety with respect to the carbaboranyl ligand, were detected in solution. The iodo analog as the tetrabutylammonium salt could be obtained from closo-[3-(PPh_3)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$] and tetrabutylammonium iodide (ref. 738).

The phosphazine-substituted carbaboranyl anion [404] reacts with [RhCl-$(PPh_3)_3$] to give a closo-[3,3-(PPh_3)-3-H-3,1,2-$RhC_2B_9H_{10}$] moiety attached to the phosphazine unit. A similar species was derived from a carbaboranyl-substituted linear phosphazine polymer (ref. 739). The complexes [405] (M = Rh; L = 4-picoline. M = Ir; L = COD) are obtained from $[RhCl(CO)_2]_2$ plus one equivalent of 4-picoline or $[IrCl(COD)]_2$ and 1-$Ph_2PCH_2C_2B_{10}H_{11}$ while

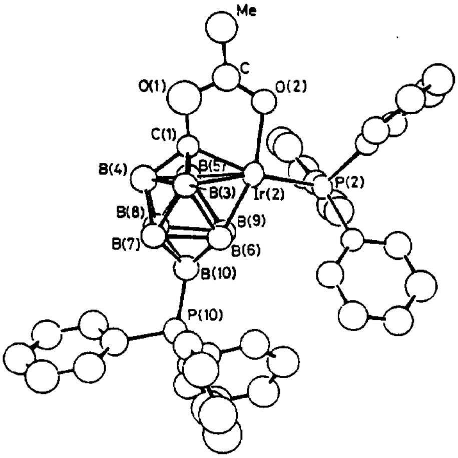


[404]



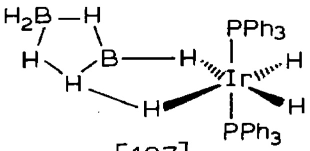
[405]

[$RhCl(PPh_3)_3$] and Na[1,7-HCB_9H_9PMe] form [2,2-$(PPh_3)_2$-2,1,7-RhCP(Me)B_9H_{10}] (refs. 740, 741). A miniscule yield of [406] is obtained as one product of the reaction of [$IrCl(CO)(PPh_3)_2$] and closo-$[B_{10}H_{10}]^{2-}$ in refluxing

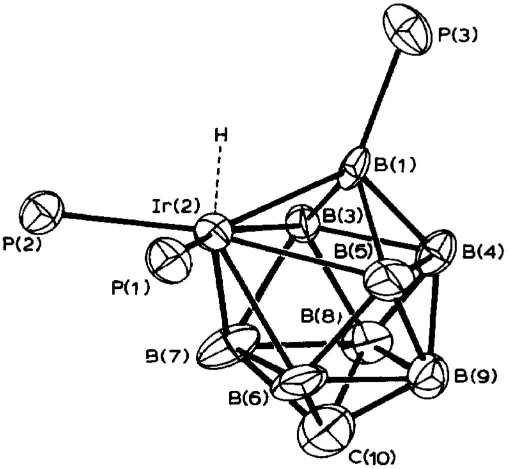


[406]

methanol. An interesting feature is the acetate group which is attached to C(1) and the metal. The hydrogen atoms were not located crystallographically but NMR measurements indicate that one is bound to the metal and the remaining seven are on boron atoms (except B(10)). The closo-structure found here is in contrast to a formally isoelectronic complex obtained earlier (J. Chem. Soc., Chem. Commun., (1981)933) which has an iso-nido structure (ref. 742). At room temperature [$IrCl(PPh_3)_3$] reacts with $Tl[B_3H_8]$ to form [407] and with $Li[B_8CH_{13}]$ one of the products is identified as closo-[1-(PPh_3)-2-H-2,2-$(PPh_3)_2$-2,10-$IrCB_8H_8$] whose skeleton is shown as [408] (refs. 743, 744). Substantial yields of [409] result from the

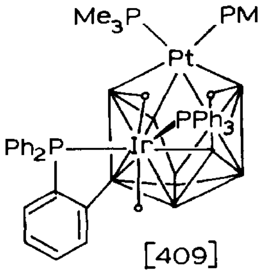


[407]



[408]

reaction of [410] with [$PtCl_2(PMe_3)_2$] and potassium hydride (ref. 745).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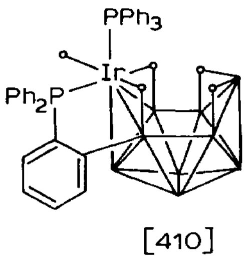
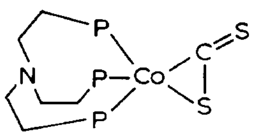

[410]

Miscellaneous Complexes

As mentioned in previous Annual Surveys, these are systems which do not fit into the categories described up to this point but which nevertheless are likely to be of interest to organometallic chemists. Interest continues in the reactions of gaseous metal ions with hydrocarbons. Using ion beam experiments, the mechanistic details of reactions of Co^+ with alkanes which have been described in previous Annual Surveys have been further probed using ^{13}C and ^{2}H labelled substrates. No carbon scrambling occurs but a considerable amount of deuterium scrambling is observed. This is presumed to occur via a series of reversible β-hydrogen (deuterium) abstractions from the initially formed alkyl complexes (ref. 746). When gaseous cobalt ions are produced by laser ionization instead of electron impact, they are less energetic and in some instances show differing reactivity patterns with hydrocarbons. For example unlike the earlier work of Beauchamp, no reaction with cyclopropane is observed. Otherwise the predominant reaction with alkanes and cycloalkanes is again insertion into carbon-carbon bonds to form alkyls or metallacycles which then undergo β-hydrogen abstraction and reductive eliminiation of dihydrogen to ultimately yield olefin complexes. By contrast the primary process by which $\{CoD\}^+$ reacts with hydrocarbons is the oxidative addition of carbon-hydrogen bonds (refs. 747-749). Reduction of $K[Co(N_2)(PMe_3)_3]$ with dialkylaluminum chlorides at low temperature yields the bis(diazenido) complex $[(Me_3P)_3CoN_2(\mu\text{-}R_2Al)_2N_2Co(PMe_3)_3]$ (R = Me, Et, Bu^s). The structure has been determined and the short cobalt-nitrogen distance observed was interpreted to indicate some degree of π-bonding between the two atoms (ref. 750). The substitution of phenyldiethylphosphonite (L') into $[CoHL_4]$(L = $PPh(OMe)_2$) to give $[CoHL_nL'_{4-n}]$ (n = 0-4) is facilitated by photolysis. In the absence of irradiation only traces of the complexes with n = 3 or 2 are seen which suggests the photolysis generates the coordinatively unsaturated species $\{CoHL_3\}$. This is supported by the observation that $[CoH(PPh(OMe)_2)_4]$ catalyzes the isomerization of allyl benzene to (E)- and (Z)-propenyl benzene under photolytic conditions (ref. 751). Addition of diethylmagnesium at -20°C in THF to $[CoH(N_2)(PPh_3)_3]$

forms $[((PPh_3)_3Co(N_2))_2Mg(THF)_4]$ which is converted to $[Li(THF)_3][(N_2)Co(PPh_3)_3]$ by butyllithium. The latter complex can also be got directly from $[CoH(N_2)(PPh_3)_3]$ and butyllithium in THF/hexane. The lithium or magnesium is coordinated to the dinitrogen ligand and on protonation of these complexes 20-30% of the dinitrogen is converted to a mixture of hydrazine and ammonia (ref. 752). The complex $[Co(PMe_3)(dmpm)_2]A$ (A = Cl, PF_6) is formed by addition of dmpm to either $[CoCl(PMe_3)_3]$ or $[Co(PMe_3)_4]PF_6$ respectively in THF. The chloride salt on standing in THF solution converts to $[CoCl_2(PMe_3)_2(dmpm)]$ while on treatment with trimethylphosphine in acetone at low temperature a mixture of $[Co(PMe_3)_3(dmpm)]Cl$ and $[(Co(PMe_3)(dmpm))_2(\mu\text{-}PMe_2)]$ forms. The former complex is fluxional and in both the dmpm ligand is monodentate (ref. 753). Addition of *n*-butyryl chloride to $[CoCl(PPh_3)_3]$ initially yields $[Pr^nC(O)CoCl(PPh_3)_3]$ which can decompose either to octan-3,4-dione or heptan-4-one and $[CoCl_2(PPh_3)_2]$. The latter path is favored in the presence of excess acid chloride and presumably proceeds *via* the intermediate formation of $[Co(Pr^n)(CO)Cl_2(PPh_3)_2]$ (ref. 754). Reduction of $[CoL_3L']$ (L = PMe_3; L' = N_2, olefin) with potassium forms $K[CoL_3L']$ which reacts with $MXPh_3$ (M = Sn; X = Cl. M = Ge; X = Br) to give $[Co(MPh_3)L_3]$. These form adducts $[Co(MPh_3)L_3L'']$ (M = Ge; L'' = CO. M = Sn; L'' = CO, C_2H_4) (ref. 755).

The reaction of $[CoH(np_3)]$ with carbon disulfide yields [411] which converts to [412] on successive treatments with methylfluorosulfonate and sodium tetrafluoroborate. Complex [412] can be reduced to [413] with sodium borohydride. An alternate synthesis of [413] is the reaction of $[CoH(np_3)]$ with carbon disulfide and sodium tetraphenylborate. Phenylisothiocyanate also reacts with $[CoH(np_3)]$ to form [414] which converts to [415] on treatment with sodium tetraphenylborate. A similar reaction occurs with phenylisocyanate but the mode of bonding of the isocyanate was not determined. In related work, $[(triphos)Co(\eta^2\text{-}CS_2)]$ undergoes electrophilic addition of chalcogens to form $[(triphos)Co(S_2C{=}E)]$ (E = O, S) and $[(triphos)Co(SSeC{=}S)]$. Similarly $[(triphos)Co(\eta^2\text{-}SCSMe)]^+$ gives $[(triphos)Co(SECSMe)]^+$ (E = S, Se) (refs. 756-758). Reduction of cobalt(II) salts with sodium borohydride in benzene containing 1,5-bis(diphenylphosphino)pentane forms [416] (ref. 759).



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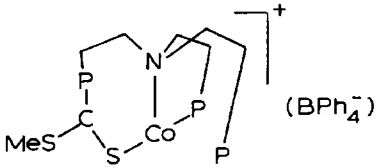

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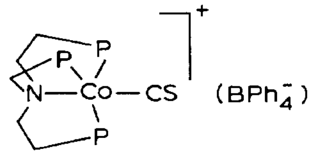
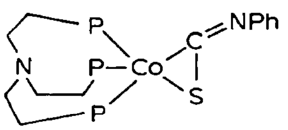
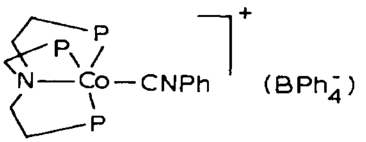


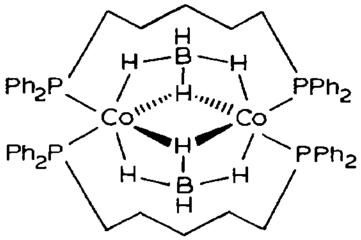
[413]



[414]



[415]

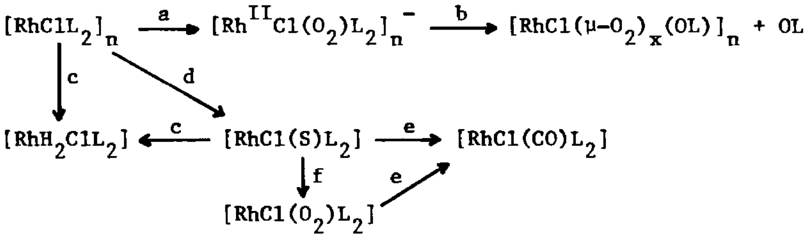


[416]

A number of applications of $[CoCl(PPh_3)_3]$ as a catalyst precursor include the reductive coupling of allylic halides in the stereospecific synthesis of squalenes (ref. 760), the reduction of diphenylacetylene to cis- and trans-stilbene (ref. 761) and the formation of indoles from diphenylacetylene and azobenzene derivatives (ref. 762). The kinetics and mechanism of styrene hydrogenation in the presence of $[CoH_3L_3]$, $[CoH(N_2)L_3]$ and $[Co(N_2)L_3]$ ($L = PPh_3$) have been studied (ref. 763) as has the homologation of methanol by syngas using $[CoI_2(PPh_3)_2]$. In the latter study when completely deuterated methanol is used the products are CD_3CHO, CD_3CH_2OH, $CD_3CH(OCD_3)_2$, $CD_3CO_2CD_3$, CD_4 and CHD_3. The observation of only CD_4 and CHD_3 in the methane formed suggests reductive elimination from species such as $[(CD_3)Co(X)L_n]$ ($X = D$ or H) which in turn indicates that the methane arises from the methanol and not from hydrogenation of carbon monoxide. It also indicates that methylene complexes are not intermediates (ref. 764).

Since, as previously demonstrated, $[RhCl(PPh_3)_3]$ is undissociated in dioxygen-free solvents, its reaction with phosphinated polymers is considered to occur by an associative process (ref. 765). The reaction of dihydrogen with $[RhCl(B)(P(p\text{-tolyl})_3)_2]$ ($B = P(p\text{-tolyl})_3$, py, THT) gives cis-dihydrido complexes in which the original phosphine ligands are trans to one another. The thermodynamics of the addition have been measured and a value for the rhodium-hydrogen bond energy of ca 58 kcal/mol derived which does not appear to be sensitive to a change in the ligand B from the phosphine to THT (ref. 766). The thionitrosyl complex $[Rh(NS)Cl_2(PPh_3)]_2$ is formed from $[RhH(PPh_3)_4]$ and $[NSCl]_3$ and can be cleaved to $[Rh(NS)Cl_2(PPh_3)_2]$ by triphenylphosphine. The iridium analog of the latter can be formed from

$[IrHCl_2(PPh_3)_3]$ (ref. 767). Reduction of hydrated rhodium(III) chloride under dinitrogen with sodium amalgam in THF containing phosphine ligands forms $[RhH(N_2)L_2]$ (L = PBu^t_3, $PPhBu^t_2$, PPr^i_3), $[Rh_2H_2L_4(\mu\text{-}N_2)]$ (L = Pcy_3, PPr^i_3) or $[RhHL_n]$ (n = 3; L = PPr^i_3, PEt_3. n = 4; L = PEt_3). With triethyl- and triisopropylphosphine the product obtained depends on the metal/ligand ratio used in the synthesis. The complexes provide catalysts for the hydrogenation of nitriles, ketones and alkynes and for H-D exchange between primary or secondary carbon-hydrogen bonds and deuterium oxide (ref. 768). In refluxing ethanol, hydrated rhodium(III) chloride reacts with np_3 to form $[RhCl_2(np_3)]Cl$. Reduction with one equivalent of sodium borohydride in dichloromethane forms $[RhCl(np_3)]$ while with two equivalents in acetone the product is $[RhH(np_3)]$. Treatment of $[RhCl_2(np_3)]Cl$ with silver hexafluorophosphate in acetonitrile forms $[RhCl(MeCN)(np_3)](PF_6)_2$ (ref. 769). Acetonitrile solutions of $[Rh(diars)_2]Cl$ react with carbon dioxide with the formation of trans-$[RhCl(\eta^1\text{-}CO_2)(diars)_2]$. The adduct formation appears to require the presence of a counterion capable of coordinating to the metal since $[Rh(diars)_2]BPh_4$ does not give a carbon dioxide adduct (ref. 770). The chemistry of $[RhCl(Pcy_3)_2]_n$ towards dioxygen differs between the solid state and solution as outlined in Scheme LXIX (L = Pcy_3); OL = $OPcy_3$; S = C_6H_6). The species $[Rh^{II}Cl(O_2)L_2]_n^-$ is paramagnetic and is formulated as a



a) O_2, solid state. b) slowly on standing. c) H_2, benzene. d) benzene. e) CO, benzene. f) O_2, benzene.

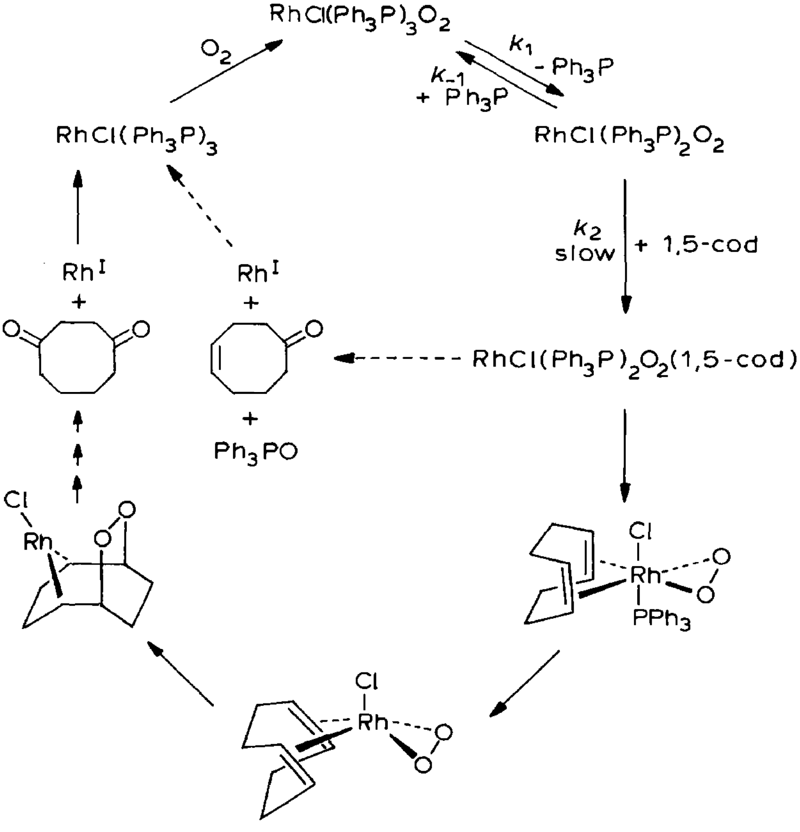
Scheme LXIX

superoxide complex; $[RhCl(O_2)L_2]$ at the bottom of the Scheme is diamagnetic and unlike the former does not form any tricyclohexylphosphine oxide even on further reaction with dioxygen. Also $[RhCl(CO)L_2]$ cannot be converted to $[RhCl(\mu\text{-}O_2)_x(OL)]_n$ by reaction with dioxygen nor can the latter be converted to the former with carbon monoxide (ref. 771). The anaerobic decomposition of $[RhCl(O_2)(PPh_3)_3]$ occurs by competing pathways which either form $[RhCl(O_2)(PPh_3)_2]_2$ or generate triphenylphosphine oxide (ref. 772).

The complex mer-$[RhCl_3(P-O)_2]$ (P-O = $Ph_2PCH_2C(O)OEt$) contains one monodentate and one chelating ligand. Abstraction of chloride with silver hexafluorophosphate yields cis-$[RhCl_2(P-O)_2]PF_6$ in which both ligands are chelated. The carboxylate oxygen is evidently rather strongly coordinated contrary to expectation since the cationic complex displays no reactivity towards carbon monoxide or other small molecules (ref. 773). Hydrated rhodium(III) chloride and o-methoxyphenyldimethylstibine(L) form $[RhCl_3L_2]$ which reacts with carbon monoxide to give $[RhCl_3(CO)L_2]$. Presumably in the former complex one of the o-methoxy groups of the ligand also coordinates to the metal. With iridium, however, the initial product is $[IrCl_3L_3]$ (ref. 774). The structure of $[RhCl(\eta^2-P_4)(PPh_3)_2]$ which was proposed from NMR studies (J. Chem. Soc., Chem. Commun., (1982)1422) has now been verified by x-ray crystallography. From molecular orbital calculations it appears that the bonding of the P_4 molecule to the metal is similar to that for an olefin although the π-type dp hybrid orbitals on the P_4 unit which would be involved in π-backbonding are more delocalized than are the corresponding π^* orbitals in an olefin. The edge of the P_4 tetrahedron opposite that bound to the metal appears unperturbed suggesting the possibility that a second metal might bind there (ref. 775).

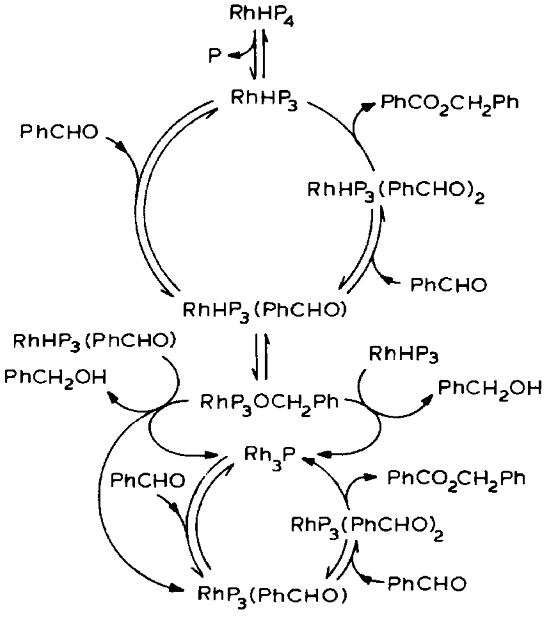
X-ray photoelectron spectra have been measured for $[RhCl(PPh_3)_3]$ and $[RhCl(O_2)(PPh_3)_3]$ in an effort to determine the nature of surface species formed in solid-state reactions of these complexes. Exposure of the former complex to air forms a labile surface species whose formation is reversible. It is thought to be a Rh(III)-oxygen complex and the observation that it readily reacts with dihydrogen is taken to indicate that oxygenated species on the surface of $[RhCl(PPh_3)_3]$ should not hinder its activity in hydrogenation catalysis (ref. 776). In a study of the mechanism of olefin hydrogenation reactions catalyzed by rhodium(I) complexes using para-enriched dihydrogen it is found that the reversible oxidative addition of dihydrogen to the metal leads to an equilibration of ortho and para forms. With $[RhCl(PPh_3)_3]$ this equilibration occurs at the same rate whether or not an olefin is present which indicates that dihydrogen oxidative addition occurs prior to olefin coordination and is the rate-determining step. With cationic species such as the $[Rh(L_2)(S)_2]^+$ complexes used in asymmetric hydrogenations, the same equilibration is observed indicating that reversible oxidative addition of dihydrogen is occurring even though a measureable concentration of a dihydride complex cannot be detected. In the presence of olefin, however, no equilibration is observed until the substrate is consumed (ref. 777). The activation energy and pre-exponential nuclear tunnelling factors for the oxidative addition of dihydrogen to $[RhCl(PPh_3)_3]$ and for the olefin insertion steps in olefin hydrogenation catalyzed by this complex have been calculated. The tunnelling process appears to be important for the stretching of the hydrogen-hydrogen bond in the former process and of the carbon-carbon double bond in the latter (ref. 778).

Systems involving $[RhCl(PPh_3)_3]$ as a catalyst include the asymmetric hydrogenation of acetamidocinnamic acid (16% optical yield) in the liquid crystal cholesteryltridecanoate at the temperature of the mesophase (refs. 779-780), the hydrogenation of acetophenone and other ketones (ref. 781) and the conversion of cyclodienes to ketones (ref. 782). In the ketone hydrogenation system the presence of triethylamine is necessary for significant activity and the observation of saturation kinetics suggests the function of the base is to convert species such as $[RhH_2ClL_n]$ to $[RhHL_n]$ ($L = PPh_3$). The beneficial effect of excess phosphine on the catalytic activity suggests that $[RhHL_3]$ is the active species and that ones with fewer ligands form catalytically inactive clusters. The mechanism of oxygenation of COD is thought to be that of Scheme LXX. Attempts to stereospecifically decarbonylate (E)-α,β-unsaturated aldehydes with $[RhCl(PPh_3)_3]$ were unsuccessful because the high temperatures required to achieve reasonable rates give a



Scheme LXX

mixture of (E)- and (Z)-olefins (ref. 783). The addition of formaldehyde to olefins is catalyzed by $[RhH_2(O_2COH)(PPr^i_3)_2]$. A 60% conversion of hex-1-ene to C_7-aldehydes was achieved with about half the product being the linear aldehyde. Under the same conditions $[RhH(CO)(PPh_3)_3]$ gave only a 6% conversion (ref. 784). In an aqueous solution of formic acid and sodium formate, the water-soluble complexes $[RhClL_3]$ (L = Ph_2P(p-$NaO_3SC_6H_4$), Ph_2P(m-$NaO_3SC_6H_4$)) catalyze the reduction of olefins such as allyl alcohol and α,β-unsaturated aldehydes (refs. 785, 786) while in non-polar media $[RhCl(PPh_3)_3]$ catalyzes the oxidation of 2-substituted anthracenes to the corresponding quinones by tert-butylhydroperoxide (ref. 787). The hydrogen-transfer reduction of α,β-unsaturated ketones by alcohols is catalyzed by $[RhH(PPh_3)_4]$ (refs. 788-790) and the same complex also catalyzes the formation of benzyl benzoate from benzaldehyde. Scheme LXXI (P = PPh_3) is proposed for the last reaction (ref. 791). Another catalytic appplication of $[RhH(PPh_3)_4]$ is the conversion of β-trimethylsilylallyl alcohols to α-trimethylsilylketones (ref. 792).

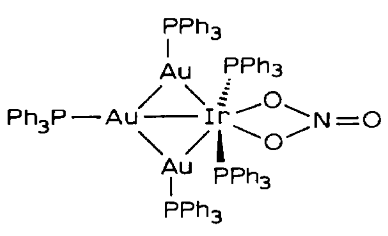


Scheme LXXI

In acidic media, $[Rh(L_2)_2]BF_4$ (L_2 = $Ph_2PCH_2CH_2SR$ (R = Me, Et, Ph)) catalyzes the air oxidation of terminal olefins, primary alcohols and secondary alcohols to ketones, acetals and ketones respectively. A dioxygen adduct of the complex could be isolated from the solution (ref. 793). Various rhodium phosphine complexes catalyze the hydroformylation of formaldehyde. The stability of the system is increased in the presence of excess ligand but the activity is decreased (ref. 794). The complex $[Rh(acac)L_2]$ ($L = P(OPh)_3$) is a catalyst precursor for the hydroformylation of hex-1-ene and the species $[Rh(acac)(CO)L]$, $[Rh(acac)H_2L_2]$ and $[Rh(acac)H(CO)L_2]$ were detected in the solution. The reaction of the last with the olefin to form an alkyl complex is proposed as the rate-determining step. When $L = PPh_3$ the catalytic hydrogenation of aromatic hydrocarbons can be achieved (refs. 795, 796).

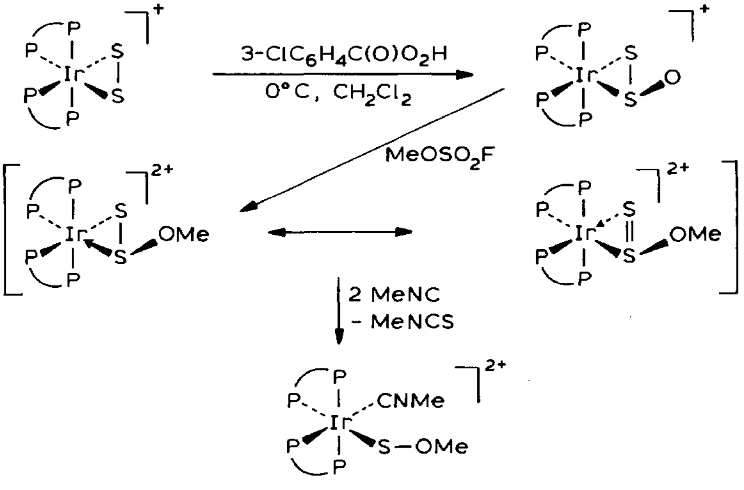
The hydrogenation of acetylene and propyne to olefins is catalyzed by $[RhCl(PPh_3)_3]$ in molten triphenylphosphine and supported on various silica gels. The use of macroporous supports and weakly coordinating solvents provides the best balance between long catalyst life and high activity (ref. 797). Organosilyl and organosiloxanyl phosphines attached to chrysotile asbestos are proposed as an effective means of heterogenizing $[RhCl(PPh_3)_3]$ (ref. 798). Fast-atom bombardment mass spectrometry provides a means of observing the molecular ions of $[RhX(PPh_3)_3]$ (X = Cl, Br) (ref. 799). Molecular orbital calculations using the SCF-Xα-scattered wave method have been performed on $[M(E_2)(PH_3)_4]$ (M = Rh; Ir; E = S, Se) as models for $[M(E_2)(L_2)_2]$ (L_2 = DPPE, dmpe) (see J. Organometal. Chem., 261(1984)103, ref. 803). From these the E-E bond order is approximately unity and the covalent interaction with the metal is in the order $RhSe_2 < IrSe_2 < RhS_2 < IrS_2$. The electronic spectra in frozen solutions show a weak band for the HOMO-LUMO transition which appears to be largely localized on the $\{E_2\}$ moiety. The lowest energy transition of significant intensity originates in a π-bonding orbital of the $\{ME_2\}$ unit. The $\{E_2^-\}$ moiety is described as having the electronic configuration $(p\sigma)^2(\pi)^3(\pi^*)^3$ (ref. 800).

Reaction of solid $[IrH_2(H_2O)_2(PPh_3)_2]BF_4$ with ammonia forms $[IrH_2(NH_3)_2(PPh_3)_2]BF_4$ while $[IrH_2(acetone)_2(PPh_3)_2]BF_4$ in dichloromethane reacts with nitrobenzene and ethyl cinnamate to form $[IrH_2(L)(PPh_3)_2]BF_4$ ($L = PhNO_2$, $PhCH{=}CHCO_2Et$) (ref. 801). In the reaction of $[Ir_3(\mu_3\text{-}H)(\mu\text{-}H)_3H_3(DPPE)_3](BF_4)_2$ with $[Au(NO_3)(PPh_3)]$, the triply-bridging hydride is replaced by a $\{Au(NO_3)\}$ moiety to form $[Ir_3(\mu_3\text{-}Au(O_2NO))(\mu\text{-}H)_3H_3(DPPE)_3]BF_4$ in which the nitrate ion bound to gold can be replaced by triphenylphosphine. However in the same reaction with $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]PF_6$, the product is [417] (ref.



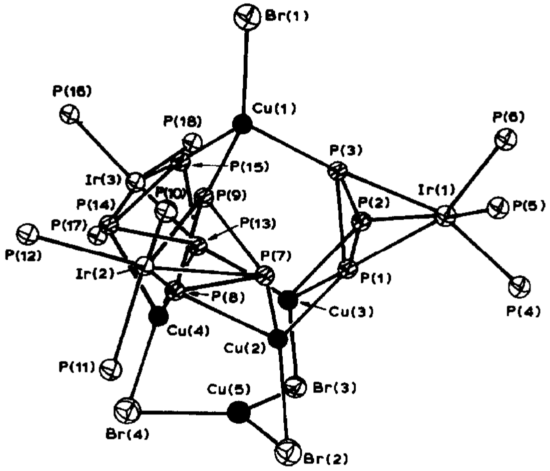
[417]

802). Reaction of $[Ir(E_2)(DPPE)_2]^+$ (E = S, Se) with methyl triflate yields $[Ir(\eta^2\text{-}E_2Me)(DPPE)_2]^{2+}$ which could be isolated as the hexafluorophosphate salt as a mixture of (Λ,S) and (Δ,R) enantiomers. The same complex reacts with triflic acid to form $[Ir(\eta^2\text{-}E_2H)(DPPE)_2]^+$ which was identified in solution. Reaction of $[Ir(\eta^2\text{-}S_2Me)(DPPE)_2]^+$ with dimethylphenylphosphine forms $[Ir(DPPE)_2]^+$, dimethylphenylphosphine sulfide and the methylthiodimethylphenylphosphonium cation possibly *via* the initial formation of $[Ir(SPMe_2Ph)(SMe)(DPPE)_2]^{2+}$. The same complex also reacts with methylisocyanide to give methylisothiocyanate and *cis*-$[Ir(SMe)(CNMe)(DPPE)_2]^{2+}$ while with cyanide ion, the product is *cis*-$[Ir(SCN)(SMe)(DPPE)_2]^+$. The reaction of $[Ir(S_2)(DPPE)_2]^+$ with *m*-chloroperoxybenzoic acid and subsequent chemistry of the initial product are outlined in Scheme LXXII (P-P = DPPE) (refs. 803, 804). Addition of Se_8 to $[Ir(dmpe)_2]Cl$ affords $[Ir(Se_4)(dmpe)_2]Cl$, in which the $\{Se_4\}$ unit is in the half-chair conformation, and small amounts of $[Ir(Se_2)(dmpe)_2]Cl$. The former product regenerates Se_8 on photolysis and reacts with triphenylphosphine to give $[Ir(Se_2)(dmpe)_2]Cl$ and triphenylphosphine selenide. Molecular orbital calculations (SCF-Xα-SW) on $[Ir(Se_4)(PH_3)_4]Cl$ as a model for the dmpe complex imply that the $\{Se_4\}$ moiety should be considered as an excited state of the Se_4 molecule which is bound *via* selenium 4*p* orbitals to iridium *p* and *d* orbitals. The selenium-selenium bonding is largely *p*σ in nature. The main features of the electronic spectra are bands due to transitions involving only the $\{Se_4\}$ unit (ref. 805).

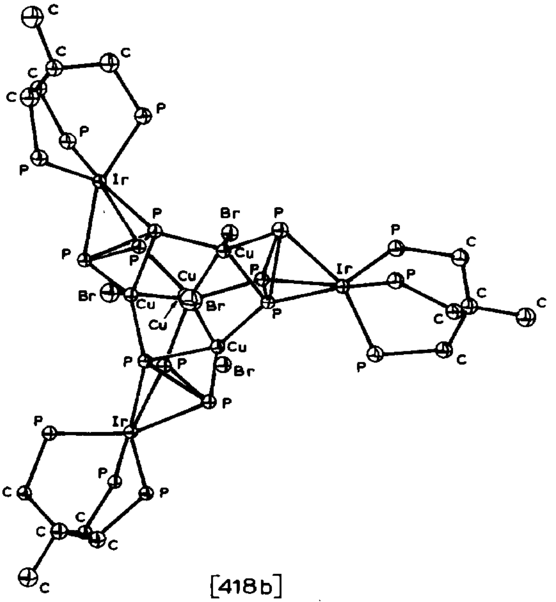


Scheme LXXII

The complex $[Ir(DIPAMP)_2]BF_4$ reacts with dihydrogen to form two diastereoisomeric, <u>cis</u>-dihydrides which subsequently isomerize intramolecularly to the <u>trans</u> isomer. Similar results were observed for the DPPE and CHIRAPHOS analogs (ref. 806). In dichloromethane, the product obtained from $[(triphos)Ir(P_3)]$ and copper(I) bromide is $[((triphos)Ir(P_3))_3Cu_5Br_4][CuBr_2]$. The framework of the cluster is shown in two views as [418a] and [418b]



[418a]



[418b]

(ref. 807). Active catalysts for the WGSR are obtained from $[Ir(NH_3)_6]^{3+}$ and $[Iren_2(NH_3)_2]^{3+}$ on zeolite supports but they show loss of activity with time. A partially carbonylated amine complex stabilized in the zeolite cages is proposed as the active species (ref. 808).

List of Abbreviations

acac = acetylacetonate
acen = bis(acetylacetone)ethylenediiminato
ADDH = 1-2-acenaphthalenedione dioximate
ARPHOS = 1-diphenylarsino-2-diphenylphosphinoethane
ATCNQ = 4-dicyanomethylenepyridinium dicyanomethanide
BAE = bis(acetylacetone)ethylenediiminato
bdpp = bis(3-diphenylphosphinopropyl)phenylphosphine
bipy = 2,2'-bipyridine
BPPFA = (R)-{1-[(S)-2,1'-bis(diphenylphosphino)ferrocenyl]ethyl} dimethylamine
BPPM = (2S,4S)-N-*tert*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine
br = 1,3-diisocyanopropane
BTMSA = bis(trimethylsilyl)acetylene
t-BuDiNC = 1,2-bis(4-*tert*-butyl-2-isocyanophenoxy)ethane
(S)-BUTAPHOS = (S)-1-diphenylphosphinoxy-2-N-ethyl-N-diphenylphosphinoaminobutane
bz = benzyl
CHIRAPHOS = (S,S)-2,3-bis(diphenylphosphino)butane
COD = cycloocta-1,5-diene
COT = cyclooctatetraene
cp = η^5-C_5H_5
cp' = η^5-C_5Me_5
cpMe = η^5-C_5H_4Me
cy = cyclohexyl
cycphos = (R)-1,2-bis(diphenylphosphino)-1-cyclohexylethane
cyoct = cyclooctene
cyttp = bis(3-dicyclohexylphosphinopropyl)phenylphosphine
DADPM = diphenylarsinodiphenylphosphinomethane
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene
DBu^{t}PF = 1,1'-bis(di(*tert*-butyl)phosphino)ferrocene
DCP = dicyclopentadiene
dct = dibenzo[a,e]cyclooctatetraene
diars = 1,2-bis(dimethylarsino)benzene

DICOL = 3α-diphenylphosphino-5α-cholestane

DIOCOL = 2,3-O-(5'α-cholestan-3',3'-ylidene)-2,3-dihydroxy-1,4-bis(diphenylphosphine)butane

DIOP = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane

DIPAMP = (R,R)-1,2-bis(*o*-anisylphenylphosphino)ethane

DIPHOL = (2R,3R)-2,3-O-isopropylidene-1,4-bis(5H-dibenzophosphol-5-yl)-2,3-butanediol

DME = dimethoxyethane

DMF = N,N-dimethylformamide

dmgH = dimethylglyoximate

dmpe = 1,2-bis(dimethylphosphino)ethane

dmpm = bis(dimethylphosphino)methane

dmpp = 1,3-bis(dimethylphosphino)propane

DMSO = dimethylsulfoxide

DPAE = 1,2-bis(diphenylarsino)ethane

(S,S)-dpcp = (S,S)-1,2-bis(diphenylphosphino)cyclopentane

DPM = bis(diphenylphosphino)methane

DPMP = bis(diphenylphosphinomethyl)phenylphosphine

DPPB = 1,4-bis(diphenylphosphino)butane

DPPE = 1,2-bis(diphenylphosphino)ethane

DPPP = 1,3-bis(diphenylphosphino)propane

en = ethylenediamine

Fc = ferrocenyl

fpz = 3,5-bis(trifluoromethyl)pyrazolate

fpzH = 3,5-bis(trifluoromethyl)pyrazole

GH = glyoximate

HFB = hexafluorobut-2-yne

Hpybzim = 2-(2'-pyridyl)benzimidazole

In = indolate

MA = maleic anhydride

MABP = (S)-6,6'dimethyl-2,2'-bis(diphenylphosphinamino)biphenyl

2-Mepy = 2-methylpyridine

4-Mepy = 4-methylpyridine

Me_3TFB = trimethyltetrafluorobenzobarrelene

MNT = maleonitriledithiolate

NBD = bicyclo[2.2.1]heptadiene

(-)NORPHOS = (R,R)-*trans*-5,6-bis(diphenylphosphino)bicyclo[2.2.1]-hept-2-ene

np_3 = tris(2-(diphenylphosphino)ethyl)amine

OEP = octaethylporphyrin

OFCOT = octafluorocylooctatetraene

ophen = 1,10-phenanthroline

PhCAPP = (2S,4S)-N-(N-phenylcarbamoyl)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine

PNP = 2-(bis(diphenylphosphino)methyl)pyridine

POP = 2-diphenylphosphinoxyethyldiphenylphosphine

PPN = bis(triphenylphosphine)iminum cation

(S)-PROLOPHOS = (S)-N-(diphenylphosphino)-2-diphenylphosphinoxymethylpyrrolidine

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

py = pyridine

pybzim = 2-(2'-pyridyl)benzimidazolate

pz = pyrazolate

pzH = pyrazole

salen = N,N'-ethylenebis(salicylideniminato)

salophen = N,N-*o*-phenylenebis(salicylideniminato)

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

TCNE = tetracyanoethylene

TCNQ = tetracyanoquinodimethane

tfacen = bis(trifluoroacetylacetone)ethylenediiminato

TFB = tetrafluorobenzobarrelene

THF = tetrahydrofuran

THT = tetrahydrothiophene

tmhd = 2,2,6,6-tetramethylheptan-3,5-dionate

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

TPM = tris(diphenylphosphino)methane

TPP = tetraphenylporphyrin

TPPS = tetrakis(4-sulfonatophenyl)porphyrin

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

vdiphos = *cis*-1,2-bis(diphenylphosphino)ethylene

vy = vinyl

WGSR = water-gas-shift reaction

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