COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1981*

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

CONTENTS

Introduction

The format of the present Survey will be that followed last year. Again, articles appearing in less-available journals will be covered in abstract form only and are so indicated in the list of references. Those reporting only the results of crystal structure determinations are not included. The majority of abbreviations to be used will be explained following their initial occurrance however because of the prevalence of the π-cyclopentadienyl group (η^5-C_5H_5), the abbreviation "cp" for it is given here.

A number of reviews dealing at least in part with cobalt, rhodium and iridium have appeared during the course of the year. Besides a general review of complexes of the cobalt group containing metal-carbon σ-bonds (ref. 1) there are discussions of the ^{13}C NMR spectra of metal-alkyl, -olefin and -allyl complexes (ref. 2), the

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* Cobalt, rhodium and iridium; Annual Survey covering the year 1980 see J. Organometal. Chem., 230 (1982) 99-206.

uses of [$HCo(CO)_4$] as a catalyst (ref. 3a), the Co-catalyzed oxidation of alkylated aromatics (ref. 3b), the hydroacylation of rhodium complexes (ref. 3c), and the mechanism of replacement of carbonyl ligands in metal carbonyl complexes (ref. 4). The subject of clusters continues to be extensively covered with a short review on the use of Pt(0) complexes in the synthesis of mixed-metal clusters (ref. 5) and an extensive survey of metal carbide clusters (ref. 6). Also in this area are a review on the relationship between metal-carbonyl clusters and supported metal catalysts (ref. 7), an extensive compilation of catalyst systems derived from supported metal carbonyls and related species (ref. 8) and a discussion of the electronic structures of clusters as derived from Extended Hückel molecular orbital methods (ref. 9).

Complexes of the cobalt group with o-quinone and catecholate type ligands have been surveyed (ref. 10) as have complexes containing a ferrocene moiety as a part of one or more ligands (ref. 11). Two reviews of ^{31}P NMR studies on phosphine complexes, the first giving general coverage (ref. 12) while the latter dealing with polydentate phosphine complexes of cobalt and rhodium (ref. 13), have appeared. [$RhCl(PPh_3)_3$] has found wide use as an olefin hydrogenation catalyst and now two reviews dealing with its chemistry and catalytic applications (ref. 14) and with a theoretical study of the mechanism of its catalysis of olefin hydrogenation (ref. 15) are available. Other reviews on the subject of catalysis by cobalt, rhodium and iridium complexes deal with heterolytic hydrogen activation (ref. 16), olefin hydrogenation (ref. 17), carbonylation (ref. 18) and hydrocarboxylation (ref. 19a), carboxylic acid synthesis and homologation (ref. 19b), phase transfer catalysis (ref. 20) and asymmetric hydrogenation of olefinic substrates (refs. 21-23).

Olefin complexes of cobalt which also contain alkalai metals have been reviewed (ref. 24) as have systems which catalyze alkyne and arene hydrogenation (ref. 25). Also available is a summary of recent developments in the use of [$cpCo(CO)_2$] to mediate the formation of annellated cyclohexadienes from α, δ, ω-diynenes (ref. 26a) and the activation of CO and acetylenes by cobalt carbonyls (ref. 26b).

Finally, reviews have appeared on the photoelectron spectra of organometallic compounds (ref. 27) and on the structures of hydride (ref. 28) and sulfur dioxide complexes (ref. 29).

Dissertations

Several dissertations dealing with metal-carbon σ-bonded complexes have appeared. The first reports the synthesis of bis(pentafluorophenyl)arene cobalt complexes by metal atom vapor techniques (ref. 30) while two more deal with cyclometallated complexes of rhodium and iridium with 2-aryl pyridines (ref. 31) and with triarylphosphites (ref. 32). This last work also reports studies of oxidative addition reactions of cationic rhodium and iridium complexes. A related study reports the mechanism of the reaction of aroyl chlorides and phenylacetyl chloride with $[RhCl(PPh_3)_3]$ (ref. 33). A final thesis describes binuclear rhodium (I) complexes of mono- and bicyclic hexaammine ligands (ref. 34).

Studies on cobalamins and related cobalt macrocycles are the subjects of three dissertations. These describe sterically unstable cobalamins (ref. 35), dimethylcobalt macrocycles (ref. 36) and factors which influence ligand exchange in alkylcobaloximes (ref. 37).

In the area of carbonyl complexes there are two studies on the mechanisms of substitution reactions of $[Co_2(CO)_8]$ (refs. 38, 39) and two on the use of supported $[Rh_{12}(CO)_{30}]^{2-}$ (ref. 40) and $[Rh_6(CO)_{16}]$ (ref. 41) for catalyzing the reduction of nitrobenzene to aniline. The latter also describes studies on the hydroformylation of olefins catalyzed by $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PPh)_2]$. Further theses describe the use of $[Ir_4(CO)_{12}]/AlCl_3$ systems as catalysts for carbon monoxide hydrogenation (ref. 42), the hydrogenolysis of $[Bu^t\text{-}CH_2CCo_3(CO)_9]$ (ref. 43) and the preparation and catalytic properties of $[cpWIr_3(CO)_{11}]$ and $[cp_2W_2Ir_2(CO)_{10}]$ (ref. 44).

The synthesis and thermolysis of $[cpIrH_2(CO)]$ (ref. 45), the synthesis and determination of the structures of diphenylphosphide- and carbonyl-bridged cobalt dimers, e.g. $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}PPh_2)](cp' = \eta^5\text{-}C_5Me_5)$ (ref. 46), the synthesis of bi- and tetranuclear rhodium complexes containing diphenylphosphide bridges (ref. 47) and the formation of mixed-metal clusters from photogenerated metal carbonyl fragments and $[cp'_2Co_2(CO)_2]$ (ref. 48) have also been described. Further studies report on the ^{31}P NMR spectra of polytertiary phosphine complexes of rhodium and iridium (ref. 49) and on the use of silver-complexed sulfonated polystyrene to absorb triphenylphosphine and thereby enhance the catalytic activity of $[RhCl(PPh_3)_3]$ and related complexes (ref. 50).

On the subject of asymmetric hydrogenation are two dissertations reporting studies of polymer-supported chiral ligands (ref. 51) and the synthesis of chiral diphosphines from a series of glycerols (ref. 52) which have been used to form chiral rhodium catalyst systems. Also reported are studies on the hydrogenation of arenes catalyzed by $[(\eta^3\text{-allyl})Co(P(OMe)_3)_3]$ (ref. 53), the preparation of functionalized metallocenes (ref. 54), the reductive substitution of $[cp_2Co]$ by tetracyclones (ref. 55) and the use of cyclopentadiene-functionalized polystyrene-divinylbenzene copolymer to anchor Rh(III) chloro species which are active hydrogenation catalysts (ref. 56).

The final three dissertations are concerned with the use of cobalt and iridium carbonyls as catalysts or co-reactants in the reactions of acetylenes with polyhedral boranes (ref. 57), the use of rhodacarbaboranes in catalysis (ref. 58) and the occurrance of closo-nido tautomerism in rhodacarbaborane chemistry (ref. 59).

Metal-Carbon σ-bonded Complexes

Based on the evident high nucleophilicity of $[CoMe(PPh_3)_3]$, this complex was anticipated to react with ketones as do Grignard reagents. However the major products of the reactions attempted were those resulting from aldol condensations. The mechanism of the reaction is unclear at present (ref. 60). Treatment of anhydrous cobalt(II) bromide with pentafluorophenyl magnesium bromide in tetrahydrofuran (THF) followed by solvent removal and dissolution of the residue in dioxane affords $[Co(C_6F_5)_2(dioxane)_2]$ from which phosphine derivatives $[Co(C_6F_5)_2L_2]$ ($L = PEt_3$, PBu^n_3, PPh_3; $L_2 = Ph_2PCH_2CH_2PPh_2$ (diphos)) are readily prepared. For the first two ligands mixtures of cis and trans isomers result while with triphenylphosphine only the trans isomer is formed (ref. 61). Treatment of the $[Co(C_6F_5)L_2]$ complexes with carbon monoxide in benzene produces unstable five-coordinate adducts, $[Co(C_6F_5)_2(CO)L_2]$ except where $L = PPh_3$ where the reaction must be performed in petroleum ether to avoid the formation of $[Co(CO)_3PPh_3]_2$. The reaction of $[Co(C_6F_5)_2(dioxane)_2]$ itself with carbon monoxide in hexane gives an unstable blue solid thought to be $[Co(CO)_3(C_6F_5)_2]$ and a yellow solution of $[Co(C_6F_5)(CO)_4]$. The latter complex reacts with phosphines ($L = PEt_3$, PBu^n_3, PPh_3) to give $[Co(C_6F_5)(CO)_3L]$ (ref. 62).

The complexes $[Co(R)(CO)_2L_2]$ (R = Me, MeCO; $L = P(OMe)_3$) show significant activity for the catalytic hydrogenation of α-olefins but more hindered olefins show much lower catalytic rates. A mechanism involving a series of Co-Me to Co-C(O)Me conversions to provide open coordination sites on the metal is proposed (ref. 63). In an exploration of the mechanism of the hydrogenolysis of metal-carbon bonds, $[cpCoMe_2(PPh_3)]$ was reacted with hydrogen to yield two equivalents of methane and one half an equivalent of $[cpCo(PPh_3)_2]$. The rate is inhibited by excess phosphine but now all the cobalt is isolated as $[cpCo(PPh_3)_2]$. Furthermore, on reaction with D_2 all the methane produced is CH_3D while D_2 reacts with $[cpCo(CD_3)_2(PPh_3)]$ to give only CD_4 even in the presence of excess 1,3-cyclohexadiene implying the absence of radical processes. An autocatalytic process is proposed in which thermal decomposition of $[cpCoMe_2(PPh_3)]$ (slow under the reaction conditions but not negligible) leads ultimately to a critical Co(I) species formulated as $[cpCo(PPh_3)]$. The subsequent hydrogenolysis then proceeds as outlined in Scheme I with the hydrogenolysis occurring in a bimolecular step.

$$[cpCoMe_2(PPh_3)] \rightleftharpoons [cpCoMe_2] + PPh_3$$

$$[cpCo(PPh_3)_2] \rightleftharpoons [cpCo(PPh_3)] + PPh_3$$

$$[cpCo(PPh_3)] + H_2 \rightleftharpoons [cpCoH_2(PPh_3)]$$

$$[cpCoH_2(PPh_3)] + [cpCoMe_2] \xrightarrow{PPh_3} 2CH_4 + [cpCo(PPh_3)]$$

Scheme I

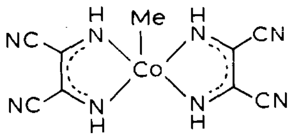
Although the proposed dihydrido intermediate could not be isolated, the analogous species [cp'CoH$_2$(PPh$_3$)] was obtained by hydrogenation of [cp'CoMe$_2$(PPh$_3$)]. The isolated dihydride could then be reacted with [cp'CoMe$_2$(PPh$_3$)] yielding two equivalents of methane. The kinetics of this process and the observation of inhibitions by excess triphenylphosphine are suggested to support a bimolecular process involving a coordinatively unsaturated intermediate as proposed in Scheme I (ref. 64). In a related system, direct transfer of a cyclopentadienyl group between cobalt centers (in the absence of hydrogen) has been demonstrated. Thus the reaction of [(η^5-C$_5$H$_4$Me)CoMe$_2$(PPh$_3$)] with [cpCo(PPh$_3$)$_2$] yields [cpCoMe$_2$(PPh$_3$)] and [(η^5-C$_5$H$_4$Me)Co(PPh$_3$)$_2$]. Since [(η^5-C$_5$H$_4$Me)CoMe$_2$(PMe$_3$)] in the same reaction yields [cpCoMe$_2$(PMe$_3$)] while the trimethylphosphine ligand does not dissociate and methyl group transfer was ruled out, this demonstrates the transfer of the cyclopentadienyl group. In additional studies, [cpCoMe$_2$(PPh$_3$)] did not react with [MCl(PPh$_3$)$_3$] (M = Rh, Ir) but on reaction with [Fe$_2$(CO)$_9$], [cpCo(CO)$_2$] was observed as a product. The course of this last reaction is proposed to be that of Scheme II (L = PPh$_3$) (ref. 65). Finally, reaction of [(η^5-C$_5$Me$_4$Et)$_2$Co$_2$Cl$_4$] with methyllithium

$$\begin{gathered}
[\mathrm{Fe_2(CO)_9}] \rightleftharpoons [\mathrm{Fe(CO)_4}] + [\mathrm{Fe(CO)_5}] \\
[\mathrm{cpCoMe_2L}] \rightleftharpoons [\mathrm{cpCoMe_2}] + \mathrm{L} \\
[\mathrm{cpCoMe_2}] + [\mathrm{Fe(CO)_5}] \longrightarrow [\mathrm{cpCo(CO)Me_2}] + [\mathrm{Fe(CO)_4}] \\
[\mathrm{cpCoMe_2L}] + [\mathrm{Fe(CO)_4}] \longrightarrow [\mathrm{cpCoMe_2}] + [\mathrm{Fe(CO)_4L}] \\
[\mathrm{cpCo(CO)Me_2}] + 2[\mathrm{Fe(CO)_5}] \longrightarrow [\mathrm{cpCo(CO)_2}] + 2[\mathrm{Fe(CO)_4}] + \mathrm{CH_3COCH_3} \\
[\mathrm{Fe(CO)_4}] + \mathrm{L} \longrightarrow [\mathrm{Fe(CO)_4L}] \\
3[\mathrm{Fe(CO)_4}] \longrightarrow [\mathrm{Fe_3(CO)_{12}}]
\end{gathered}$$

Scheme II

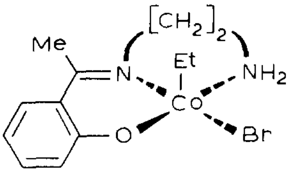
at -70° C in the presence of various ligands yields [(η^5-C$_5$Me$_4$Et)CoMe$_2$L] (L = C$_2$H$_4$, C$_3$H$_6$, PPh$_3$). In solution the olefin complexes undergo olefin exchange and on longer reaction times olefin insertion into the Co-CH$_3$ bonds occurs (ref. 66).

The metal-metal bond in [(H$_2$O)Co(C$_2$(CN)$_2$(NH)$_2$)$_2$]$_2$ can be cleaved by reaction with hydrazine or sodium amalgam to give monomeric [Co(C$_2$(CN)$_2$(NH)$_2$)$_2$]$^-$ which on reaction with methyl iodide yields [1]. This can also be prepared directly from

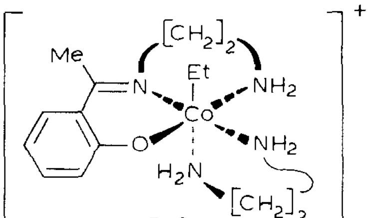


[1]

the dimer using methylhydrazine in the presence of oxygen. The structure of the cyano analog of [1] was determined from which it was concluded that the complex contains di-iminosuccinonitrile ligands (ref. 67). Condensation of o-hydroxyacetophenone with ethylenediamine in the presence of Co(II) ions followed by borohydride reduction and alkylation with ethyl bromide yields, in addition to the expected Schiff-base complex [2], a cationic species [3]. Although the structural study of [3] showed the Co-N bond trans to the alkyl group to be



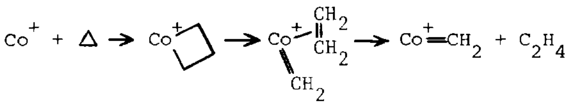
[2]



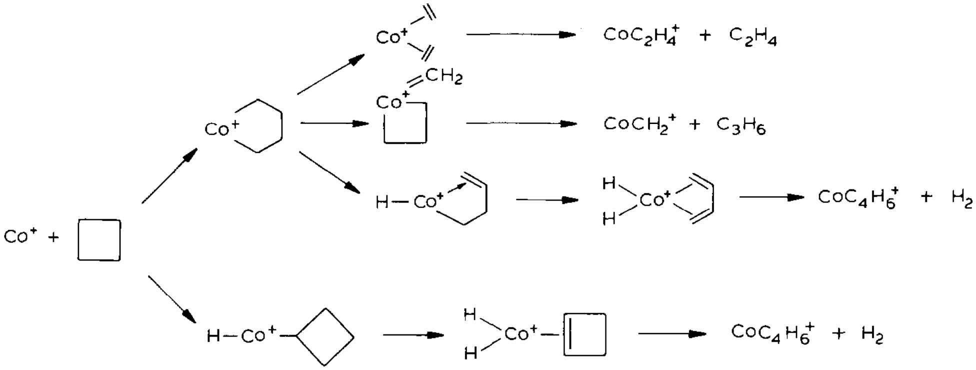
[3]

significantly lengthened, ligand substitution of this site does not readily occur in contrast to what is usually seen for Lewis base adducts of alkylcobaloximes and related complexes. Also in contrast to these latter types of complexes, the alkyl group in [3] is readily cleaved by dilute acids (ref. 68). Oxidation of $[Co(CN)_5]^{3-}$ by hydrogen peroxide in dimethyl sulfoxide yields $[MeCo(CN)_5]^{3-}$ and $[Co(CN)_5(H_2O)]^{2-}$. The formation of the methyl-cobalt complex is proposed to result from reaction of the starting material with methyl radicals formed by the attack of hydroxyl radicals on the solvent (ref. 69). Alkyl-cobalt intermediates have been proposed to be involved in the hydrodimerization of methyl acrylate catalyzed by $[CoCl(PPh_3)_3]$ in methanol (ref. 70).

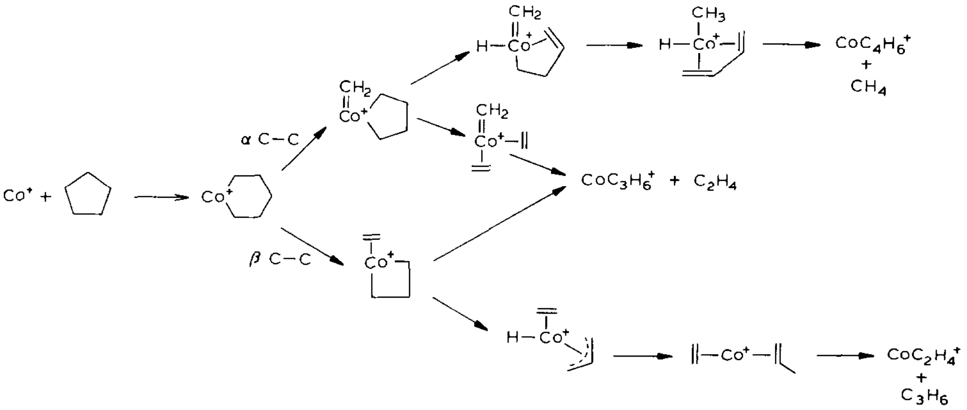
The reaction of $Co^+_{(g)}$ with alkanes, alkenes and cycloalkanes have been extensively studied by ion-beam techniques. For the first two systems, the major reaction at all energies appears to involve the oxidative addition of C-H and C-C bonds to Co^+ followed where possible by a facile β-hydrogen abstraction and the elimination of H_2 or the neutral hydrocarbon. For the alkenes, oxidative addition to allylic bonds appears to be preferred with the product distribution in the case of butenes indicating the presence of a common allyl hydride intermediate. The cleavage products observed for the butenes and branched pentenes and hexanes suggest the formation of metallacyclobutanes but this has not yet been confirmed. For cyclopropane reaction according to Scheme III is proposed while Schemes IV and V provide a rationale for the products observed from reaction of Co^+ with



Scheme III

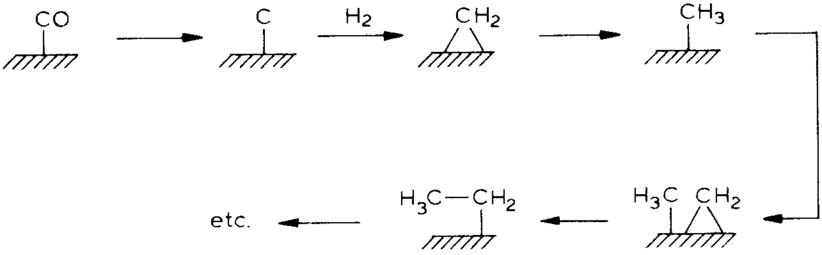


Scheme IV



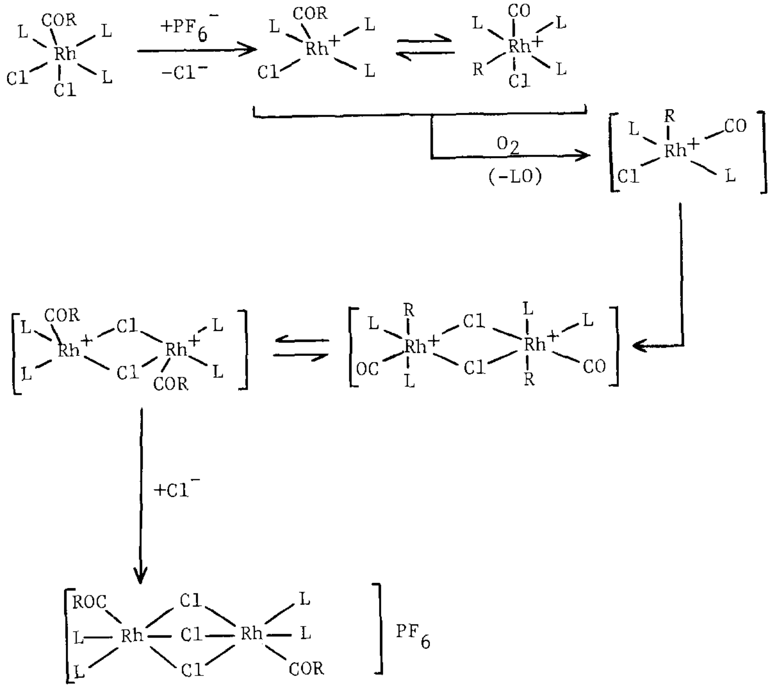
Scheme V

cyclobutane and cyclopentane respectively. In the latter cases, the intermediacy of metallacycles is equivocal but there appears to be a preference for the ring cleavage to occur as symmetrically as possible (refs. 71-75). In a study of the mechanism of the Fischer-Tropsch reaction, a mixture of diazomethane, hydrogen and carbon monoxide was passed over a supported cobalt catalyst. Consideration of the distribution of product hydrocarbons and the distribution of the ^{13}C label in propene formed when the feed gas contained ^{13}CO and $^{12}CH_2N_2$ indicated that the mechanism of Scheme VI best explained the results. Mechanisms involving condensation of surface hydroxymethylene groups or CO insertion into M-C bonds appeared inconsistent with the results of the labelling study (ref. 76).



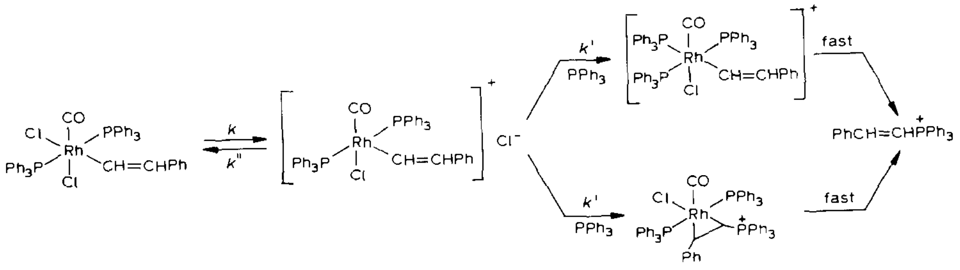
Scheme VI

Addition of ammonium hexafluorophosphate to an acetone/dichloromethane solution of $[RhCl_2(COR)(PMe_2Ph)_3]$ or reaction of $[RhCl(C_2H_4)_2]_2$ with RCOCl (R = Me, Et) in the presence of four moles of dimethylphenylphosphine and hexafluorophosphate ion in benzene yielded the dimeric acyl complexes [4] (Scheme VII) (ref. 77). In a continuation of studies on the decarbonylation of acid chlorides by $[RhCl(PPh_3)_3]$ it was found that the reaction with (E)-RCH=CHCOCl (R = Ph, Me, Bu^n) produced no vinyl chlorides but rather the phosphonium salts $[(E)\text{-}RCH{=}CHPPh_3]Cl$ and $[Rh(CO)Cl(PPh_3)_2]$. Control, crossover and competition experiments excluded the possibility that the phosphonium salts resulted from reaction of preformed vinyl chlorides with triphenylphosphine or rhodium-phosphine complexes or from triphenylphosphine and the starting acid chloride. The fact that the styryl complex $[RhCl_2(CO)(CH{=}CHPh)(PPh_3)_2]$ can be isolated from the reaction when R = Ph and that the acyl $[RhCl_2(C(O)CH{=}CHPh)(PPh_3)_2]$ can be detected early in the reaction indicates that the usual steps of oxidative addition followed by migration of the styryl moiety do occur. Evidently the Rh-C(vinylic) bond is sufficiently strong as to preclude reductive elimination of β-chlorostyrene as occurs when saturated acid chlorides are employed. Possible routes to phosphonium salt formation are detailed in Scheme VIII (ref. 78). The kinetics of addition of methyl iodide to $[Rh(CO)ClL_2]$ (L = $P(\underline{n}\text{-}C_8H_{17})_3$, PBu^n_3, $P(\underline{n}\text{-}C_{18}H_{37})_3$) have been studied. The rate



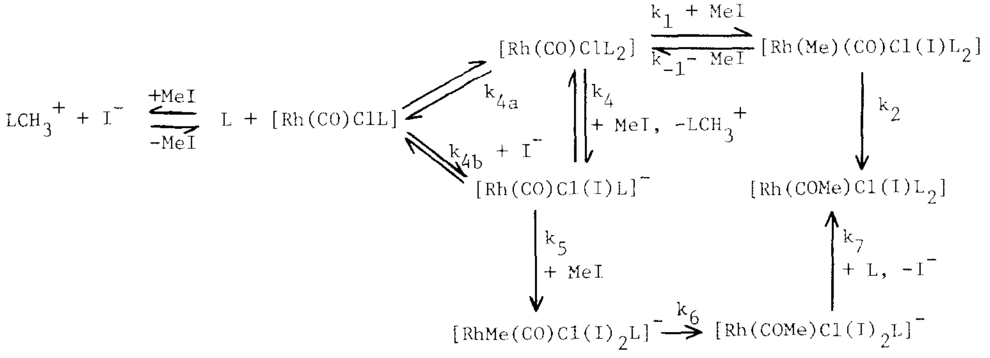
[4]

Scheme VII



Scheme VIII

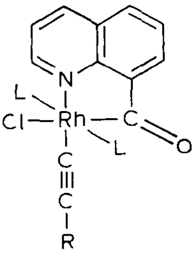
decreases with change in L in the order given above and no acyl species were detected, both observations being attributed to steric effects. With L = $P(\underline{p}\text{-}RC_6H_4)_3$ (R = Bu^n, Et, $\underline{n}\text{-}C_6H_{13}$) and PPh_3 the rates decrease in the order shown and are all less than those observed for the trialkylphosphine complexes but acyl complexes are detected. The ordering here is thought to reflect a combination of steric, electronic and solvation effects. The mechanism of Scheme IX is proposed with the interesting suggestion that $k_2 \ll k_4$, k_5, k_6 and k_7 implying that



Scheme IX

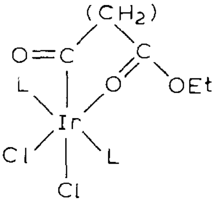
[RhClI(Me)(CO)L_2] is not a significant species in the formation of the acyl complexes (ref. 79). Stoichiometric methylation of alkenyl, alkynyl and aryl mercurials by [Rh(Me)$I_2(PPh_3)_2$] has been reported. In the case of [Hg(C≡CBu^t)$_2$] the rhodium complex functions catalytically in the presence of excess methyl iodide to afford a convenient synthesis of 4,4-dimethylpent-2-yne (ref. 80).

Refluxing hydrated rhodium(III) chloride with 2-arylpyridines (aryl = $\underline{p}\text{-}NO_2C_6H_4$, $\underline{o}\text{-}MeC_6H_4$, $\underline{p}\text{-}BrC_6H_4$), in aqueous methanol leads to chloro-bridged dimers containing two arylpyridine ligands which are coordinated through nitrogen and in addition have been $\underline{o}$-metallated on the aryl substituent. Monomeric diethyldithiocarbamate derivatives are obtained by bridge-splitting reactions with NaS_2CNEt_2 in refluxing acetone. Iridium analogs were also prepared (ref. 81). Related complexes result from the reaction of $[RhCl_3(PBu_3^n)_2]_2$ with 2- or 3-thienyl-2-pyridine and are formulated as $[Rh(N\text{-}C)(PBu_3^n)Cl_2]_2$ where "N-C" represents a cyclometallated thienylpyridine moiety which is coordinated through nitrogen and also bound with a Rh-C bond at the 3 or 2 position of the thiophene ring respectively (ref. 82). In refluxing dichloromethane $[RhCl(PPh_3)_3]$ reacts with 8-quinolinyl-$\underline{t}$-butylacetylenyl ketone to form [5] (L = PPh_3, R = Bu^t). The phenyl analog was also prepared and these provide an example of the directed cleavage of an sp-sp^2 carbon-carbon bond. By contrast, 8-quinolinyl-trans-β-styryl ketone is not cleaved under analogous conditions but rather functions only as a bidentate ligand coordinating through nitrogen and the carbon-carbon double bond (ref. 83). The thermal decomposition of the metallacycles [cp'M$(CH_2)_n(PPh_3)$] (M = Rh, Ir; n = 4,5. M = Rh, n = 6) has been followed by thermogravimetric analysis and differential scanning calorimetry. For M = Rh, both hydrocarbon moieties are lost at approximately the same temperature while for M = Ir, the metallacyclic portion decomposes first followed by loss of the cp' moiety at higher temperatures. Analysis of the hydrocarbon products suggested that the initial step in the metallacycle decomposition involves homolysis of a metal-carbon bond followed by intra- or intermolecular hydrogen abstractions (ref. 84).



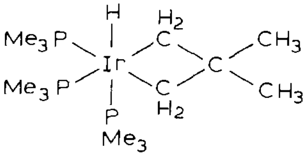
[5]

The oxidative addition of acid chlorides to Rh(I) and Ir(I) centers continues to be studied. From [MCl$(PMe_2Ph)_3$] are obtained mer-[MCl$_2$(COR)$(PMe_2Ph)_3$] (M = Rh, Ir; R = Me, Pr^i. M = Rh; R = Et. M = Ir; R = Pr^n). When the iridium complexes (R = Me, Pr^n) are treated with hexafluorophosphate ion under nitrogen, the salts mer-[IrCl(CO)R$(PMe_2Ph)_3$]PF_6 are formed but alkyl migration does not occur when R = Pr^i. The corresponding reaction where M = Rh and R = Me gives an equilibrium mixture of [RhCl(COMe)$(PMe_2Ph)_3$]PF_6 and mer-[RhCl(CO)(Me)$(PMe_2Ph)_3$]PF_6 (2:1 at -70° C). In the square pyramidal acyl species, a structural study shows a close contact between the chloride ligand and the methyl group which displaces the chloride in the direction of the vacant coordination site leading to the suggestion that this might be a reasonable model for the transition state for the alkyl migration process (ref. 85). This migration reaction has been studied further using the neutral five-coordinate acyl complexes [IrCl$_2$(COR)$(PPh_3)_2$] (R = CH_2Cl, CH_2OPh, CO_2Et, $CH_2CH_2CO_2Me$, C(O)Me) which were prepared from [Ir(N_2)Cl$(PPh_3)_2$] and the corresponding acid chlorides in benzene. Heating the acyl complexes in the solid state or allowing them to stand in solution at room temperature afforded the six-coordinate alkyl carbonyl complexes except where R = C(O)Me where the predominant product was $[IrCl_2(CO)Me(PPh_3)_2]$. This last product is stated to not arise via a migration reaction of the expected acetyl complex. In the above study, the rate of the alkyl migration reaction decreases as R becomes more electronegative. In the synthesis of the acyl complexes, use of ethyl malonyl chloride produced the six-coordinate acyl complex [6] (ref. 86). The enthalpies of the oxidative addition of acetyl chloride to $[Ir(CO)ClL_2]$ (L = tertiary phosphine or phosphite) and of a variety of other acid chlorides to $[Ir(CO)Cl(PMe_2Ph)_2]$ have been measured and a value of the dissociation energy of the Ir-C(O)Me bond of 205 ± 46 kJ/mol derived. The measured enthalpies correlate well with the Tolman cone angle for the various ligands used (ref. 87).



[6]

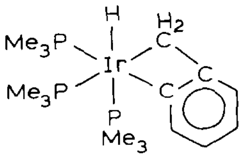
Treatment of $[Ir(PMe_3)_4]Cl$ with neopentyllithium in hexane at room temperature produces the metallacycle [7] which surprisingly shows no evidence of decomposition after being heated for 24 hours at 90° C and is unreactive towards ethylene and



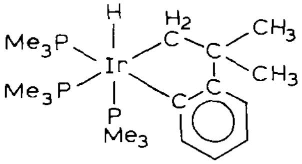
[7]

carbon monoxide. With trimethylsilylmethyllithium $[Ir(PMe_3)_4]Cl$ initially yields $[Ir(PMe_3)_3CH_2SiMe_3]$ which can be converted into a metallacycle analogous to [7] on heating. The reactions of $[Ir(PMe_3)_4]Cl$ with benzylmagnesium chloride and $LiCH_2CMe_2Ph$ yield the metallacycles [8] and [9] respectively. In all these reactions the final products are presumed to form via oxidative addition of a C-H bond in an intermediate iridium alkyl complex (ref. 88). In a related study,

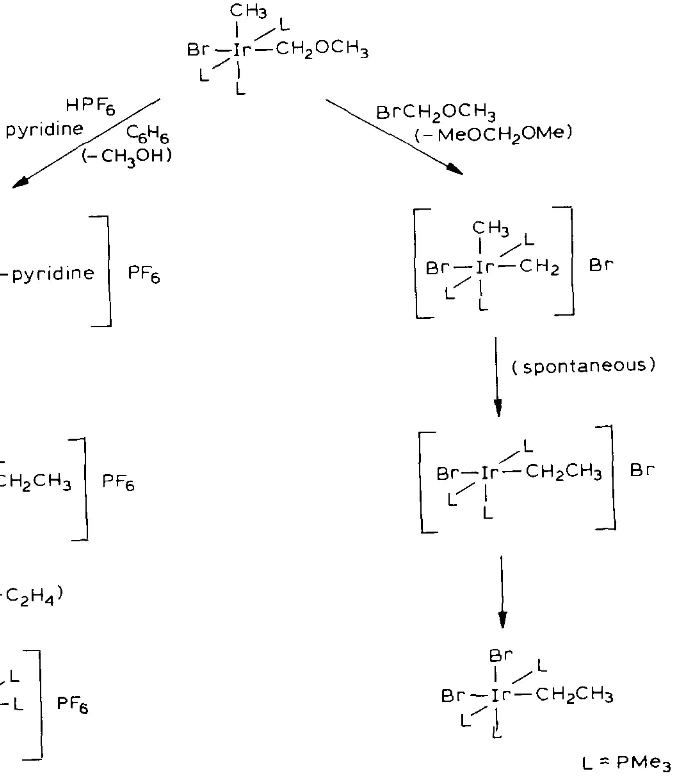
$[Ir(Me)(PMe_3)_4]$ reacts with ethylene to give $[Ir(Me)(C_2H_4)(PMe_3)_3]$ which on treatment with bromomethyl methyl ether yields <u>mer</u>-$[Ir(Me)Br(CH_2OMe)(PMe_3)_3]$. This last complex reacts with HPF_6 in pyridine(py) to give <u>mer</u>-$[Ir(Me)Br(CH_2$-pyridine$(PMe_3)_3]PF_6$ which on heating converts to <u>mer</u>-$[Ir(H)Br(py)(PMe_3)_3]PF_6$ and ethylene or with excess bromomethyl methyl ether in benzene to yield <u>mer</u>-$[Ir(Et)Br_2(PMe_3)_3]$ and dimethyoxymethane. The results are interpreted as indicating the migration of the methyl group to a coordinated methylene moiety as depicted in Scheme X (ref. 89).



[8]

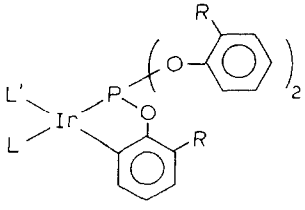


[9]

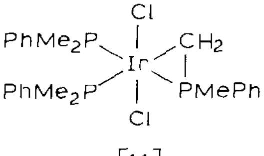


Scheme X

An intermolecular methyl group transfer occurs when [cp_2TiMe_2] is photolyzed in the presence of either [$IrCl_3(CO)(PPh_3)_2$] or [$IrCl(CO)(PPh_3)_2$] to yield [$cp_2TiMeCl$] and [$Ir(Me)Cl_2(CO)(PPh_3)_2$]. In the first reaction, [$IrMe_2Cl(CO)(PPh_3)_2$] is also formed (ref. 90). The cyclometallated phosphite complex [10] (L' = 1,5-cyclooctadiene (COD); L = ($\underline{o}$-$RC_6H_4O)_3P$ (R = H, Me)) in refluxing benzene undergoes substitution of the ligand L by a wide variety of phosphines and phosphites (L") while with carbon monoxide replacement of COD by two carbonyl ligands occurs instead. By contrast if the substitution reaction is performed in refluxing toluene, COD is lost and further ortho-metallation occurs to give [IrH(P-C)$_2$L"] (P-C = mono-ortho-metallated ($\underline{o}$-$RC_6H_4O)_3P$) (ref. 91). In an attempt to prepare metallacycles, mer-[$IrCl_3(PMe_2Ph)_3$] was reacted with 1,5-dilithiopentane. However, the lithium reagent appears to function simply as a base to deprotonate a methyl group on one phosphine since the metallated phosphine complex [11] was the only product isolated. An analogous species metallated at the benzyl carbon of one ligand was obtained from mer-[$IrCl_3(PMe(CH_2Ph)_2)_3$]. Reaction of both these metallated complexes with HCl in ether yields mer-[$IrCl_3L_3$] (L = PMe_2Ph, $PMe(CH_2Ph)_2$) while [11] reacts with halogens to give mer-[$IrCl_2X(PMe_2Ph)_2(PMePh$-$CH_2X)$] (X = Cl, Br, I) (ref. 92). The first example of an Ir(V) organometallic complex, [$cp'IrMe_4$] is obtained from [$cp'_2Ir_2Cl_4$] and trimethylaluminum (ref. 93).

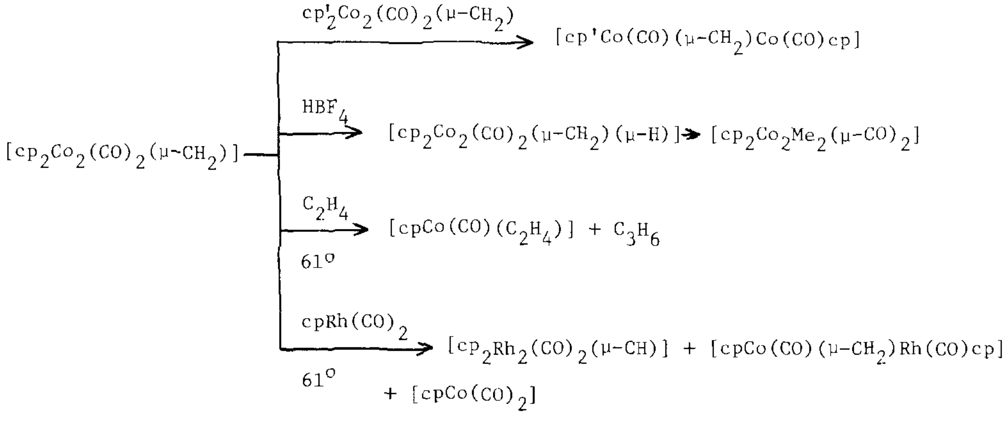


[10]

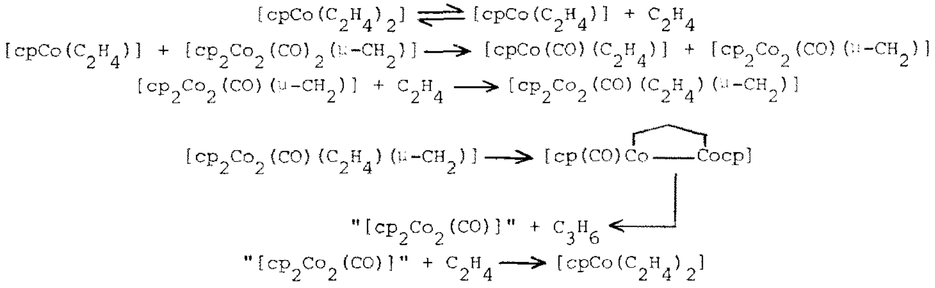


[11]

Interest remains high in the chemistry of binuclear complexes containing bridging methylene groups. Treatment of the radical anion $[cp_2Co_2(CO)_2]^{\dot{-}}$ with diiodomethane in THF yields $[cp_2Co_2(CO)_2(\mu\text{-}CH_2)]$ and $[cp_2Co_2(CO)_2]$. Further chemistry of the former complex is outlined in Scheme XI. Reaction of $[cp_2Co_2(\mu\text{-}CO)_2]$ with ethylene proceeds rapidly to yield $[cpCo(CO)_2]$ and $[cpCo(C_2H_4)_2]$ which undergo a slower redistribution to give $[cpCo(CO)(C_2H_4)]$. This result is proposed to provide support for the structure assigned to the ethylene complex produced from $[cp_2Co_2(CO)_2(\mu\text{-}CH_2)]$ as shown in Scheme XI. The rate of the reaction of ethylene with $[cp_2Co_2(CO)_2(\mu\text{-}CH_2)]$ is inhibited by carbon monoxide and other ligands including tetrafluoroethylene indicating that the inhibition involves more than just repression of carbon monoxide dissociation particularly since no olefin complexes which could be formed reversibly from $[cp_2Co_2(CO)_2(\mu\text{-}CH_2)]$ were detected. The results are interpreted to indicate that the inhibitors scavenge species which are catalysts for the reaction since the reaction appears to be autocatalytic. The proposed mechanism is shown in Scheme XII. Although it is not clear how the process is initiated, it is possible that a small amount of decomposition of $[cp_2Co_2(CO)_2(\mu\text{-}CH_2)]$ to $[cp_2Co_2(CO)_2]$ may occur since as noted above, this last species reacts rapidly with ethylene to give $[cpCo(C_2H_4)_2]$. Once this species is generated, the reaction can proceed as indicated (ref. 94). An alternative route to related complexes is the reaction of $[cp'_2Co_2(\mu\text{-}CO)_2]$ with diazo compounds. Depending on the nature of the diazo species one obtains $[cp'_2Co_2(CO)_2(\mu\text{-}CHCF_3)]$, $[cp'_2Co_2(\mu\text{-}CO)(\mu\text{-}CPh_2)]$ or $[cp'_2Co_2(\mu\text{-}CO)_2(\mu\text{-}CRR')]$ ($R = H$, $R' = CO_2Et$; $R = R' = CO_2Et$; $RR' = CCl{=}CClCCl{=}CCl$, 2,2'-biphenylyl) (ref. 95). Reaction of $[cp'_2Rh_2Cl_4]$ with methyllithium produces [12] which under some conditions isomerized to the trans isomer. This trans isomer is also the product of the reaction of $[cp'_2Rh_2Cl_4]$ with trimethylaluminum. Thermal decomposition of [12] and its trans



Scheme XI



$$[cpCo(C_2H_4)_2] \rightleftharpoons [cpCo(C_2H_4)] + C_2H_4$$

$$[cpCo(C_2H_4)] + [cp_2Co_2(CO)_2(\mu\text{-}CH_2)] \longrightarrow [cpCo(CO)(C_2H_4)] + [cp_2Co_2(CO)(\mu\text{-}CH_2)]$$

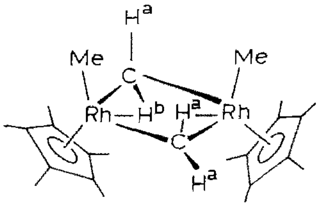
$$[cp_2Co_2(CO)(\mu\text{-}CH_2)] + C_2H_4 \longrightarrow [cp_2Co_2(CO)(C_2H_4)(\mu\text{-}CH_2)]$$

$$[cp_2Co_2(CO)(C_2H_4)(\mu\text{-}CH_2)] \longrightarrow [cp(CO)Co\text{---}Cocp]$$

$$\text{"}[cp_2Co_2(CO)]\text{"} + C_3H_6 \longleftarrow$$

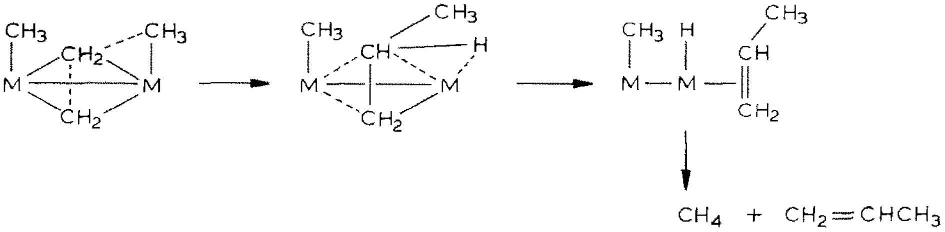
$$\text{"}[cp_2Co_2(CO)]\text{"} + C_2H_4 \longrightarrow [cpCo(C_2H_4)_2]$$

Scheme XII



[12]

isomer produced mainly methane, ethylene and propene plus traces of ethane (Scheme XIII) suggesting that these complexes may be models for Fischer-Tropsch catalysis

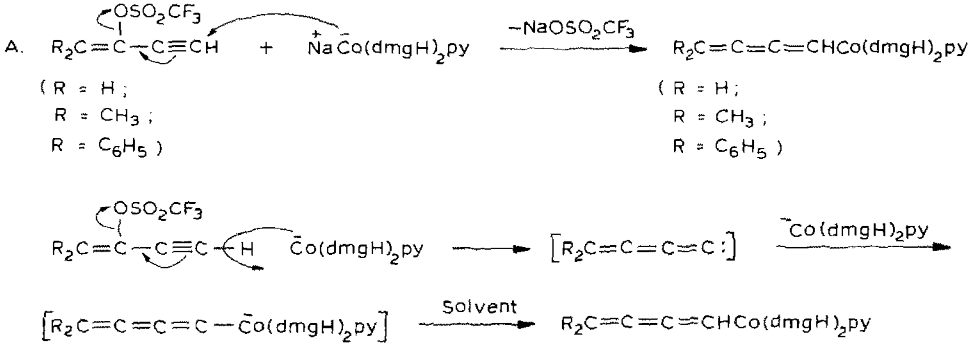


Scheme XIII

via polymerization of methylene groups (ref. 96). The metal-metal bond in $[cp_2Rh_2(CO)_2(\mu\text{-}CH_2)]$ is reversibly protonated in ether at -80° C to give

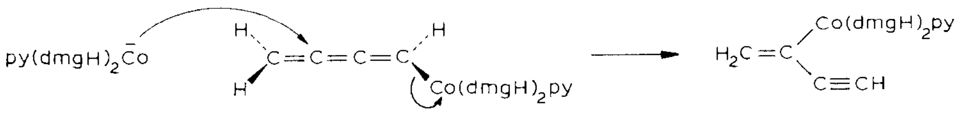
$[cp_2Rh_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}H)]X$ (X = Cl^-, Br^-, BF_4^-, CF_3COO^-, FSO_3^-). On warming one obtains either $[cp_2Rh_2(X)Me(\mu\text{-}CO)_2]$ (X =Cl, Br) or $[cp_3Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)]$ (X = BF_4^-, CF_3COO^-, FSO_3^-) plus $[cpRh(CO)_2]$, methane and hydrogen. The results of labelling experiments imply that the thermal reactions proceed via species such as $[cp_2Rh_2(CO)_2(\mu\text{-}CH_3)]$. In THF, the trinuclear species is formed directly when protonation by HX (X = BF_4^-, CF_3COO^-, FSO_3^-) is attempted. Protonation of the metal-metal bond also occurs when $[cp_2Rh_2(CO)_2(\mu\text{-}CO)]$ reacts with HBF_4 in ether at -20° C to give $[cp_2Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)]BF_4$. On warming, this complex reacts further yielding $[cpRh(CO)_2]$ and $[cp_3Rh_3(\mu\text{-}CO)_3]$ (ref. 97). Diazo compounds react with $[cp'_2Rh_2(\mu\text{-}CO)_2]$ in a manner analogous to that described earlier for the corresponding cobalt complex. Thus at -80° C one obtains $[cp_2'Rh_2(\mu\text{-}CO)_2(\mu\text{-}CHRR')]$ (R = H; R' = H, Me, CO_2Et. R = R' = CO_2Me, Ph. RR' = CX=CXCX=CX (X = Cl, Br), *o,o'*-$(C_6H_4)_2CO$) which on warming rearrange to $[cp_2'Rh_2(CO)_2(\mu\text{-}CRR')]$ (R = H; R' = H, Me, CO_2Et. R = R' = CO_2Me, Ph) or lose CO to give $[cp_2'Rh_2(\mu\text{-}CO)(\mu\text{-}CRR')]$ (RR' = CX=CXCX=CX (X = Cl, Br), *o,o'*-$(C_6H_4)_2CO$) (ref. 98). The analogous complex $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}CPh_2)]$ can be obtained by the same route and, as it presumably contains a rhodium-rhodium double bond as does $[cp_2Rh_2(\mu\text{-}CO)_2]$, reacts further with diazomethane to yield $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}CPh_2)(\mu\text{-}CH_2)]$ (ref. 99).

In the area of cobaloxime chemistry, the reaction of $Na[Co(dmgH)_2py]$ (dmgH = dimethylglyoximate) with the enynes $R_2C{=}C(OSO_2CF_3)C{\equiv}CH$ (R = Me, Ph) produces the cumulenyl compounds $[R_2C{=}C{=}C{=}CHCo(dmgH)_2py]$ according to Scheme XIV (mechanism A preferred) however for R = H, $[H_2C{=}C(C{\equiv}CH)Co(dmgH)_2py]$ is the product (Scheme XV) (ref. 100). Standard methods have been employed for the synthesis of $[RCo(dmgH)_2B]$ (R = Me, CH_2Br, Et, Pr^i; B = substituted adenines) and the equilibrium constants for the dissociation of B determined (ref. 101). A variety of allyl(pyridine)

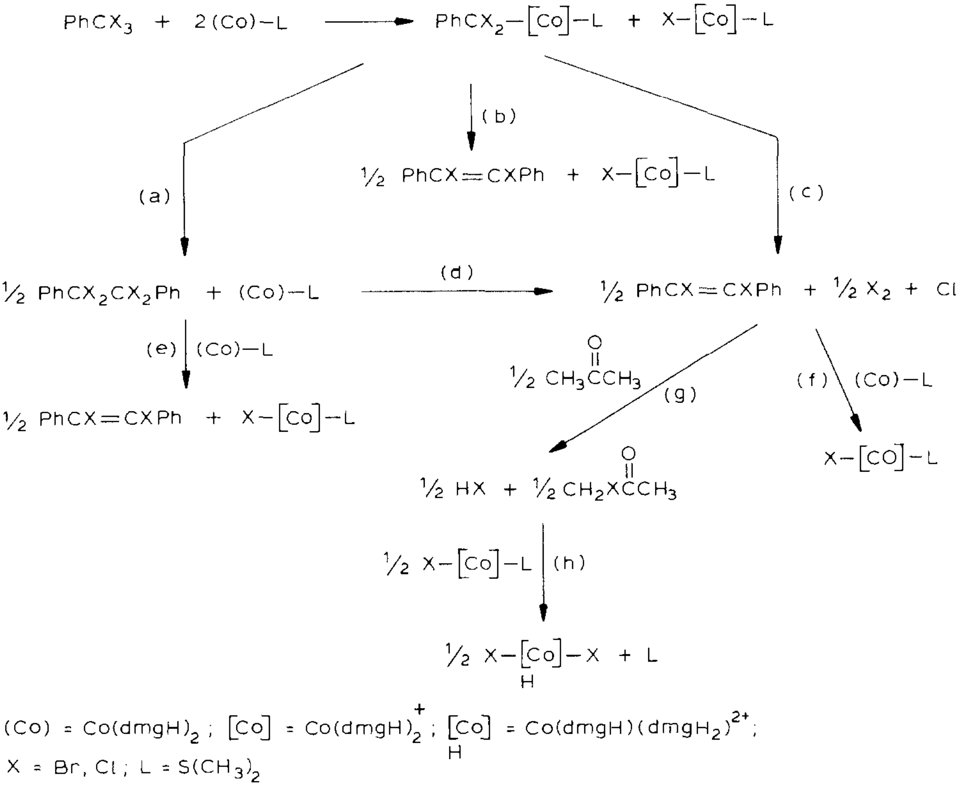


Scheme XIV

cobaloximes have been reacted with N,N-dimethylsulfamoyl chloride to prepare S-allyl-N,N-dimethylsulfonamides. The reaction is proposed to occur via attack of the N,N-dimethylsulfamoyl radical on the γ carbon of the allyl group with displacement of a divalent cobaloxime moiety (ref. 102). Dimethylsulfide cobaloxime(II) functions as a promoter for the coupling of $PhCX_3$ (X = Cl, Br) according to Scheme XVI. For X = Cl, path a is the primary one while for X = Br

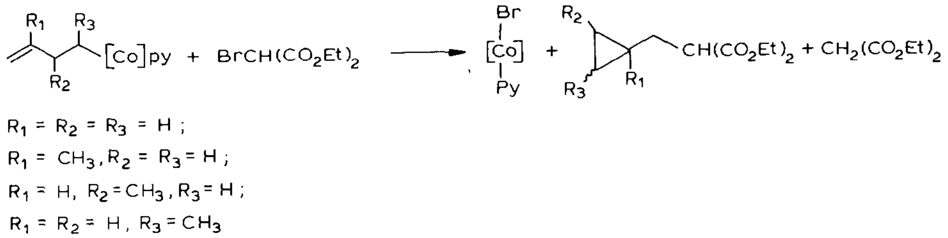


Scheme XV



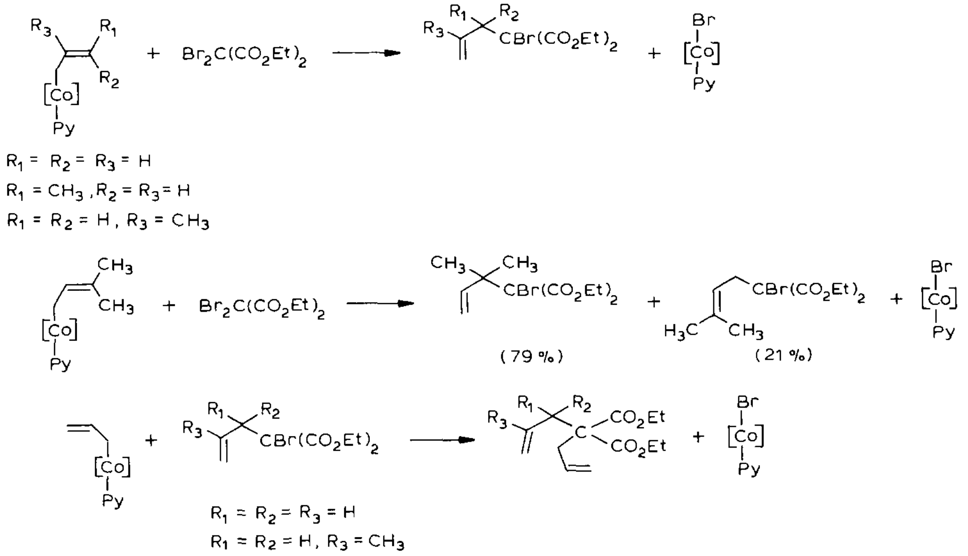
Scheme XVI

the authors favor path b (ref. 103). Bromotrichloromethane reacts with $[PhCH_2Co(dmgH)_2py]$ to give benzyl bromide and $PhCH_2CCl_3$ in approximately equal amounts while in the presence of an excess of imidazole the major product is $PhCH_2CCl_3$. The high yield of $PhCH_2CCl_3$ and the absence of bibenzyl implies direct attack of trichloromethyl radical on the benzyl cobaloxime and this is favored by the presence of an axial base which is strongly coordinated (ref. 104). In another example of the use of cobaloxime derivatives in organic synthesis, allyl- and but-3-enylcobaloximes react with a variety of brominated esters to give malonic or acetoacetic esters containing secondary or tertiary allyl substituents. These transformations are detailed in Schemes XVII-XX (ref. 105). Acid chlorides readily



$R_1 = R_2 = R_3 = H$;
$R_1 = CH_3, R_2 = R_3 = H$;
$R_1 = H, R_2 = CH_3, R_3 = H$;
$R_1 = R_2 = H, R_3 = CH_3$

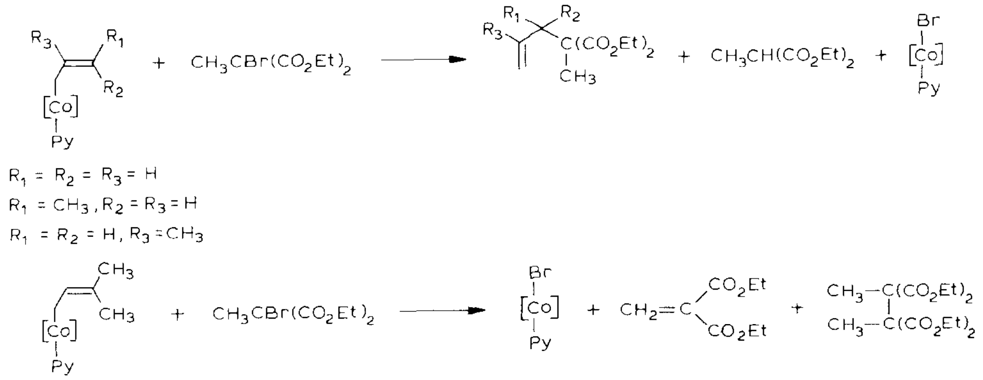
Scheme XVII



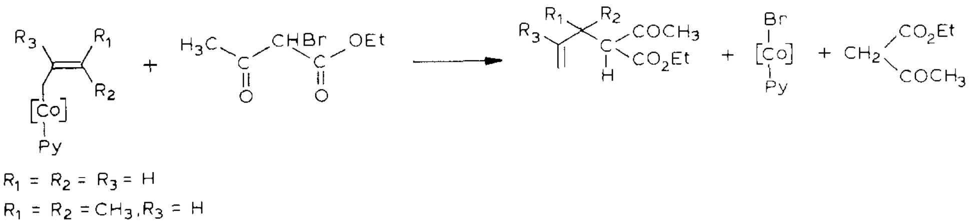
$R_1 = R_2 = R_3 = H$
$R_1 = CH_3, R_2 = R_3 = H$
$R_1 = R_2 = H, R_3 = CH_3$

$R_1 = R_2 = R_3 = H$
$R_1 = R_2 = H, R_3 = CH_3$

Scheme XVIII



Scheme XIX



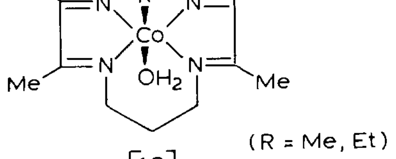
Scheme XX

acylate [Co(salen)] (salen = N,N'-bis(salicylidene)ethylenediamino) and the resulting acyl complexes function as acyl transfer agents with Grignard reagents and thiols for the synthesis of unsymmetrical ketones (ref. 106).

Fluorine-19 NMR studies have been made on [m-and p-$FC_6H_4Co(dmgH)_2L$] (L = substituted pyridines, PPh_3, amines, CN^-, SCN^-) and the fluorine chemical shifts correlated with those of monosubstituted fluorobenzenes via the Taft dual substituent parameter equation to obtain appropriate inductive and resonance parameters for the cobaloxime moieties. The results indicate the presence of significant π-donotion from cobalt to the fluorophenyl ligand which is favored by the presence of strong σ-bases (ref. 107). The pKa's of the carboxyl group in [$HO_2CCH_2CH_2Co(dmgH)_2B$] (B = substituted pyridines, primary amines, S-methylsulfides) have been correlated with those for several substituted propionic acids obtain inductive parameters for the cobalt centers. These correlate with the pKb's of the axial bases, B, within each series but no overall correlation could be found (ref. 108). The base hydrolysis of $[EtCo(dmgH)_2(H_2O)]$ in D_2O/OD^- has been studied. The increase in the proportion of C_2H_5D in the liberated ethane with time and the observation that deuteration of the ligand methyl groups also occurs is taken to indicate that only about one third of the ethyl fragments produced are protonated by solvent; the remainder abstract hydrogen from the ligand methyl groups. While homolytic cleavage of the Co-Et bond appears to occur, the results of the methyl analog suggest heterolytic ($Me^- + Co^+$) cleavage of the Co-Me bond (refs. 109,110).

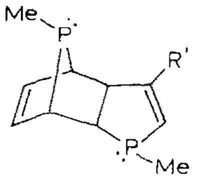
Methylcobalamin reacts with tin(II) chloride in aqueous hydrochloric acid under aerobic conditions to give aquocobalamin and methyltrichlorotin(IV) but unless aquocobalamin is present under anaerobic conditions, no reaction is observed. The proposed mechanism involves bimolecular homolytic attack of tin(II) chloride at carbon to give a methyltin(III) radical which on further reaction with dioxygen or aquocobalamin yields the final tin species (ref. 111). Methylation of Tl(IV), Hg(II), Pb(IV) and Au(III) in related systems is affected by the concentration and nature of halide ion also present. The data are interpreted in terms of the effect the halide ions have on the electrophilicity of the metal towards the methyl group (ref. 112). In coenzyme B_{12}, reversible Co-Me bond cleavage has been observed to be catalyzed by methylmalonyl-CoA mutase derived from P. shermanii (ref. 113).

The optically active cobaloximes $[RCo(dmgH)_2B]$ ($R = CH_3CHX$ ($X = CN, CO_2Me$); $B = H_2O$, py, optically active amines) have been prepared and their circular dichroism (CD) spectra measured. From these it appears that the optical rotation is dominated by the contribution from the alkyl group (ref. 114). Optical rotatory dispersion (ORD) and CD spectra have also been measured for the α- and β-isomers of methylcobalamin, cobyric acid and p-cresylcobamide (ref. 115). Activation parameters have been determined for the substitution of water in $[MeCo(dmgH)_2(H_2O)]$ and [13] by SCN^-, NH_3 and thiourea. Comparison of these with those for the corresponding reactions of aquocobalamin imply that the increased lability of the latter



[13]

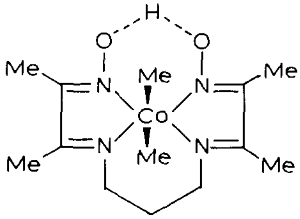
complex is due to entropy effects (ref. 116). The phosphine-bridged cobaloximes $[(MeCo(dmgH)_2)_2(L_2)]$ (L_2 = syn and anti isomers of [14] have been synthesized to



[14] (R = Me, H)

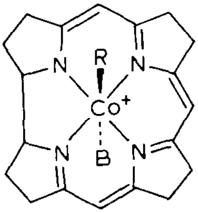
provide examples of the coordinating abilities of these ligands. Two interesting features of the ligand which are retained on complexation are the chemical shift of the bridgehead phosphorus which is much further downfield for the syn isomer than for the anti isomer and $^3J_{P-P}$ which is ca. 24 Hz in the former and below the limit of detection in the latter (ref. 117).

The kinetics of the reaction of $[(p\text{-}XC_6H_4CH_2)Co(dmgH)_2py]$ (X = H, Cl, NO_2, Me, OMe) with iodine to give $p\text{-}XC_6H_4CH_2I$ and $[Co(I)(dmgH)_2py]$ suggest that the rate-determining step is dissociation of pyridine with a subsequent rapid reaction of the base-off cobaloxime with iodine in an inner-sphere process (ref. 118). The conversion of aryl olefins to α-aryl alcohols is catalyzed by $[CoCl(dmgH)_2py]$ in the presence of borohydride. The mechanism is suggested to involve initial reduction of the cobaloxime to a Co(II) species which attacks the olefin to yield an alkylcobaloxime. This then reacts with oxygen to form an alkylperoxocobaloxime which is subsequently hydrolyzed (ref. 119). Photolysis of $[RCo(dmgH)_2py]$ (R = 2-phenyl- or 2-ethoxycarbonylpentanone-2-ylmethyl) produces the corresponding 3-substituted cyclohex-2-enones. A radical process is proposed and the reaction is considered to be a model for ester migration reactions mediated by vitamin B_{12} (ref. 120). Studies of $[Me_2Co(DPNH)]$ ([15]) have involved photolysis and electrochemical oxidation. Photolysis in acetonitrile yields methane and even in dichloromethane or chloroform, methane is still the major product. Some hydrogen abstraction from the ligand by methyl radicals also occurs (ref. 121). On oxidation the complex is strongly labilized towards loss of one methyl group with the intermediate formation of Co(IV) cations being suggested. Homolytic cleavage of the Co-C bond appears to occur (ref. 122). Reduction of the diiodo analog of [15], $[CoI_2(DPNH)]$, by sodium borohydride in methanolic base under carbon monoxide yields [Co(CO)(DPNH)]. Initial reduction to a Co(II) species followed by base-induced disproportionation with one Co(I) product being captured by CO is proposed to be the mechanism. The carbonyl derivative undergoes oxidative addition with alkyl halides (RX = MeI, Bu^nBr, $PhCH_2Cl$, $MeC(CO_2Et)CH_2Br$, 4-chloro-2-dioxolane).



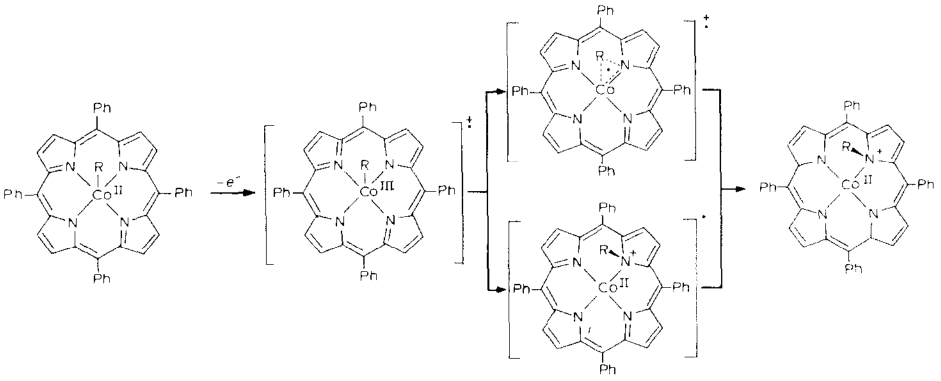
[15]

The [RCoX(DPNH)] products react with silver hexafluorophosphate in the presence of water or pyridine (B) to yield the cations $[RCo(DPNH)B]PF_6$. They also show significant dissociation of the axial halide ligand in methanol solution (ref. 123). Electrochemical studies on [16] suggest that this complex is a better model



[16]

for the electrochemical behavior of vitamin B_{12} than are the more commonly studied cobaloximes (Ref. 124). Polarographic studies on the $[Co^{III}L(R)]/[Co^{IV}L(R)]$ (R = Et, Ph; L = salen, N,N'-ethylene(acetylacetonediiminato)(acen)) couple indicate that following oxidation, the Co-C bond underdoes homolysis and that solvent coordination in the vacated axial position is coupled with the electron transfer (ref. 125). Electrochemical reduction of methylcobaloximes and related complexes has been investigated in dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF). In the first system, two one-electron steps to Co(II) and Co(I) species were identified and Co-C bond cleavage occurred. Reoxidation of the species formed on coulometric reduction provided substantial recovery of the starting alkylcobaloximes implying a reversible trapping of the alkyl radical by the equatorial ligand (ref. 126). In DMF there was a linear correlation of the half-wave potentials and electronic spectral parameters between compounds with equatorial ligands having comparable opportunities for charge delocalization (ref. 127). A similar metal-to-ligand migration of an alkyl group occurs upon one-electron oxidation of [EtCo(TPP)] (TPP = tetraphenylporphyrin) (Scheme XXI). The starting material can be regenerated upon borohydride reduction presumably by an intermolecular process. An analogous process is observed with [EtO_2CCo(TPP)] but at low temperature the site of oxidation is on the porphrin ring to give a π-cation radical. On warming rearrangement occurs to give the N-alkylated product (ref. 128).



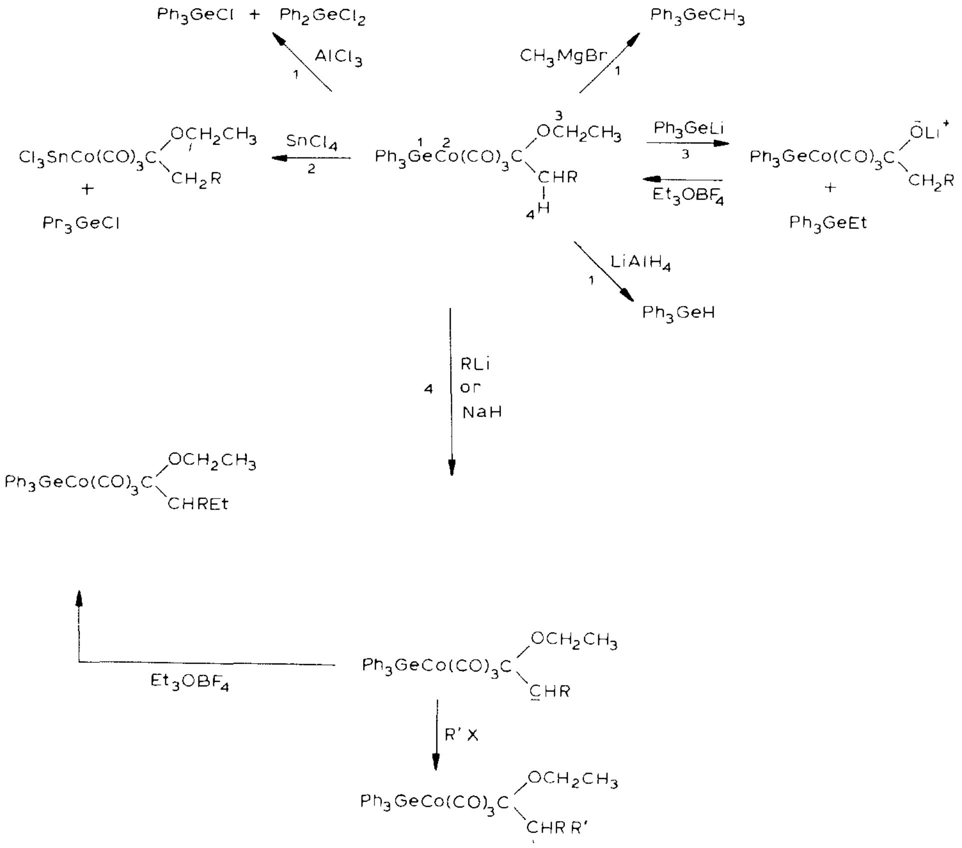
Scheme XXI

Exposure of a single crystal of [((R)-1-cyanoethyl)((S)-α-methylbenzylamine) $Co(dmgH)_2$] to x-rays causes a slow change to the disordered racemate implying epimerization has occurred. ESR results confirm cleavage of the Co-C bond occurs. From the structural study there appears to be sufficient space in the vicinity of the cyanoethyl group for it to epimerize following Co-C bond cleavage without disturbing the remainder of the structure (ref. 129). Additional studies which continue attempts to define the factors influencing the strengths of the axial bonds in cobaloximes include structure determinations of [RCo(dmgH)py] (R = Me_3CCH_2, Me_3SiCH_2, NO_2CH_2). In the first two the results indicate considerable steric interaction between the alkyl group and the equatorial ligands and this steric pressure is suggested to be significant in the ease of substitution of the axial base (ref. 130). In the last, prepared from [$CoCl(dmgH)_2py$] and silver oxide in nitromethane, the Co-N(py) bond is significantly shorter than in related alkylcobaloximes indicating a low trans influence for the CH_2NO_2 ligand (ref. 131). In neopentyl and benzyl cobalamins prepared from vitamin B_{12}s, homolysis of the Co-C bond is facilitated by coordination of an axial base. Presumably in the "base-off" form, the conformation of the corrin ring is such as to minimize steric interaction with the axial alkyl group but on coordination of the axial base (here dimethylbenzimidazole is used), the corrin ring is displaced upwards towards the alkyl group with the resulting steric pressure aiding Co-C bond cleavage. It is further suggested that the energy requirements for Co-C bond cleavage in related enzyme systems can be reduced by protein-corrin interactions which enhance these conformational changes (ref. 132). The asymmetric hydrogenation of α-diketones, α-ketocarboxylates and related compounds is catalyzed by $[Co(dmgH)_2(quinine)]$ with up to 70% enantiomeric excess being obtained. The site determining the enantioselectivity appears to be different than the catalytic site and the results suggest that protonation of the chiral base is important. The proposed mechanism involves heterolytic activation of hydrogen to produce a hydrido cobaloxime and protonated base. Reaction of the hydrido species with substrate produces an alkylcobaloxime which undergoes protonolysis to product with the required proton being delivered enantioselectively by the protonated base (ref. 133).

Addition of one equivalent of trimethylphosphite to $[Rh(OEP)]_2$(OEP = octaethylporphyrin) cleaves the dimer to give [MeRh(OEP)] and $[Rh(OEP)(P(O)(OMe)_2)]$. Use of excess phosphite gives only the latter complex and a greater than stoichiometric quantity of $MeP(O)(OMe)_2$. A radical chain mechanism involving attack of methyl radical on the excess phosphite is proposed (ref. 134). Treatment of [HRh(OEP)] with carbon monoxide produces the formyl complex [Rh(CHO)(OEP)] which loses CO to give $[Rh(OEP)]_2$. The dimer can be reconverted to the formyl by reaction with hydrogen and carbon monoxide (ref. 135). Flash photolysis of $[Pr^iRh(dmgH)_2(PPh_3)]$ in ethanol causes homolysis of the Rh-C bond and the rate constants for the reaction of the $[\cdot Rh^{II}(dmgH)_2(PPh_3)]$ species produced with organic halides have been evaluated. The rate-determining step appears to be halogen abstraction from the organic halide (refs. 136, 137).

Metal Carbene Complexes

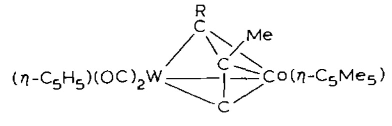
Reaction of $[Ph_3SiCo(CO)_4]$ with phenyllithium at -78° C in ether yields the acyl complex $Li[Ph_3SiCo(CO)_3(COPh)]$ which on warming or treatment with Et_3OBF_4 produces $Ph_3SiC(O)Ph$. The silyl ketone is also obtained directly if the original reaction is performed at room temperature. The same reaction with an optically active silyl substituent indicates that formation of the silyl ketone occurs with retention of configuration. However reaction of butyllithium with $[Ph_3SiCo(CO)_4]$ at -78° C followed by hydrolysis produced only Ph_3SiOH indicating that in this instance the acyl complex was not formed. By contrast, the acyl produced by alkylation of $[Ph_3GeCo(CO)_4]$ with RLi (R = Me, Et, Pr^n, Bu^n, Ph) forms alkoxycarbene complexes, $[Ph_3Co(CO)_3(C(R)OEt)]$, on further alkylation with Et_3OBF_4. This reaction sequence does not occur with [Ph$_3$GeCo(CO)$_3$(PPh$_3$)] however. Further reactions of [Ph$_3$GeCo(CO)$_3$(C(R)OEt)] (R = Ph) are detailed in Scheme XXII(ref.138). The bridging carbyne



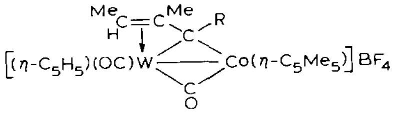
The different sites of attack by the indicated reagents are marked by numbers.

Scheme XXII

complex [cp(CO)$_2$W(μ-*p*-tolylC)Co(CO)cp'] reacts with but-2-yne to yield [17] (R = *p*-tolyl) which can be protonated to give [18]. Complex [18] can also be obtained from [19] which is synthesized by protonation of the original carbyne complex. Reaction of [19] with dimethylphenylphosphine produces [20] (R = *p*-tolyl) (ref. 139). Reaction of cobalt(II) chloride with trimethylsilylmethyllithium in benzene yields substantial amounts of tetramethylsilane together with some 1,2-bis(trimethylsilyl)ethylene. The results are interpreted as indicating the formation of the unstable carbene species $\{Co{=}CHSiMe_3\}$ (ref. 140).



[17]



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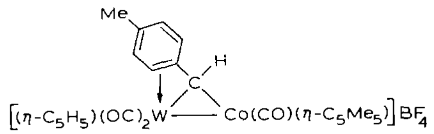

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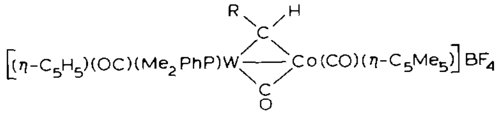
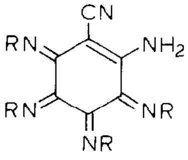


[20]

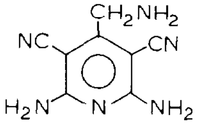
Metal Isocyanide Complexes

Isocyanides react with $[Co(NMA)_3 \cdot 3H_2O]$ (NMA = nitromalonaldehyde) to give the ionic species $[Co(CNR)_5][Co(NMA)_3]$ (R = p-XC_6H_4 (X = Me, MeO, NO_2, Cl)). Analogous species are obtained from $[Co(hfac)_2] \cdot 2H_2O$ (hfac = hexafluoroacetylacetonate) and formulated as $[Co(CNR)_5][Co(hfac)_3]$ (ref. 141). The oligomer- or co-oligomerization of the active methylene compounds $CH_2R'R''$ (R' = R" = CN, CO_2Me, CO_2Et) with RNC (R = 2,6-$Me_2C_6H_3$) is catalyzed by $[Co_2(CO)_8]$ and $[Co_2(CNR)_8]$ yielding [21] and [22] for R' = R' = CN and [23] for the others (ref. 142). Proton and ^{59}Co NMR spectra have been reported for $[CoX(CNcy)(dmgH)_2]$ (X = Cl, Br, I, NO_2; cy = cyclohexyl) (ref. 143).

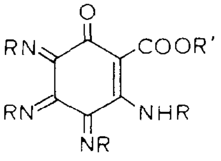
Considerable interest continues to be shown in binuclear rhodium complexes bridged by diisocyanide ligands. Photolysis of an acetone solution of $[Mn_2(CO)_{10}]$ and $[Rh_2(TM4\text{-}br)_4](PF_6)_2$ (TM4-br = 2,5-dimethyl-2,5-diisocyanohexane) yields $[(OC)_5MnRh(TM4\text{-}Br)_4RhMn(CO)_5](PF_6)_2$ with the primary photoprocess presumed to be homolysis of the Mn-Mn bond. Photolysis of the product complex leaves it substantially unchanged implying it is either stable or undergoes rapid recombination of photochemically generated fragments. However in the presence of oxygen, photolysis regenerates $[Rh_2(TM4\text{-}br)_4]^{2+}$ and unidentified manganese species (ref. 144). Oxidation of $[\mathrm{Rh_2br_4}]^{2+}$ (br = 1,3-diisocyanopropane) in 1 M sulfuric acid leads to dimerization and the formation of $[\mathrm{Rh_4br_8}]^{6+}$ which associates with two equivalents of $[\mathrm{Rh_2(TM4\text{-}br)_4}]^{2+}$ to give $[(\mathrm{Rh_2(TM4\text{-}br)_4})(\mathrm{Rh_4br_8})(\mathrm{Rh_2(TM4\text{-}br)_4})]^{10+}$. Air oxidation of the octanuclear ion yields $[(\mathrm{Rh_2(TM4\text{-}br)_4})(\mathrm{Rh_2br_4})]^{6+}$.



[21]



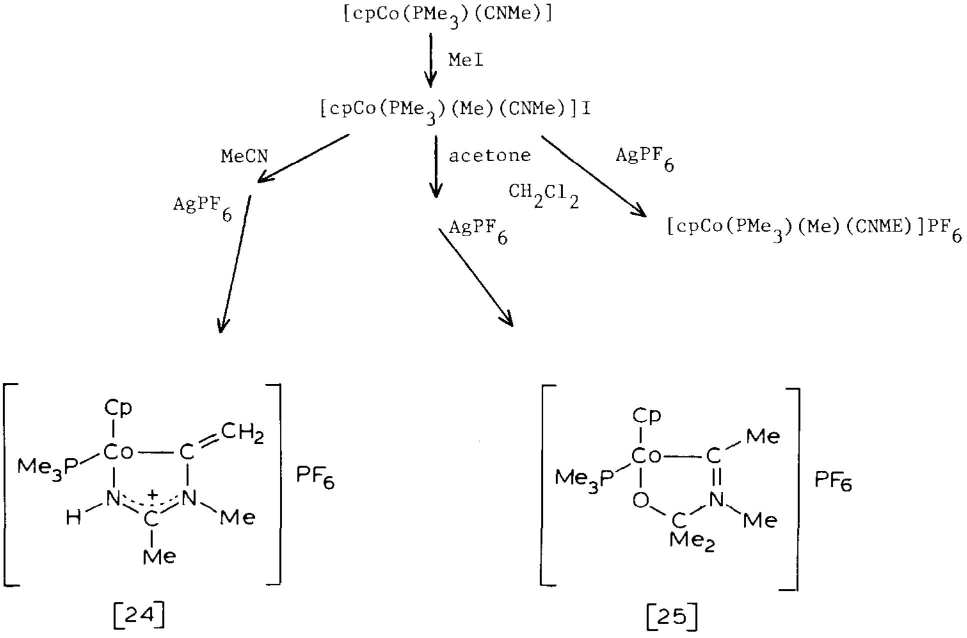
[22]



[23]

However when $[\mathrm{Rh_4br_8}]^{6+}$ is present in excess only one end of the tetramer becomes capped giving $[(\mathrm{Rh_4br_8})(\mathrm{Rh_2(TM4\text{-}br)_4})]^{8+}$ which subsequently dimerizes to $[\mathrm{Rh_2(TM4\text{-}br)_4)(Rh_4br_8)_2(Rh_2(TM4\text{-}br)_4})]^{16+}$ (ref. 145). The polarized single-crystal and the time-resolved resonance raman spectra of $[\mathrm{Rh_2br_4}]^{2+}$ show that $\nu_{\mathrm{Rh-Rh}}$ increases by a factor of ca. 1.8 on going to the $^3A_{2u}$ excited state indicating a significantly greater amount of metal metal bonding in the excited state than in the ground state (refs. 146, 147). The redox behavior of $[\mathrm{Rh_4br_8}]^{6+}$ at a rotating glassy carbon electrode shows that the oxidation potential is lowered when chloride is added implying chloride binds more strongly to the oxidized species. The reduction behavior is more complex and is interpreted in terms of the formation of a film of oligomerized complex on the electrode surface (ref. 148). Related dimers $[\mathrm{Rh_2(L_2)_4}]^{2+}$ ($\mathrm{L_2}$ = meso-1,3-diisocyanocyclohexane (cybr), meso-2,4-diisocyanopentane (mebr)) have been synthesized from $[\mathrm{RhCl(COD)}]_2$ and have been observed to dimerize in methanol although to a lesser extent than does $[\mathrm{Rh_2br_4}]^{2+}$. $[\mathrm{Rh_2(cybr)_4}]^{2+}$ reacts rapidly in the dark with concentrated hydrochloric acid to generate hydrogen and $[\mathrm{Rh_2(cybr)_4Cl}]^{4+}$ which slowly evolves more hydrogen with formation of $[\mathrm{Rh_2(cybr)_4Cl_2}]^{2+}$. This last complex reacts with water to form $[\mathrm{Rh_2(cybr)_4Cl_2}]_2^{4+}$ but no oxygen or hydrogen peroxide was observed. The iridium analogs, $[\mathrm{Ir_2(L_2)_2}]^{2+}$ were also synthesized (refs. 149, 150).

Oxidative addition of methyl iodide to $[\mathrm{cpRh(PMe_3)(CNMe)}]$ occurs in pentane to give $[\mathrm{cpRh(PMe_3)(Me)(CNMe)}]\mathrm{I}$ which on refluxing in acetone rearranges to the acetimidoyl complex $[\mathrm{cpRh(PMe_3)(I)(C(Me){=}NMe)}]$. The initial oxidative adduct formed in the analogous cobalt system is unstable and its subsequent reactions are detailed in Scheme XXIII (ref. 151). Addition of the lithium salt of TCNQ radical anion (TCNQ = tetracyano-p-p-quinodimethane) to solutions of $[\mathrm{Rh(CNR)_4}]\mathrm{ClO_4}$ (R = $\mathrm{Bu^t}$, cy, p-tolyl, p-$\mathrm{MeOC_6H_4}$, m-xylyl, mesityl) yields $[\mathrm{Rh(CNR)_4}][\mathrm{TCNQ}^{\dot{-}}]$ however for R = Ph, the mixed salt $[\mathrm{Rh(CNPh)_4}](\mathrm{TCNQ}^{\dot{-}})_{0.67}(\mathrm{ClO_4})_{0.33}$ forms. Refluxing the simple salts with TCNQ in acetonitrile yields $[Rh(CNR)_4][(TCNQ)_2^{\cdot-}]$. Most of these are semi-conductors (ref. 152). Methyllithium reacts with $[RhCl(CNBu^t)_4]$ at -20° C to yield $[RhMe(CNBu^t)_4]$ which is proposed to have a trigonal bipyramidal structure. It reacts with methyl iodide and tetracyanoethylene but the products were not characterized (ref. 153). Like a variety of other Lewis bases, tert-butylisocyanide forms a simple axial adduct, $[Rh_2(O_2CMe)_4(CNBu^t)_2]$, with $[Rh_2(O_2CMe)_4]$ (ref.154).

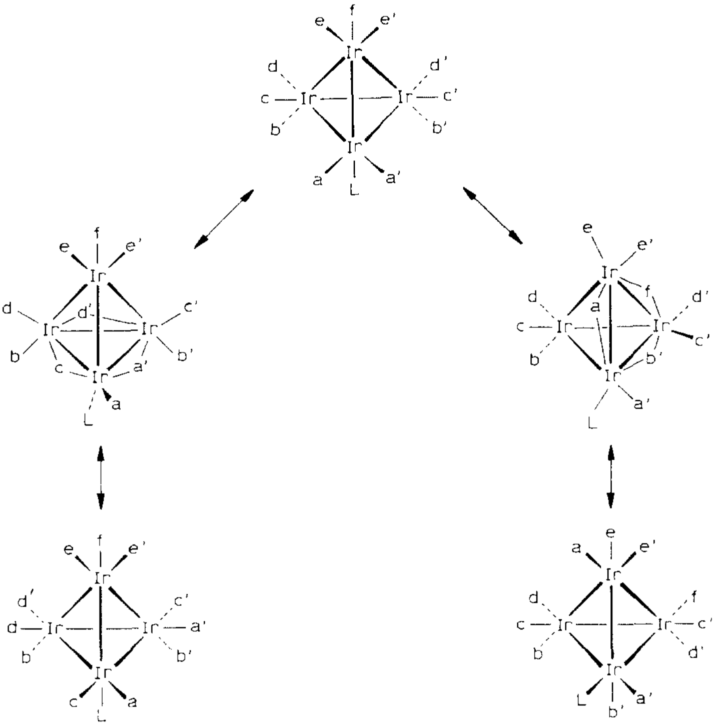


Scheme XXIII

The substitution of isocyanides on metal carbonyls is catalyzed by $[M(CO)Cl(PPh_3)_2]$ (M = Rh, Ir) and by $[RhCl(PPh_3)_3]$ either homogeneously or supported on phosphinated styrene-divinylbenzene copolymer. Rhodium or iridium isocyanide complexes are proposed as intermediates (refs. 155, 156).

The chemisorption of methylisocyanide on alumina-supported rhodium occurs in a non-dissociative fashion on isolated and crystalline rhodium sites. No isomerization of the isocyanide occurs. When added to supported $\{Rh(CO)_2\}$ sites, the isocyanide displaces carbon monoxide apparently with the formation of $\{Rh(CO)(CNMe)\}$ species (refs. 157, 158).

The trimethylamine oxide-assisted substitution of isocyanide in $[Ir_4(CO)_{12}]$ yields $[Ir_4(CO)_{12-x}(CNR)_x]$ (R = Me, Bu^t; x = 1-4). Except for R = Bu^t and x = 3, 4 where bridging carbonyls are present, the products contain only terminal ligands. The occurrance of bridging carbonyl ligands in the two cases mentioned is attributed to steric factors. The kinetics of the substitution reactions show the rates to be much faster than with triphenylphosphine and each step is second order. The complexes with R = Bu^t are fluxional at room temperature and the processes of Scheme XXIV are proposed to explain the carbonyl site exchange in a typical example (ref. 159).

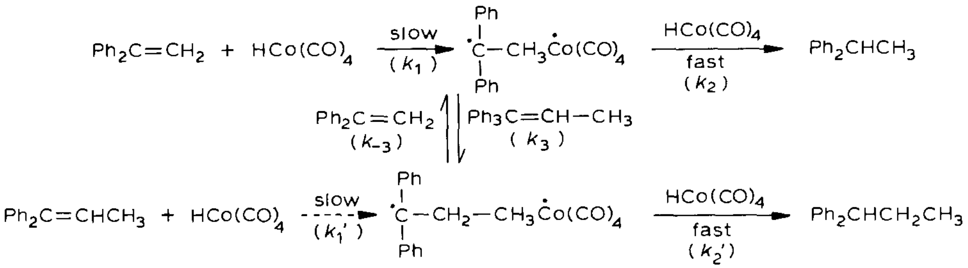


Scheme XXIV

Metal Carbonyl Complexes and Related Compounds

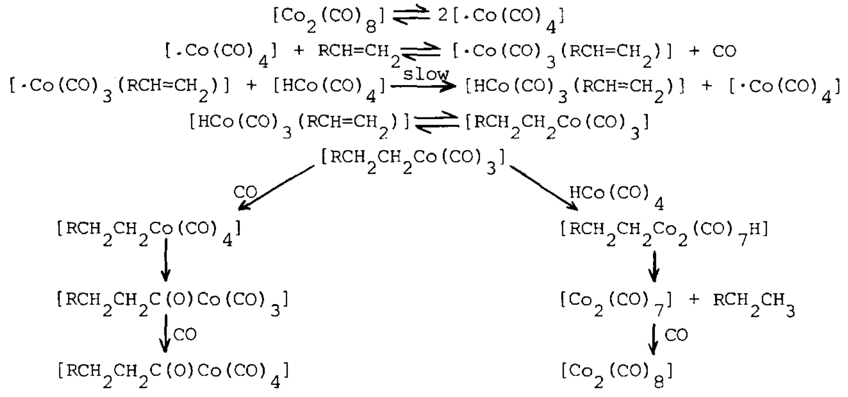
a) Homonuclear Carbonyl Compounds

Considerable study has been made of the use of $[HCo(CO)_4]$ in stoichiometric and catalytic hydrogenations. The relatively rapid hydrogenation of bifluorenylidene and α-cyanostyrene to bifluorenyl and α-cyanoethylbenzene respectively together with the fact that both species can form stable radicals is taken as evidence that hydrogenations with $[HCo(CO)_4]$ involve radical intermediates (ref. 160). In a related study reaction of $[DCo(CO)_4]$ with 9-benzylidenefluorene gives 9-deuterio-9-(α-deuteriobenzyl)fluorene. However the fact that the $[DCo(CO)_4]$ used could be prepared by an exchange reaction of $[HCo(CO)_4]$and 2,4,6-trideuterio-3,5-dimethoxybenzene in dichloromethane under carbon monoxide is taken to indicate the protic nature of the hydrogen in [$HCo(CO)_4$] (ref. 161). Two more radical processes are proposed for the hydrogenation of a variety of ring-substituted styrene and 1,1-diphenylmethanes and 1,1-diphenylprop-1-ene by [$HCo(CO)_4$] (Scheme XXV) and for the



Scheme XXV

reaction of [$HCo(CO)_4$] with α-olefins in the presence of [$Co_2(CO)_8$] in which the primary products are saturated hydrocarbons and acyl cobalt tetracarbonyls (Scheme XXVI) (refs. 162, 163). At -78° C in hexane, [$HCo(CO)_4$] reacts with amines, NR_3



Scheme XXVI

(R = Me, Et), to yield species which from structural studies are best formulated as [HNR_3][$Co(CO)_4$]. However the hydrogen remains aligned with the C_3 axis of the anion and the Co-H distance is 2.85(7) Å implying the existence of specific contact ion pairing. This is also evident from infrared studies (ref. 164).

Complexes of the formula [$HCo(CO)_3(PBu^n_3)$] can be generated photochemically from either [$Co_2(CO)_8$] or Co(II) acetate and the phosphine in methanol under 80 atm of CO/H_2. They are active hydroformylation catalysts giving high selectivities to straight-chain aldehydes. In hydrocarbon solvents however no photoinitiated hydroformylation occurs in the absence of phosphine but when it is added, a photocatalytic hydrogenation of olefins is seen (ref. 165). A kinetic analysis of the $[\mathrm{HCo(CO)_4}]$-mediated reduction of aldehydes to alcohols reveals that previous mechanisms are not in accord with an inverse square dependence of rate on CO pressure. Scheme XXVII is proposed instead (ref. 166). Other related studies

$$\begin{gathered}
[\mathrm{HCo(CO)_4}] \rightleftharpoons [\mathrm{HCo(CO)_3}] + \mathrm{CO} \\
[\mathrm{HCo(CO)_3}] \overset{\mathrm{H_2}}{\rightleftharpoons} [\mathrm{H_3Co(CO)_3}] \\
[\mathrm{H_3Co(CO)_3}] \rightleftharpoons [\mathrm{H_3Co(CO)_2}] + \mathrm{CO} \\
[\mathrm{H_3Co(CO)_2}] + \mathrm{RCHO} \longrightarrow \text{Products}
\end{gathered}$$

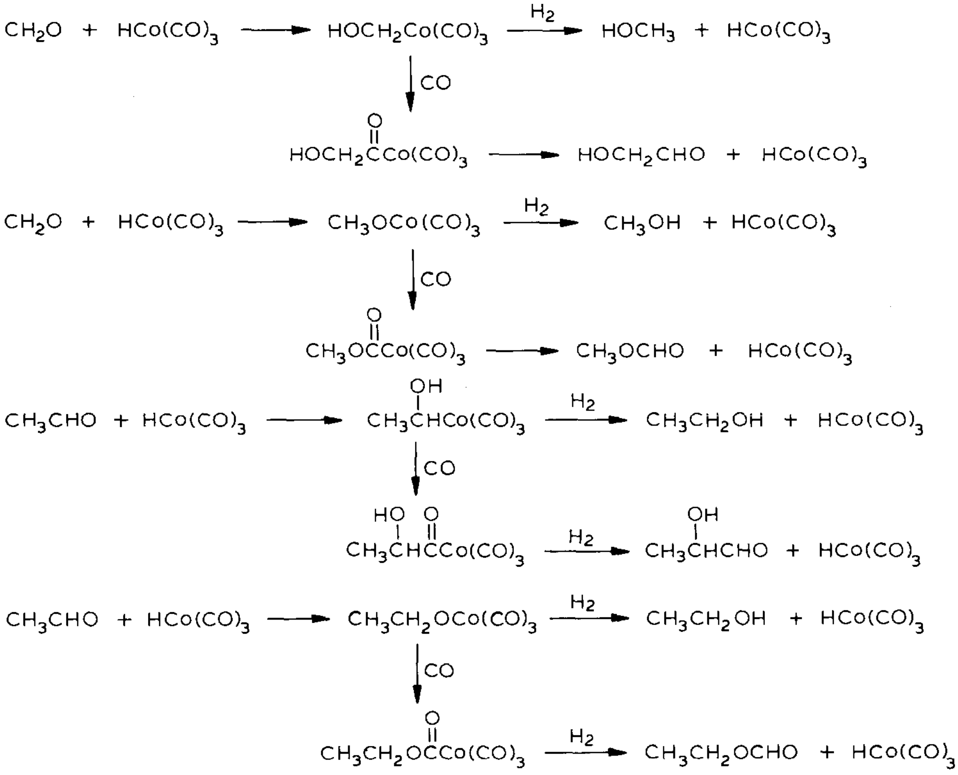
Scheme XXVII

include the extent of poisoning by oxygen of the $[\mathrm{HCo(CO)_4}]$-catalyzed hydroxycarbonylation of ethylene (ref. 167), the effect of added $[\mathrm{Fe(CO)_5}]$ on the $[\mathrm{HCo(CO)_3(PBu^n{}_3)}]$-catalyzed hydroformylation of propene (ref. 168) and a theoretical treatment of $[\mathrm{HCo(CO)_4}]$-catalyzed propene hydroformylation (ref. 169). In the second study the catalyst activity is decreased to a minimum at Fe/Co = 1 presumably because of the formation of an inactive iron-cobalt complex while in the third, it is concluded that the aldehyde isomer ratio is determined by the extent to which non-bonded interactions influence the insertion of the olefin into the Co-H bond.

An extensive study of the use of $[\mathrm{Co_2(CO)_8}]$ and $[\mathrm{Rh(CO)_2acac}]$ as catalyst precursors for the hydrogenation of carbon monoxide in tetraglyme. For the cobalt system it is proposed that the ethylene glycol and methanol products derive from a common intermediate and that cluster formation is unimportant. Cluster species appear to be significant in the rhodium system however. Both catalyst systems convert paraformaldehyde to methanol and ethylene glycol. Thus it is proposed that formaldehyde is a possible intermediate in the catalytic sequence although since 1,3-dioxolane is seen under some conditions the formaldehyde is considered to not always be coordinated to the metal. Possible reaction paths are presented in Scheme XXVIII (ref. 170). The geometries of possible intermediates in the cobalt system have been investigated theoretically with the preferred geometry for $[\mathrm{Co(CO)_3CHO}]$ being square planar. For $[\mathrm{Co(H)_2(CO)_3CHO}]$ the <u>mer</u> and <u>fac</u> isomers are nearly of the same energy while for $[\mathrm{CoH(CO)_3CH_2O}]$ a square pyramidal geometry with an apical monohapto $\mathrm{CH_2O}$ group is preferred to a considerable extent over one with this group bound as a hydroxycarbene (ref. 171).

Reaction of $\mathrm{Na[Co(CO)_4]}$ with $\mathrm{RO_2CCH_2X}$ (R = Et, $\mathrm{Bu^t}$, $\mathrm{PhCH_2}$, (S)-(-)-2-MeBu, (1R,3R,4S)-(-)-menthyl(Men*); X = Cl, Br) yields $[\mathrm{RO_2CCH_2Co(CO)_4}]$ rather than $[\mathrm{ROOCCH_2C(O)Co(CO)_3}]$ as has been proposed previously (ref. 173b). The products are in fact unreactive towards carbon monoxide but do react with Group V ligands

(L = PPh_3, $AsPh_3$, $SbPh_3$) at 0° C to give mixtures of $[RO_2CCH_2Co(CO)_3L]$ and $[RO_2CCH_2C(O)Co(CO)_3L]$. On warming to room temperature, the acyl complex reverts to the alkyl species. The CD spectra of $[Men^*O_2CCH_2Co(CO)_3L]$ (L = PPh_2Men^*, PPh_3) have been measured and the complexes found to display significantly greater optical rotations than the chiral starting materials suggesting the existence of chiral rotomers in solution (refs. 172, 173a). Reduction of Co(II) acetate by sodium hydride in the presence of sodium tert-amylate (t-AmONa) and carbon monoxide in THF gives high yields of $Na[Co(CO)_4]$ and the heterogeneous mixture is an effective catalyst for the carbonylation of aryl halides. An $S_{RN}1$ mechanism (Scheme XXIX) is proposed and although the electron source was not definitely identified, sodium hydride is considered important to the initiation step. An active photostimulated catalyst system for the same process is $Na[Co(CO)_4]$/t-AmONa/CO for which the mechanism of Scheme XXX is proposed. Finally, reaction of $[Co_2(CO)_8]$ with NaH/t-AmONa/CO in THF is reported as a convenient synthesis of $Na[Co(CO)_4]$ (ref. 174).



$$CH_2O + HCo(CO)_3 \longrightarrow HOCH_2Co(CO)_3 \xrightarrow{H_2} HOCH_3 + HCo(CO)_3$$
$$HOCH_2Co(CO)_3 \xrightarrow{CO} HOCH_2\overset{O}{\overset{\|}{C}}Co(CO)_3 \longrightarrow HOCH_2CHO + HCo(CO)_3$$
$$CH_2O + HCo(CO)_3 \longrightarrow CH_3OCo(CO)_3 \xrightarrow{H_2} CH_3OH + HCo(CO)_3$$
$$CH_3OCo(CO)_3 \xrightarrow{CO} CH_3O\overset{O}{\overset{\|}{C}}Co(CO)_3 \longrightarrow CH_3OCHO + HCo(CO)_3$$
$$CH_3CHO + HCo(CO)_3 \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCo(CO)_3 \xrightarrow{H_2} CH_3CH_2OH + HCo(CO)_3$$
$$CH_3\overset{OH}{\overset{|}{C}}HCo(CO)_3 \xrightarrow{CO} CH_3\overset{HO}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}Co(CO)_3 \xrightarrow{H_2} CH_3\overset{OH}{\overset{|}{C}}HCHO + HCo(CO)_3$$
$$CH_3CHO + HCo(CO)_3 \longrightarrow CH_3CH_2OCo(CO)_3 \xrightarrow{H_2} CH_3CH_2OH + HCo(CO)_3$$
$$CH_3CH_2OCo(CO)_3 \xrightarrow{CO} CH_3CH_2O\overset{O}{\overset{\|}{C}}Co(CO)_3 \xrightarrow{H_2} CH_3CH_2OCHO + HCo(CO)_3$$

Scheme XXVIII

$$[\text{electron source}] + ArX \longrightarrow ArX^{\dot{-}} \longrightarrow Ar^{\cdot} + X^{-}$$

$$Ar^{\cdot} + Co(CO)_4^{-} \longrightarrow ArCo(CO)_4^{\dot{-}}$$

$$\begin{tikzcd} ArX + ArCo(CO)_4^{\dot{-}} \arrow[r] & ArCo(CO)_4 \arrow[d] & + ArX^{\dot{-}} \arrow[d] \\ & \text{Carbonylation Products} & \text{Propagation} \end{tikzcd}$$

Scheme XXIX

Initiation step

$$C_6H_5Br + NaCo(CO)_4 \rightleftharpoons C_6H_5Br,NaCo(CO)_4 \xrightarrow{h\nu} [C_6H_5Br]^{\dot{-}}Na^{+} + {\cdot}Co(CO)_4$$

$$\text{or } NaCo(CO)_4 \xrightarrow{h\nu} [NaCo(CO)_4]^{*} \xrightarrow{C_6H_5Br}$$

Propagation steps

$$[C_6H_5Br]^{\dot{-}}Na^{+} \longrightarrow C_6H_5^{\cdot} + NaBr$$

$$C_6H_5^{\cdot} + NaCo(CO)_4 \longrightarrow [C_6H_5CoCO_4]^{\dot{-}}Na^{+}$$

$$[C_6H_5Co(CO)_4]^{\dot{-}}Na^{+} + C_6H_5Br \longrightarrow C_6H_5Co(CO)_4 + [C_6H_5Br]^{\dot{-}}$$

$$C_6H_5Co(CO)_4 + CO \longrightarrow C_6H_5COCo(CO)_4$$

$$C_6H_5COCo(CO)_4 + \underline{t}\text{-AmONa} \longrightarrow C_6H_5COO\underline{t}\text{-Am} + NaCo(CO)_4$$

Termination steps

$$C_6H_5Co(CO)_4 \longrightarrow C_6H_5^{\cdot} + {\cdot}Co(CO)_4$$

$$C_6H_5^{\cdot} + THF \longrightarrow C_6H_6$$

$$C_6H_5COCo(CO)_4 \longrightarrow C_6H_5CO^{\cdot} + {\cdot}Co(CO)_4$$

$$C_6H_5CO^{\cdot} + THF \longrightarrow C_6H_5CHO$$

Hydrolysis

$$\begin{tikzcd} C_6H_5COCo(CO)_4 + NaOH \arrow[r] & C_6H_5COOH + NaCo(CO)_4 \arrow[d, "NaOH"] \\ & C_6H_5COONa + H_2O \end{tikzcd}$$

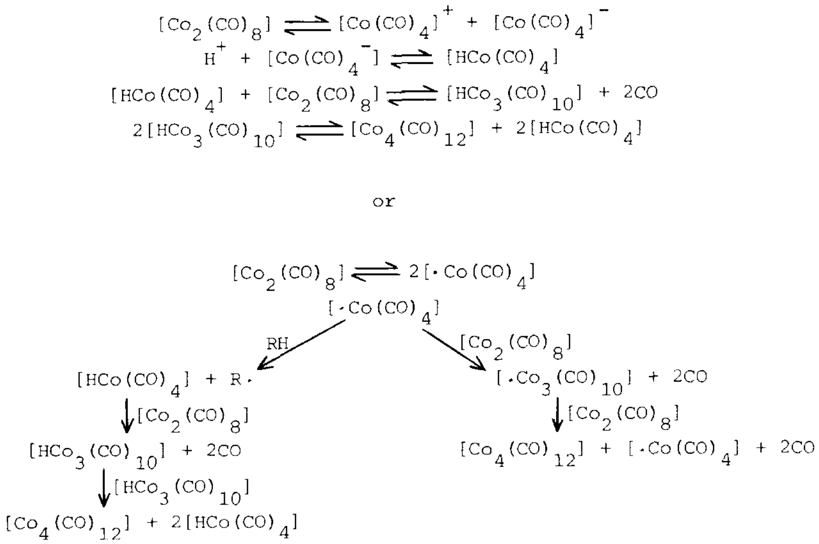
Scheme XXX

Electrolysis of pyridine solutions of tertiary phosphines containing tetrabutylammonium bromide in a carbon monoxide atmosphere at a cobalt anode produces $[Co(CO)_4]^-$, $[CoBr(CO)_2L_2]$, $[Co_2(CO)_5L_3]$ and $[Co_2(CO)_4L_4]$ ($L = PMe_3$). In the presence of triphenylphosphine, only $[Co(CO)_4]^-$ is formed (ref. 175). Vacuum pyrolysis of $[Co(CO)_3(PBu^n_3)_2][Co(CO)_4]$ is reported as a convenient synthesis of $[Co(CO)_3PBu^n_3]_2$ (ref. 176). The photocatalytic hydroformylation of propene in methanol containing Co(II) acetate and tri-n-butylphosphine produces n-butyraldehyde almost exclusively. The same reaction using $[Co_2(CO)_8]$ proceeds more rapidly but gives roughly equal amounts of straight- and branched-chain aldehyde and is unaffected by irradiation (ref. 177).

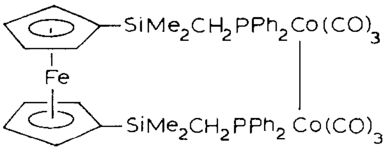
Infrared studies indicate that solutions of Na[Co(CO)$_4$] in moist ether show a weak association of the ions which is increased as the solution is dried by adding sodium. Addition of tetrabutylammonium ion yields a spectrum characteristic of an undistorted [Co(CO)$_4$]$^-$ ion and [Bu$^n{}_4$N][Co(CO)$_4$] then precipitates. Addition of lithium ion to the dried Na[Co(CO)$_4$] solution gives a tight ion-pair, Li$^+$...-{Co(CO)$_4$$^-$}which is disrupted on subsequent addition of water. Some evidence for [Co$_3$(CO)$_{10}$]$^-$ in these solutions is also found (ref. 178). The photochemistry of {Co(CO)$_4$} moieties attached to silica surfaces has been studied by Fourier-transform infrared, photoacoustic spectroscopy. Labelling studies indicate that the primary process following excitation is CO dissociation. At -50° C in the presence of olefins an anchored {Co(CO)$_3$(olefin)} species appears to form. The technique used for detection of surface species is proposed to have comparable specificity to infrared spectroscopy in solution (refs. 179,180). A number of other studies of supported cobalt species have appeared. Using CO and CO/H$_2$ mixtures and CoO supported on alumina, terminal carbonyl groups bound to Co^{2+} ions and to Co in oxygen-rich and oxygen-poor environments have been identified. Also bridging carbonyls and {H-Co-CO} moieties are seen (ref. 181). With MgO-supported CoO, mono- and polynuclear cobalt carbonyl species are detected (ref. 182). Cobalt carbonyls supported on large-pore silica are catalysts for carbon monoxide hydrogenation with the surface area of the support having only minimal effect on the activity (ref. 183).

The kinetics of the conversion of [Co$_2$(CO)$_8$] to [Co$_4$(CO)$_{12}$] have been studied and the data are considered to be inconsistent with the dimerization of [Co$_2$(CO)$_6$] units. The rate is very dependent on reaction conditions and inhibition by CO is observed. A modest acceleration by irradiation and a significant acceleration by ethanol are observed although no ethanol-derived products are seen. Evidence for autocatalysis and autoinhibition is reported leading to the postulate of the mechanism of Scheme XXXI (ref. 184). The steric and electronic effects on the mechanism of substitution of [Co$_2$(CO)$_8$] by PR$_3$ (R = Pr^i, Bu^t, CH$_2$CH$_2$CN) have been studied. For the latter two ligands, the reaction proceeds by a rate-determining loss of CO from [Co$_2$(CO)$_8$] while for the first a radical chain mechanism, previously proposed for the reaction with tri-n-butylphosphine (see 1980 Annual Survey), is operative. The slower rate with triisopropylphosphine is attributed to steric inhibition of either the preequilibrium or of the electron-transfer step. It is concluded that the radical mechanism will occur if possible but if the entering ligand is too bulky to associate with [Co$_2$(CO)$_8$] (e.g. PBu$^t{}_3$) or is insufficiently basic to initiate Co-Co cleavage following association (e.g. P(CH$_2$CH$_2$CN)$_3$) then the CO-dissociation mechanism occurs by default (ref. 185). Reaction of [Co$_2$(CO)$_8$] with 1,1'-bis(diphenylphosphinomethyldimethylsilyl)ferrocene yields [26] which can be reduced to [27] with potassium hydride or oxidized to 1,1'-bis(diphenylphosphorylmethyldimethylsilyl)ferrocene by oxygen (ref. 186). Treatment of

$[(\eta^6\text{-}1,4\text{-}(SiMe_2H)_2C_6H_4)Cr(CO)_3]$ with $[Co_2(CO)_8]$ yields $[(\eta^6\text{-}1,4\text{-}(SiMe_2Co(CO)_4)_2\text{-}C_6H_4)Cr(CO)_3]$ while with $1,4\text{-}(SiMe_2H)_2C_6H_4$ itself, $[1,4\text{-}(SiMe_2Co(CO)_4)_2C_6H_4]$ is obtained. The former complex appears more stable (ref. 187). Coordination of a $\{Co(CO)_4\}$ moiety to ytterbium through the oxygen atom of a carbonyl group occurs in $[cp'_2Yb(THF)(OCCo(CO)_3)]$ prepared from $[cp'_2Yb(OEt)_2]$ and $[Co_2(CO)_8]$ in toluene followed by recrystallization from THF (ref. 188). Sulfur-capped trinuclear cobalt clusters are formed from $[Co_2(CO)_8]$ and thioamides, RC(S)NHR' (R = Me, Ph; R' = cy), [28] or dimethylthiocarbamoyl chloride [29]. In [28], both the capping sulfur atom and the RCNR' moiety are thought to derive from the same thioamide molecule (refs. 189, 190).



Scheme XXXI



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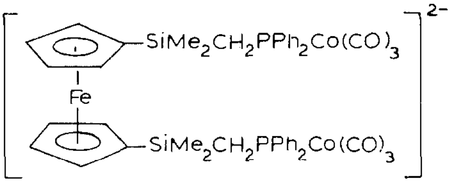

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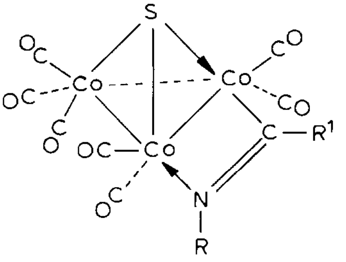

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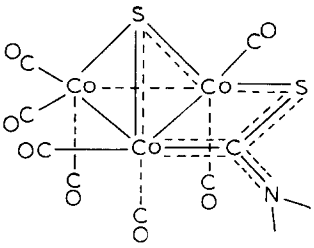


[29]

A convenient synthesis of $Et_4N[Co(CO)_4]$ by the phase transfer-catalyzed reduction of $[Co_2(CO)_8]$ with sodium borohydride has been reported (ref. 191). Also in this area are examples of the carbonylation of aryl and vinyl bromides to unsaturated acids using $[Co_2(CO)_8]/MeOH/C_6H_6/Bu^n{}_4NBr$ as the transfer catalyst under photolytic conditions (ref. 192), the regiospecific acylation (adjacent to the exocyclic double bond) of fulvenes using methyl iodide and carbon monoxide in the presence of $[Co_2(CO)_8]/PhCH_2Et_3NCl/NaOH/H_2O/C_6H_6$ (ref. 193) and the conversion of allenes to unsaturated hydroxyketones and dienones using methyl iodide and carbon monoxide catalyzed by $[Co_2(CO)_8]/cetylMe_3NBr/NaOH/H_2O/C_6H_6$ (ref. 194).

The isomerization of octenes catalyzed by $[Co_2(CO)_8]$ is enhanced by γ-irradiation using a ^{60}Co source. Since the product distribution is unaffected by the irradiation, an increase in the concentration of active species such as $[\cdot Co(CO)_4]$ or $[Co_2(CO)_7]$ is proposed (ref. 195). A variety of cobalt-based catalyst systems operating under hydroformylation conditions have been described. A $[Co_2(CO)_8]/$ diphos (diphos = 1,2-bis(diphenylphosphino)ethane) (ca. 1:0.75) mixture catalyzes the hydrogenation of α, β-unsaturated ketones and aldehydes (ref. 196) while $[Co_2(CO)_8]$ and diphos or $Ph_2PC{\equiv}CPPh_2$ are effective catalysts for the hydroformylation of allyl acetate and allyl formate (ref. 197). In related systems, aqueous dioxane functions as the hydrogen source under water-gas-shift conditions to catalyze the conversion of propene and ethylene to dipropyl- and diethyl ketone respectively at high olefin concentrations (refs. 198, 199) while at lower olefin concentrations the major product from propene is butyraldehyde (ref. 200). Although, as mentioned earlier, $[Fe(CO)_5]$ inhibits hydroformylation catalyzed by

$[HCo(CO)_3(PBu^n{}_3)]$, a catalyst mixture prepared from $[Co_2(CO)_8]$, $[Fe(CO)_5]$ and N-methylpyrrolidine has been found to be effective for the hydroformylation of C_{11} olefins (ref. 201).

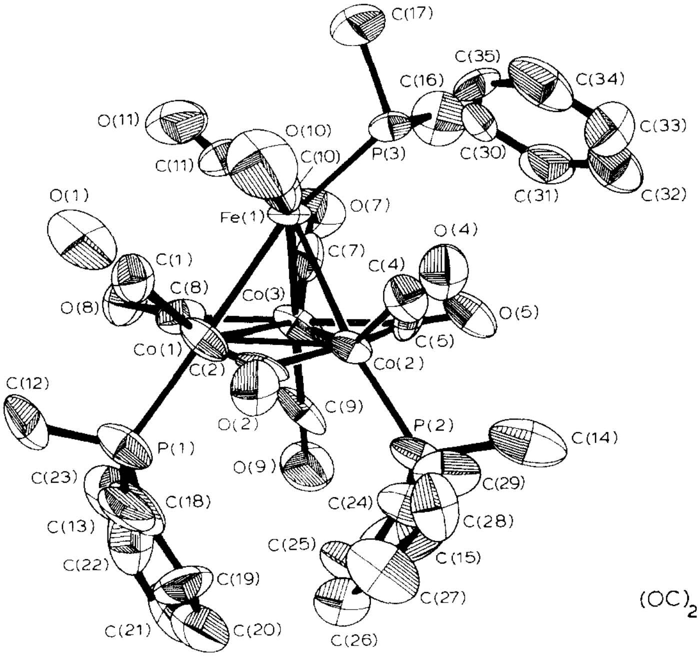
The use of ^{13}C labelling studies to probe the course of carbon monoxide hydrogenation using $[Co_4(CO)_{12}]$ as the catalyst precursor in glyme-type solvents showed that only about 5% of the ethanol produced originated wholly from carbon monoxide. The rest appeared to derive from the reaction of solvent fragments with the initial reduction products (ref. 202). Unlike some systems mentioned earlier, the hydroformylation of oct-1-ene and cyclohexene catalyzed by species derived from $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$ is strongly inhibited when the reaction mixture is photolyzed. This is proposed to result from the interception of $[HCo(CO)_4]$ by $[\cdot Co(CO)_4]$ produced by the photolysis. It was also found that irradiation of methylcyclohexane solutions of $[Co_2(CO)_6(PBu^n{}_3)_2]$ in the presence of $HSi(OEt)_3$ or under an atmosphere of carbon monoxide and hydrogen does not yield $[HCo(CO)_3(PBu^n{}_3)]$ implying that 17-electron species such as $[\cdot Co(CO)_3(PBu^n{}_3)]$ are unable to activate hydrogen, carbon monoxide or to abstract hydrogen from silanes or solvent (ref. 203). The reactivity of isomeric n-dodecenes towards hydroformylation in the presence of $[Co_2(CO)_8]$ and $[RhH(CO)(PPh_3)_3]$ shows that the selectivity for the α-olefin is significantly higher for rhodium than for cobalt presumably reflecting differences in the ease of access of the various olefins to the active site (ref. 204). The hydroformylation of C_{10}-C_{13} alkenes catalyzed by $[Co_2(CO)_8]/PBu^n{}_3$ mixtures, the hydrocarboxylation of (Z)-cis-1,4-hexadiene catalyzed by $[Co_2(CO)_8]$ in the presence of γ-picoline and the hydrocarboxylation of ethylene in ketonic solvents have also been reported (refs. 205-207).

The effectiveness of additives varying in σ-donor and π-donor or π-acceptor ability on the $[Co_2(CO)_8]$-catalyzed hydrosilylation of olefins has been studied. The results are discussed in terms of the effects of the additives on the stabilities of intermediates and/or transition states in the reaction (ref. 208). The preparation of anchored $\{SiCo(CO)_4\}$ moieties on the surface of silica or alumina has been achieved by reacting $[Co_2(CO)_8]$ with Si-H functionalities on the surface. Photolysis in the presence of triphenylphosphite yields a supported $\{SiCo(CO)_3(P(OPh)_3)\}$ moiety while in the presence of triethylsilane, $[Et_3SiCo(CO)_4]$ is liberated. Photolysis in the presence of pent-1-ene gives free $[Co_4(CO)_{12}]$ and a surface-bound pentenylsilyl moiety while in the presence of both pent-1-ene and triethylsilane, isomerization of the pentene occurs together with the formation of pentyltriethylsilane and small amounts of pentane. As this is basically what is observed when the same reaction is run using free $[R_3SiCo(CO)_4]$, the photocatalysis is considered to be due to the release of $\{Co(CO)_n\}$ fragments from the surface. The supported species however is easier to handle (ref. 209). Grafting of 4-vinylpyridine onto polypropylene provides a means of heterogenizing cobalt carbonyls for use as hydroformylation catalysts. They are reported to be of comparable activity to analogous homogeneous systems and provide much better selectivity to straight-chain aldehyde products. The selectivity is thought to be influenced by both the pendant pyridyl group and the polymer backbone (ref. 210). [$Co_2(CO)_8$] supported on NaY zeolite catalyzes the hydrogenation of carbon monoxide at 250° C giving 42% conversion to methane plus a mixture of other hydrocarbons up to C_{10} (ref. 211). The same complex supported on alumina provides a stoichiometric process for the room temperature reduction of nitroarenes to the corresponding anilines. A small amount of coupling product is also observed and this contrasts with the homogeneous reaction where the coupling product is the major species produced. The fact that the yield of amine decreased when the alumina is dried at high temperature is interpreted as indicating that cobalt hydride species are produced _via_ CO_2 loss from a metallocarboxylic acid generated from the attack of surface hydroxyl groups on a coordinated carbonyl group (ref. 212).

Two syntheses of [$Co_2(CO)_8$] have been reported. These involve high pressure carbonylation of [$Co(O_2CR)_2$] (R = Me, CF_3, $C_{16}H_{31}$) (ref. 213) and the γ-irradiation (^{60}Co source) of cobalt(II) hydroxide in the presence of carbon monoxide (ref.214). An autocatalytic mechanism involving radiochemically produced solvent radicals is proposed in the latter case.

The laser photodissociation of [$Co_2(CO)_8$] in the gas phase yields Co^+ and Co_2^+ species in a 10:1 ratio. The data are more consistent with the dimeric ion arising from ionization of a Co_2 fragment than from combination of cobalt atoms with cobalt ions. This method is proposed to be an efficient means of producing bare metal clusters in the gas phase (ref. 215). The He(I) and He(II) photoelectron spectra (PES) of [$Co_4(CO)_{12}$] in the gas phase have been measured but the quality of the spectrum was poor. The absence of a band at _ca_. 10.5 ev previously observed in the solid-state spectrum was taken to indicate that this band may have been due to a surface species and not to [$Co_4(CO)_{12}$]. Attempts to obtain spectra of the rhodium and iridium analogs were foiled by decomposition (ref. 216). The ESR spectrum of [$Co_2(CO)_6(PBu^n{}_3)_2]^{\dot{-}}$ has been measured and it was found that a multi-configuration ground state including spin-polarization terms was required to model the experimental results (ref. 217). The effects of substitutents on the "flap angle" (dihedral angle of the two Co(μ-CO)Co planes) in derivatives of [$Co_2(CO)_8$] have been explored using extended Hückel calculations. The complexes studied were [$Co_2(CO)_6(C_2H_4)_2$], [$Co_2(CO)_4$(_cis_-$C_4H_6)_2$] and [$cp_2Co_2(CO)_2$] for both _cis_ and _trans_ isomers. Only the _cis_ isomers were puckered and the extent was dependent on the substituent (_cis_-$C_4H_6 > C_2H_4 >$ cp) but not on the number of carbonyl groups replaced (ref. 218).

In the area of alkylidenenonacarbonyltricobalt complexes, is found first a synthesis of [$RCCo_3(CO)_9$] (R = mesityl) by prolonged reaction of 2,4,6-$Me_3C_6H_2$-COCl with Na[$Co(CO)_4$]. In the same paper, Na[$Co(CO)_4$] is reported to react with Me_2PCl_3 to give [$Co_4(CO)_{12}$] plus [30] and with iron(III) chloride followed by addition of dimethylphenylphosphine to yield $[Co_2(CO)_6(PMe_2Ph)_2]$ and [31] (ref. 219). The latter complex contains a hydride presumably bridging an Fe-Co bond but it was not located crystallographically. A one-step phase-transfer catalyzed synthesis of $[YCCo_3(CO)_9]$ from CX_3Y (X = Y = Cl, Br; X = Br, Y = H) and $[Co(H_2O)_6](NO_3)_2$ involves treatment of the Co(II) salt with sodium dithionite and carbon monoxide in aqueous ammonia followed by CX_3Y in the presence of benzene and $[(cetyl)Me_3N]Br$ as the phase-transfer agent (ref. 220). After one day, the reaction of $Na[Co(CO)_4]$ with $Me_2ClSiSiClMe_2$ gives $[Me_2ClSiSiMe_2Co(CO)_4]$ as an oil. However on prolonged reaction (∿1 week), $[(CO)_3Co(\mu\text{-}SiMe_2)_2Co(CO)_3]$ and [32] are formed. Complex [32] can also be formed from $[Me_2ClSiSiMe_2Co(CO)_4]$ and $Na[OCCo_3(CO)_9]$ (ref. 221). Hydrogenation of $[RC(O)CCo_3(CO)_9]$ in benzene under carbon monoxide yields $[RCH_2CCo_3(CO)_9]$ (R = H) or $[RCH(OH)CCo_3(CO)_9]$ [R = Me, Et, Bu^n, Ph, p-XC_6H_4 (X = Br, Cl, F, Me)). In the presence of acid the yield of alcohol is



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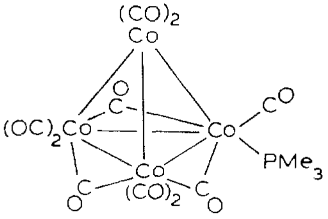

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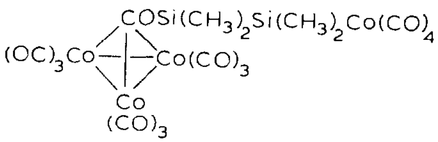
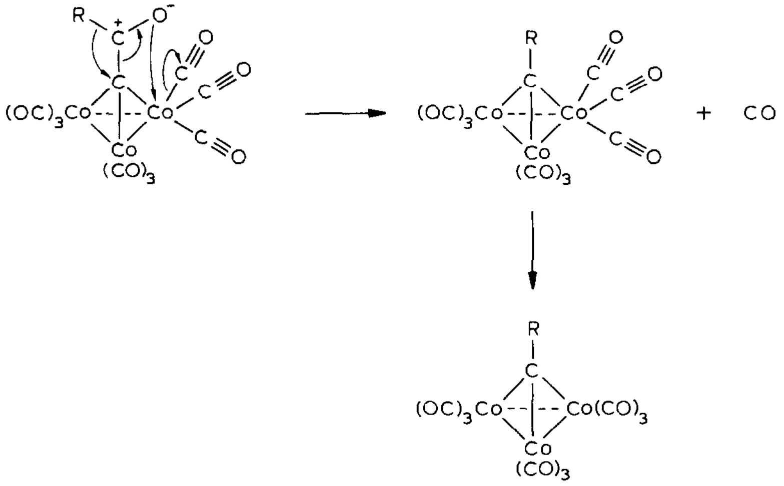
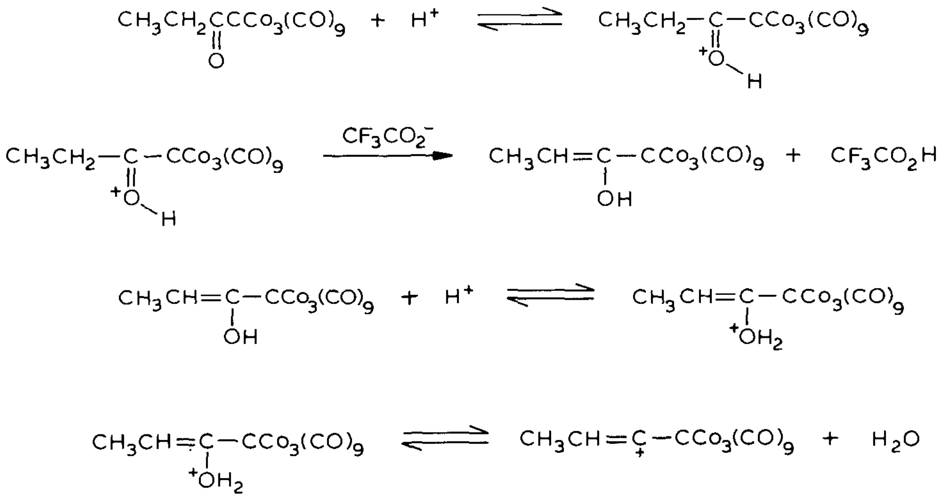


[32]

increased while on heating the alcohols in base reconversion to the ketones occurs. Heating the ketones under nitrogen leads to decarbonylation to [$RCCo_3(CO)_9$]. The proposed mechanisms for the various reactions are given in Schemes XXXII - XXXIV (ref. 222). Treatment of Li[$Co_3(CO)_{10}$]·Et_2O with diphenyl ether in vacuo yields the unsolvated species which on protonation at -80° C with HCl in toluene, briefly warming to -17° C and subsequent carbonylation at -65° C yields the thermally unstable complex [$HOCCo_3(CO)_9$]. The triethylamine adduct of this complex can be synthesized from [$Et_3N{\cdot}HCo(CO)_4$] and [$Co_2(CO)_8$] and this together with other studies indicates that the interconversions of Scheme XXXV occur. It is proposed that



Scheme XXXII



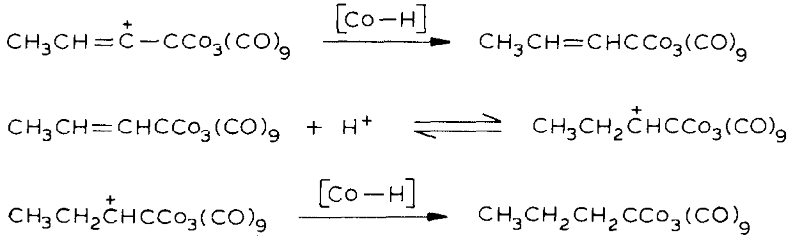
$$CH_3CH_2\underset{\underset{O}{\|}}{C}CCo_3(CO)_9 + H^+ \rightleftharpoons CH_3CH_2{-}\underset{\underset{{}^+O{\diagdown}H}{\|}}{C}{-}CCo_3(CO)_9$$

$$CH_3CH_2{-}\underset{\underset{{}^+O{\diagdown}H}{\|}}{C}{-}CCo_3(CO)_9 \xrightarrow{CF_3CO_2^-} CH_3CH{=}\underset{\underset{OH}{|}}{C}{-}CCo_3(CO)_9 + CF_3CO_2H$$

$$CH_3CH{=}\underset{\underset{OH}{|}}{C}{-}CCo_3(CO)_9 + H^+ \rightleftharpoons CH_3CH{=}\underset{\underset{{}^+OH_2}{|}}{C}{-}CCo_3(CO)_9$$

$$CH_3CH{=}\underset{\underset{{}^+OH_2}{|}}{C}{-}CCo_3(CO)_9 \rightleftharpoons CH_3CH{=}\underset{+}{C}{-}CCo_3(CO)_9 + H_2O$$

Scheme XXXIII

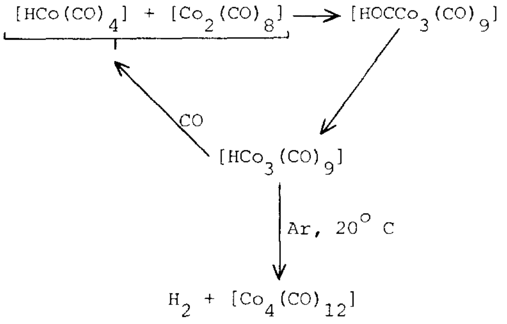


$$CH_3CH{=}\overset{+}{C}{-}CCo_3(CO)_9 \xrightarrow{[Co-H]} CH_3CH{=}CHCCo_3(CO)_9$$

$$CH_3CH{=}CHCCo_3(CO)_9 + H^+ \rightleftharpoons CH_3CH_2\overset{+}{C}HCCo_3(CO)_9$$

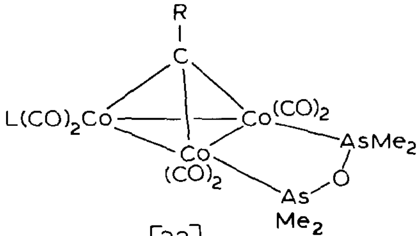
$$CH_3CH_2\overset{+}{C}HCCo_3(CO)_9 \xrightarrow{[Co-H]} CH_3CH_2CH_2CCo_3(CO)_9$$

Scheme XXXIV



Scheme XXXV

$[HOCCo_3(CO)_9]$ is a model for the hydrogenation of carbon monoxide to methanol (refs. 223, 224). In a related study $[XCCo_3(CO)_9]$ ($X = MeO, H, Bu^n$) was hydroformylated in the presence of $[Co_2(CO)_8]$ to yield $[HCo(CO)_4]$ and $[Co_2(CO)_8]$ as the metal-containing products. For X = MeO, dimethyl ether and 2-methoxyethanol were also obtained while for X = H or Bu^n, C_2 and C_6 aldehydes resulted. In the latter case, prolonged reaction reduced the aldehydes to alcohols (ref. 225). Silyl substituted alkylidynenonacarbonyltricobalt complexes can be prepared by reaction of chlorosilanes with $[HCCo_3(CO)_9]$. Subsequent reaction of $[MePhSiClCCo_3(CO)_9]$ with methanol yielded $[MePhSi(OMe)CCo_3(CO)_9]$ which could be fluorinated to $[MePhSiFCCo_3(CO)_9]$ with $BF_3{\cdot}Et_2O$ and reduced to $[MePhSiHCCo_3(CO)_9]$ with diisobutylaluminum hydride. However reduction with lithium aluminum hydride only decomposed the complex. Although $Me_2Si[CCo_3(CO)_9]_2$ could not be synthesized, the original synthesis using $MeSiCl_2H$ gave $[MeSiCl_2CCo_3(CO)_9]$ which could be converted into $[MeSi(OMe)_2CCo_3(CO)_9]$ and then $[MeSiF_2CCo_3(CO)_9]$ as described above. Optically active analogs, $[MePh(1\text{-naphthyl})ECCo_3(CO)_9]$ (E = Si, Ge) were also synthesized by analogous procedures (ref. 226). The series $[RCCo_3(CO)_{9-n}L_n]$ (R = $CONMe_2$, Cl, H, Me, Ph; L = PMe_3, $P(OMe)_3$; n = 0-2) on reaction with dimethylaminodimethylarsine give extremely moisture-sensitive products which generally hydrolyzed on workup to species containing $(Me_2As)_2O$ (e.g. [33]) although an impure sample of $[MeCCo_3(CO)_8$-$(Me_2AsNMe_2)]$ was identified. Direct reaction of $[RCCo_3(CO)_9]$ with $(Me_2As)_2O$ yielded mixtures of [34] and [35]. Redistribution reactions to give [36] were also



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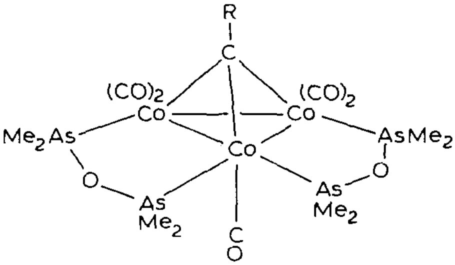

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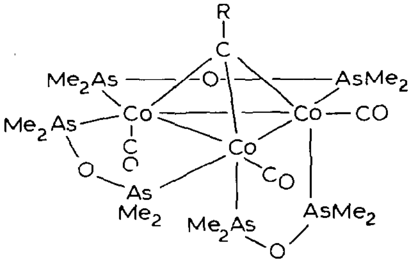

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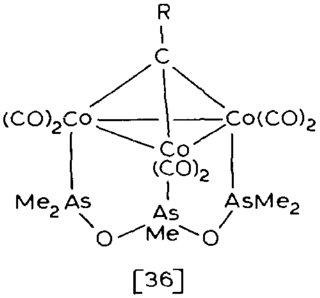


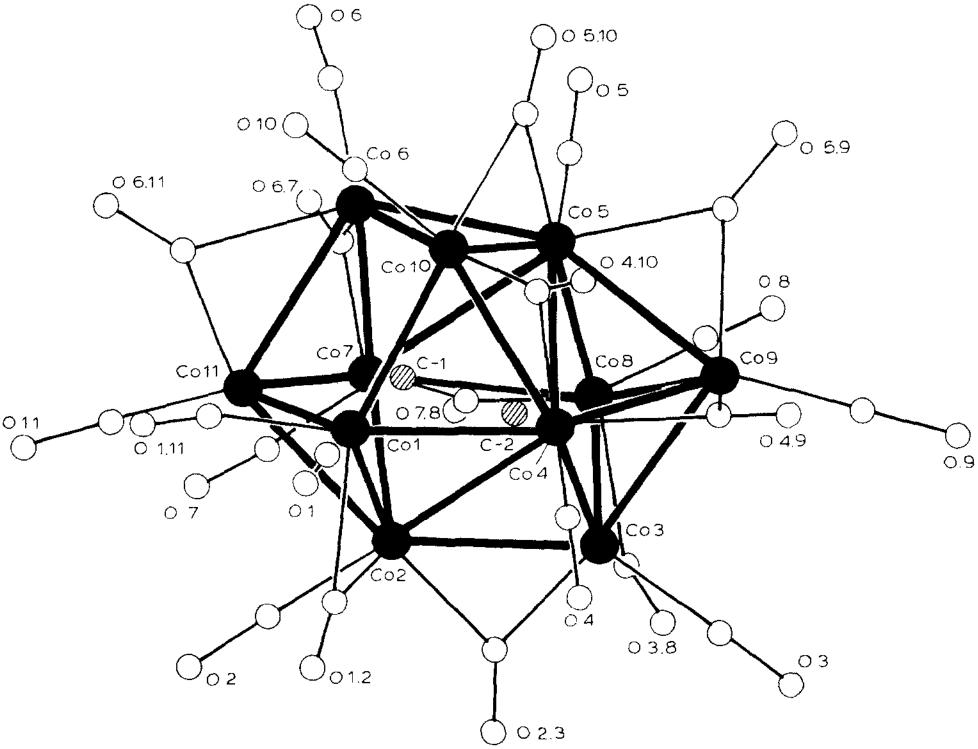
[36]

observed (ref. 227). The "permetallated" isocyanide $[(CO)_5CrC{\equiv}NCCo_3(CO)_9]$ has been synthesized from $[Cr(CO)_5(CNCCl_3)]$ and $[Co_2(CO)_8]$ while the analogous species $[(PPh_3)Cl_2PtC{\equiv}NCCo_3(CO)_9]$ is obtained from $[Pt(C_2H_4)(PPh_3)_2]$ and $[Cl_2CNCCo_3(CO)_9]$ which in turn was synthesized from $[CO_2(CO)_8]$ and $Cl_3CN{=}CCl_2$ (ref. 228). Although the alkalidynenonacarbonyltricobalt compounds are numerous, efforts to prepare rhodium analogs have generally been unsuccessful. Thus reactions of $Na[Rh(CO)_2(PPh_3)_2]$ with tetra- or trihalomethanes or trichloroacetyl chloride yielded only $[RhX(CO)(PPh_3)_2]$ or $[RhCl_3(CO)(PPh_3)_2]$ with the high thermodynamic stability of these monomeric species apparently dominating the course of the reaction. Reaction of the rhodium anion with several perfluoroacid anhydrides gave $[Rh(CO)_2(PPh_3)_2COR]$ ($R = CF_3$, C_2F_5, $\underline{n}$-C_3F_7) which did not undergo any rearrangement even on heating to 120° C (ref. 229). The complexes $[ECo_3(CO)_9]$ function as ligands and from $[M(CO)_y(THF)]$ one obtains $[(CO)_yMECo_3(CO)_9]$ (E = P, As; M = Fe; y = 4. E = As; M = Mo, W; y = 5). Analogous reactions with $[E_2Co_2(CO)_6]$ were unsuccessful, however, on photolysis of this complex in the presence of $[M(CO)_6]$ a mixture of $[(CO)_5MECo_3(CO)_9]$ and $[E_3Co_9(CO)_{24}]$ (E = P; M = Cr, Mo, W. E = As; M = W) was obtained. Similarly, $[As_3Co(CO)_3]$ failed to react with $[W(CO)_6]$ or $[W(CO)_5(THF)]$ but when it was photolyzed in the presence of $[Co_2(CO)_8]$ and $[W(CO)_6]$, $[As_2Co_2(CO)_6]$, $[As_3Co_9(CO)_{24}]$ and $[(CO)_5WAsCo_3(CO)_9]$ were obtained. Finally, although no isolable products could be obtained from $[AsCo_3(CO)_9]$ and tertiary phosphines, it reacted readily with triphenylphosphite to yield $[AsCo_3(CO)_8(P(OPh)_3)]$ and $[As_2Co_2(CO)_5(P(OPh)_3)]$. The pattern of reactivity of these cobalt-pnicogen clusters appears to be that on reaction with electrophiles the products contain fewer pnicogen atoms while with nucleophiles they contain more. This is rationalized on the basis of the optimum filling of cluster orbitals (ref. 230).

Several groups have examined the ultraviolet and He(I) PES spectra of $[RCCo_3(CO)_9]$ (R = H, Me, OMe, F, Cl, Br, I). From these it is concluded that the cluster behaves as an electron sink capable of π-interaction with the apical substituent. In particular, the fact that the lowest energy band, attributed to ionization from a delocalized orbital which is Co-C and Co-Co bonding, appears at an energy more comparable to the appropriate band for $HC{\equiv}CX$ than to that for H_3CX (X = halogen) is interpreted to indicate that the bonding of the RC moiety to the $Co_3(CO)_9$ cluster is best described as a dative, two-electron, bond from an approximately sp-hybridized carbon to the Co_3 unit with the p orbitals on carbon forming multicenter π-bonds to it as well. It is further suggested that the hybridization on the apical carbon is determined primarily by the nature of the substituent, R, rather than by the number of metal atoms to which it is attached (refs. 231, 232). Comparison of the PES spectra of $[MeCCo_3(CO)_9]$ and the isoelectronic $[MeCFe_3(CO)_9(\mu\text{-}H)_3]$ suggests that the presence of the edge-bridging hydride ligands markedly stabilize orbitals which have significant amplitude between the metal atoms (ref. 233). For R = H, Me, the ionizations from the C-H portion correlate with the spectra of C-H units adsorbed on Ni and Pt surfaces if the C-H axis is not perpendicular to the surface while those from the C-Me portion correlate with the spectra of a C-Me unit normal to a Pt(1,1,1) face (ref. 234). Detailed vibrational analyses have been performed on $[RCCo_3(CO)_9]$ (R = H, D, Me, F, Cl, Br). For the halogen derivatives, the high value of the C-R stretch is attributed to substantial coupling with the symmetric Co-C stretch. For R = H, the ν_{C-H} and δ_{C-H} vibrations appear at energies quite comparable to those observed for acetylene adsorbed on Ni(1,1,1) suggesting the possibility that the chemisorbed species may be $\{HCNi_3\}$. Similarly for R = Me, the vibrations associated with the $MeCCo_3$ unit bear strong resemblences both in energy and intensity to those observed for ethylene chemisorbed on Pt(1,1,1) suggesting that the surface species may be a CH_3-C moiety (refs. 235-237). The Co-S stretching vibrations have been assigned for $[Co_3(CO)_9S]$ and $[cp_3Co_3S(CS)]$ and it appears that they are not significantly coupled to the Co-Co vibrations (ref. 238).

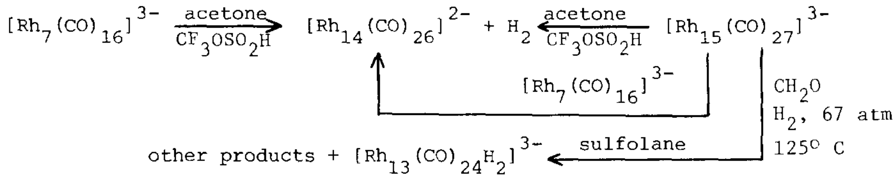
Room temperature reaction of $[Co_2(CO)_8]$ with carbon disulfide produces a plethora of products (at least 13) of which $[Co_6C(CO)_{12}S_2]$ was crystallographically characterized. The structure consists of a trigonal prism of $Co(CO)_2$ units with the carbide at the body-center and the triangular faces each capped by a sulfur atom (ref. 239). An excess of sodium acetylide in THF converts $[Co_4(CO)_{12}]$ into $[Co_6(CO)_{15}]^{2-}$ after a short reaction time but on prolonged contact, $[Co_6(CO)_{14}]^{4-}$ and $[Co(CO)_4]^-$ are formed (ref. 240). An alternate synthesis of $[Co_6(CO)_{16}]^{2-}$ involves electrochemical reduction of $[Co(acac)_3]$ in the presence of carbon monoxide and ethanol. In most instances however $[Co(CO)_4]^-$ is the major product (ref. 241). Protonation of aqueous $[Co_6(CO)_{15}]^{2-}$ by concentrated hydrochloric acid yields $[HCo_6(CO)_{15}]^-$. A neutron diffraction study of the bis(triphenylphosphine)-iminium (PPN^+) salt located the hydrogen atom at the center of the cluster. Ten of the carbonyl groups are terminally bound while the remainder are μ_2-bridging with all but one binding in an asymmetric fashion (ref. 242). Thermolysis of $Na_2[Co_6C(CO)_{15}]$ in diglyme produces several anionic clusters of which $[Co_{13}(C)_2(CO)_{24}]^{4-}$ and $[Co_{11}C_2(CO)_{22}]^{3-}$ have been isolated as benzyltrimethylammonium salts with the former being the major product. The structure of the latter showed it to be [37] (ref. 243).

A considerable amount of work on rhodium carbonyl clusters has been reported by the Union Carbide group. The usual starting rhodium complex is $[Rh(CO)_2(acac)]$ and the identity of the complexes produced is very dependent on reaction conditions. Prolonged reaction at 150° C under 1 atm of carbon monoxide in aqueous 18-crown-6 as the solvent and in the presence of cesium benzoate yields salts of $[Rh_{15}(CO)_{27}]^{3-}$ and $[Rh_{22}(CO)_{35}H_{x+n}]^{(5-n)-}$ (n = 0,1; x uncertain). A crystal of the latter fraction was found by x-ray diffraction to be $[Cs_9(crown)_{14}][Rh_{22}(CO)_{35}H_x]$-$[Rh_{22}(CO)_{35}H_{x+1}]$. The metal atom frameworks of the anions are fragments of a cubic-close-packed array of rhodium atoms. The presence of hydrogen atoms in the clusters was determined by proton NMR and observation of reversible changes in the carbonyl region of the infrared spectrum on treatment of the sample with acid or base (ref. 244). If the reaction is carried out in ethylene glycol as solvent at 15 atm pressure of a 1:1 mixture of carbon monoxide and hydrogen in the presence of N-methylmorpholine for 4 h, $[Cs(crown)]_3[Rh_{15}(CO)_{30}]$ is obtained. The structure consists of a body-centered-cubic array of rhodium atoms surrounded by six terminal

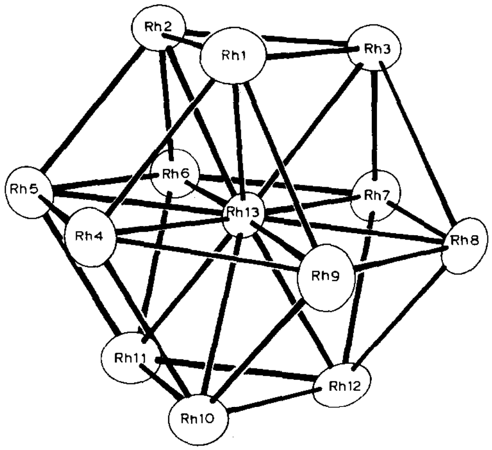


[37]

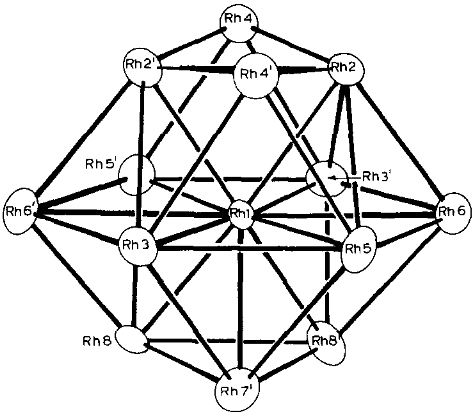
and twenty four doubly-bridging carbonyl ligands. It is proposed as an intermediate in the conversion of $[Rh_{15}(CO)_{27}]^{3-}$ to $[Rh_{14}(CO)_{25}]^{4-}$ (ref. 245). Support for this proposal comes from a study of a related system in which the crown ether is absent and the solvent is tetraglyme. Here $[Rh_{13}(CO)_{24}H_2]^{3-}$ forms within ten minutes but if the reaction is continued one obtains $[Rh_{15}(CO)_{27}]^{3-}$ after one hour and $[Rh_{14}(CO)_{25}H]^{3-}$ plus $[Rh_{14}(CO)_{25}]^{4-}$ after three hours. Related rhodium cluster chemistry is given in Scheme XXXVI. In this scheme, the counterion is PPN^+. However protonation of $Cs[Rh_{15}(CO)_{27}]$ with trifluoromethanesulfonic acid yields $[Rh_{22}(CO)_{35}H_x]^{(5-x)-}$ instead, indicating an influence of the counterion on the course of the reaction. The metal-atom polyhedra of $[Rh_{13}(CO)_{24}H_2]^{3-}$ and $[Rh_{14}(CO)_{26}]^{2-}$ are shown as [38] and [39] respectively (ref. 246). A new synthesis of $Cs_4[Rh_{14}(CO)_{25}]$ is reported together with the structure of the tetraethylammonium salt of this cluster. A ^{13}C NMR study of the cluster shows that all carbonyl groups become equivalent at 80° C but that a nearly static structure exists at -40° C (ref. 247).



Scheme XXXVI



[38]



[39]

An extensive study of the fragmentation-aggregation reactions of rhodium carbonyl clusters under high pressures of carbon monoxide and/or hydrogen yielded the results depicted in Scheme XXXVII. In addition, treatment of $[Rh_4(CO)_{12}]$ with hydrogen and carbon monoxide at 1320 atm or of $[Rh(CO)_4]^-$ with acid under similar conditions showed the production of some $[HRh(CO)_4]$ detected in situ by infrared spectroscopy. It was also determined that the acidity of the cobalt triad hydrido tetracarbonyls is $[HRh(CO)_4] > [HCo(CO)_4] > [HIr(CO)_4]$. In those reactions using hydrogen and carbon monoxide together, no hydrogenation of carbon monoxide was observed. The overall study concluded that the tendency for fragmentation of the clusters increases with an increase of the ratio of the negative charge to the

$$[Rh_7(CO)_{16}]^{3-} \overset{\mathrm{CO}}{\rightleftharpoons} [Rh_5(CO)_{15}]^- + 2[Rh(CO)_4]^-$$

$$[Rh_{12}(CO)_{30}]^{2-} \overset{\mathrm{CO/base}}{\rightleftharpoons} 2[Rh_5(CO)_{15}]^- + 2[Rh(CO)_4]^-$$

$$\begin{tikzcd} {[Rh_{13}(CO)_{24}H_3]^{2-}} \arrow[r, "\mathrm{CO}", "\mathrm{base}"'] \arrow[d, shift right, "\mathrm{CO}"'] & {[Rh_{13}(CO)_{24}H_2]^{3-}} \arrow[d, shift right, "\mathrm{CO}"'] \\ {2[Rh_5(CO)_{15}]^- + 3[HRh(CO)_4]} \arrow[u, shift right, "H_2"'] & {2[Rh_5(CO)_{15}]^- + 3[Rh(CO)_4]^-} \arrow[u, shift right, "H_2"'] \end{tikzcd}$$

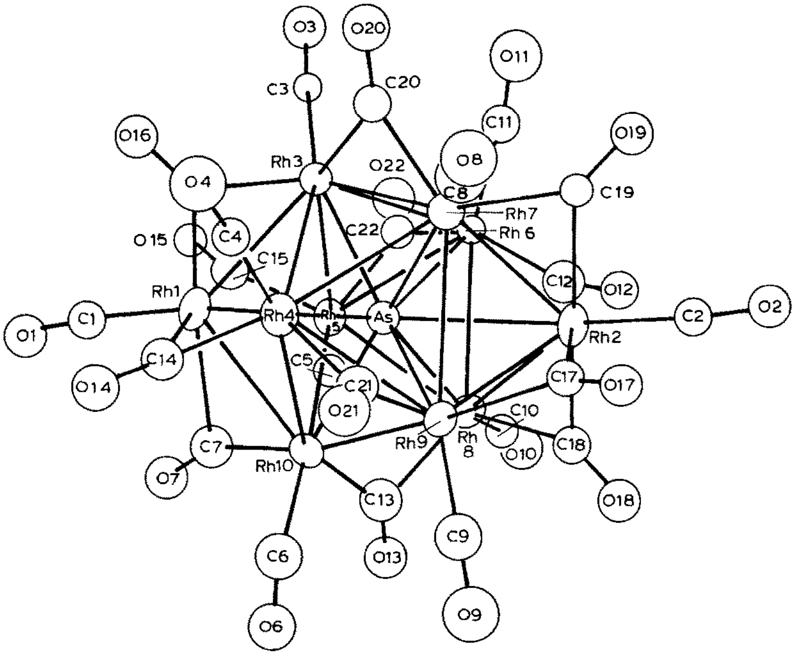
$$[Rh_5(CO)_{15}]^- \overset{\mathrm{CO}}{\rightleftharpoons} 2[Rh_2(CO)_8] + [Rh(CO)_4]^-$$

$$[Rh_{15}(CO)_{27}]^{3-} \overset{\mathrm{CO/MeCN}}{\rightleftharpoons} [Rh_{14}(CO)_{25}]^{4-} + [Rh(CO)_2(MeCN)_2]^+$$

$$[Rh_{17}S_2(CO)_{30}]^{3-} \overset{\mathrm{CO}}{\rightleftharpoons} 6[Rh_2(CO)_8] + 3[Rh(CO)_4]^- + [Rh(CO)_2SH]_2$$

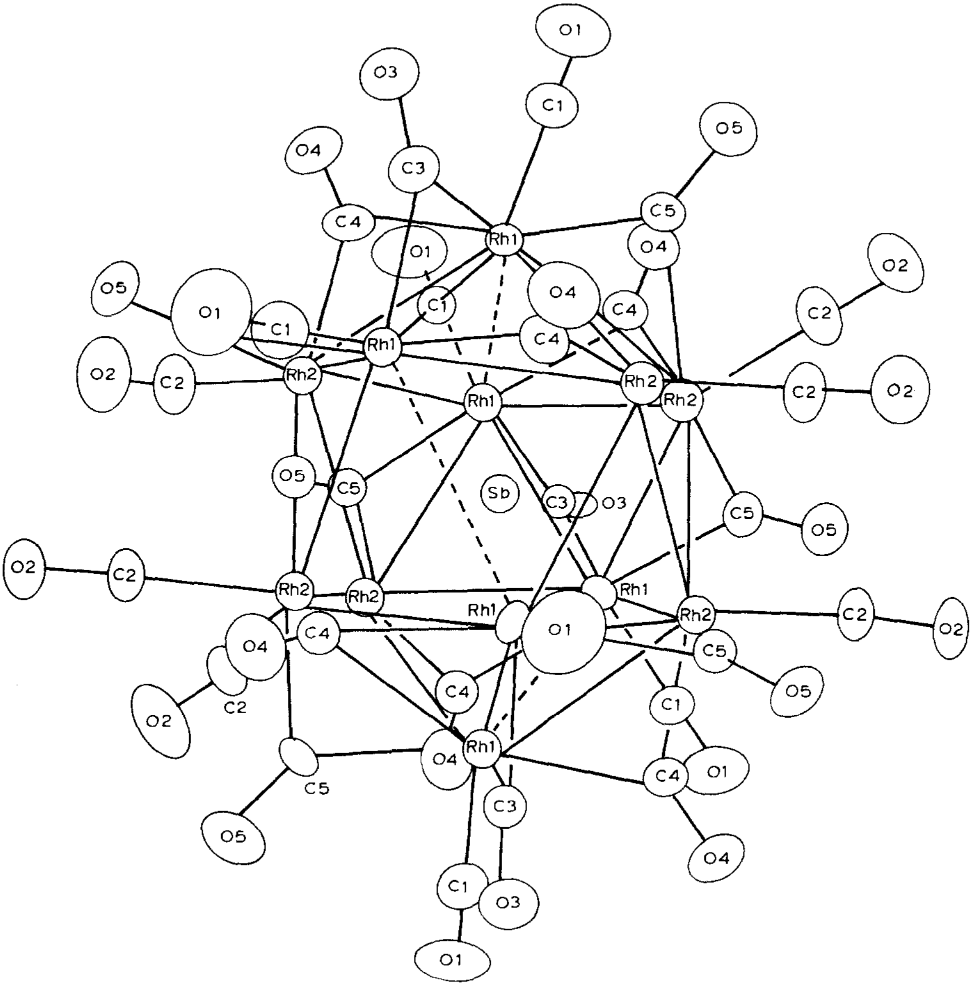
Scheme XXXVII

number of metal atoms (refs. 248, 249). Large rhodium carbonyl clusters appear to be significantly stabilized against fragmentation when interstitial pnicogen atoms are present although under severe conditions this can still occur. If $[Rh(CO)_2acac]$ is heated at 150° C in glyme-type solvents under 250-500 atm of carbon monoxide in the presence of cesium benzoate and EPh_3 (E = P, As, Sb), the clusters $[Rh_{10}E(CO)_{22}]^{3-}$ (E = P, As), $[Rh_9As(CO)_{21}]^{2-}$ and $[Rh_{12}Sb(CO)_{27}]^{3-}$ can be prepared. The Rh_{10} clusters have the structure [40] while the antimony complex is [41]. NMR studies show all the carbonyl groups to equilibrate at 40° C and from the ^{31}P NMR spectrum of [40] (E = P), the metal framework also appears fluxional even at -45° C. Under extreme conditions (200° C, 862 atm CO) fragmentation of $[Rh_{10}E(CO)_{22}]^{3-}$ to $[Rh_9E(CO)_{21}]^{2-}$ and $[Rh(CO)_4]^-$ (E = P, As) occurs (refs. 250-252). The hydrogenation of carbon monoxide to alcohols is catalyzed by $[Rh_{17}(CO)_{30}S_2]^{3-}$ and from *in situ* infrared studies it is concluded that the cluster remains intact. Also the lithium triethylborohydride reduction of $[Ir_4(CO)_{12}]$ was examined and the formation of methanol, acetaldehyde and cluster formyls was detected (refs. 253, 254). The cluster $[Rh_{17}(CO)_{30}]^{3-}$ has also been isolated as one of several products from the reaction of $[Rh_4(CO)_{12}]$ with sodium hydroxide in isopropanol. From the crystallographic study it is found to be [42]. It is air sensitive and reacts with acetonitrile and halide ions but apart from $[Rh(CO)_2X_2]^-$ (X = halide) detected in the latter reaction, none of the products has yet been identified. Although it is not protonated by trifluoroacetic acid in THF, its reduction product with potassium hydroxide, which also is a 17-metal cluster does protonate readily (ref. 255). Thiocyanate ion replaces two carbonyl groups in $[Rh_6(CO)_{16}]$ to give $[Rh_6(CO)_{14}(SCN)_2]^{2-}$ which was isolated as the PPN^+ salt. Slow recrystallization of the salt from THF/isopropanol caused a complex decomposition process with $(PPN)_2[Rh_{10}(CO)_{10}(\mu\text{-}CO)_{12}S]$ being the only characterized product. It was shown to have the same structure as $[Rh_{10}P(CO)_{22}]^{3-}$ (ref. 256). Decarbonylation of $K_2[Rh_6C(CO)_{15}]$ occurs together with decomposition in refluxing isopropanol. From the product mixture $(PPh_4)_2[Rh_6C(CO)_7(\mu\text{-}CO)_6]$ could be isolated on addition of the tetraphenylphosphonium cation. This product takes up carbon monoxide to regenerate the starting complex (ref. 257). These two rhodium carbonyl carbides have been studied by ^{13}C and $^{13}C\{^{103}Rh\}$ NMR spectroscopy. The lowest energy carbonyl migration process occurring in $[Rh_6C(CO)_{13}]^{2-}$ is depicted in Scheme XXXVIII. When enriched at all carbon sites, carbon-carbon coupling between the carbide carbon and both the migrating carbonyl ligands as well as those on Rh_A was observed. $[Rh_6C(CO)_{15}]^{2-}$ was



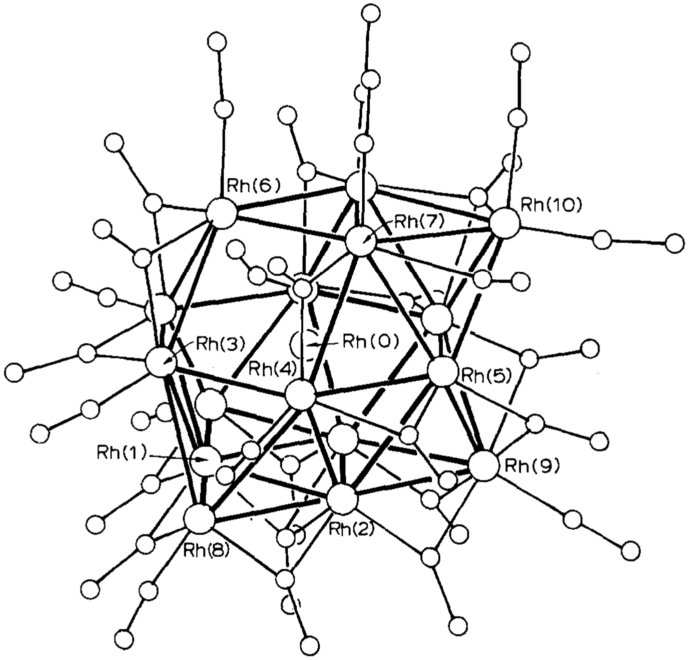
[40]

shown to undergo intermolecular carbonyl exchange by a dissociative process at sites associated with the longest metal-metal bonds (ref. 258). The conversion of $[Rh_{12}(CO)_{30}]^{2-}$ to $[Rh_5(CO)_{15}]^-$ mentioned earlier (Scheme XXXVII) has also been studied by ^{13}C NMR under carbon monoxide pressure at -52°C. At this temperature the conversion is slow and is unaffected by the addition of hydrogen however it becomes



[41]

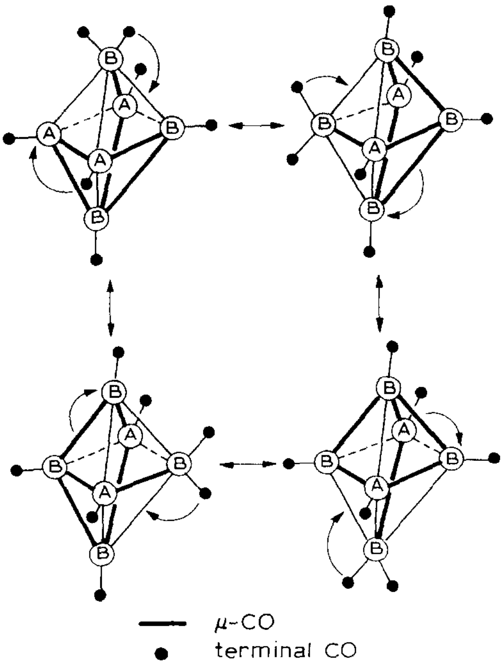
rapid at room temperature. Also at the low temperature the exchange of CO with the cluster is relatively slow on the NMR time scale (ref. 259). In another study, $[Rh_6(CO)_{12}(P(OPh)_3)_4]$ was shown by ^{13}C and ^{31}P NMR spectroscopy to be rigid below 60° C. Above this temperature, exchange of carbonyl groups between doubly and triply bridging sites is seen. The appearance of fluxional behavior parallels the onset of catalytic activity of the complex for hex-1-ene hydrogenation (ref. 260).



[42]

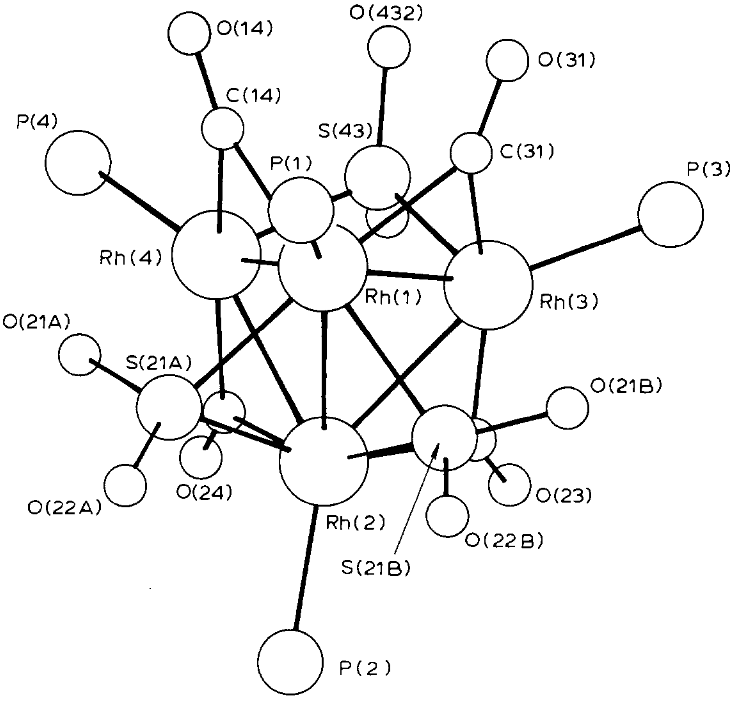
Sulfur dioxide reacts readily with $[Rh_4(CO)_8(P(OPh)_3)_4]$ to form $[Rh(\mu\text{-}CO)_4\text{-}(\mu\text{-}SO_2)_3(P(OPh)_3)_4]$ which adopts a butterfly structure [43]. The two sulfur dioxide molecules bridging the hinge appear to interact with the wingtip rhodium atoms through oxygen (O(21A) and O(21B)) (ref. 261). Reaction of $[Rh(CO)_2Cl]_2$ with two equivalents of diphenylphosphine in benzene yields a mixture of products one of which has been characterized as [44]. As it has two electrons in excess of that predicted for a closed triangular cluster, it is proposed that these occupy a metal-metal antibonding orbital. Carbonylation of [44] yields [45] which can also be got from $[Rh(CO)_2Cl]_2$ and one equivalent of diphenylphosphine in the presence of diethylamine. Reconversion of [45] to [44] occurs on reaction with carbon tetrachloride (refs. 262, 263). Complex [45] undergoes decarbonylation and rearrangement in solution to give a tetranuclear species which has been structurally characterized as [46] (ref. 264).

Alkoxide attack on a carbonyl group of $[Ir_4(CO)_{12}]$ occurs in the corresponding alcohol solution to give $[Ir_4(CO)_8(\mu\text{-}CO)_3CO_2R]^-$ (R = Me, Et). Also $[Ir_4(CO)_8(\mu\text{-}CO)_3CO_2Me]^-$ can be converted to the ethyl and isopropyl esters by heating

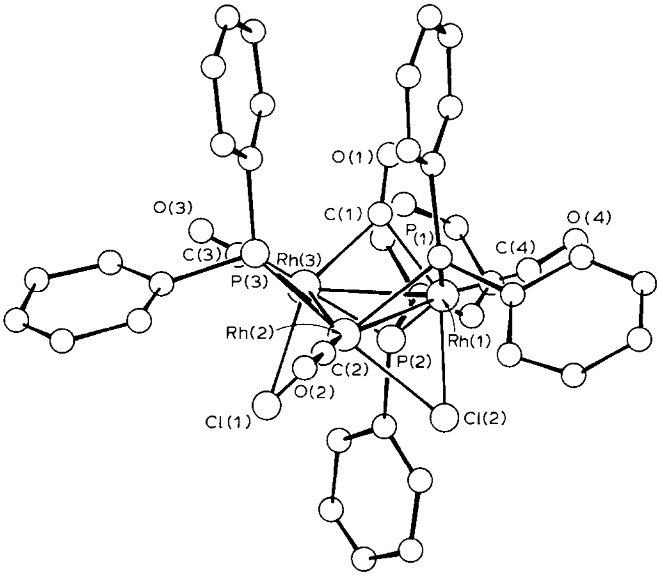


Scheme XXXVIII

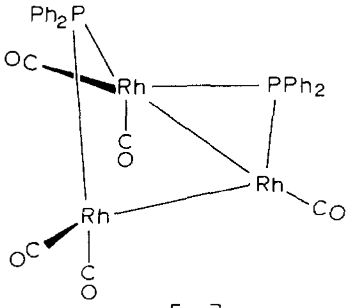
in the appropriate alcohol. Carbonylation of $[Ir_4(CO)_8(\mu\text{-}CO)_3CO_2Me]^-$ in aqueous methanol in the presence of potassium carbonate yields $[HIr_4(CO)_{11}]^-$ while reaction with acetic acid regenerates $[Ir_4(CO)_{12}]$ (ref. 265). Reduction of $[Ir_4(CO)_{12}]$ with potassium hydroxide in dimethoxyethane yields $[Ir_8(CO)_{22}]^{2-}$ whose structure can be described as two $[Ir_4(CO)_8(\mu\text{-}CO)_3]^-$ units joined by an Ir-Ir bond. The length of this bond, 2.8657(1) Å, suggests a partial localization of the negative charge in this portion of the anion. Cleavage by triphenylphosphine, hydrogen or iodine is facile and produces $[Ir_4(CO)_{12-n}(PPh_3)_n]$ (n = 1-3) or $[Ir_4(CO)_{11}X]^-$ (X = H, I) as well as some $[Ir_4(CO)_{12}]$ (ref. 266).


O(14)
O(432)
O(31)
C(14)
P(4)
S(43)
C(31)
P(1)
P(3)
Rh(4)
Rh(1)
Rh(3)
O(21A)
S(21A)
O(21B)
O(24)
O(22A)
O(23)
Rh(2)
O(22B)
S(21B)
P(2)

[43]

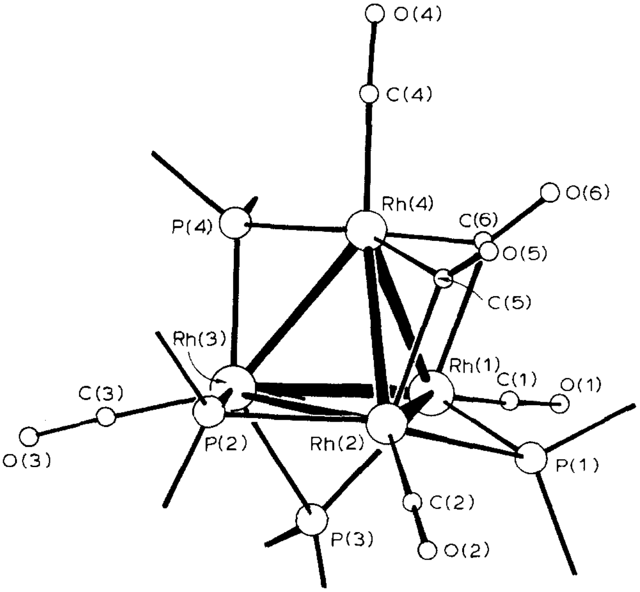

O(1)
O(3)
C(1)
O(4)
P(1)
C(4)
C(3)
Rh(3)
P(3)
Rh(2)
C(2)
P(2)
Rh(1)
O(2)
Cl(1)
Cl(2)

[44]



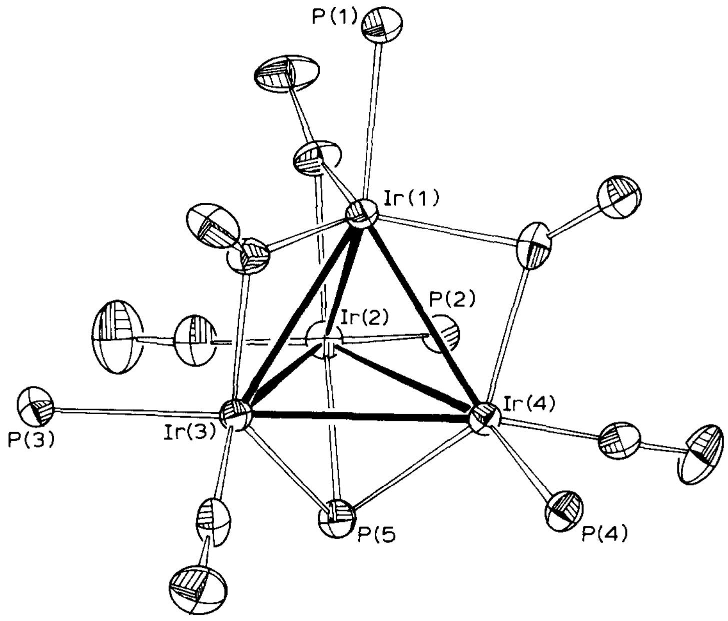
[45]

A number of papers have reported on substitution reactions of $[M_4(CO)_{12}]$ *(M = Co, Rh, Ir).* For example, the enrichment of $[Co_4(CO)_{12}]$ with ^{13}CO is facilitated by small amounts of tri-n-butylphosphine oxide however an excess of the phosphine oxide decomposes the cluster to a blue oil possibly $[Co(OPBu^n{}_3)_6][Co(CO)_4]_2$ (ref. 267). Use of the appropriate stoichiometric quantities of $[Rh_4(CO)_{12}]$ and triphenylphosphite allows reasonably clean syntheses of $[Rh_4(CO)_{12-n}(P(OPh)_3)_n]$ (n =



[46]

1-3) to be achieved. In hexane a single isomer of $[Rh_4(CO)_{12-x}(PPh_3)_x]$ (x = 1, 2) can be synthesized using appropriate stoichiometries but in toluene mixtures of isomers are obtained. The structures of $[Rh_4(CO)_{10}(PPh_3)_2]$ and $[Rh_4(CO)_9(P(OPh)_3)_3]$ were also determined. In solution, redistribution reactions are observed between the various substituted products prepared and a process involving cluster fragmentation is proposed (ref. 268). In an attempt to prepare $[Ir_4(CO)_8(PPh_3)_4]$, $[Ir_4(CO)_{12}]$ and an excess of triphenylphosphine were refluxed in toluene to give a mixture of products from which a low yield of [47] was obtained (ref. 269). The



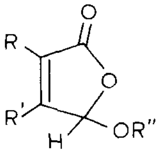
[47]

kinetics of the substitution of $[Ir_4(CO)_{12}]$ by the ligands L (L = PBu^n_3, PPh_3, $P(OPh)_3$, $AsPh_3$) have been studied and a two-term rate law was found to apply. For L = PPh_3, mono- and trisubstitution products were observed to form sequentially while for L = $P(OPh)_3$ $[Ir_4(CO)_{12-x}L_x]$ (x = 1-4) appeared with those with x = 3 and 4 being the major end products. For L = PBu^n_3 those with x = 2-4 were identified with the trisubstituted species predominating at low temperature and the tetrasubstituted species at high temperature. The proposed mechanism is depicted in Scheme XXXIX with the associative path accounting for ca. 95% of the reaction in the case of the phosphorus ligands. A similar scheme applies to the subsequent substitution steps (ref. 270). In a complementary study, the reaction of carbon monoxide with $[Ir_4(CO)_8(PMe_3)_4]$ to produce $[Ir_4(CO)_9(PMe_3)_3]$ has been studied and found to proceed via a dissociative mechanism. The fact that it occurs much more slowly than with the triethylphosphine analog suggests that steric factors are important (ref. 271).

$$\begin{tikzcd}
{[Ir_4(CO_{12}]} \arrow[r, shift left, "+L"] \arrow[d, "-CO"] & {[Ir_4(CO)_{12}L]} \arrow[l, shift left, "-L"] \arrow[d, "-CO"] \\
{[Ir_4(CO)_{11}]} \arrow[r, "+L"] & {[Ir_4(CO)_{11}L]}
\end{tikzcd}$$

Scheme XXXIX

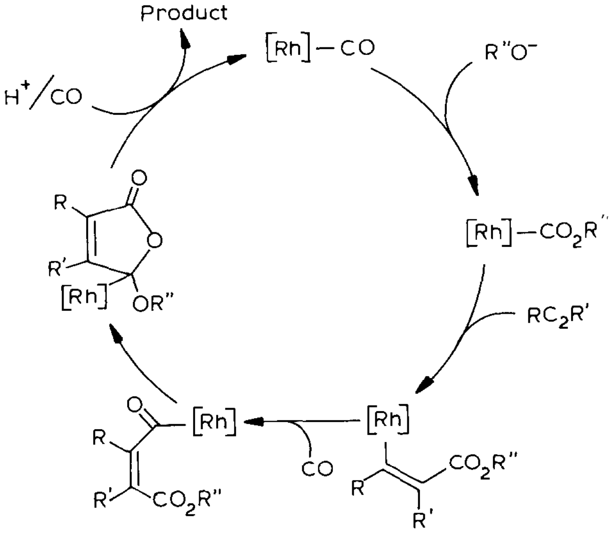
The trimethylamine oxide-promoted decarbonylation of $[Ir_4(CO)_{12}]$ has been used to effect the attachment of $[Ir_4(CO)_{12-n}]$ clusters to phosphinated silica. The clusters are stable below 330 K but degrade at higher temperatures particularly in the presence of hydrogen and/or olefins with the ultimate formation of aggregates on the surface. Most of the ethylene hydrogenation catalyzed by this system appears to involve these decomposition products as the active catalyst rather than the tetranuclear clusters (ref. 272). The condensation of disubstituted acetylenes with alcohols in the presence of base (e.g. Na_2CO_3, $NaHCO_3$) to yield the pseudo-esters [48] (R = R' = Ph; R" = Me, Et, Pr^n, Pr^i, n-octyl. R" = Et; R = Me, Ph; R' = Ph, Me) is catalyzed by $[Rh_4(CO)_{12}]$ under carbon monoxide. Although the question



[48]

of cluster integrity is not addressed, the mechanism of Scheme XL is proposed (ref. 273). The catalysis by $[Rh_6(CO)_{16}]$ or $[Co_2(CO)_8]$ of ylide transfer of allyl methyl sulfide and the cyclopropanation of olefins by ethyldiazoacetate has been reported (refs. 274-277). The hydrogenation of benzaldehyde to benzyl alcohol is catalyzed by $[Rh_6(CO)_{16}]$ in aqueous, alcoholic potassium hydroxide. The observed increase in rate with decreasing rhodium concentration is taken to indicate cluster fragmentation and infrared spectra of the reaction mixture indicate the presence of

$[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_5(CO)_{15}]^-$. From the earlier discussion of rhodium cluster carbonyls, $[Rh(CO)_4]^-$ is likely to be present as well. The data are interpreted as indicating that a metal hydride reacts with the aldehyde to generate a $PhCH_2$-O-Rh species which is then hydrolyzed (ref. 278). An earlier report that rhodium and cobalt carbonyls in the presence of aluminum chloride catalyze the Fischer-Tropsch alkylation of benzene (ref. 279a) has now been shown to be suspect since very similar products can be obtained in the absence of the carbonyl complexes (ref. 279b). In light of these results, the report that the Fischer-Tropsch synthesis of



Scheme XL

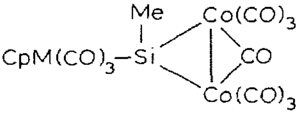
C_1-C_5 hydrocarbons can be catalyzed by $[Rh_4(CO)_{12}]/AlBr_3$ in the presence of magnesium or aluminum should be viewed with caution (ref. 280). Under water-gas-shift conditions, $[Rh_6(CO)_{16}]$ is reported to catalyze the reduction of nitrobenzene to aniline and the carbonylation of α-olefins to alcohols in the presence of γ-picoline and 4-dimethylaminopyridine respectively (refs. 281, 282). A full report of the catalysis of carbon monoxide reduction by $[Ir_4(CO)_{12}]$ in a sodium chloride/aluminum chloride melt using a flow system has now appeared. In the initial fast stage of the reaction, propane is the major product while in the later, slower stage, isobutylene predominates. Other products are C_1-C_8 hydrocarbons including methylcyclopentane and methylcyclohexane and with long contact times ethane is the major product. It is concluded that methyl chloride is not a likely initial product and although the active catalytic species were not identified it was felt that at least some of the Ir-CO moieties had a Lewis acid bound to the carbonyl oxygen (ref. 283). Using toluene solutions of $[Ir_4(CO)_{12}]$ in a static system containing carbon monoxide and hydrogen, modest amounts of methane were produced and it was determined that this did not arise from the solvent. Methane was also produced in the presence of added trimethylphosphite but here, labelling studies showed that most of it arose from ligand decomposition (ref. 284).

Further reports have appeared on the nature of the species present when $[Rh_6(CO)_{16}]$ is supported on alumina. From X-ray PES measurements, the initial supported complex appears to interact weakly with the support. On exposure to air, decarbonylation occurs but the Rh_6 unit appears to persist. The new data support the conclusions described in the 1980 Annual Survey (refs. 285, 286). A comparison has been made of $[Rh_4(CO)_{12}]$ and $[Rh(CO)_2Cl]_2$ supported on alumina with the homogeneous systems for the hydrogenation of pent-1-yne and pent-2-yne. The supported species favor hydrogenation to pentane while the homogeneous systems yield much larger proportions of pentenes. Although it was concluded that metal particles did not form on the surface, the nature of the surface species was not further determined (ref. 287). The temperature programmed decomposition (TPDE) of $[M_4(CO)_{12}]$ (M = Co, Rh, Ir), $[Rh_6(CO)_{16}]$ and $[Co_2(CO)_8]$ supported on calcined alumina in flowing hydrogen has been shown to give primarily methane with only traces of C_2 hydrocarbons and carbon dioxide. No correlation of the methane yield with the activities of the metals themselves as methanation catalysts was found and as the methane yield did not depend significantly on cluster size it was concluded that clusters are not significantly better than monomeric species for catalyzing carbon monoxide hydrogenation (ref. 288). The inelastic electron tunnelling spectrum (IETS) of carbon monoxide adsorbed on rhodium supported on alumina indicates the presence of $\{Rh(CO)_3\}$, $\{Rh(CO)\}$ and carbonyl-bridged species on the surface. Heating the sample in hydrogen causes carbon monoxide hydrogenation and the dominant surface species is an ethylidene moiety. That no oxygen-containing species are seen on the surface suggests that polymerization of surface methylene groups formed by reduction of carbon monoxide may be occurring. Similar studies using cobalt indicated the possible presence of surface methylene groups but other surface species were not identified and the hydrocarbons formed on hydrogenation were not the same as with rhodium. A caution has been raised concerning this method of detecting surface species. If the atomic radius of the metal used for the upper part of the tunnel junction is significantly different from that of the metal under study, the IETS may not be very similar to the infrared and Raman spectra of the same surface species in the absence of the junction (refs. 289-291). Rhodium and iridium carbonyl clusters supported on MgO, La_2O_3 or ZrO_2 catalyze the hydrogenation of carbon monoxide to methanol with 65-98% selectivity. By-products are ethanol, methane and carbon dioxide (ref. 292). The activities of $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ supported on silica towards saturated hydrocarbons have been studied. As noted previously, $[Rh_6(CO)_{16}]$ appears to physisorb without change however $[Rh_4(CO)_{12}]$ appears to dimerize on contact with the support. Contact of the catalyst activated by flushing with nitrogen at 120° C followed by hydrogenation at 320-350° C with an n-heptane/hydrogen stream at temperatures below 300° C gave low conversions to methane. Some dehydrocyclization also was observed (ref. 293). A thermally regenerable ion exchange resin (Sirotherm^{TM}) has been used to support rhodium complexes for catalytic carbonylation reactions. At the operating temperature the complexes are released into solution but become reimmobilized on cooling (ref. 294). The rhodium clusters $[Rh_6(CO)_{15}]^{2-}$, $[Rh_7(CO)_{16}]^{3-}$ and $[Rh_{13}(CO)_{23}H_2]^{3-}$ on impregnation into silica containing titanium or zirconium react with the surface hydroxyl groups to give supported $[Rh_6(CO)_{15}H]^-$ and $[Rh_{13}(CO)_{23}H_3]^{2-}$ which catalyze carbon monoxide hydrogenation with an increased selectivity to ethanol. The heteroatoms in the support are thought to prevent aggregation of the rhodium on the surface (ref. 295).

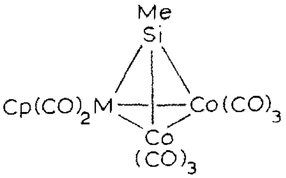
A new method has been presented for the derivation of metal-metal bond energies in $[Co_2(CO)_8]$, $[M_4(CO)_{12}]$ (M = Co, Rh, Ir) and $[Rh_6(CO)_{16}]$. The values obtained are lower than those previously determined (ref. 296). Infrared and Raman spectra of $[M_4(CO)_{12}]$ (M = Rh, Ir) in the metal-metal stretching region have been measured and it is concluded that a band at 200 cm^{-1} previously assigned as a component of the ν_3 vibration was due to an impurity. Thus there is little if any splitting of this band which implies the metal skeleton has full tetrahedral symmetry (ref. 297). In a paper using electron-pair repulsion theory to explain the difference in structure between $[Ir_4(CO)_{12}]$ and its cobalt and rhodium analogs it is felt that contrary to the Johnson-Benfield model reported in the last Annual Survey the steric requirement of the M_4 tetrahedron inside the $(CO)_{12}$ polyhydron is an insufficient criterion. Instead, the differences are thought to be due to an increase in metal-metal bonding or differences in the M-C bonds (ref. 298). Two other cluster classification and bonding models have been proposed (refs. 299-300).

b) Heteronuclear Metal-Metal Bonded Compounds

The use of ligands to promote the formation of heterometallic clusters continues to attract interest. Extended reaction of $[cpM(CO)_3SiH_2Me]$ (M = Mo, W) with $[Co_2(CO)_8]$ at room temperature produces [49] which on refluxing in benzene converts to [50]. The germanium analog of [50] (M = Mo) can be obtained by refluxing $[MeGeCo_3(CO)_9]$ and $[cpMo(CO)_3]_2$ in benzene (ref. 301). Related alkylidyne trimetal complexes are prepared thermally or photochemically from $[MeCCo_3(CO)_9]$ and $[L_nMML_n]$ (ML_n = $cpMo(CO)_3$, $cpW(CO)_3$, $cpFe(CO)_2$, $cpNi(CO)$). These have the structure [51] (ML_m = $cpMo(CO)_2$, $cpW(CO)_2$, $cpFe(CO)$, $cpNi$). Reaction of $[cp_2Ni_2(CO)_2]$ with $[Co_4(CO)_{12}]$ yields $[cpNiCo_3(CO)_9]$ containing a tetrahedron of metal atoms and terminal carbonyl groups while [51] (ML_m = $cpMo(CO)_2$) reacts with $[cp_2Ni_2(CO)_2]$ to give a low yield of the optically active clusters [52] (ref. 302). The chromium dimer

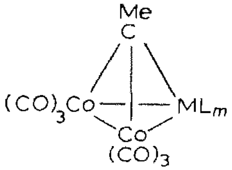


[49]



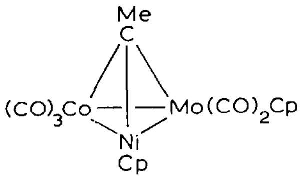
[50]

$[cp_2Cr_2(\mu\text{-}S)(\mu\text{-}SBu^t)_2]$ reacts with $[Co_2(CO)_8]$ to give [53] which on refluxing with diphenyl acetylene in toluene condenses to [54]. Complex [53] is considered to be the first example of a cluster with a metallacyclic skeleton which shows antiferromagnetic behavior (refs. 303, 304). At -20° C in the presence of alcohols *trans*-$[W(N_2)_2(diphos)_2]$ and $[HCo(CO)_4]$ yield $[W(OR)(NNH_2)(diphos)_2][Co(CO)_4]$ (R = Me, Et) while with $[HFeCo_3(CO)_{12}]$ the product is $[W(OR)(NNH_2)(diphos)_2][FeCo_3\text{-}(CO)_{12}]$ (R = Me, Et, Pr^i) (ref. 305). Fragmentation of $[(\eta^5\text{-}C_5H_4Me)(CO)Mn(\mu\text{-}CO)_2\text{-}Co(PMe_3)cp]$ occurs on reaction with R_2S_2 (R = Ph, $PhCH_2$) or $N(SCF_3)_3$ to give



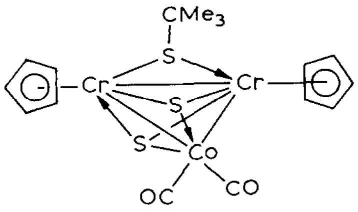
[51]

$[(\eta^5\text{-}C_5H_4Me)Mn(CO)_3]$ and $[cpCo(PMe_3)(SR')]$ (R' = Ph, $PhCH_2$, CH_3). Alkylation of $[cpCo(PMe_3)(SPh)_2]$ with trimethyloxonium tetrafluoroborate proceeds *via* the postulated intermediate $[cpCo(PMe_3)(SPhMe)_2](BF_4)_2$ to $[cp_2Co_2(PMe_3)_2(\mu\text{-}SPh)_2](BF_4)_2$. This is cleaved by phosphines or phosphites to $[cpCo(PMe_3)(L)(SPh)]BF_4$ (L = PMe_3, $P(OMe)_3$) which can be alkylated as before to yield $[cpCo(PMe_3)(L)(SMePh)](BF_4)_2$ (ref. 306). The diazabutadiene(DAB) complexes $[M(CO)_3Br(DAB)]$ react with

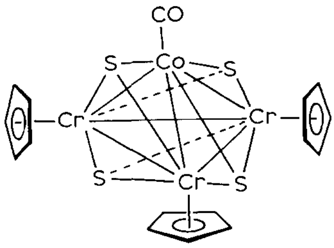


[52]

[Co(CO)$_4$]$^-$ to yield the dimers [55] (M = Mn, Re; R = Me, R' = *cyclo*-C$_3$H$_5$; R = H, R' = *cyclo*-C$_3$H$_5$, *cyclo*-C$_6$H$_{11}$, Bu^t) presumably by nucleophilic displacement of bromide by [Co(CO)$_4$]$^-$. The ^{13}C NMR spectra show that the imine carbon has a chemical shift close to that for the free ligand while the one coordinated to

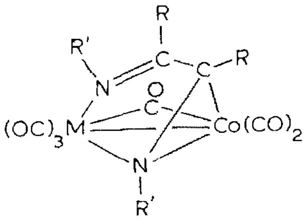


[53]



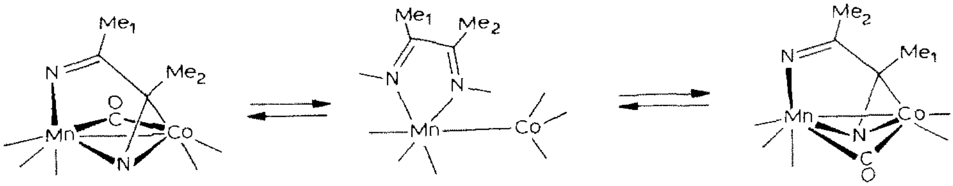
[54]

cobalt is shifted upfield by *ca*. 100 ppm. For the cyclopropyl complexes the DAB ligand with R = H appears a better π-acceptor from the ^{13}C chemical shifts. The complexes with R = Me are fluxional and the rearrangement process depicted in Scheme XLI is proposed. Because of the thermal lability and non-volatility of these complexes normal mass spectrometric techniques are unsuitable. However the use of field-desorption mass spectrometry has made it possible to observe the molecular



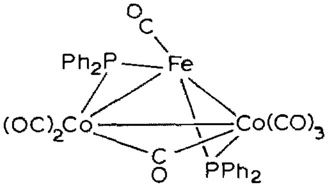
[55]

ion in most cases (refs. 307-309). A complete analysis of the infrared spectra of $[MCo(CO)_9]$ (M = Mn, Tc, Re) has been reported. The force constants for the C-O stretching vibrations are largest in the technetium complex indicating considerable polarization ($Tc^{\delta+} \rightarrow Co^{\delta-}$) in the metal-metal bond (ref. 310).



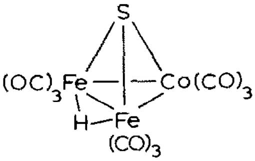
Scheme XLI

In refluxing hexane $[Co_2(CO)_8]$ reacts with $[Fe(CO)_4(P_2Ph_4)]$ to yield [56]. The ^{13}C NMR spectrum indicates the occurrance of bridge-terminal CO exchange along the Co-Co edge *via* a species with two bridging carbonyl ligands. Cyclic voltammetric measurements show the presence of three one-electron reduction steps but the reduction products were not identified (ref. 311). Reaction of $[Co_2(CO)_8]$ with $[Fe_3(CO)_9S]^{2-}$ in dichloromethane or with $[Fe(CO)_5]$ and sodium sulfide in ethanol under carbon monoxide followed by protonation with HCl yields [57] which is deprotonated to $[Fe_2Co(CO)_9S]^-$ by tetraethylammonium hydroxide in pyridine. Reaction of this anion with sodium nitrite in acidified methanol produces [58] (ref. 312). $[Co_2(CO)_8]$ also reacts with $[Fe_2(CO)_6(\mu\text{-}S_2)]$ or $[Fe_2(CO)_6(\mu\text{-}PPhH)_2]$ to yield [59] (E = S, PPh) (ref. 313). At room temperature the product of the reaction of $[Fe_2(CO)_5(PMe_2H)(\mu\text{-}SMe)_2]$ with $[(\eta^3\text{-}C_3H_5)Co(CO)_3]$ is [60] while at



[56]

65° C $[Fe_2(CO)_5(PMe_2H)(\mu\text{-}PMe_2)_2]$ yields [61] (ref. 314). The kinetics of the cleavage of the Fe→Co bond in $[FeCo(CO)_7(\mu\text{-}AsMe_2)]$ by ligands to give $[Fe(CO)_4(\mu\text{-}AsMe_2)Co(CO)_3L]$ (L = $P(cyclohexyl)_3$, $PPhEt_2$, PPh_2Et, $P(OMe)_3$, PPh_3, $P(OPh)_3$, $AsPh_3$, $SbPh_3$, $P(OCH_2)_3CEt$) have been interpreted to show that the reaction follows



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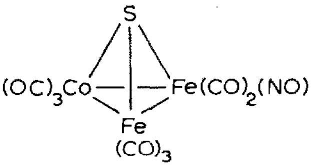
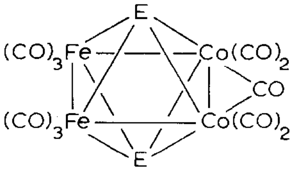
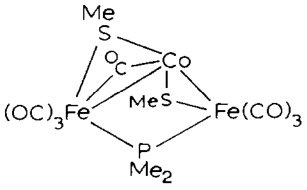


[58]

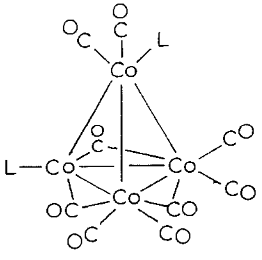


[59]

an I_d process for poor nucleophiles but for good nucleophiles it more closely resembles an I_a process (ref. 315). Treatment of the vinylidene-bridged complex [cp$_2$-Fe$_2$(CO)$_2$(μ-CO)(μ-C=CH$_2$)] with [Co$_2$(CO)$_8$] at room temperature or with [Co$_4$(CO)$_{12}$] in refluxing toluene produces the cluster [62] (ref. 316). The first example of a cluster containing a gold atom bonded to three other transition metal atoms is [63] which is prepared from [FeCo$_3$(CO)$_{12}$]$^-$ and [PPh$_3$AuNO$_3$] in acetone. Since



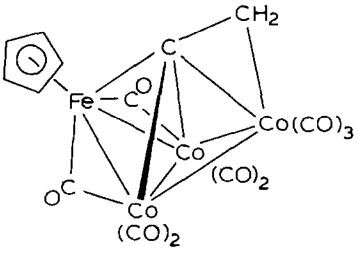
[60]



[61]

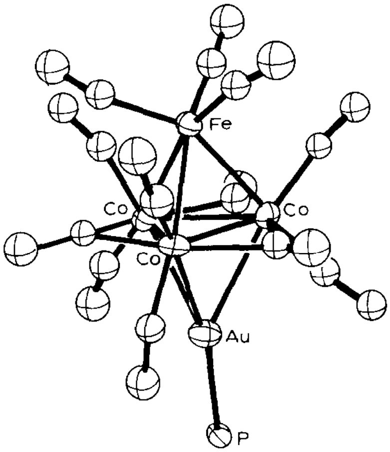
L = PMe$_2$(CH$_2$CH=CH$_2$)

[63] has the same structure as [HFeCo$_3$(CO)$_{12}$], the AuPPh$_3$ moiety is considered to be a hydride equivalent (ref. 317). The ^{17}O NMR spectra of the isoelectronic clusters [Co$_4$(CO)$_{12}$] and [HFeCo$_3$(CO)$_{12}$] both show four resonances at low temperatures confirming that the C_{3v} structure found in the solid state persists in solution. On warming, the spectrum of [Co$_4$(CO)$_{12}$] shows a non-selective broadening indicating that a species of T_d symmetry is involved in the fluxional process. For the other, several processes are detected, the first involving the bridging carbonyls and one terminal carbonyl on each cobalt, the second all the carbonyls on cobalt and finally an exchange of all carbonyl groups. The chemical shifts of oxygen atoms of the terminal and bridging carbonyl groups are separated by



[62]

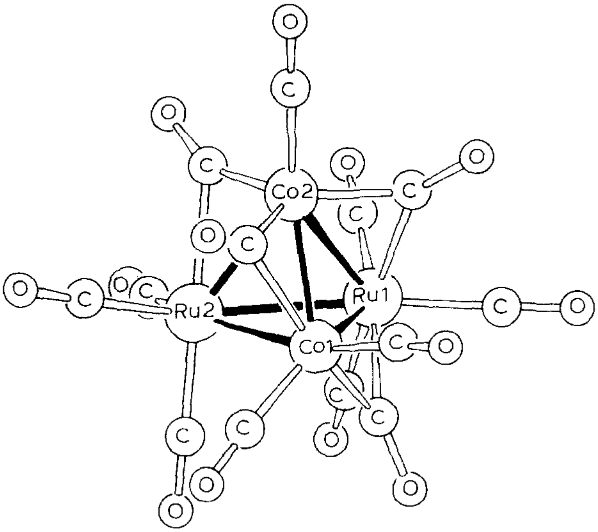
ca. 120 ppm in the low temperature spectra (ref. 318). A reversible one-electron reduction step is seen for $[FeCo_2(CO)_9(\mu_3\text{-}S)]$ which appears at approximately the same potential as that observed for $[FCCo_3(CO)_9]$. Coordination of a $Cr(CO)_5$ moiety to the sulfur has little effect on the reduction potential but substitution of trimethylphosphite for a carbonyl group increases it presumably because the HOMO is



[63]

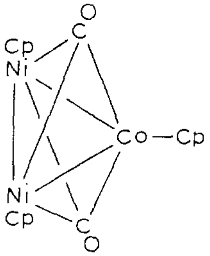
stabilized. ESR studies on the reduced complex and the corresponding reduced species from $[Co_3(CO)_9(\mu_3\text{-}S)]$ suggest that replacement of cobalt by iron results in the mixing of Co $3d_{z^2}$ character into the primarily $3d_{xy}$ antibonding orbital. An estimate of 60% of the spin density appears to reside on the equivalent cobalt atoms in the mixed cluster (ref. 319).

Another example of nucleophilic displacement of halide by $[Co(CO)_4]^-$ occurs with $[Ru(CO)_3Cl_2]_2$ from which $[RuCo_2(CO)_{11}]$ is obtained. This cluster reacts over three days in hexane to yield a mixture of $[Ru_3(CO)_{12}]$, $[Co_4(CO)_{12}]$ and [64] (ref. 320). Under 50 atm pressure of carbon monoxide $[Co_2(CO)_8]$ and $[Rh_4(CO)_{12}]$ react at



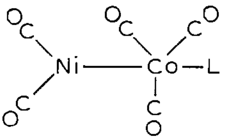
[64]

70° C to give a species proposed to be $[(OC)_4CoRh(CO)_3]$ which contains no bridging carbonyls. On attempted isolation the binuclear complex decomposes to produce $[Co_2Rh_2(CO)_{12}]$ and $[Co_3Rh(CO)_{12}]$ (ref. 321). Prolonged reflux of $[cpCo(CO)_2]$ with $[cp_2Ni_2(CO)_2]$ in hexane yields [65]. Related clusters were also obtained from

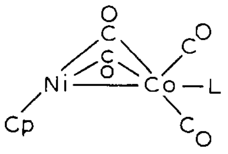


[65]

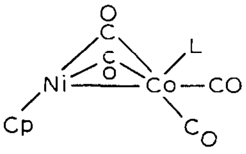
$[(\eta^5\text{-}C_5H_{5-n}Me_n)Co(CO)_2]$ (n = 1,5). The absence of a trinickel cluster suggests that the reaction proceeds via attack of a $\{cpCo(CO)\}$ fragment on the intact nickel dimer. The complexes are isoelectronic with $[cp_3Ni_3(CO)_2]^+$ which has not been synthesized and thus provide a means, by comparison of their metal-metal distances with those of $[cp_3Ni_3(CO)_2]$, of determining the nature of the orbital which the odd electron in this last compound occupies. As the mixed-metal clusters have shorter distances it was concluded that the odd electron occupies an in-plane, M_3 anti-bonding orbital (ref. 322). Displacement of halide on [cpNi(L)Br] by $[Co(CO)_4]^-$ is accompanied by migration of L to cobalt and formation of $[cpNiCo(CO)_4L]$ (L = PEt_3, PPh$_3$, (*p*-X-C$_6$H$_4$)$_3$P (X = F, Cl, MeO), PPh$_2$(*o*-tolyl), PBu$^n{}_3$, P(CH$_2$Ph)$_3$, PPh(*o*-tolyl)$_2$, AsMe$_3$), which appears to exist in solution as a mixture of isomers [66a-c]. An



[66a]

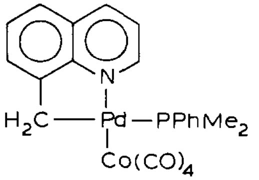


[66b]



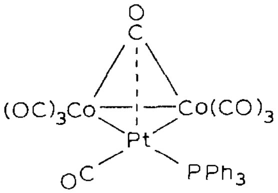
[66c]

analogous series has been prepared from [(η^5-C$_5$H$_4$Me)Ni(L)Br] (L = PPh(cyclohexyl)$_2$, PPh$_2$(cyclohexyl), PPh(CHPh)$_2$, PPh$_3$, P(*p*-tolyl)$_3$, P(*p*-MeOC$_6$H$_4$)$_3$) (ref. 323). Complex [67] is prepared by displacement of chloride from the corresponding palladium complex by [Co(CO)$_4$]$^-$. Analogs with pyridine and carbon monoxide in place of the phosphine were also synthesized (ref. 324). Other mixed metal clusters which have been studied as catalysts for the homologation of methanol with

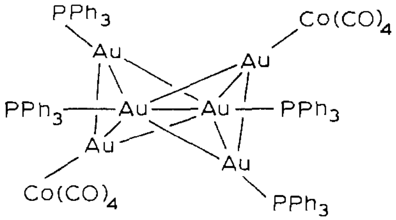


[67]

synthesis gas are [(diphos)MCo$_2$(CO)$_7$] (M = Pd, Pt) and Na[RuCo$_3$(CO)$_{12}$] and are prepared from Na[Co(CO)$_4$] and [MCl$_2$(diphos)] or [Pt(C$_2$Ph)diphos] and hydrated ruthenium(III) chloride respectively. The palladium complex generates more acetaldehyde than [Co$_2$(CO)$_8$] or [Co$_4$(CO)$_{12}$] alone but the yield of ethanol is about the same. With the ruthenium cluster, 35-40% C$_2$ products containing roughly equal amounts of ethanol and dimethyl ether are obtained at 45% conversion (ref. 325). The redox behavior of [PtCo$_2$(μ-CO)(CO)$_6$(diphos)] and [PtCo$_2$(μ-CO)(CO)$_7$(PPh$_3$)] show that both undergo an irreversible, one-electron reduction with loss of [Co(CO)$_4$]$^-$. The latter complex also yields [Pt$_2$Co$_2$(μ-CO)$_3$(CO)$_5$(PPh$_3$)$_2$] presumably *via* dimerization of a [$\cdot$PtCo(CO)$_4$PPh$_3$] fragment. Both complexes undergo a reversible one-electron oxidation but further oxidation leads to passivation of the electrode (ref. 326). The Pt_2Co_2 complex has also been obtained together with [68] from $[Co_2(CO)_8]$ and $[Pt_5(CO)_6(PPh_3)_4]$ (ref. 327) while an analog of the tetranuclear species supported on phosphinated styrene divinylbenzene copolymer is a catalyst for ethylene hydrogenation under mild conditions (ref. 328). While $PPN[Co(CO)_4]$ reacts with $[Au(C_6F_5)_3(THT)]$ (THT = tetrahydrothiophene) to give $PPN[(C_6F_5)_3$-$AuCo(CO)_4]$, the same reaction with $[Au(C_6F_5)_2Cl(PPh_3)]$, $[AuCl_3(THT)]$, $[Au(C_6F_5)_2$-$Cl]_2$ or $[Au(C_6F_5)_2Cl_2]^-$ leads only to reduction to Au(I) or Au(O) species. On the other hand the reaction of $[Au(C_6F_5)(THT)]$ yields $[Au(Co(CO)_4)_2]^-$ and $[Au(C_6F_5)_2]^-$ while $[(C_6F_5)_3AuCo(CO)_4]^-$ undergoes substitution at cobalt to yield $[(C_6F_5)_3$-$AuCo(CO)_3L]^-$ (L = PPh_3, $P(OPh)_3$) (ref. 329). Finally, $[Au_8(PPh_3)_7](NO_3)_2$ reacts with two equivalents of $Li[Co(CO)_4]$ to give [69] (ref. 330).



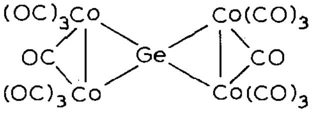
[68]

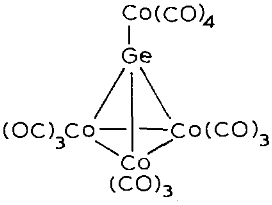


[69]

Reaction of $[Co(CO)_4]^-$ with GeI_4 or reaction of $[Co_2(CO)_8]$ with GeH_4 for extended periods of time yields [70] and a variety of anionic complexes. Heating [70] above 40° C converts it to [71]. Complex [70] also results from the first reaction when run in the presence of sodium amalgam and [72] is now also formed which is characterized as the first example of a cobalt-cobalt bond bridged by mercury (refs. 331-332). Carbenoid character is attributed to $[Pd(diphos)_2]$ in its reaction with $[Hg(Co(CO)_4)_2]$ where it inserts into a mercury-cobalt bond to produce $[(CO)_4CoHgPd(diphos)Co(CO)_4]$ (ref. 333). The stereochemistry of the cleavage of

Co-Si and Co-Ge bonds in $[(CO)_3LCoMRR'R'']$ (L = CO, PPh_3, $P(OPh)_3$; M = Si, Ge; R = Me; R' = Ph; R" = 1-naphthyl) by hydride to give MHRR'R" has been investigated. The reaction proceeds with inversion to a substantial extent, being slightly greater with silicon than with germanium and showing a significantly greater loss of stereochemistry with L = PPh_3 than with the other complexes (ref. 334). A phase-transfer catalyst system composed of $NaBH_4/PhCH_2Et_3NCl/H_2O/CH_2Cl_2$ has been found effective for the preparation of $[Ph_3SnCo(CO)_4]$ from $[Co_2(CO)_8]$ and Ph_3SnCl (ref. 335). Other tin-cobalt complexes reported are $[W(CO)_5(Sn(Co(CO)_4)_2)]$ prepared from $Na[Co(CO)_4]$ and $[W(CO)_5(SnCl_2)\ THF]$ and [73] from $Me_2\overline{SiOSi(Me)_2CH_2Sn(Cl)_2CH_2}$ (refs. 336, 337).


[70]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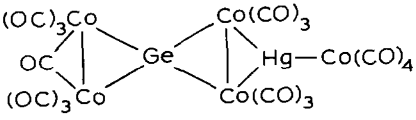
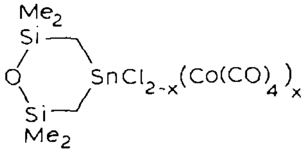
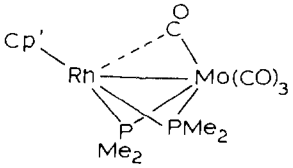

[72]

One of several products obtained from the reaction of $[cp'_2Rh_2Cl_4]$ and $[Mo(CO)_4(PMe_2Li)_2]$ at -78° C is [74]. Although a static NMR spectrum was not obtained for this fluxional molecule, the observation of a single ^{13}C resonance for the carbonyl groups and the absence of P-C coupling led to the suggestion that the rearrangement involves cleavage of one Mo-P bond and rotation of the square-pyramidal molybdenum unit about the remaining Mo-P bond (ref. 338). Using catalysts prepared from $[Co(CO)_4]^-$ or $[Rh_{12}(CO)_{34}]^{2-}$ and either $[MoH_3(PMePh_2)_3]^+$ or $[WH_5(PMePh_2)_4]^+$ some ethylene glycol was detected when the mixture was heated under pressure of carbon monoxide and hydrogen (ref. 339). Reaction of $[(\eta^3\text{-}C_3H_5)_2RhCl]_2$ with four mols of $[Fe(CO)_4(PPh_2H)]$ under CO



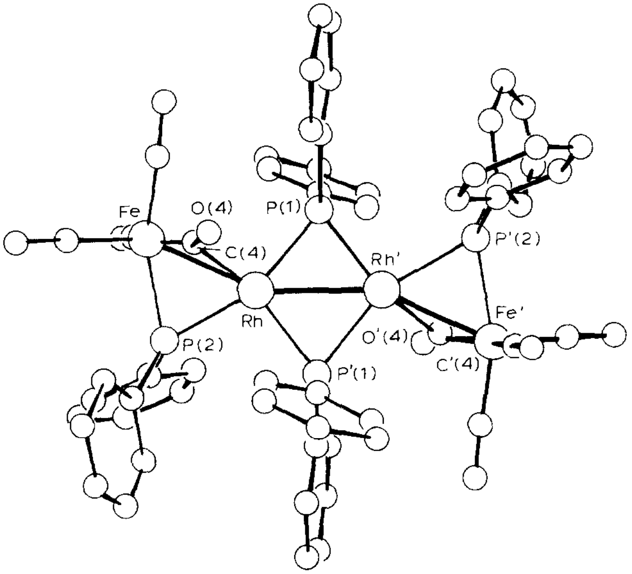
[73]

(x = 1,2)



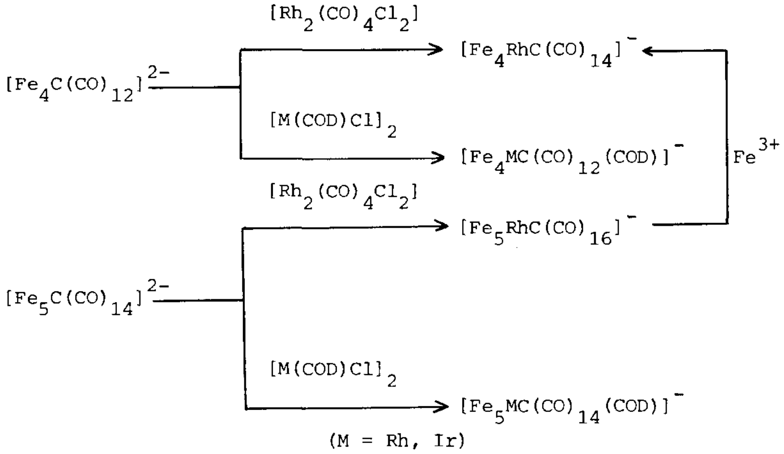
[74]

yields [75]. In solution, a mixture of cis and trans isomers is seen (ref. 340). A full report has now appeared on the preparation of mixed-metal clusters from



[75]

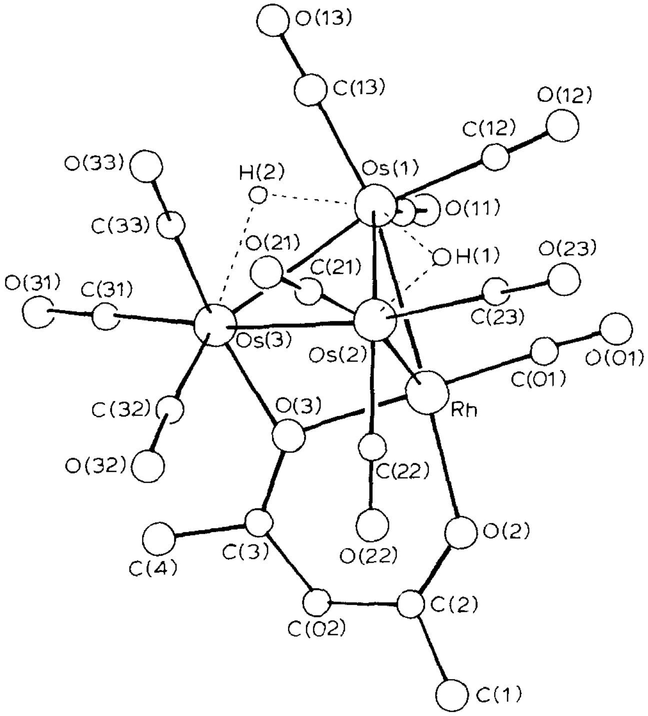
$[Fe_4C(CO)_{12}]^{2-}$ and $[Fe_5C(CO)_{14}]^{2-}$ as detailed in Scheme XLII. For the Fe_4M clusters, the heteroatom occuries a basal position in the square pyramidal array of metal atoms. The octahedral clusters show facile carbonyl rearrangements while those for the square pyramidal complexes occur with greater difficulty (ref. 341).



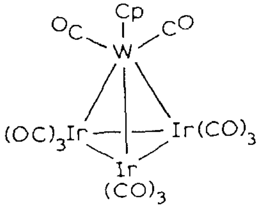
Scheme XLII

The coordinatively unsaturated cluster $[H_2Os_3(CO)_{12}]$ reacts with $[Rh(C_2H_4)_2acac]$ to yield the butterfly complex [76]. An unusual feature is the bridging function of the acetylacetonate ligand which functions as a 5-electron donor. From the proton NMR spectrum it is evident that the hydride ligands are fluxional but as no Rh-H coupling is observed, they evidently remain on the Os_3 portion of the molecule. Complex [76] is cleaved by carbon monoxide to $[Rh(CO)_2acac]$ and $[H_2Os_3(CO)_{11}]$ (ref. 342).

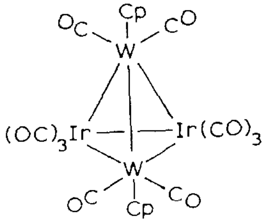
The tetrahedral clusters [77] and [78] are prepared from $[IrCl(CO)_2$(*p*-toluidine)] and $[cpWH(CO)_3]$ by zinc reduction under carbon monoxide and $Na[cpW(CO)_3]$ respectively. Heating [78] at 110° C under carbon monoxide converts it to [77]. Both complexes have been supported on alumina and studied by TPDE in flowing hydrogen. The majority of the carbonyl groups are hydrogenated as decomposition occurs but for [78] the yield of methane relative to liberated carbon monoxide is lower than for the other. Supported [77] shows a 70% selectivity to ethane in the hydrogenolysis of *n*-butane but for [78] it is no greater than 50%. Retention of Ir-W bonding is suggested for the latter under these conditions (ref. 343). The reactions of $[cp'_2Ir_2Cl_4]$ with $[Fe_3(CO)_{12}]$ in benzene are detailed in Scheme XLIII (ref. 344). Room temperature reaction of $[Ir_4(CO)_{12}]$ with five mols of hydrated ruthenium(III) chloride and sodium hydroxide in methanol solution under carbon monoxide yields $[RuIr_4(CO)_{15}]^{2-}$ ([79]) isolated as the PPN^+ salt. The complex is



[76]

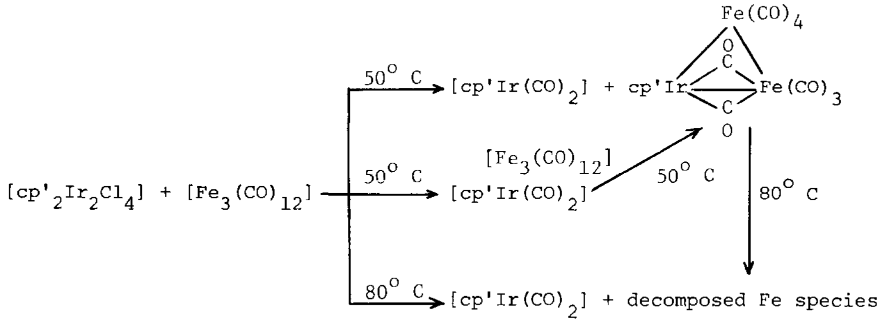


[77]

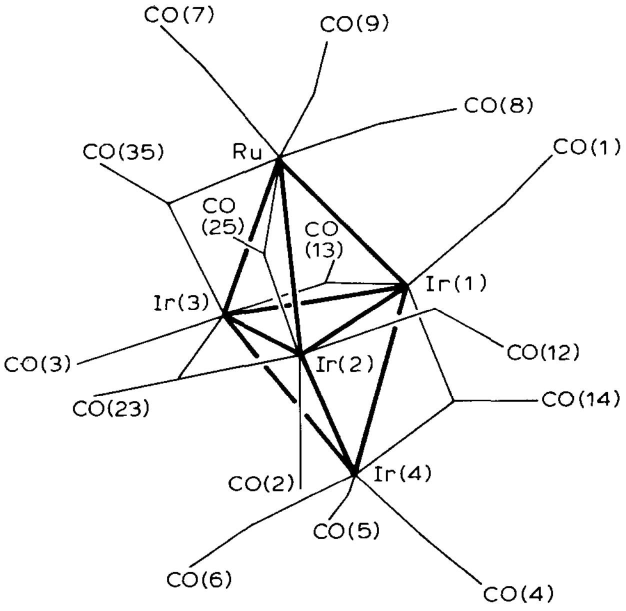


[78]

unstable in the absence of carbon monoxide and decomposes to a black material of unknown composition. The course of the original reaction is very dependent on conditions and unless a large excess of ruthenium and hydroxide is used one obtains $[HIr_4(CO)_{11}]^-$ or $[Ir_6(CO)_{15}]^{2-}$ (ref. 345).



Scheme XLIII



[79]

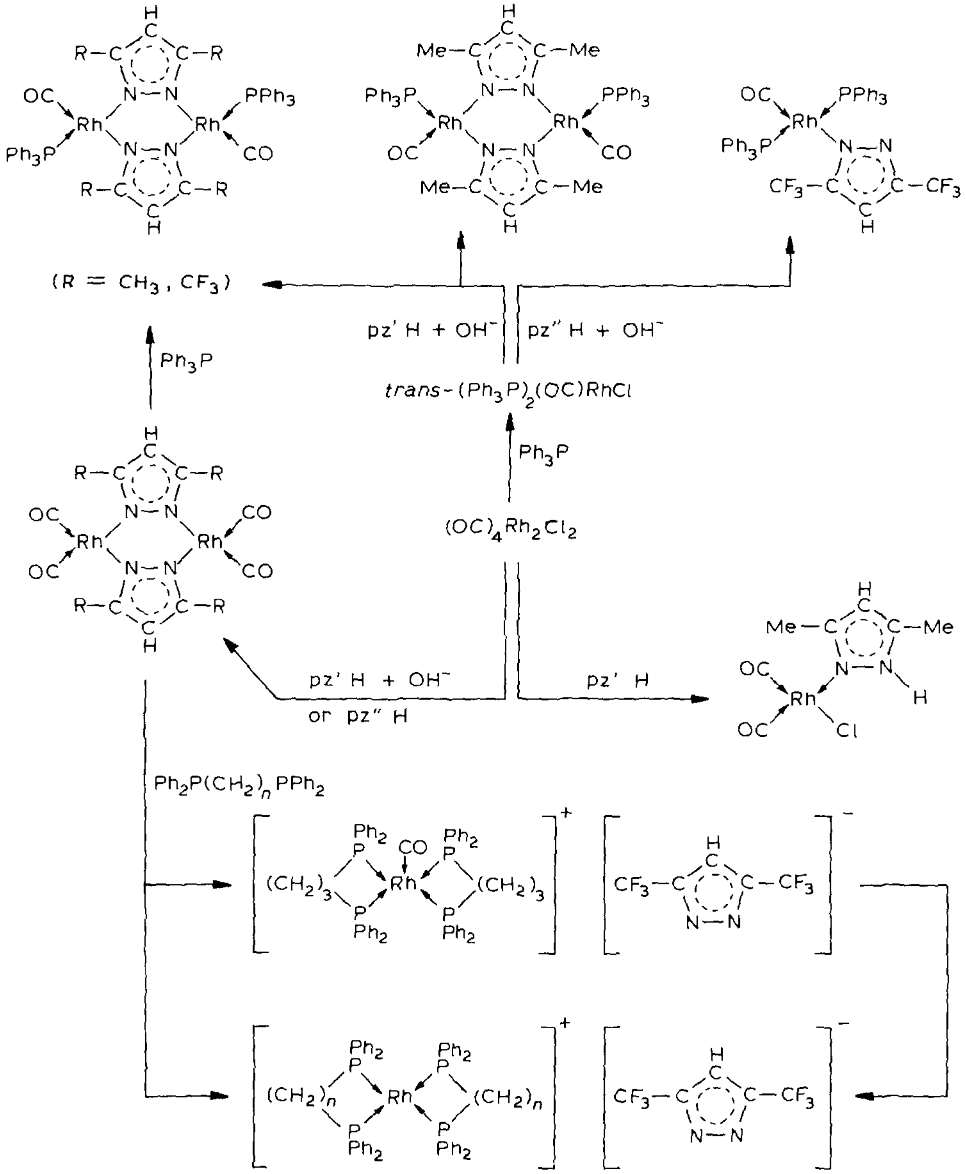
c) Metal(I), -(II) and -(III) Compounds

Polystyrene-divinylbenzene copolymer functionalized with pendant cyclopentadiene or $-CH_2C_5H_6$ groups has been used to generate supported analogs of $[cpCo(CO)_2]$. The former polymer on photolysis yields "cpCo" moieties from which the original dicarbonyl species can be generated on carbonylation at 100 atm CO and 200° C. The same treatment of the second polymer yields supported analogs of $[cp_2Co_2(\mu\text{-}CO)_2]$ and $[cp_2Co_2(CO)_2(\mu\text{-}CO)]$ which on heating lose all carbonyl groups. Carbonylation of this species regenerates the original supported monomeric dicarbonyl moieties.

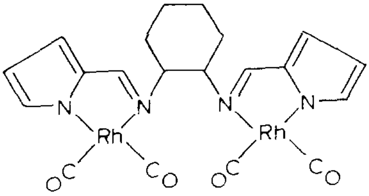
The supported complexes catalyze some hydroformylation of pent-1-ene but with poor selectivity. Although some hydrocarbon synthesis is observed in these systems under Fischer-Tropsch conditions, their activity is very low (ref. 346). Attempts to prepare medium-sized heterocyclic rings using $[HCo(CO)_4]$, $[Co_2(CO)_8]$ and $[RhH(CO)(PPh_3)_3]$ as catalysts for the hydroformylation of bis olefinic amines after the fashion of the cyclizations of 4-pentenals mediated by rhodium complexes were unsuccessful. Using various diallylamines the products were pyrrolidones and/or hydroformylation products of only the double bonds (ref. 347). Based on infrared spectral data, it was concluded that N-diphenylphosphinopyrrole and its 2,5-dimethyl analog (L) are better π-acceptors than triphenylphosphine in $[Rh(CO)ClL_2]$ (ref. 348). A number of mono- and binuclear rhodium complexes have been synthesized from 3,5-dimethylpyrazole(pz'H) or its trifluoromethyl analog(pz"H) as detailed in Scheme XLIV (ref. 349). The INEPT method of proton polarization transfer has been used to obtain the ^{103}Rh NMR spectrum of [80] in which the chemical shift of the metal is one of the highest yet seen (ref. 350).

The chemistry of Rh(I) complexes of the α-diimines RN=CHCH=NR, L, (R = Bu^t, $CEtMe_2$) is detailed in Scheme XLV (L' = 2,4,6-trimethylpyridine). The products are rather unstable and air-sensitive and only $[RhCl(CO)(C_2H_4)L]$ and $[RhCl(CO)_2L]$ were isolated; the rest were identified in solution. The diimine ligand is proposed to function as a chelate ligand and as the complexes indicated in the Scheme can be isolated only if the α-carbon of the terminal substituents bears no hydrogen atoms it is felt that steric factors stabilize these species. This is shown by the fact that with the diimines RN=C(R')C(R")=NR (R' = R" = H; R = Pr^i, $CHPr^i_2$, *m*-xylyl. R' = H, R" = Me; R = Pr^i. R' = R" = Me; R' = *p*-tolyl), the products obtained are $[Rh(CO)_2L][Rh(CO)_2Cl_2]$ although at low temperatures the initial product is the ligand-bridged dimer, $[(Rh(CO)_2Cl)_2L]$. At room temperature fast exchange between the dimer and the ionic species occurs (refs. 351, 352). A number of other N-donor ligands forming rhodium complexes are *o*-aminopyridine(AP), 7- or 8-methylquinoline(Q), *o*-and *p*-aminobenzoic acid(Q), 2-aminobiphenyl(Q) and a series of *o*-alkylanilines(L). With $[Rh(CO)_2X_2]^-$ (X = Cl, Br) or $[Rh(CO)_2Cl]_2$ these give $[Rh(AP)_2X]$, $[Rh(CO)_2Cl(Q)]$ and $[Rh(CO)_2(L)]$. For the last, proton NMR studies indicate interaction of the benzylic protons with the metal while $[Rh(CO)_2Cl$-(*o*-aminobenzoic acid)] in the presence of triphenylphosphine is a catalyst precursor for propene hydroformylation (refs. 353-356). In the same area, complexes of formula $[Rh(CO)_2Cl(A)]$ (A = $MeNH_2$, Me_2NH, $EtNH_2$, Et_2NH, pyridine, benzothiazole, benzimidazole, benzotriazole) have been prepared from $[Rh(CO)_2Cl$-(2,1,3-benzothiadiazole)] by ligand displacement (ref.357). The reaction of $[Rh(CO)Cl(PPh_3)_2]$ with diethylaluminum cyanide are depicted in Scheme XLVI(ref.358).

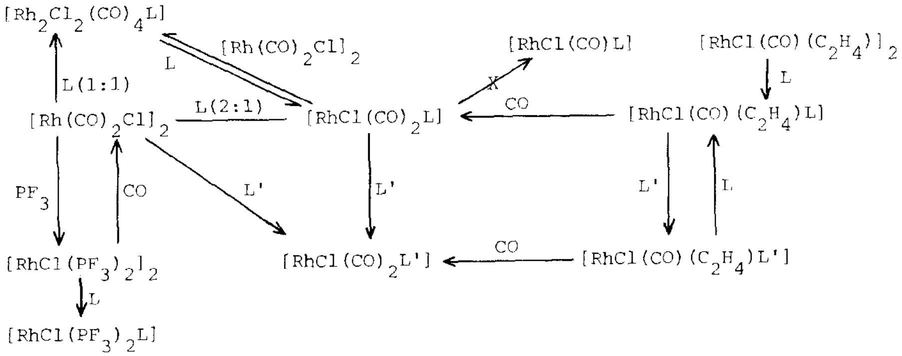
Other standard reactions of $[Rh(CO)_2Cl]_2$ have been used to prepare complexes of long-chain phosphines, $[Rh(CO)ClL_2]$ (L = $P(C_nH_{2n+1})_3$ (n = 4,8,14,16,18), $P(\underline{p}\text{-}R\text{-}C_6H_4)_3$ (R = C_nH_{2+1} (n = 2-7, 9))), many of which are oils (ref. 359) and of


(R = CH3, CF3)
pz' H + OH⁻
pz" H + OH⁻
trans-(Ph3P)2(OC)RhCl
Ph3P
Ph3P
(OC)4Rh2Cl2
pz' H + OH⁻
or pz" H
pz' H
Ph2P(CH2)nPPh2

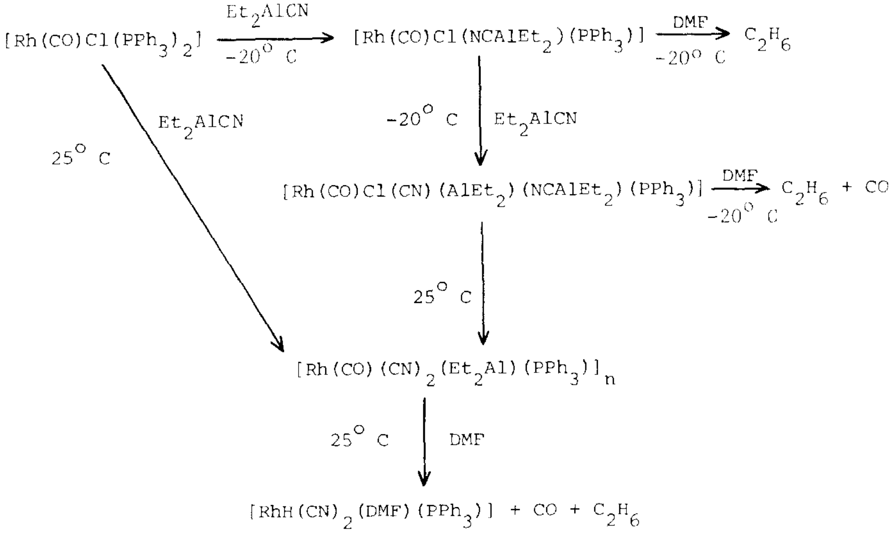
Scheme XLIV



[80]



Scheme XLV

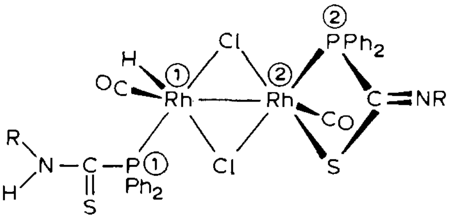


Scheme XLVI

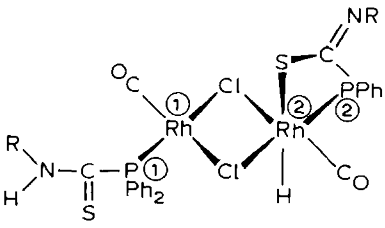
phosphites. In the latter study, the products are $[Rh(CO)ClL_2]$ or $[RhClL_2]_2$ (L = phosphite) depending on the ratio of reactants used. In the presence of moisture, hydrolysis of the ligands occurs and the complexes $[Rh(CO)Cl(P(O)(OR)_2)_2]$ are obtained (ref. 360). Finally, an improved reactor for the synthesis of $[Rh(CO)_2Cl]_2$ which eliminates the need of manually removing the water produced in the early stages of the reaction has been reported (ref. 361).

Cationic Rh(I) complexes containing one or two readily replaceable ligands (e.g. acetone) react with $[Au(Im)PPh_3]$ (Im = imidazole) to form $[(COD)(PPh_3)Rh(\mu\text{-}Im)\text{-}AuPPh_3]ClO_4$ and $[Y_2Rh((\mu\text{-}Im)AuPPh_3)_2]ClO_4$ (Y_2 = COD, $(CO)_2$, $(CO)PPh_3$) respectively while with $[Au(pz)PPh_3]$ (pz = pyrazolate) one obtains mixtures of $[(COD)Rh(\mu\text{-}pz)]_2$ and $[Au(PPh_3)_2]ClO_4$ or $[Y_2Rh(\mu\text{-}pz)]_2$ and $[(PPh_3)Au(\mu\text{-}pz)]_2ClO_4$ respectively. On the other hand, $[Rh(COD)Cl]_2$ reacts with the two gold complexes to yield $[(COD)Rh\text{-}(\mu\text{-}Im)]_3$ and $[(COD)Rh(\mu\text{-}pz)]_2$ plus $[AuCl(PPh_3)]$ respectively. The acetone solvate $[(COD)Rh(acetone)_x]Cl_4$ also reacts with $[L_2M(diphos)]$ (L = pz, M = Pd; L = Im, M = Pt) to yield $[(COD)Rh(\mu\text{-}pz)_2Pt(diphos)]ClO_4$ and $[(COD)_2Rh_2(\mu\text{-}Im)_4Pt_2(diphos)_2]\text{-}(ClO_4)_2$. In the majority of these complexes, the COD ligands could be replaced by carbon monoxide without disrupting the remainder of the molecule (ref. 362). The tropolonate complexes, $[Rh(trop)(CO)_2]$, can be prepared from $[Rh(COD)(trop)]$ and carbon monoxide, $[Rh(CO)_2Cl]_2$ and thallium tropolonate or $[Rh(CO)_2Cl_2]^-$ and tropolone. Only one carbonyl group can be substituted by phosphines. In the presence of potassium hydroxide, they catalyze the hydrogen transfer from isopropanol to acetophenone. A number of Schiff-base complexes derived from salicylaldehyde were also prepared (ref. 363). Both enantiomers of $[Rh(CO)_2(3\text{-trifluoromethylcamphorate})]$ have been obtained separately as yellow crystals. However a 1:1 enantiomeric mixture crystallizes as a red-green dichroic racemate. The same color arises when equimolar solutions of the separate enantiomers are mixed or when a solid mixture of the two is moistened with chloroform. It is concluded that the racemate is a stoichiometric, binary compound (ref. 364).

Further work on the reactions of $[Rh(CO)_2Cl]_2$ with $Ph_2PC(S)NHR$ (R = Me, Ph) has appeared. In toluene the initial product is a dimer which is believed to exist in solution in the rapidly interconverting tautomers [81a] and [81b]. Treatment of

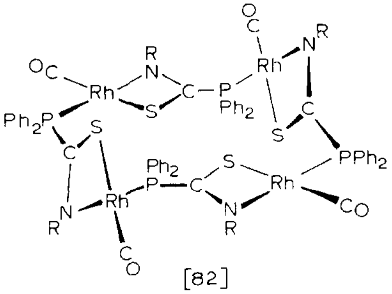


[81a]

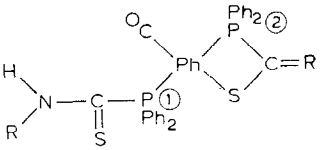


[81b]

[81a, b] with triethylamine or performing the original reaction in the presence of amine yields the tetramer [82] which can be cleaved to [83] on reaction with further $Ph_2PC(S)NHR$. Complex [83] can also be obtained directly from [81a, b] on reaction with $Ph_2PC(S)NHR$ and base while if this last reaction is carried out stepwise, it is seen to proceed <u>via</u> the intermediate, <u>trans</u>-$[Rh(CO)Cl(Ph_2PC(S)NHR)_2]$ (ref. 365). Sodium pyrazolate reacts with $[Rh(CS)Cl(PPh_3)_2]$ at -50° C to



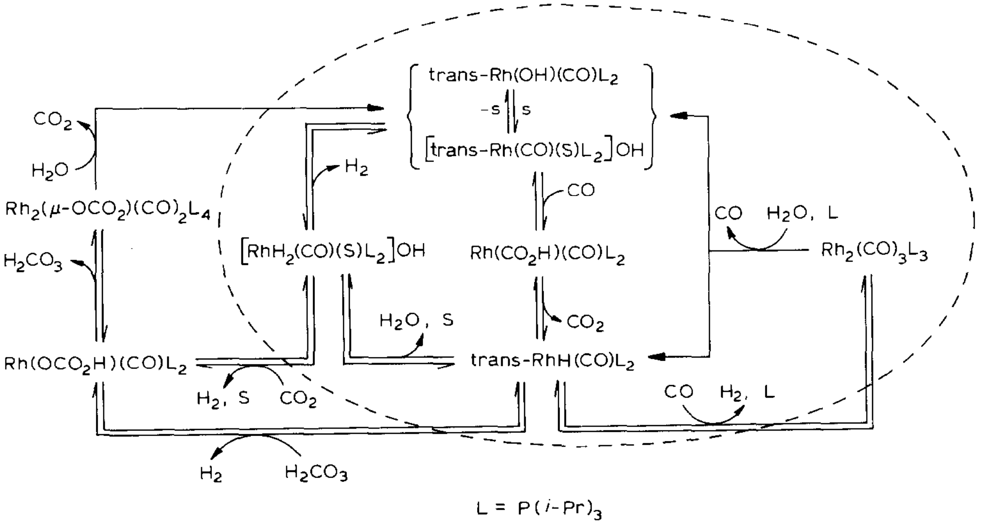
[82]



[83]

give $[Rh(CS)(pz)(PPh_3)_2]$ which on warming to room temperature condenses to $[Rh(CS)(pz)PPh_3]_2$. This is reversibly protonated with perchloric acid to $[Rh(CS)(Hpz)(PPh_3)_2]ClO_4$ which can also be got from $[Rh(CS)Cl(PPh_3)_2]$ by successive reactions with silver perchlorate and pyrazole in acetone (ref. 366). Both $[Rh(CO)Cl(PPh_3)_2]$ and $[RhCl(PPh_3)_3]$ are reported to react with NSOH to produce $[Rh(NSO)_2Cl(PPh_3)(H_2O)]_2$ which can be cleaved with triphenylphosphine to give $[Rh(NSO)_2Cl(H_2O)(PPh_3)_2]$ (ref. 367). Carbon monoxide replacement in $[Rh(CO)_3L_2]ClO_4$ ($L = P(\underline{p}\text{-}RC_6H_4)_3$ (R = Cl, F, Me, MeO)) occurs in acetonitrile with N-donor ligands to give $[Rh(CO)L_2L']ClO_4$ (L' = MeCN, py, bipy, ophen) (ref. 368). The photolysis of $[L_2ML'_2]$ (L_2 = acac or its trifluoro(tfac) or hexafluoro(hfac) analogs; L' = CO, C_2H_4; M = Rh, Ir) in frozen matrices has been studied. In methane and dinitrogen matrices $[Rh(tfac)(CO)_2]$ yields $[Rh(tfac)(CO)]$ and $[Rh(tfac)(CO)(N_2)]$ while in carbon monoxide no $[Rh(tfac)(CO)_3]$ is seen in contrast to what occurs with $[cpCo(CO)_2]$ under similar conditions. Under prolonged photolysis a small amount of a species thought to be $[Rh(\eta^1\text{-tfac})(CO)_2]$ is seen (ref. 369). A low temperature ^{31}P NMR study of mixtures of $[Rh(CO)_2acac]$ or $[RhH(CO)(PPh_3)_3]$ and triphenylphosphine together with hydrogen or carbon monoxide indicated the presence of $[RhH(CO)_2(PPh_3)_2]$ and $[Rh(CO)(PPh_3)_2]_2$ except at high phosphine/rhodium ratios where $[RhH(CO)(PPh_3)_3]$ is the major species. The last on standing in the presence of an aldehyde is converted into the dimer. A mechanism for hydroformylation is proposed wherein $[RhH(CO)(PPh_3)_2]$ is the species reacting with the substrate olefin (ref. 370).

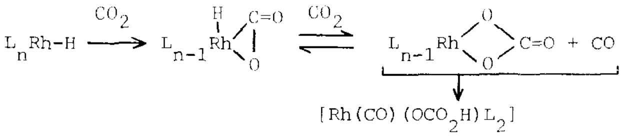
In an extensive study of water-gas-shift catalysis by rhodium complexes, $[RhHL_3]$ ($L = PEt_3$, PPr^i_3), $[Rh_2H_2(\mu\text{-}N_2)(P(cyclohexyl)_3)_4]$, $[RhH(N_2)(PPhBu^t_2)_2]$ and $[RhH(PBu^t_3)_2]$ were examined as catalyst precursors. In pyridine or acetone solution over the range 50°-100° C, the first three gave significantly more active systems than the last two with the triisopropylphosphine complex being the best. At the conclusion of the experiment in pyridine solution, complexes of formula $[Rh(CO)(py)L_2]BPh_4$ could be isolated from the first three systems while in acetone, the second and third systems yielded $[Rh(CO)(OH)(PPr^{i}_3)_2]$ and $[RhH(CO)(P(cyclohexyl)_3)_2]$ respectively. These last two complexes gave active catalyst solutions and are suggested as important in the overall catalytic cycle. The proposed cycle is presented in Scheme XLVII and the plausibility of the majority of the steps have been supported by separate experiments. The oxidative addition of water is shown



Scheme XLVII

by the formation of $[RhH_2py_2L_2]OH$ (L = PPr^{i}_3, $P(cyclohexyl)_3$) from $[RhH(PPr^{i}_3)_3]$ and $[Rh_2H_2(\mu\text{-}N_2)(P(cyclohexyl)_3)_4]$ in aqueous pyridine. These complexes, isolated as tetraphenylborate salts, convert to $[Rh(CO)(py)L_2]BPh_4$ (the final product of the catalytic systems) with the reductive elimination of hydrogen on carbonylation.

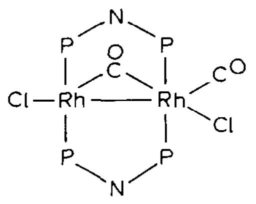
The details of the reaction of the hydride complexes with carbon monoxide were obtained from observing that $[RhH_2(PEt_3)_3]BPh_4$ adds CO to give $[RhH_2(CO)(PEt_3)_3]$-BPh_4 which on heating in aqueous pyridine eliminated hydrogen to yield $[Rh(CO)py(PEt_3)_2]BPh_4$. Also $[RhH(PPr^i_3)_3]$ adds CO to give first the unstable $[Rh(CO)_3(PPr^i_3)]_n$ (probably dimeric) and then $[Rh_2(CO)_4(PPr^i_3)_3]$ on further carbonylation or $[Rh_2(CO)_3(PPr^i_3)_3]$ on flushing with nitrogen. The last complex reacts with aqueous pyridine in the presence of phosphine to again give $[Rh(CO)py(PPr^i_3)_2]^+$ and hydrogen. Reentry of $[Rh(CO)py(PPr^i_3)_2]$ into the cycle for CO_2 production is demonstrated by its reaction with hydroxide (generated by the previous oxidative additions of water) to give $[Rh(CO)(OH)(PPr^i_3)_2]$ which on carbonylation in aqueous THF produces $[Rh_2(CO)_3(PPr^i_3)_3]$ and $[Rh_2(\mu\text{-}OCO_2)(CO)_2(PPr^i_3)_4]$. The last can be hydrolyzed in aqueous pyridine to generate CO_2 and reform $[Rh(CO)(OH)(PPr^i_3)_2]$ (refs. 371, 372). In related systems carbonylation of $[RhH(CO)(PPh_3)_3]$ yields a mixture of $[RhH(CO)_2(PPh_3)_2]$ and $[Rh_2(CO)_4(PPh_3)_4]$ which react with carbon dioxide at 5° C *via* at least two intermediates to give the bicarbonate complex *trans*-$[Rh(CO)(OCO_2H)(PPh_3)_2]$ which on flushing with argon at 0° C releases carbon dioxide, triphenylphosphine and possibly water to form a species proposed to be $[Rh_2(CO)_2(PPh_3)_3(\mu\text{-}CO)_3]$. Labelling experiments indicate the course of the reaction is unaffected by the presence of water. A mechanism involving reductive disproportionation of carbon dioxide is proposed (Scheme XLVIII) (ref. 373). The same bicarbonate complex and its iridium analog are formed by carbon monoxide attack on $[M(OH)(CO)(PPh_3)_2]$ (M = Rh, Ir) but here the presence of water retards the reaction. The rate data were not further interpreted however (ref. 374). Aqueous phosphoric acid converts $[RhH(PPr^i_3)_3]$ to $[RhH_2(H_2O)(PPr^i_3)_2]$ which can be photolyzed to $[RhH(H_2O)_3(PPr^i_3)_2]^{2+}$ and hydrogen (ref. 375). Using one equivalent of carbon monoxide $[Rh_2(\mu\text{-}H)_2(P(OPr^i)_3)_4]$ is converted to $[Rh_2(\mu\text{-}H)_2(\mu\text{-}CO)(P(OPr^i)_3)_4]$ while with an excess, cleavage of the dimer occurs and $[RhH(CO)_n(P(OPr^i)_3)_{4-n}]$ (n = 1, 2) is formed. Interestingly, when n = 1, carbon monoxide dissociation is observed in contrast to the phosphine dissociation observed with $[RhH(CO)(PPh_3)_3]$. If $[Rh_2(\mu\text{-}H)_2(\mu\text{-}CO)(P(OPr^i)_3)_4]$ is allowed to stand in solution, $[Rh_2(\mu\text{-}CO)_2(P(OPr^i)_3)_4]$ and a species tentatively identified as a hydride form. The former species reacts with hydrogen to give a green species showing no Rh-H bands in the infrared spectrum and with carbon monoxide to yield $[Rh_2(CO)_2(\mu\text{-}CO)_2(P(OPr^i)_3)_4]$ which does not readily degrade to monomeric species (ref. 375).



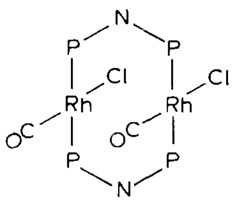
Scheme XLVIII

Reduction of $[Rh(CO)Cl(PMe_3)_2]$ with sodium amalgam gives $[Rh_2H_2(\mu\text{-}CO)_2(PMe_3)_6]$ while the same treatment of $[RhCl(PMe_3)_3]$ or $[Rh(PMe_3)_4]Cl$ produces $[Hg_6(Rh(PMe_3)_3)_4]$ containing an octahedron of mercury atoms and four, face-bridging $Rh(PMe_3)_3$ units. In benzene $[RhCl(PMe_3)_3]$ or $[Rh(PMe_3)_4]Cl$ react with sodium alone to give $[RhCl(PMe_2Ph)(PMe_3)_2]$ while $[Rh(PMe_3)_4]Cl$ with sodium cyclopentadienide, methyllithium or oxygen in the presence of moisture yields $[cpRh(PMe_3)_2]$, $[RhMe(PMe_3)_3]$ and $[Rh(O_2)(PMe_3)_4]^+$ respectively (ref. 377). The solvated complex $[Rh(diphos)(MeOH)_2]BF_4$ reacts in methanol with *mer*-$[IrH_3(PEt_3)_3]$ and sodium tetraphenylborate to give $[(diphos)Rh(\mu\text{-}H)_3Ir(PEt_3)_3]$ which can be carbonylated to *fac*-$[IrH_2(CO)(PEt_3)_3]^+$ and unidentified rhodium complexes (ref. 378).

The study of binuclear complexes of the A-frame type continues unabated. With $PhSCH_2SPh$ and $[Rh(CO)_2Cl]_2$ in equimolar quantities the dimer $[Rh(CO)Cl(PhSCH_2SPh)_2Rh(CO)Cl]$ is formed which loses carbon monoxide to yield $[Rh_2Cl_2(\mu\text{-}CO)(PhSCH_2SPh)_2]$. With two equivalents of the ligands $PhS(CH_2)_nSPh$ (n = 1-6) are obtained air-sensitive oily or waxy materials which were difficult to characterize. For n = 2, 4 however these were identified as $[Rh(CO)_2Cl(PhS(CH_2)_nSPh)Rh(CO)_2Cl]$. One equivalent of the mixed ligand $Ph_2P(CH_2)_2SPh$ reacts with $[Rh(CO)_2Cl]_2$ to give the chelate complex $[Rh(CO)Cl(Ph_2P(CH_2)_2SPh)]$ while with an excess, $[Rh(CO)Cl(Ph_2P(CH_2)_2SPh)_2]$ is obtained where the ligand is bound only through phosphorus (ref. 379). Carbonylation of mixtures of $[RhCl(COD)]_2$ and potassium halides in acetone/methanol followed by addition of ligands, L_2, (L_2 = bis(diphenylphosphino)methane (DPM), bis(diphenylarsino)methane (DAM)) yields the A-frame complexes $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}X)(L_2)_2]^+$ (X = Cl, Br, I) or the face-to-face dimers $[Rh_2(CO)_4X_2(L_2)_2]$ (X = CN,NCS). The bromo complexes slowly lose the bridging carbonyl ligand while the cyano complex (L_2 = DPM) loses one carbonyl to give $[Rh_2(CO)_2(CN)_2(\mu\text{-}CO)(DPM)_2]$. Its DAM analog loses two carbonyl groups. The original reaction with potassium cyanate or potassium azide gives $[Rh_2(NCO)_2(CO)_2(L_2)_2]$ and $[Rh_2Cl(N_3)(CO)_2(L_2)_2]$ respectively (ref. 380). Reaction of $[Rh(CO)_2Cl]_2$ with the ligands $EtN(P(OR)_2)_2$ (R = Me, Ph) yields [84] and [85] respectively. In chloroform solution, the terminal carbonyl group [84] is lost (ref. 381). Reduction of [85] with zinc amalgam under carbon monoxide yields [86] which appears

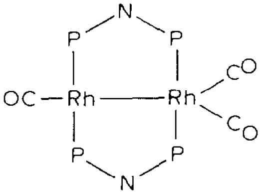


[84]



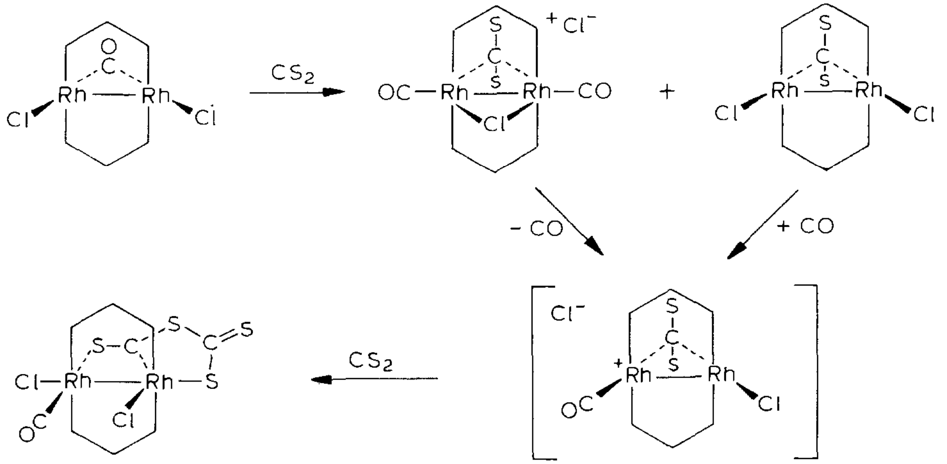
[85]

fluxional by ^{31}P NMR (ref. 382). A full report of the structure of $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$ has appeared and details of its preparation are given in Scheme XLIX (ref. 383).



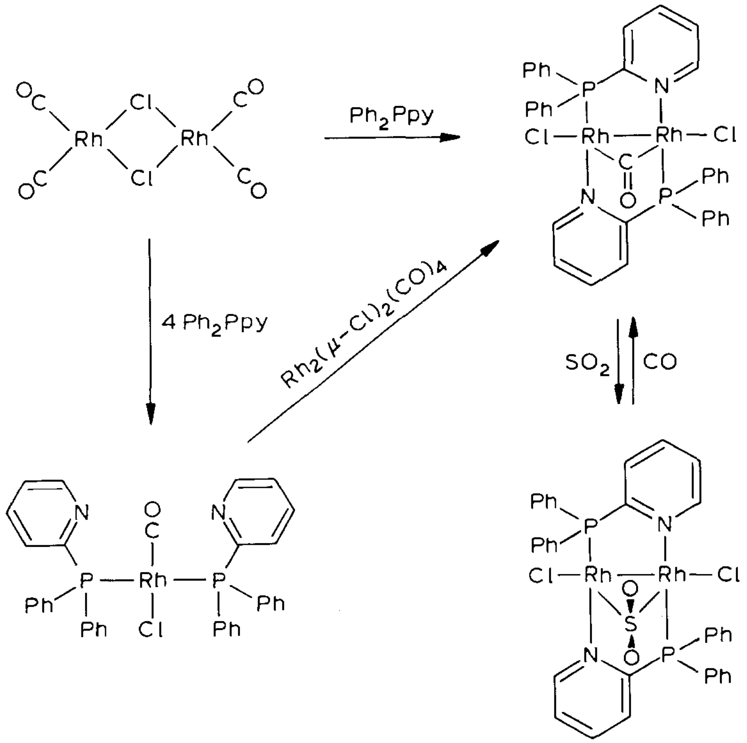
[86]

Full reports of the reactions of $[Rh(CO)_2Cl]_2$ with 2-pyridyldiphenylphosphine and the structure of one of the products are now available and are depicted in Scheme L. The failure to obtain strict analogs of the DPM-bridged dimers is attributed to the smaller bite of the ligand used here (ref. 384). The DPM derivative $(Ph_2P)_2CHMe$ reacts with $[Rh(CO)_2Cl]_2$ to give $[Rh_2(CO)_2Cl((Ph_2P)_2CHMe)_2][Rh(CO)_2Cl_2]$ which is thought to be an A-frame complex. However with



Scheme XLIX

$[RhCl(cyclooctene)_2]_2$ the chelate complex $[Rh((Ph_2P)_2CHMe)_2]^+$ is formed. Analogs with DPM and diphos were also prepared while with 1,3-bis(diphenylphosphino)propane (DPPP) the product was $[Rh(DPPP)_2]BF_4 \cdot \frac{1}{2}[RhCl(cyclooctene)_2]$. All four complexes reversibly add HCl to give <u>trans</u>-$[RhHCl(L_2)_2]^+$ (L_2 = DPM, diphos, DPPP, $(Ph_2P)_2CHMe$) and all but the diphos complex add dioxygen to give $[Rh(O_2)(L_2)_2]^+$ (ref. 385). An extensive series of molecular orbital calculations on rhodium A-frame complexes has appeared which supports the proposal made on the basis of structural studies that the bridging carbonyl group in $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-MeO}_2C{=}CCO_2Me)(DPM)_2]$ should be considered as a ketonic carbonyl (ref. 386).

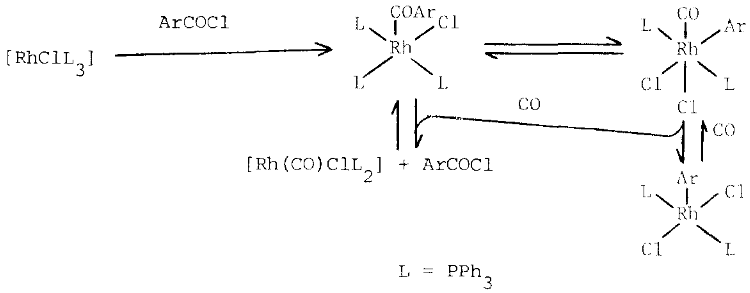


Scheme L

Reaction of the phospha-alkene $Ph_2C{=}P(mesityl)$ (L) with $[RhCl(PPh_3)_3]$, $[Rh(CO)_2Cl]_2$ and $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ produces *trans*-$[RhCl(L)(PPh_3)_2]$, trans-$[Rh(CO)ClL_2]$ and $[(\eta^5\text{-}C_9H_7)RhL_2]$ respectively. In all cases the phospha-alkene is bound through phosphorus (ref. 387).

Hydroformylation of olefins catalyzed by $[Rh(CO)ClL_2]$ and $[RhH(CO)L_3]$ (L = tertiary phosphine) has been the subject of several studies. Use of the former (L = PPh_3) converts 3-substituted-1,1-diethoxybut-2-enes into the corresponding derivatives of glutaraldehyde monoethylacetal which are intermediates in the synthesis of optically active pyridines. Also $[RhH(CO)(PPh_3)_3]$ is useful for the conversion of (S)-2-methyl-2-(2-*sec*-butylallyl)-1,3-dithiane into (S)-3-*sec*-butyl-4-(1,3-dithiane-2-methyl-2-yl)-butanal (ref. 388). The presence of *p*-alkyl groups on triarylphosphines are effective for increasing the selectivity to *n*-heptanal in the hydroformylation of hex-1-ene catalyzed by $[Rh(CO)ClL_2]$ with the optimum system containing L = $P(p\text{-}Bu^nC_6H_4)_3$. In these systems, trialkylphosphine complexes enhance the isomerization of the feedstock olefin and with long-chain alkyl substituents the yield of aldehyde is significantly decreased (ref. 389). The same system with L = PPh_3 has been studied as a function of the concentration of added phosphine and total pressure to optimize the selectivity to *n*-heptanal. The selectivity appears independent of catalyst concentration so long as the rate is not controlled by the rate of diffusion of the gaseous reactants to the catalyst. Also, while the gas phase hydroformylation of hex-1-ene is much slower than the liquid phase system, the selectivity is greatly enhanced (refs. 390, 391). Dissolution of $[RhH(CO)(PPh_3)_3]$ in molten triphenyl- or tri(*p*-tolyl)phosphine followed by supporting the mixture on silica provides an active catalyst for the gas phase hydroformylation of allyl alcohol to 4-hydroxybutyraldehyde with high selectivity (ref. 392). In the hydroformylation of propylene to *n*-butanol and 2-ethylcyclohexanol, only the initial step which forms *n*-butyraldehyde is considered to involve catalysis by $[RhH(CO)(PPh_3)_3]$ (ref. 393).

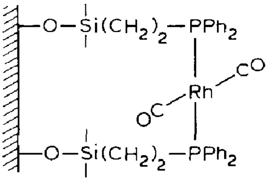
In contrast to other acid chlorides, chlorobenzene is not the product of the stoichiometric decarbonylation of benzoyl chloride with $[RhCl(PPh_3)_3]$ at moderate temperatures. At 80° C the only product observed after fifteen minutes is $[Rh(CO)Cl_2(Ph)(PPh_3)_2]$ while after a longer time $[Rh(CO)Cl(PPh_3)_2]$ and $[RhCl_2(Ph)(PPh_3)_2]$ are seen but chlorobenzene is absent. In dichloroethane solution at 80° C equimolar quantities of $[RhCl(PPh_3)_3]$ and *p*-tolylCOCl react over 24 hr. to give roughly equal quantities of $[Rh(CO)Cl(PPh_3)_2]$ and $[RhCl_2($*p*-tolyl$)(PPh_3)_2]$ together with *p*-tolylCOCl which was shown in a separate experiment to arise from reaction of $[RhCl_2($*p*-tolylCO$)(PPh_3)_2]$ with $[RhCl_2(CO)($*p*-tolyl$)(PPh_3)_2]$ rather than simply being unreacted starting material. The results are interpreted according to Scheme LI (ref. 394). These results notwithstanding, $[RhCl(PPh_3)_3]$ has found use in effecting the decarbonylation of an aldehyde intermediate in the synthesis of a cholestadienone (ref. 395).



Scheme LI

The hydrogenation of nitrobenzene and hept-1-ene is reported to be catalyzed by $[Rh(CO)ClL_2]$ (L = 2,3:4,5-diisopropylidenefructopyranose-1-tetraethyldiamidophosphite) (ref. 396). A phase-transfer catalyst composed of $[Rh(CO)_2Cl]_2/C_6H_6/$-$NaOH/H_2O$/tetraalkylammonium halide is reported to be effective for the isomerization of allyl aromatics (ref. 397). The carbonylation of phenyl azide to phenyl isocyanate is catalyzed by $[Rh(CO)Cl(PPh_3)_2]$ and $[Rh(diphos)_2]Cl$ at temperatures below 80° C. Interestingly, $[Ir(diphos)_2]Cl$ was inactive while $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2Cl_2]^-$ showed low activity (ref. 398). Under hydroformylation conditions, $[RhCl(PPh_3)_3]$ and $[RhCl(CO)(PPh_3)_2]$ are poor catalysts for the conversion of *o*-nitroallylbenzene to the corresponding aldehyde while $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ are inactive (ref. 399). The oxidation of α-methylstyrene is inhibited by $[Rh(CO)$-$Cl(PPh_3)_2]$ but $[Ir(CO)Cl(PPh_3)_2]$ and $[Rh(diphos)_2]Cl$ accelerate the process to a modest extent. Unlike other olefin oxidations, the metal appears not to react with organic peroxides formed in the main radical chain process and the possible direct activation and transfer of oxygen in the initial part of the reaction is suggested (ref. 400).

Phosphinated styrene-divinylbenzene copolymer has been used to support $\{RhCl(CO)\}$ and $\{RhCl(PR_3)\}$ moieties to be used for the catalysis of hexene and benzene hydrogenation. Apparently several types of sites exist and the structure of the support significantly influences the evolution of the catalyst activity (ref. 401). A comparison of $[Rh(CO)_2Cl]_2$ in homogeneous media and supported on alumina for the catalytic hydrogenation of *trans*-1,3-pentadiene to primarily *trans*-pent-2-ene showed that the latter system, although more active initially, lost activity with time. Thus the homogeneous system appears to be the better catalyst (ref. 402). The complex $[Rh(CO)ClL_2]$ (L = $Ph_2P(CH_2)_2Si(OEt)_3$) reacts with silica and alumina surfaces to become attached *via* silyloxy groups of both ligands. On silica the initial species, [87], carbonylates to [88] at 100° C under pressure and with prolonged exposure to high pressure of carbon monoxide and hydrogen [89] is seen. Depressurization leads to reformation of [88]. On alumina one sees [87], [88] and the new species [90] (ref. 403). Species [87] is an effective and highly selective catalyst for the hydroformylation of hex-1-ene to *n*-heptanal (ref. 404). Silica



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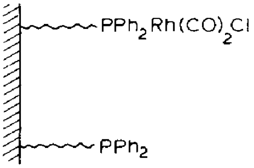
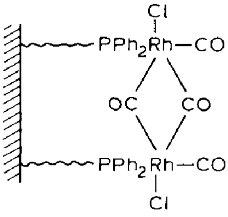
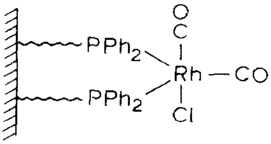


[88]



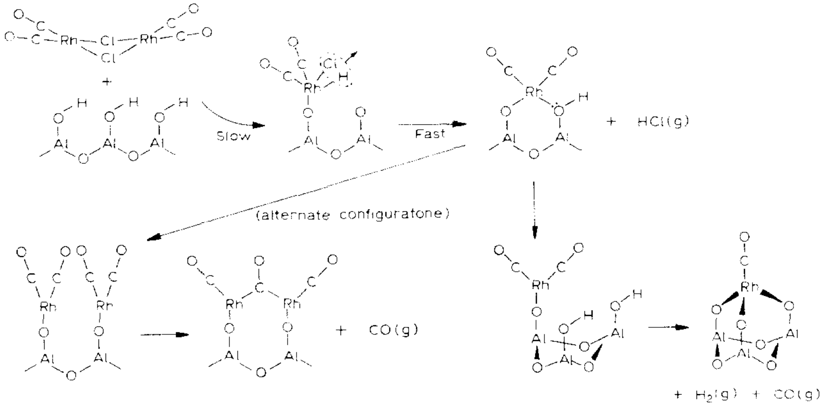
[89]

gel-supported $\{Rh(CO)_2\}$ and $\{Rh_2(CO)_4\}$ moieties are catalysts for the oxidation of hex-1-ene to 2-hexanone in the presence of acid and Cu(II). The mononuclear species appears more active (ref. 405). Reaction of $[Rh(CO)Cl(L)]_2$ (L = CO, PPh_3, P(p-tolyl)$_3$) with polystyrene-bound pyridine or bipyridine ligands produces



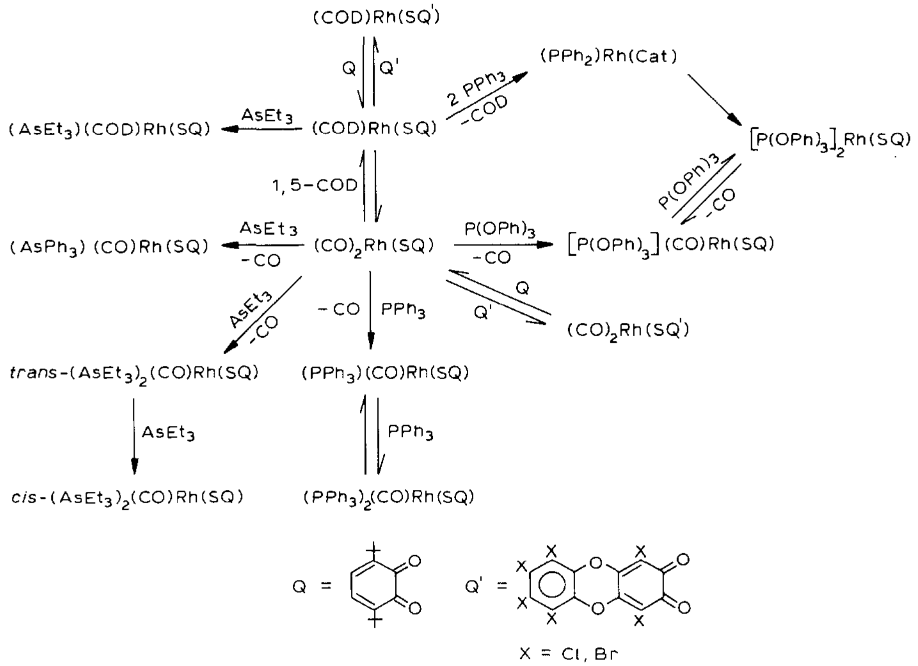
[90]

supported $\{Rh(CO)ClL\}$ or $\{Rh(CO)Cl\}$ and $\{RhLCl\}$ moieties respectively. The latter system has been studied as an olefin hydrogenation catalyst and some reduction to Rh(O) species occurs (refs. 406, 407). Anion exchange resins will support $[Rh(CO)_2I_2]^-$ and the system catalyzes the carbonylation of methanol. In low polarity solvents, catalyst leaching is minimized (ref. 408). Olefin hydroformylation is catalyzed by $[RhH(CO)(PPh_3)_3]$ dissolved in molten triphenylphosphine and supported on chromosorb or silica gel with high selectivity to straight-chain aldehydes (refs. 409-410). Finally, the interaction of $[Rh(CO)_2Cl]_2$ with alumina surfaces has been studied by IETS. The mechanism of adsorption is depicted in Scheme LII (ref. 411).



Scheme LII

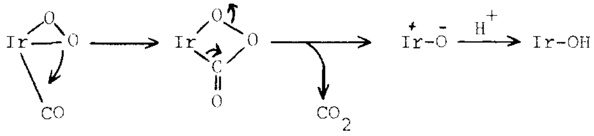
Phosphorus-31 NMR studies of the reactions of $[RhH(CO)(PPh_3)_3]$ with the bidentate phosphine ligands trans-1,2-bis(diphenylphosphinomethyl)cyclobutane, 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane(DIOP), 1,1'-bis-(diphenylphosphino)ferrocene and 1,1'-bis(bis(p-trifluoromethyl)phenylphosphino)-ferrocene indicate the existence of $[L_2RhH(CO)(PPh_3)]$, $[Rh(L_2)_2H(CO)]$ and $[L_2RhH(CO)(\mu\text{-}L_2)RhH(CO)L_2]$ (L_2 = ditertiary phosphine). In the second complex one phosphine is monodentate (ref. 412). Also studied were variable temperature ^{31}P NMR spectra of $[Rh(CO)XL_2]$ (L = $PMeBu^t_2$, PBu^t_2Cl, $PPhBu^t_2$; X = Cl, Br, I) which were interpreted in terms of hindered rotations of the ligands about the Rh-P bonds (ref. 413). Extended Hückel molecular orbital calculations have been performed on $[RhClL_3]$ (L = PMe_3, PPh_3), $[Rh(CO)ClL_2]$ (L = PMe_2Ph, $PHBu^t_2$) and $[Ir(CO)Cl(PHBu^t_2)_2]$ to determine $^2J_{PP}$ (ref. 414) while LCAO-MO-SCF calculations on $[Rh(PH_3)_3]^+$ and $[Rh(PH_3)_2(Ph_2CH{=}CH_2)]^+$ have been used to model geometrical distortions in $[Rh(PPh_3)_3]^+$. In the latter study, the approach of the species to a T-shaped structure as the minimum energy configuration is attributed to the interaction of a phenyl group with the metal. However the torsional orientation of this group is such that o-metallation is predicted to be unfavorable and indeed this process has not yet been observed (ref. 415). Scheme LIII details the chemistry of a series of o-benzosemiquinolate complexes prepared from $[Rh(CO)_2Cl]_2$ and the appropriate thallium o-benzosemiquinolate. The ESR spectra of these complexes of



Scheme LIII

spin-labelled ligands were also measured (ref. 416). Also available are the He(I) PES of $[Rh(CO)_2Br]_2$, $[Rh(PF_3)_2X]_2$ (X = Cl, Br) and $[Ir(PF_3)_2Cl]_2$ (ref. 417).

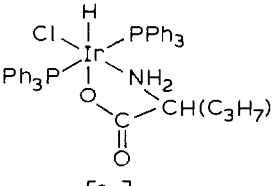
Carbonylation of $[IrF_5]$ at 260-80° C and 1 atm yields $[Ir(CO)_{2.5}F_2]$ which under pressure reacts further to give $[Ir(CO)_3F_2]$ and $[Ir(CO)_2F_2]$ (ref. 418). The tridentate phosphine $PhP((CH_2)_3PPh_2)_2$ (BDPP) reacts with $[IrCl(cyclooctene)_2]_2$ to yield [IrCl(BDPP)] which can be successively carbonylated to [IrCl(CO)(BDPP)] and $[Ir(CO)_2(BDPP)]Cl$. Both are proposed to have trigonal bipyramidal structures with the carbonyl ligands in equatorial sites. Oxidative addition reactions of [IrCl(BDPP)] with hydrogen and hydrogen chloride have also been recorded (ref. 419). In benzene solution, the carbonyl ligand in $[Ir(CO)Cl(L_2)]$ (L_2 = o-diphenylphosphino-N,N-dimethylaniline (PN), o-diphenylphosphino-N,N-dimethylbenzylamine (PCN)) can be oxidized by dioxygen to carbon dioxide with $[Ir(OH)(O_2)(L_2)]_2Cl_2$ being the other product. Since these types of complexes are known to form dioxygen adducts, the process detailed in Scheme LIV is proposed although it is not clear what is the



Scheme LIV

source of the proton since the reaction proceeds in rigorously dried solvents and no acceleration is observed in the presence of water (ref. 420). Oxidative addition of RCH_2SO_2Cl (R = H, p-tolyl, o-$NO_2C_6H_4$) to $[Ir(CO)Cl(PPh_3)_2]$ yields $[IrCl_2(CO)(SO_2CH_2R)(PPh_3)_2]$ but attempts at dehydrohalogenation did not give clean reactions (ref. 421). The first thiazate complex $[Ir(CO)(NSO)Cl_2(PPh_3)_2]$ is reported to be obtained from $[Ir(CO)Cl(PPh_3)_2]$ and thionitrosyl chloride in air. Under nitrogen, the product is $[Ir(CO)(NS)Cl_2(PPh_3)_2]$ (ref. 422).

Oxidative addition of acids to $[IrCl(L)(PPh_3)_2]$ in polar solvents gives trans-$[IrH(X)(L)Cl(PPh_3)_2]$ (L = CO, N_2; X = BF_4, $OSO_2C_4F_7$. L = CO, X = OSO_2CF_3) while for L = CO, cis isomers are formed in non-polar solvents. Displacement of the weakly-coordinated tetrafluoroborate ligand by a variety of species occurs in trans-$[IrH(FBF_3)(CO)Cl(PPh_3)_2]$ to give trans-$[IrH(B)Cl(CO)(PPh_3)_2]BF_4$ (B = C_2H_4, C_3H_6, PPh_3, CO, MeCN, H_2O, acetone, THF) or trans-$[IrH(ECN)Cl(CO)(PPh_3)_2]$ (E = S, Se). In the latter, the thiocyanate is S-bonded while both N- and Se-binding is observed in the other. The selenocyanate complex reacts further with trans-$[IrH(FBF_3)(CO)$-$Cl(PPh_3)_2]$ to yield the selenocyanate-bridged species $[(IrH(CO)Cl(PPh_3)_2)_2SeCN]BF_4$. Reaction of $[IrH(FBF_3)Cl(N_2)(PPh_3)_2]$ with diphos or triphenylphosphine gives trans-$[IrHCl(diphos)_2]BF_4$ and trans-$[IrHCl(PPh_3)_3]BF_4$ respectively while with valinate or diethyldithiocarbamate ions [91] and [92] are obtained. The dinitrogen complex also functions as a catalyst for the hydrogenation of cyclohexanes and the isomerization of COD (refs. 423, 424). Oxidative addition of Si-H bonds in $P(SiH_3)_3$ to $[Ir(CO)I(PPh_3)_2]$ occurs in benzene using phosphine:metal ratios of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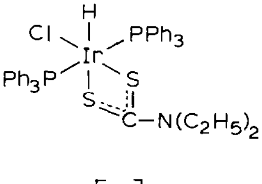
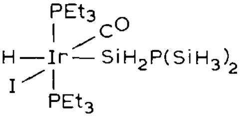

[92]

1:1, 0.5:1 and 0.25:1 to yield [93]-[95] respectively. Analogs of [93] and [94] are formed using $N(SiH_3)_3$. With $Y(SiH_3)_2$ (Y = O, S, Se) the reaction yields mixtures of trans-$[(IrI(CO)(PPh_3)_2(H)SiH_2)_2Y]$ and trans-$[IrH(SiH_2YSiH_3)(CO)I(PPh_3)_2]$ (ref. 425). Reaction of $[IrH(CO)(PPh_3)_3]$ with MH_3Q (M = Si; Q = H, F, Cl, Br, I, Me, $SiMe_3$. M = Ge; Q = H, F, Cl, Br, I) gives, in most instances, either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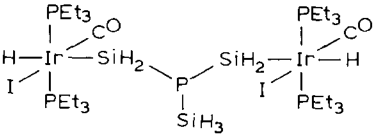
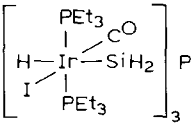
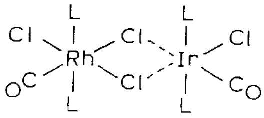

[94]


[95]

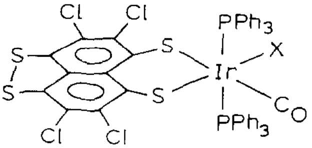
fac-$[IrH_3(CO)(MH_2Q)(PPh_3)]$ or $[IrH_2(CO)(MH_2Q)(PPh_3)_2]$. For M = Si, the second complex is the major product and only for Q = $SiMe_3$ is the yield of this species less than 75% of the total. For M = Ge the only instance where the first complex is less than 80% of the total yield is when Q = H. An extensive analysis of the ^1H NMR spectra has been performed and couplings are seen between Ir-H and M-H protons. For Q = I and M = Si, the two silyl protons are separated by 1.3 ppm and show saturation transfer (ref. 426). At -50° C, the phosphine ligands PF_2Q add to $[Ir(CO)X(PEt_3)_2]$ (X = Q = Cl, Br, I; X = I, Q = H) to give $[Ir(CO)X(PF_2Q)(PEt_3)_2]$ (PEt_3 ligands axial) but on warming oxidative addition occurs to yield $[Ir(CO)X(Q)(PF_2)(PEt_3)_2]$ (ref. 427). Oxidation of $[IrCl(CO)(PMe_2Ph)_2]$ by $[RhCl_3(CO)(PMe_2Ph)_2]$ gives $[IrCl_3(CO)(PMe_2Ph)_2]$ and $[RhCl(CO)(PMe_2Ph)_2]$ while with

$[IrCl_3(CO)(PEt_2Ph)_2]$ one sees initially $[Ir(CO)Cl(PEt_2Ph)_2]$ and $[IrCl_3(CO)(PMe_2Ph)_2]$ although over longer times phosphine scrambling also occurs. The absence of an induction period is taken to indicate the absence of radical intermediates. No exchange of phosphines occurs between $[RhCl_3(CO)(PEt_2Ph)_2]$ and $[RhCl_3(CO)(PMe_2Ph)_2]$ but when a small quantity of $[Rh(CO)Cl(PMe_2Ph)_2]$ is added, the Rh(I) species disappears and mixed-ligand Rh(III) complexes plus $[Rh(CO)Cl(PEt_2Ph)_2]$ are seen. The results are taken to imply the formation of intermediates such as [96] (ref. 428).

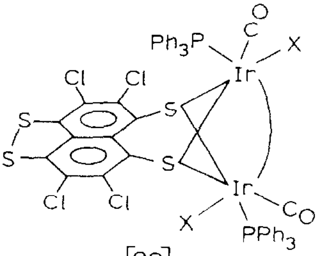


[96]

Borohydride reduction of $[Ir(CO)Cl(PPh_3)_2]$ in acetonitrile under hydrogen yields first mer- and then fac-$[IrH_3(CO)(PPh_3)_2]$ which were separated by fractional crystallization. Both species isomerize in solution, particularly in the presence of hydrogen to an equilibrium mixture containing a slight excess of the fac isomer. The kinetics of the isomerization and the observation of a reaction of the mixture with CH_2Cl_2 in the absence of hydrogen were interpreted as indicating the formation of Ir(I) intermediates via a slow, unimolecular loss of hydrogen. This was supported by the observation that the reaction of the trihydrides with triphenylphosphine was independent of phosphine concentration. These results together with others for the oxidative addition of Group IV hydrides to $[Ir(CO)Cl(PPh_3)_2]$ indicate that the kinetically favored isomer is the one where the original phosphine ligands migrate to cis positions which are trans to the addend molecule (ref. 429). Reaction of tetrachlorotetrathionaphthalene with one or two equivalents of $[Ir(CO)X(PPh_3)_2]$ yields [97] (X = H, Cl) and [98] (X = H, Cl, Br, I) respectively. Complex [98] reacts with $[Pt(PPh_3)_4]$ to yield [99] while with two

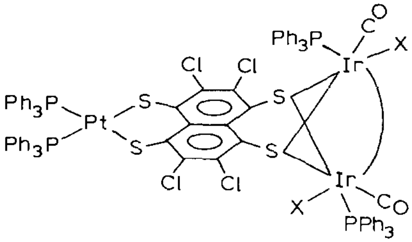


[97]



[98]

equivalents of [IrH(CO)$(PPh_3)_3$] (X = I) the product is [100] (ref. 430). Reduction of [Ir$(CO)_2$Cl(p-toluidine)] with zinc in the presence of carbon monoxide and trans-1,2-bis(diphenylphosphino)ethylene in aqueous THF gives the trinuclear cluster [101] (ref. 431).



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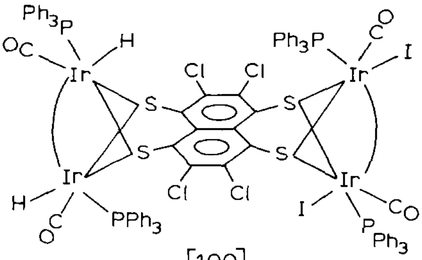
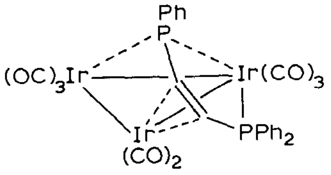


[100]



[101]

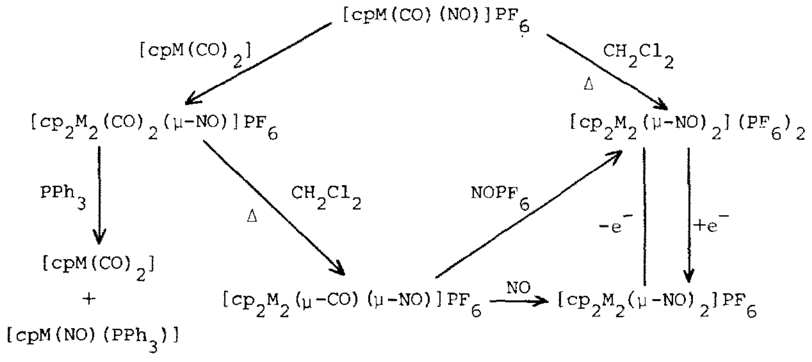
Equilibrium constants for the protonation of [Ir(CO)XL_2] (X = Cl, Br, I; L = PPh_3, $PMePh_2$, PMe_2Ph. X = Cl; L = $AsPh_3$, $AsMe_2Ph$, $AsMePh_2$, PMe_2Bu^t, PEt_2Bu^t, $PMeBu^t{}_2$, $PEtBu^t{}_2$) by CF_3SO_3H in methanol have been measured. The fact that these values are comparable to those for hydrogen chloride addition to [Ir(CO)XL_2] [X = Cl, Br; L = $PMePh_2$, PMe_2Ph, PPh_3) is taken to indicate that chloride and methanol are bound to the metal trans to hydrogen with about the same strength. The kinetics of the reactions suggest that either methanol or chloride coordinates first followed by protonation (ref. 432). The oxidative addition of iodides, RI (R = I, H, Me, Et, Pr^n, Pr^i, $PhCH_2$, MeCO), to [Ir(CO)Cl$(PMe_3)_2$] in dichloroethane has been studied by adiabatic titration calorimetry and enthalpies for the reaction determined. From the thermochemical data, Ir-R bond energies were determined and found to decrease in the order $H > Me \sim I \sim MeCO > Et > Pr^n > Pr^i > PhCH_2$. The enthalpy change for acyl formation from the corresponding methyl iridium complex by methyl migration to coordinated carbon monoxide is ca. -47 kJ/mol in accord with the observed reversibility of this reaction (ref. 433). Lewis acids AlX_3 (X = F, Cl, Br, Et) react with [Ir$(CO)_2(CO_2Me)(PPh_3)_2$] to give a species thought to contain coordinated carbon dioxide which in turn reacts with carbon monoxide yielding $[Ir(CO)X(PPh_3)_2]$ (ref. 434).

The complexes $[M(CO)Cl(PPh_3)_2]$, $[MH(CO)(PPh_3)_3]$ (M = Rh, Ir) and $[IrH_2Cl(PPh_3)_3]$ catalyze the carbonylation of nitrobenzene to methyl-N-phenylcarbamate in methanol but yields were less than 30% (ref. 435). A mixture of $[Ir(CO)Cl(PPh_3)]$ and tert-butylhydroperoxide initiates the polymerization of styrene and methylmethacrylate by a radical mechanism but the role of the metal complex was not determined (ref. 436). The same complex catalyzes the addition of pentaborane-9 to acetylenes to give 2-(CHR=CR')B_5H_8 (R = R' = H, Me; R = Me, R' = H) in low yield. The addition of the B-H bond occurs cis and, with propyne, in a predominately anti-Markownikoff fashion. With $[Co_2(CO)_6(RC_2R')]$ the same reaction occurs but here the internal alkyne is more reactive and addition occurs in a Markownikoff fashion (ref. 437). $[Ir(CO)Cl(PPh_3)_2]$ supported on phosphinated styrene-divinylbenzene co-polymer catalyzes the transfer of hydrogen from formic acid to vinyl ethers and the isomerization of alkyl benzenes and alcohols. In the former system the activity increases somewhat with time, the coordination of substrate to catalyst is considered to be the rate-determining step and the yields are better than with the unsupported complex. From infrared evidence, the active catalyst is thought to be different from the original Ir(I) complex. In the latter system, no increase in activity with time is seen. By contrast when $[Ir(CO)Cl(PPh_3)_2]$ is supported on phosphinated polystyrene, it is less active than the unsupported complex as a catalyst for the isomerization of allyl benzenes and alcohols although it is less prone to cause disproportionation of the alcohols or to be deactivated. In the isomerization processes, $[RhCl(PPh_3)_3]$ on the same supports is more active but is subject to severe leaching particularly on recycling (ref. 438-440). An iridium-exchanged NaY zeolite when carbonylated at 447 K generates water and carbon dioxide and forms a carbonyl species tentatively identified as $\{Ir^{I}(CO)_3\}$. The carbon dioxide and water are thought to arise from the reaction of carbon monoxide with a $\{Ir^{III}(OH)_2\}$ moiety. The supported carbonyl species is an active catalyst for the vapor phase carbonylation of methanol to methyl acetate (ref. 441).

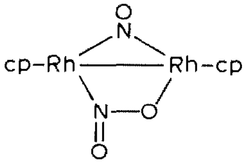
The infrared spectrum of $[Ir(CO)_2(\mu\text{-}SPh)_2Ir(CO)_2]$ in the solid state shows only seven carbonyl absorptions indicating the absence of coupling between the sets of dimers and infinite chains shown to be present in the solid (ref. 442). A linear correlation has been found between the basicity of tertiary phosphines and the ^{31}P chemical shifts of their oxides. These chemical shifts also correlate with the rate of reduction elimination of hydrogen from $[IrH_2(CO)_2L_2]^+$ (L = tertiary phosphine) promoted by trimethylphosphite, the rate of hydroformylation of hex-1-ene catalyzed by $[HCo(CO)_3L]$ and the values $^1J_{Rh-P}$ in $[Rh(CO)ClL_2]$. These are proposed as a means of assessing ligand basicity and therefore the reactivity of their complexes in catalytic systems (ref. 443).

Metal Nitrosyl and Aryldiazo Compounds

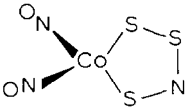
Nitrosyl hexafluorophosphate converts [cpM(CO)$_2$] (M = Co, Rh) into [cpM(CO)(NO)]PF$_6$ which undergoes further reactions as outlined in Scheme LV (ref. 444). By contrast the reaction of [cpRh(CO)$_2$] with nitric oxide in the presence of traces of oxygen yields [cp$_2$Rh$_2$(μ-NO)$_2$], [102] and a mixture of [cp$_3$Rh$_3$(NO)$_2$] and [cp$_3$Rh$_3$(CO)$_3$] in very low yield. Low yields of [cp$_2$Rh$_2$(NO)$_2$] and [cp$_3$Rh$_3$(NO)$_2$] are also obtained from [Rh(CO)$_2$Cl]$_2$ by successive treatment with nitric oxide and thallium cyclopentadienide. Heating the dimer converts it to the trimer (ref. 445). Reduction of [cp$_2$Co$_2$(μ-NO)$_2$] with sodium amalgam produces Na[cpCo(NO)] which reacts with alkyl iodides to give thermally unstable [cpCo(R)NO] (R = Me, Et). This in turn reacts with triphenylphosphine above 0° C to give [cpCo(N(O)R)PPh$_3$] as the first example of alkyl migration to a coordinated nitrosyl ligand (ref. 446). Tetrasulfurtetranitride reacts with [Co$_2$(CO)$_8$] to give an uncharacterized black precipitate which reacts further with nitric oxide to yield [103] (ref. 447). Use of [Co(NO)$_2$Br]$_2$ and [Co(NO)$_2$BrL] (L = tertiary phosphine) as nitrosylating agents has been described. With [cpV(CO)$_4$] the former yields [Co(NO)(CO)$_3$], [cpV(NO)$_2$(CO)]



Scheme LV

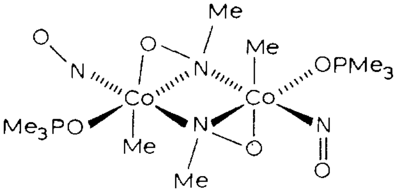


[102]

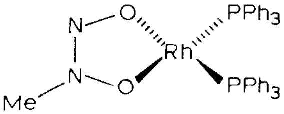


[103]

and an unidentified cluster containing cobalt, bromine and vanadium while the latter gives [cpV(NO)$_2$L], [Co(NO)$_2$Br]$_2$, [Co(NO)(CO)$_3$] and the same cluster (ref. 448). Reaction of [CoMe$_3$(PMe$_3$)$_3$] with nitric oxide yields [CoMe(NO)(OPMe$_3$)$_3$] and [104] while [RhMe(PPh$_3$)$_3$] with nitric oxide gives [105] (ref. 449). Nitric oxide reacts with [Co(H$_2$O)$_6$](NO$_3$)$_2$ in ethanol containing phosphorus ligands to yield

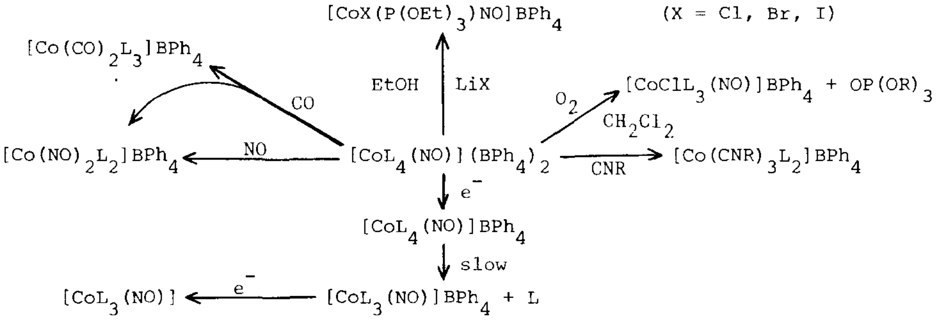


[104]



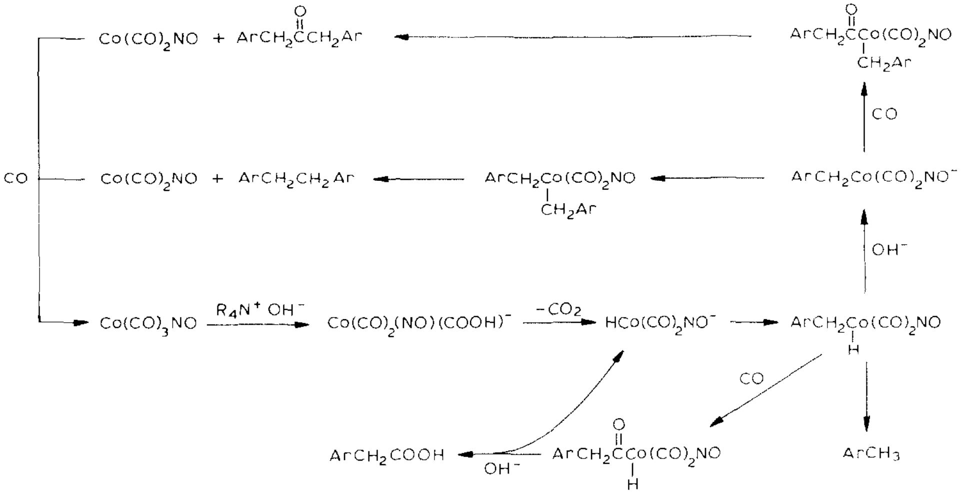
[105]

[CoL$_4$(NO)]$^{2+}$ (L = P(OR)$_3$ (R = Me, Et), PPh(OEt)$_2$) which was isolated as the tetraphenylborate salt. It is proposed to have a trigonal bipyramidal structure with an equatorial, linear nitrosyl group. Its chemistry is detailed in Scheme LVI (ref. 450). Nitrosylation of cobalt(II) acetate in methanol followed by reaction with sodium maleonitriledithiolate (Na$_2$MNT) and phosphine ligands yields [Co(NO)(MNT)L$_2$] (L$_2$ = (PPh$_3$)$_2$, diphos). From the infrared spectra of the nitrosyl group, the diphos complex is proposed to have a square-pyramidal structure with a bent nitrosyl ligand while the other is trigonal bipyramidal with a linear nitrosyl (ref. 451).



Scheme LVI

A considerable amount of work has been published on $[Co(NO)(CO)_3]$. It reacts with methyl arsine to give a very unstable complex formulated as $[Co(NO)(CO)_2(AsMeH_2)]$, with E_2Me_4 (E = P, As) to yield $[Co(NO)(CO)_2(E_2Me_4)]$ as dark red oils and with an excess of $[Cr(CO)_4(P_2Me_4)_2]$ to give $[(OC)_4Cr((\mu\text{-}Me_2PPMe_2)Co(NO)(CO)_2)_2]$. Using a 1:1 stoichiometry, $[(OC)_4Cr(P_2Me_4)((\mu\text{-}Me_2PPMe_2)Co(NO)(CO)_2)]$ is formed which on heating is converted into $[(OC)_4Cr(\mu\text{-}Me_2PPMe_2)_2Co(NO)(CO)]$. Molybdenum and tungsten analogs were also prepared. The analogous complex $[(OC)_4Cr((\mu\text{-}Me_2PPMe_2)Cocp(CO)_2)_2]$ is obtained from the same chromium complex and an excess of $[cpCo(CO)_2]$. Heating $[Co(NO)(CO)_2E_2Me_4]$ yields $[(Co(NO)(CO))_2(\mu\text{-}Me_2PPMe_2)_2]$ and $[(Co(NO)(CO)_2)_2(\mu\text{-}Me_2AsAsMe_2)]$ while refluxing $[Cr(CO)_5(\mu\text{-}Me_2PPMe_2)Co(CO)_2NO]$ with $[Co(NO)(CO)_3]$ in methyl cyclopentane gives $[(CO)(NO)Co((\mu\text{-}Me_2PPMe_2)Cr(CO)_5)_2]$ (refs. 452-454). The phase-transfer carbonylation of organic halides to the corresponding carboxylic acids is catalyzed by $[Co(NO)(CO)_3]$ and unlike the $[Co_2(CO)_8]$-catalyzed process, no double carbonylation is observed (Scheme LVII) (ref. 455). According to molecular orbital calculations, the excited state produced by irridation of the metal-ligand charge transfer (MLCT) bond of $[Co(NO)(CO)_3]$ should contain a bent nitrosyl ligand. Thus the reactions of this excited state should be those of NO^- if the reagent can attack the nitrosyl group or if not should result in nucleophilic attack at the metal. These predictions have been substantiated by experiment (ref. 456). On the other hand, photolysis of the complex in the vacuum ultraviolet leads to a one-step loss of all ligands. From this work an estimate of 58-85 kcal/mol for the Co-NO bond energy was obtained which is significantly larger than the Co-CO bond energies previously reported (ref. 457). Molecular orbital calculations on the molecule using the projected $X\alpha$-SW method are reported to be better than those using Hartree-Fock methods in predicting ionization potentials that can be measured by PES and support the idea that the electronic structure of the complex can be readily derived from those for $[Ni(CO)_4]$ or $[Fe(CO)_5]$ by symmetry lowering (ref. 458). Finally, the Auger spectrum of carbon in $[Co(NO)(CO)_3]$ has been measured and it is considered that some features of the line shapes reflect the amount of π-backbonding (ref. 459).



Scheme LVII

The ^{119}Sn NMR of the complexes $[Co(NO)(CO)_2L]$ ($L = P(Me_3Sn)_nBu^t_{3-n}$ ($n = 1-3$)) have been measured together with $^2J_{Sn-H}$ and $^1J_{Sn-P}$. As n increases, the tin chemical shift progress to lower field and $^1J_{Sn-P}$ increases significantly (ref. 460).

Reaction of $[Rh(NO)(PPh_3)_3]$, or $[Rh(NO)Cl_2(PPh_3)_2]$ with $(NSCl)_3$ yields $[Rh(NS)Cl_2(PPh_3)]_2$ which can be cleaved to $[Rh(NS)Cl_2(PPh_3)L]$ ($L = PPh_3$, $AsPh_3$) on reaction with the appropriate ligand. The significant increase in the N-S stretching frequency on going from the dimer to the monomer is taken to indicate that the former contains bridging thionitrosyl ligands (refs. 461, 462). The chloro-bridged thionitrosyl complex $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ can be got in the same way from $[Rh(CO)Cl(PPh_3)_2]$ or $[RhH(CO)(PPh_3)_3]$. In refluxing dichloromethane it reacts with triphenylphosphine to give $[Rh(CO)(NS)(PPh_3)_2]$ while at room temperature it produces $[Rh(CO)(NS)Cl_2(PPh_3)_2]$ which reacts with NOX (X = Cl, Br) to give $[Rh(CO)(NO)ClX(PPh_3)_2]$. This last complex can also be prepared directly from $[Rh(CO)Cl(PPh_3)_2]$ and NOX (refs. 463, 464).

Nitric oxide reacts with [RhH(OEP)] to give hydrogen and [Rh(NO)(OEP)] which is formulated as an NO$^-$ derivative of Rh(III). With [RhCl(OEP)] or its TPP analog the initial product is [Rh(OEP)Cl(NO)] which reacts further to give [Rh(NO)(OEP)] and nitrosyl chloride (ref. 465).

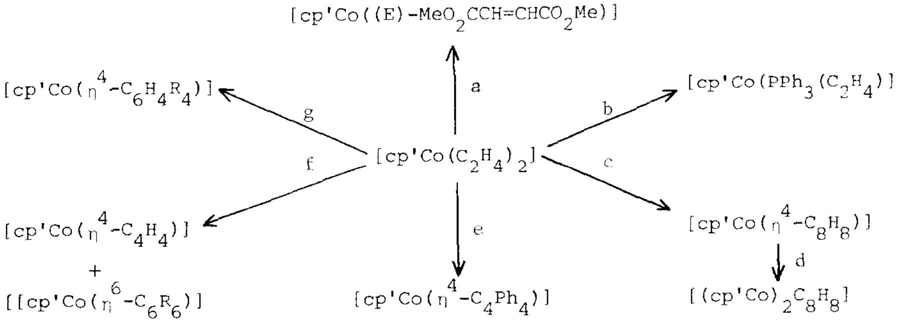
The hydrogenation of hex-1-ene, cyclohexene and styrene is catalyzed by [Rh(NO)-(PPh$_3$)(*p*-benzoquinone)]. The best rates are obtained if the system is treated with hydrogen prior to introduction of olefin and a Rh(0) species is proposed to be the active catalyst (ref. 466). In DMF solution $[Rh(NO)_2(PPh_3)_2]PF_6$ catalyzes the conversion of nitric oxide and carbon monoxide to carbon dioxide and nitrogen dioxide. From the kinetics of the reaction, the formation of a dimeric rhodium complex is proposed to occur (ref. 467).

Reaction of $[Ir(CO)Cl(PPh_3)_2]$ with N_2O_3 yields $[Ir(CO)(NO)(NO_2)Cl(PPh_3)_2]$ which can be oxidized to $[Ir(CO)(NO_2)(NO_3)Cl(PPh_3)_2]$ by dioxygen. The same complex is also obtained from N_2O_3 and either $[Ir(O_2)(CO)Cl(PPh_3)_2]$ or $[Ir(H_2S)(CO)Cl(PPh_3)_2]$ while with $[IrH(CO)(PPh_3)_3]$ and $[Ir(SO_2)(CO)Cl(PPh_3)_2]$ one obtains $[IrH(CO)(NO)(NO_2)(PPh_3)]$ and $[Ir(CO)(NO)(NO_3)Cl(PPh_3)_2]$ respectively (ref. 468). With NOX (X = Cl, Br), $[Ir(CO)Cl(PPh_3)_2]$ yields $[Ir(CO)(NO)ClX(PPh_3)_2]$ while with $NOBr_3$ the product is $[Ir(CO)(NO)Br_2(PPh_3)_2]$. The last complex can be oxidized to $[Ir(CO)(NO_3)Br_2(PPh_3)_2]$. Reaction of nitrosyl chloride with $[IrH(CO)(PPh_3)_3]$ gives $[Ir(CO)Cl_3(PPh_3)_2]\cdot 0.5\,NOCl$ from which the nitrosyl chloride is removed on heating while with $[Ir(SO_2)(CO)Cl(PPh_3)_2]$ is obtained $[(Ir(CO)Cl_2(PPh_3)_2)_2N_2O_2]$ (ref. 469).

A variety of Ir(I) and Rh(I) complexes of the neutral diazo ligands, RN_2 (R = tetrahalocyclopentadienyl, 9-fluorenyl) have been prepared and their reactions with carbonyl sulfide investigated. Three general reactivity patterns were observed: 1) decomposition to metal carbonyl complex, 2) formation of dithiocarbamate complexes and 3) rearrangement to give metal sulfide or thiolate complexes (ref. 470).

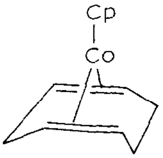
Metal Alkene Compounds

Reduction of $[cp'CoI_2]_2$ with sodium amalgam in an ethylene atmosphere yields $[cp'Co(C_2H_4)_2]$ which has proved to be a versatile synthetic intermediate as indicated in Scheme LVIII. When refluxed in light petroleum it provides a good yield of $[cp'_2Co_2(\mu\text{-}CO)_2]$ (ref. 471). Reaction of $[cpCo(CO)_2]$ with cyclohepta-1,3-diene or cyclohepta-1,3,5-triene yields $[cpCo(\eta^4\text{-}C_7H_{10})]$ and $[cpCo(\eta^4\text{-}C_7H_8)]$ respectively. Reaction of the diene complex with trityl tetrafluoroborate or protonation of the triene complex with tetrafluoroboric acid produces $[cpCo(\eta^5\text{-}C_7H_9)]BF_4$. This last complex reacts with sodium borohydride in moist ether to yield [106] and reversibly with triisopropylphosphine to give [107]. Deprotonation of $[cpCo(\eta^4\text{-}C_7H_8)]$ with trityl tetrafluoroborate gave a mixture which was not separated but with butyllithium $[cpCo(\eta^3\text{-}C_7H_7)]^-$ was obtained which underwent deuteration with D_2O in an *exo* fashion (ref. 472). Reaction of [cpCo(COT)] (COT = cyclooctatetraene) with $[Mo(CO)_3(diglyme)]$, $[Cr(CO)_3(MeCN)_3]$ or $[W(CO)_3(DMF)_3]$ gives



a) (E)- or (Z)-MeO$_2$CCH=CHCO$_2$Me, hexane reflux. b) PPh$_3$, hexane, reflux. c) C$_8$H$_8$, hexane, reflux. d) [cp'Co(C$_2$H$_4$)$_2$], hexane, reflux. e) Ph$_2$C$_2$, hexane, reflux. f) R$_2$C$_2$ (R = CO$_2$Me), hexane, 25° C. g) R$_2$C$_2$ (R = CO$_2$Me), toluene, 25° C.

Scheme LVIII



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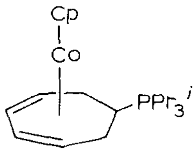
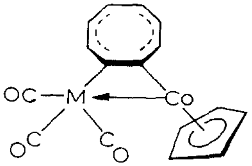


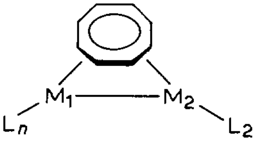
[107]

[108] (M = Cr, Mo, W) however under comparable conditions, no reaction was observed with [cpRh(COT)]. Related rhodium complexes could however be prepared from

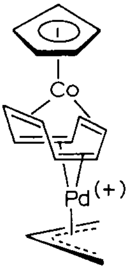


[108]

$[RhL_2(acetone)_x]BF_4$ and $[L_nM_1(COT)]$ and are of structure [109] (M_2 = Rh; L_2 = $(CO)_2$, COD, NBD; L_nM_1 = $Fe(CO)_3$, cpCo, cpRh. M_2 = Ir; L_2 = COD; L_nM_1 = cpCo). These react with phosphines to give random substitution and therefore complex mixtures of products. One interesting result is the formation of [110] from [cpCo(COT)] and $[(\eta^3\text{-}C_3H_5)Pd(acetone)_x]^+$ (refs. 473, 474). Under either thermal or photochemical conditions, $[Co_2(CO)_8]$ and COD produce $[(COD)Co(CO)_3]$ which undergoes substitution with triphenylphosphine to give $[(COD)Co(CO)_2(PPh_3)]$ (ref. 475).



[109]

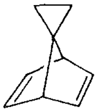


[110]

Electronegatively-substituted olefins react with cyanocobaltate complexes prepared in aqueous base under hydrogen to yield $[Co(CN)_4(ol)]^-$ (ol = $C_2(CN)_4$, $PhCH{=}C(CN)_2$, <u>cis</u>- and <u>trans</u>-PhCH=CHCN, (E)-$PhCH{=}C(CN)CO_2Et$, (E)-$PhCH{=}C(CN)CO_2K$, <u>cis</u>- and <u>trans</u>-$RO_2CCH{=}CHCO_2R$ (R = Me, Et, Na)) which were identified in solution. The maleate complexes were observed to isomerize to fumarate derivatives and an electron-transfer mechanism was proposed (ref. 476). The bipyridyl complex $[Co(bipy)_2]$ has been synthesized by metal-atom vapor techniques and reacts with tetracyanoethylene (TCNE) to give [Co(bipy)(TCNE)]. From the infrared spectrum, it appears that considerable negative charge resides on the TCNE ligand (ref. 477). The cyclopropanation of optically active fumarate esters by dibromomethane is effected by cobalt(II) chloride in acetonitrile in the presence of zinc and sodium iodide. From 40-70% enantiomeric excesses are realized and an olefin-cobalt species is proposed to be an intermediate in the reaction (ref. 478). A mixture of [Co(acac)$_2$] and triethylaluminum is used to prepare a cobalt complex of <u>cis</u>-<u>trans</u>-<u>trans</u>-cyclododeca-1,5,9-triene. Similar reactions with α-olefins produce cobalt complexes of these olefins as well (ref. 479). Ethylene and propylene are adsorbed nondissociatively on the surface of a CoO/MgO/MoO$_3$ mixed oxide and from infrared spectra, π-complexation of the olefins with the cobalt is proposed to occur (ref. 480).

Triarylphosphines, L (L = P(<u>p</u>-RC$_6$H$_4$)$_3$ (R = Cl, F, Me, MeO)) react with [Rh(NBD)Cl]$_2$ (NBD = norbornadiene) in the presence of sodium perchlorate or tetraphenylborate to yield [Rh(NBD)L$_2$]A (A = ClO$_4$, BPh$_4$). The diolefin is removed on carbonylation to yield [Rh(CO)$_3$L$_2$]A. In acetone, the diolefin is hydrogenated to give [RhH$_2$L$_2$(acetone)$_2$]ClO$_4$ or [RhL$_2$(η-C$_6$H$_5$BPh$_3$)] (ref. 481). The same research group has also made extensive studies of rhodium diolefin complexes containing nitrogen- and/or oxygen-donor ligands. Thus by an analogous route, the complexes [Rh(diolef)L$_2$]ClO$_4$ (diolef = COD, NBD, tetrafluorobenzobarrelene (TFB); L$_2$ = 2,2'-biimidazole, 2,2'-bibenzimidazole, (pyrazole)$_2$, (imidazole)$_2$). The COD complexes carbonylate to [Rh(CO)$_2$L$_2$]ClO$_4$ and where L$_2$ is a bidentate ligand react further with tertiary phosphines (L') to give [Rh(CO)L'L$_2$]ClO$_4$ (ref. 482). In the presence of sodium hydroxide, 5-methyl-8-hydroxyquinoline (moqH) reacts with [Rh(COD)Cl]$_2$ to give [Rh(moq)(COD)] which carbonylates to [Rh(moq)(CO)$_2$]. Reaction of the carbonyl complex with phosphines gives [Rh(moq)(diphos)] and [Rh(moq)L(CO)] (L = P(<u>p</u>-RC$_6$H$_4$)$_3$ (R = Cl, H, Me, MeO)). Mercury(II) chloride forms a 1:1 adduct with [Rh(moq)(CO)(P(p-tolyl)$_3$)] (ref. 483). Sodium or triethylammonium pyrazolate reacts with [Rh(diolef)Cl]$_2$ (diolef = COD, NBD, TFB) in methanol to yield the dimers [Rh(diolef)(pz)]$_2$ (pz = pyrazolate). These can also be prepared directly from pyrazole by reaction with [Rh(diolef)(acac)]. The analogous ethylene complex, [Rh(C$_2$H$_4$)$_2$(pz)]$_2$ can be got from [Rh(C$_2$H$_4$)$_2$Cl]$_2$ and Napz in the presence of sodium hydroxide. Although [Rh(diolef)(pz)]$_2$ is unreactive towards phosphines or thallium cyclopentadienide, reaction occurs in the presence of carbon monoxide to yield [Rh(CO)L(pz)]$_2$ (L = P(OPh)$_3$, PPh$_3$, P(<u>p</u>-RC$_6$H$_4$)$_3$ (R = Cl, Me, MeO)). [Rh(CO)(PPh$_3$)(pz)]$_2$ is also obtained from [Rh(CO)(PPh$_3$)(acac)] and pyrazole. Also, triethylammonium pyrazolate converts [Rh(CO)$_2$Cl]$_2$ to [Rh(CO)$_2$(pz)]$_2$ (ref. 484). The ionic species [Rh(diolef)L$_2$]ClO$_4$ (diolef = COD, NBD, TFB; L = 4-aminopyridine, 2-aminopyridine, 4-cyanopyridine. diolef = COD, TFB; L = 2-cyanopyridine) are prepared from [Rh(diolef)$_2$]ClO$_4$ or [Rh(diolef)Cl]$_2$ plus silver perchlorate and stoichiometric quantities of ligand. The ligand appears bound <u>via</u> the heterocyclic nitrogen. These carbonylate to [Rh(CO)$_2$L$_2$]ClO$_4$ although only the 4-aminopyridine complex was isolated and the carbonyl products react with triphenylphosphine to give $[Rh(CO)(PPh_3)L_2]ClO_4$. These last species are also obtained from the reaction of $[Rh(CO)Cl(PPh_3)]_2$ with silver perchlorate followed by addition of ligand (L = 4-aminopyridine, 4-cyanopyridine, ½(4,4'-bipyridyl)). The $[Rh(diolef)_2]ClO_4$ complexes react with bidentate ligands to give $[Rh(diolef)(L_2)]_n(ClO_4)_n$ (n = 2 in the solid but lower in solution. L_2 = 4,4'-bipyridyl, pyrazine). The diolefin is removed by reaction with carbon monoxide to give analogous dicarbonyl species (ref. 485). Reaction of $[Rh(COD)Cl]_2$ with silver perchlorate in acetone followed by addition of a range of substituted pyridine-N-oxides (pyNO) gives $[Rh(COD)(pyNO)_2]$-ClO_4 which react with one equivalent of triphenylphosphine to yield $[Rh(COD)(PPh_3)$-$(pyNO)]ClO_4$. Reaction of 4-methylpyridine-N-oxide(4-mepyNO) with $[Rh(COD)(RCN)_2]^+$ (R = $PhCH_2$, p-tolyl) also gives $[Rh(COD)(4\text{-mepyNO})_2]^+$ from which $[Rh(COD)L(4\text{-MepyNO})]^+$ (L = 2-methylimidazole, 4-aminopyridine) or $[Rh(COD)L_2]^+$ (L_2 = $(py)_2$, $(PPh_3)_2$, bipyridyl, o-phenanthroline) can be obtained using respectively stoichiometric and excess quantities of the appropriate ligands (ref. 486). Mixtures of $[Rh(NBD)_2]ClO_4$ and group V ligands including diamines, nitriles, substituted quinolines and mono- and ditertiary phosphines in the presence of potassium hydroxide catalyze the hydrogen transfer from isopropanol to acetophenone, cylohexene, hex-1-ene and styrene (ref. 487). The mixed diolefin complexes $[Rh(diolef)(TFB)]ClO_4$ can be prepared from $[Rh(diolef)Cl]_2$ (diolef = COD, NBD) and TFB or from $[Rh(TFB)Cl]_2$ and the diolefin (diolef = 2-methylbutadiene, 2,3-dimethylbutadiene) by reaction with silver perchlorate in acetone. Also reaction of $[Rh(TFB)Cl]_2$ with silver perchlorate in the presence of arenes gives $[Rh(TFB)$-$(arene)]ClO_4$ (arene = C_6Me_6, mesitylene, p-xylene). Most of the complexes explode on heating and except for the hexamethylbenzene derivative, the arene complexes tend to dissociate arene in acetone solution. The structures of the arene complexes have been determined showing that the C_6Me_6 ligand eclipses the TFB ligand while in the other two complexes the arene and TFB ligands are staggered (ref. 488). Also prepared were complexes of formula [Rh(diolef)(tropolonate)] (diolef = COD, NBD, TFB) which were found to be useful intermediates in the synthesis of a variety of neutral and cationic Rh(I) complexes (ref. 489).

Electrochemical studies of the complexes $[M(COD)(A)]PF_6$ (M = Rh, Ir; A = Schiff base ligands from pyridine-2-aldehyde) show the presence of two reversible, one-electron reduction steps and one oxidation step, The reduction steps were complicated by adsorption phenomena and chemical side reactions (ref. 490). The spirocyclic diene [111] (L_2) forms the rhodium complex $[Rh(L_2)Cl]_2$ which can facilitate the homo- and codimerization of [111] and NBD (ref. 491). During the reaction of $[Rh(NBD)Cl]_2$ with tin(II) bromide in the presence of phosphines, scrambling of halogen can occur and the products isolated are $[Rh(NBD)L_2$-$(SnCl_xBr_{3-x})]$ (L = $PEtPh_2$; x = 0,1,3. L = PPh_3; x = 0,1. L = $P(p\text{-tolyl})_3$, $P(m\text{-tolyl})_3$, $P(p\text{-XC}_6H_4)_3$ (X = F, Cl); x = 1). The ^{31}P and ^{119}Sn NMR spectra have



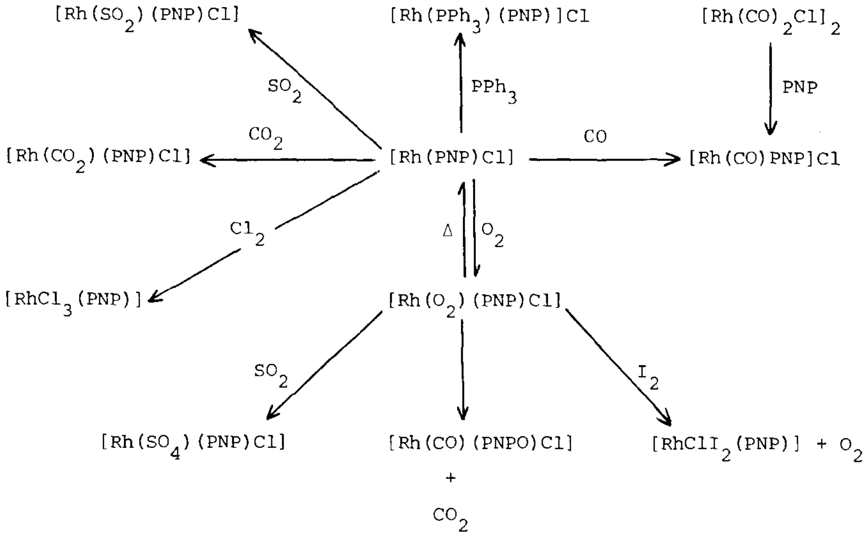
[111]

been measured and $^{1}J_{Rh-Sn}$ was found to correlate with the ^{119}Sn chemical shifts and with the sum of the Pauling electronegativities of the halogen atoms on tin in the complexes with ethyldiphenylphosphine (ref. 492). Reaction of $[Rh(CO)_2(acac)]$ with various diolefins in refluxing benzene yields [Rh(diolef)(acac)] which is converted into [cpRh(diolef)] (diolef = COD, 2-R-NBD (R = H, CHO, CH_2OH, CO_2Me), 2-carbomethoxyl-1,4,5,6,7,7-hexachloronorbornadiene) (ref. 493). A redetermination of the equilibrium constant for

$$[RhCl(NBD)]_2 + 2\ NBD \rightleftharpoons 2[Rh(NBD)_2Cl]$$

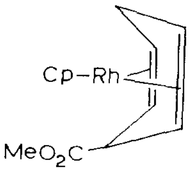
in chloroform shows the equilibrium to be far to the left at 40° C but it shifts to the right on cooling. The significance of this is that it is at 40° C that $[RhCl(NBD)]_2$ catalyzes the isomerization of quadricyclane to NBD. Hence even in the presence of the excess NBD thus produced, the rhodium is essentially all in the dimer form and it is concluded that the dimer is the active catalyst. At 1° C the isomerization is more rapid in the presence of excess NBD indicating that here the monomer is a more active catalyst. Both monomer and dimer show exchange of NBD with excess ligand in solution and, contrary to earlier reports, no monomer is seen in benzene, carbon tetrachloride or toluene solutions (ref. 494). The tridentate ligand 2,6-bis(diphenylphosphinomethyl)pyridine(PNP) reacts with $[RhCl(cyclooctene)_2]_2$ to give [Rh(PNP)Cl] or $[Rh_2(PNP)_3]Cl_2$ depending on whether the PNP is present in limiting or excess amounts. In the dimer, one PNP ligand bridges the metals and is coordinated only through phosphorus. The chemistry of [Rh(PNP)Cl] in benzene solution is detailed in Scheme LIX (ref. 495). Reaction of either $[RhCl(C_2H_4)L_2]$ or $[Rh_2Cl_2(L_2)_2]$ (L_2 = $(PEt_3)_2$, diphos) with $[IrH_5(PEt_3)_2]$ yields $[L_2Rh(\mu-H)(\mu-Cl)IrH_2(PEt_3)_2]$. The diphos complex is an olefin hydrogenation catalyst (ref. 496).

Methyllithium reacts with $[Rh(COD)Cl]_2$ at -78° C in ether to give $[Rh_2(COD)_2(\mu-CH_3)_2]$ however with the iridium analog the product is $[Ir_2(COD)_2(\mu-CH_2)_2]$. The structure of the rhodium complex shows the Rh_2C_2 unit to be non-planar and the Rh-Rh distance to be 2.6579(5) A. The molecule is fluxional with the process

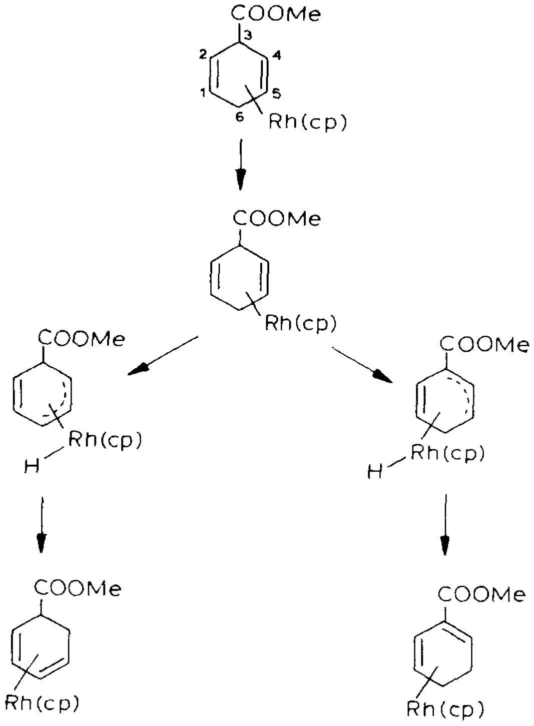


Scheme LIX

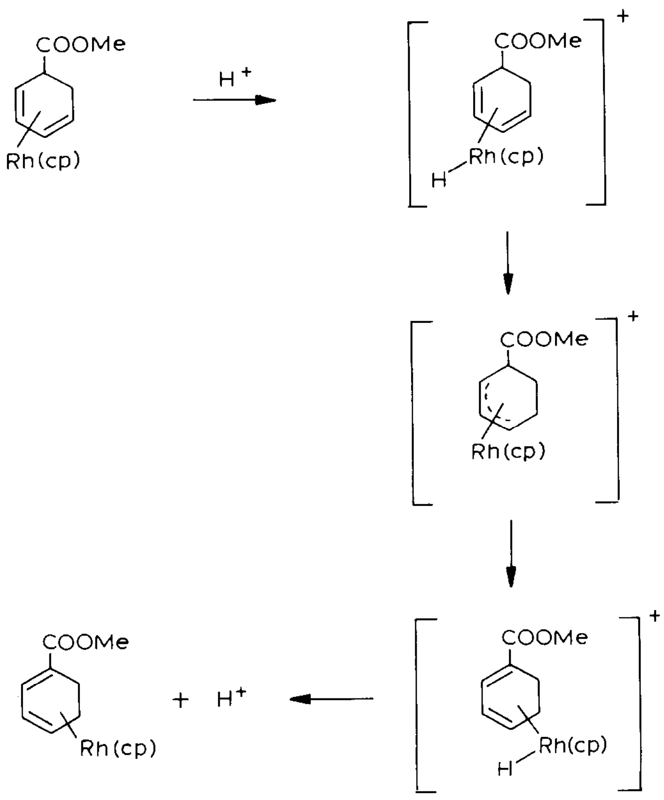
possibly involving a planar intermediate and on warming to room temperature it decomposes to hydrogen, methane and several other rhodium complexes. One of these is tentatively identified as $[Rh_2(COD)_2(\mu\text{-}CH_2)_2]$ while another appears to be a polynuclear hydride complex. The thermal decomposition of $[Rh_2(COD)_2(\mu\text{-}CD_3)_2]$ gives no products showing Rh-H stretches in the infrared implying that all the hydrogen atoms which end up bound to rhodium in the decomposition products originate in the bridging methyl groups. Also in this system the majority of the methane is CD_3H indicating that the methane is produced by hydrogen abstraction from the COD ligands. From $[Rh(COD)Cl]_2$ and trimethylsilylmethyllithium the analogous $[Rh_2(COD)_2(\mu\text{-}CH_2SiMe_3)_2]$ is obtained but with other lithium reagents only phenyllithium gives the corresponding dimer. In this case the initial product is very reactive and rapidly decomposes to polynuclear hydride complexes. With ethyllithium and benzyllithium the products are $[H_4Rh_4(\eta^5\text{-}C_8H_{11})_4]$ and $[Rh_4(CH_2Ph)_4]$ respectively although the latter has not been thoroughly characterized (ref. 497). Reaction of $[RhCl(C_2H_4)_2]_2$ with 3-methoxycarbonylcyclohexa-1,4-diene followed by treatment with thallium cyclopentadienide yields [112] which isomerizes on heating according to Scheme LX. In the presence of acid the major product of this first isomerization undergoes further reaction as shown in Scheme LXI (ref. 498). Although the carbon suboxide C_3O_2 does not react with $[Rh(COD)Cl]_2$ or $[cpRh(C_2H_4)_2]$ it does so with $[RhCl(cyclooctene)_2]_2$ to give a species tentatively formulated as [113]. This is cleaved with pyridine to give $[Rh(cyclooctene)(CO)(C_2O)(py)Cl]_2$. With $[RhCl(PPh_3)_3]$, C_3O_2 gives $[Rh(CO)Cl(PPh_3)_2]$ and $(C_2O)_n$ (ref.499).



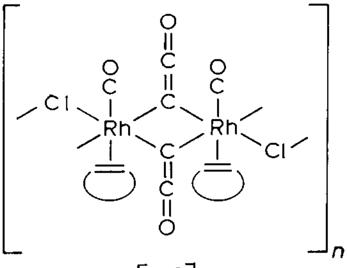
[112]



Scheme LX

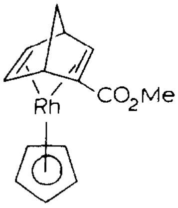


Scheme LXI

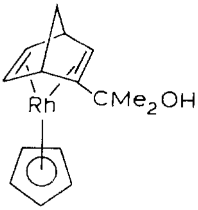


[113]

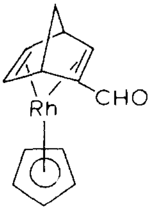
Methyllithium reacts with [114] to give [115] while with [116] and a series of organolithium reagents [117] (R = Me, Ph, CpFe(η^5-C_5H_4)) is produced indicating that attack of the carbon nucleophile occurs exo. When [117] (R = Me) is synthesized by reaction of thallium cyclopentadienide with [Rh(acac)(C_7H_7-CH(Me)OH)], the diasteromer [118] is also obtained which was separated from [117] by fractional crystallization. Protonation of [117] and [118] gave the allylic complexes [119] and [120] respectively which could be stereospecifically reconverted to the corresponding diene alcohols with hydroxide ion again indicating the preference for exo attack (refs. 500-502). Protonation of [121] at -40° C followed by warming yields [122] or [123] (R = H, Me; R' = Ph; M = Rh, Ir; Y = BF_4, PF_6; X = Cl, Br) depending on the acid used. From labelling studies the protonation occurs in an endo fashion but no metal-hydride intermediate was detected. Complex [121] (R = Bu^t) can be reduced to the corresponding alcohol complex with lithium aluminum hydride which on protonation gives an allyl species analogous to [123]. This undergoes dehydration on heating in the presence of acid to give [124]. For M = Ir, a trans β-elimination of water is indicated but the reaction is not as



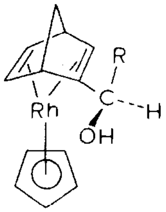
[114]



[115]

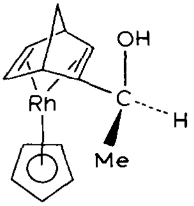


[116]

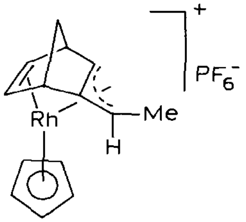


[117]

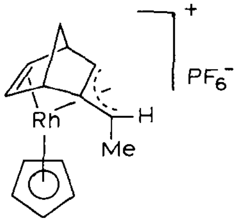
selective for M = Rh indicating protonation at oxygen may also occur (refs. 503, 504).



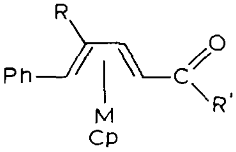
[118]



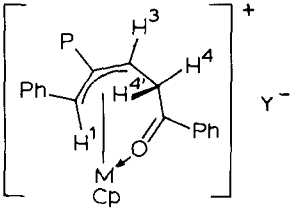
[119]



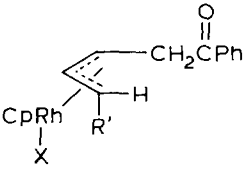
[120]



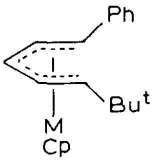
[121]



[122]



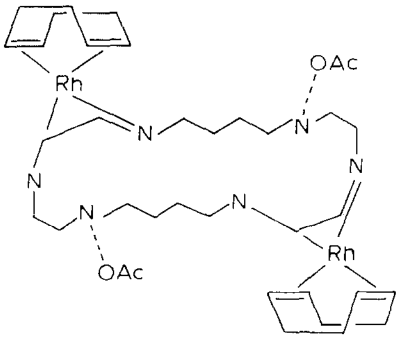
[123]



[124]

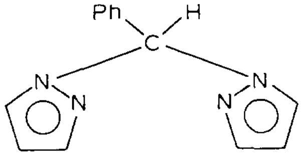
The solvent exchange process in $[ML_2(S)_2]PF_6$ (M = Rh, Ir; L = PPh_3, S = acetone; L = $P(cyclohexyl)_3$, S = MeCN), prepared by hydrogenation of the corresponding COD complexes, has been investigated. The acetone complexes are much more labile and in both instances a dissociative mechanism is proposed (ref. 505). Reaction of

$[Rh(COD)Cl]_2$ with silver tetrafluoroborate in acetone followed by addition of excess DPPP or 1,4-bis(diphenylphosphino)butane(DPPB) gives $[Rh(L_2)_2]BF_4$ (L_2 = DPPP, DPPB) but with a stoichiometric quantity, $[Rh(COD)(DPPB)]BF_4$ can be obtained. In the solid state $[Rh(DPPB)_2]^+$ is four-coordinate with a pronounced tetrahedral distortion from the expected square planar geometry. The observation that one Rh-P bond is 0.05 Å, longer than the rest is consistent with the tendency of this system to give DPPB-bridged dimers which is evident from the extremely complex ^{31}P NMR spectrum observed at low temperature. An acetone solution of $[Rh(DPPP)_2]^+$ at low temperature exhibits a ^{31}P NMR spectrum consistent with a trigonal bipyramidal structure implying coordination of acetone in an equatorial position (ref. 506). Ethylenediamine(en) reacts with $[Rh(COD)(O_2CMe)]_2$ to give $[Rh(en)(COD)]O_2CMe$. However the hexaamine 1,4,7,12,15,18-hexaazacyclodocosane yields the dimer [125].



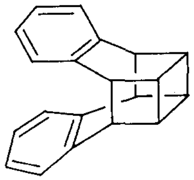
[125]

A possible trimer is produced with 1,4,7,13,16,19-hexaazacyclotetracosane but this species was not fully characterized. Hydrogenation of [125] followed by addition of diphos gave a species containing both diphos and the macrocyclic amine but no COD (ref. 507). A variety of vinyl silanes replace ethylene in $[Rh(C_2H_4)_2acac]$ to give $[Rh(H_2C{=}CHR)_2(acac)]$ (R = $SiMe_3$, $SiMe_2OEt$, $SiMe(OEt)_2$, CH_2SiMe_3). The bidentate divinyl silanes $R_2Si(CH{=}CH_2)_2$ (R = Me, Ph) and $(H_2C{=}CHSiMe_2)_2O$ also formed analogous complexes. From NMR studies the monovinyl silanes showed no rotation about the rhodium-olefin bond at room temperature and adopted a conformation with the R groups trans to one another. The ^{13}C chemical shifts of the olefinic carbons suggest that the vinyl silanes are better π-acceptors than the corresponding hydrocarbon ligands. Some decrease in the carbon-silicon pπ-dπ bonding appeared to occur on coordination (ref. 508). The pyrazole-derived ligand [126](LL) reacts with $[Rh(C_2H_4)_2Cl]_2$ to give $[Rh(C_2H_4)(LL)Cl]_x$, of unknown structure and with

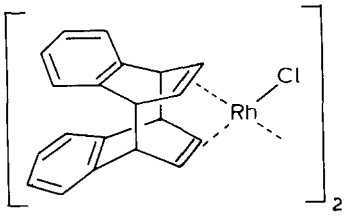


[126]

$[Rh(COD)Cl]_2$ to give $[(Rh(COD)Cl)_2LL]$ which is thought to be a ligand-bridged dimer (ref. 509). The trigonal bipyramidal complexes $[Rh(C_2H_4)_3(MeCN)_2]BF_4$, $[IrBr(CO)(TCNE)(PPh_3)_2]$, $[IrH(CO)(\underline{trans}\text{-}NCCH{=}CHCN)(PPh_3)_2]$, $[IrCl(C_2H_4)_4]$, $[\overline{Ir(C_2H_4)_2P(C_6H_4})Ph_2(PPh_3)]$ and $[\overline{Ir(C_2H_4)_2PC_3H_6}Pr^i_2(PPr^i_3)]$ are considered to more closely resemble $[Pt(C_2H_4)(PPh_3)_2]$ than $[Pt(C_2H_4)Cl_3]^-$ in that the C-C axis of the olefin is nearly parallel to the equatorial plane rather than being perpendicular to it (ref. 510). The polycyclic hydrocarbon [127] forms [128] on reaction with $[Rh(NBD)Cl]_2$ (ref. 511).

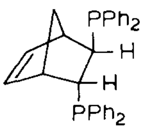


[127]

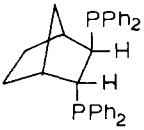


[128]

The large number of papers devoted to asymmetric hydrogenation of prochiral olefins by rhodium complexes of chiral phosphines can be largely divided into two groups, those concerned with mechanistic details and those concerned simply with maximizing optical yield. In the first category, the ligands [129] ((-)-NORPHOS) and [130] both form the complexes $[Rh(NBD)(L_2)]ClO_4$ (L_2 = [129], [130]) which on

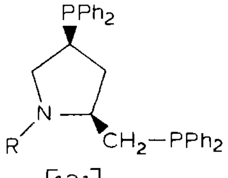


[129]



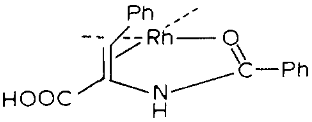
[130]

hydrogenation yield species showing identical ^{31}P NMR spectra indicating that complexed [129] has been hydrogenated to [130]. Thus both catalyst systems contain the saturated ligand and are able to catalyze the hydrogenation of (Z)-α-acetamidocinnamic acid to (+)-(S)-N-acetylphenylalanine in 95% optical yield. The structure of the rhodium complex [Rh(NBD)((+)-NORPHOS)]ClO_4 shows a considerable decrease in the dihedral angle between the two phosphorus atoms in the complex over that in the free ligand leading to a disposition of the phenyl groups which closely resembles that in the corresponding complex of CHIRAPHOS (CHIRAPHOS = (2S,3S)-bis(diphenylphosphino)butane). Thus it is suggested that it is the chiral arrangement of the phenyl groups which is the source of the asymmetric induction (ref 512). The complexes $[Rh(NBD)(L_2)]^+$ (L_2 = [131] (R = H(PPM), CO_2Bu^t(BPPM), COPh(BZPPM)) have

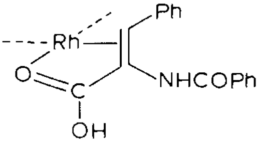


[131]

been studied by ^{31}P NMR. For the BPPM complex two disatereomeric complexes are observed while for the BZPPM complex only one is present. Hydrogenation of these in methanol produces two and one diastereomeric solvates respectively. The PPM complex is unreactive towards hydrogen due to the fact that the pyrrolidine nitrogen atom also coordinates to the metal. Addition of (Z)-α-benzamidocinnamic acid to $[Rh(BZPPM)(MeOH)_2]^+$ in the absence and presence of triethylamine produces [132] and [133] respectively. With $[Rh(BPPM)(MeOH)_2]^+$, several species are seen in solution. However if the methyl ester of the substrate is used, species identified

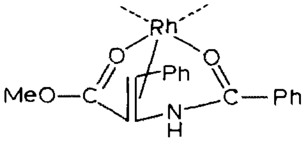


[132]



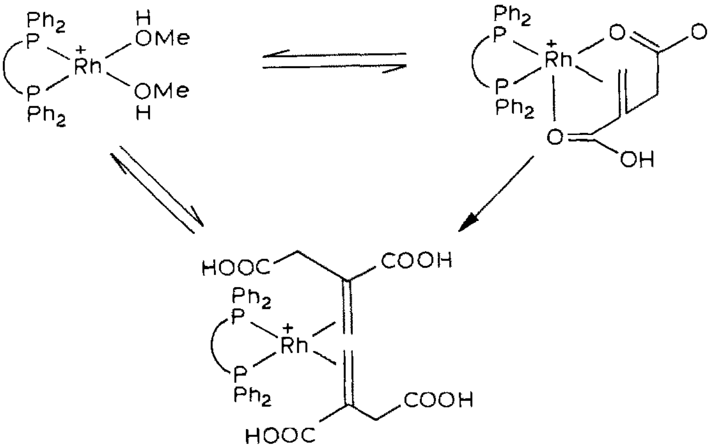
[133]

as analogs of [132] and [134] are seen in the absence of base while in its presence, four species having a structure analogous to [133] were detected.



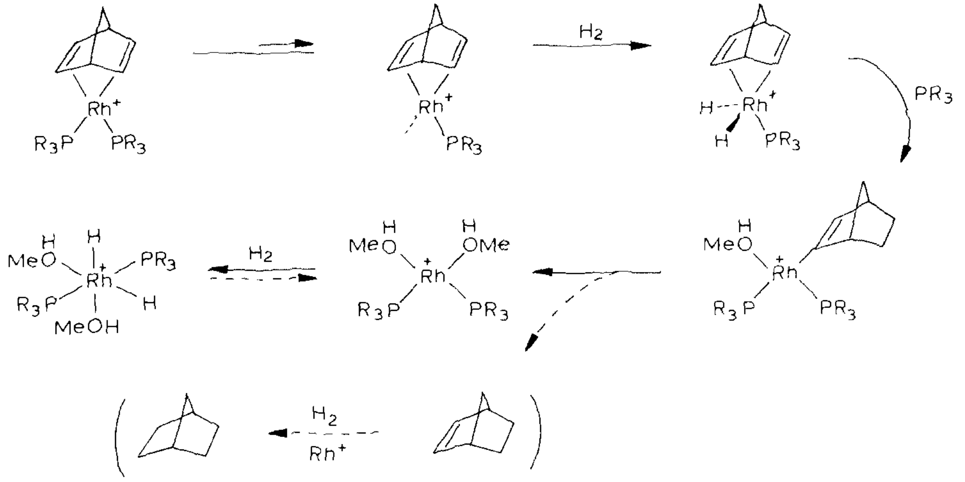
[134]

Reaction of $[Rh(BPPM)(MeOH)_2]^+$ with itaconic acid is proposed to occur as detailed in Scheme LXII (ref. 513). Unlike many of the precursors to chiral catalysts,



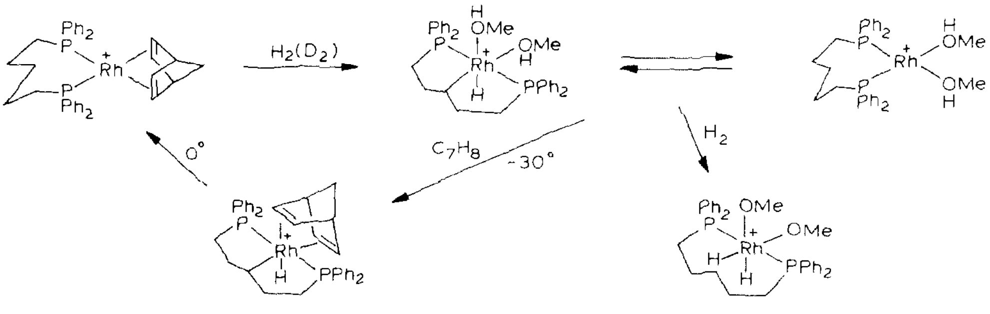
Scheme LXII

$[Rh(NBD)(PPh_3)_2]BF_4$ on hydrogenation forms $[RhH_2(MeOH)_2(PPh_3)_2]BF_4$ which is stable under argon when the concentration is 0.01 M while at 0.025 M concentration some $[Rh(PPh_3)_2(MeOH)_2]BF_4$ is detected after standing under reduced pressure. This latter complex is the sole product when an 0.05 M solution of the NBD complex is hydrogenated suggesting that the solvated Rh(I) complex is in fact oligomeric. The complex $[Rh(NBD)L_2]BF_4$ (L = PMePh(o-tolyl)) exists in two diastereomeric forms which hydrogenate to give a mixture of $[RhH_2L_2(MeOH)_2]BF_4$ and $[RhL_2(MeOH)_2]BF_4$ however if the reaction is carried out for less than ten seconds only the latter is observed. Scheme LXIII details the proposed hydrogenation process for this system



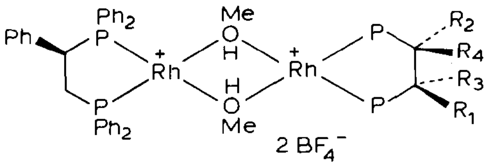
Scheme LXIII

while that for $[Rh(NBD)(Ph_2P(CH_2)_5PPh_2)]BF_4$ is shown in Scheme LXIV. Hydrogenation



Scheme LXIV

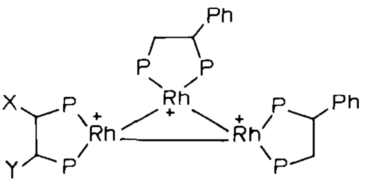
of $[Rh(NBD)(L_2)]BF_4$ (L_2 = (R)-1,2-bis(diphenylphosphino)-1-phenylethane) in methanol yields a mixture of four dimeric solvates [135a-d] while the same reaction in the presence of trimethylamine yields the mixture of trimers [136a,b]



[135]

a R_1 = Ph
b R_2 = Ph
c R_3 = Ph
d R_4 = Ph
else R=H

(coordinated amine omitted) (ref. 514). Another complex forming a stable dihydride is $[Rh(COD)(DIOXOP)]ClO_4$ (DIOXOP = (2R,4R)-bis(diphenylphosphinomethyl)-1,3-dioxolane) but unlike many of the systems discussed above only one complex is

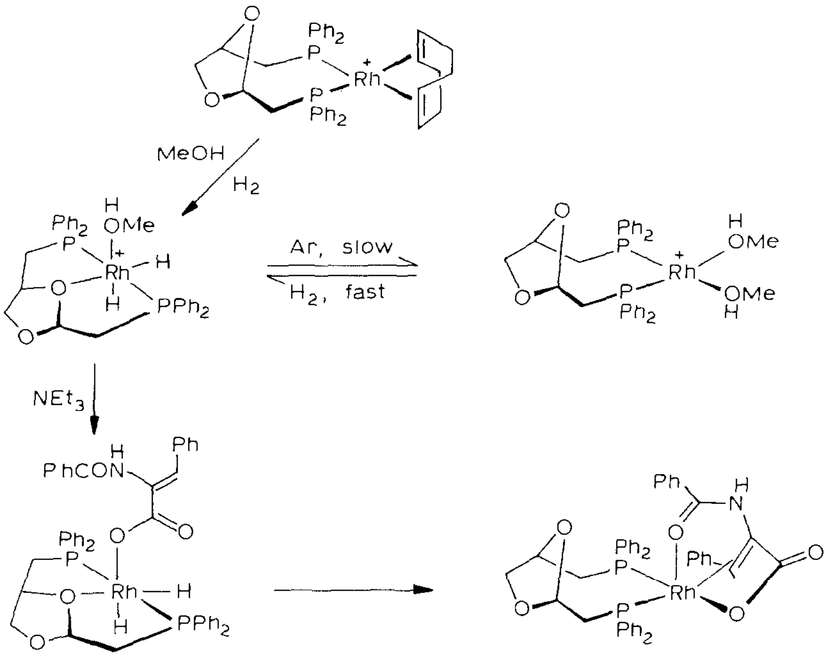


a) x = Ph, y = H
b) x = H, y = Ph

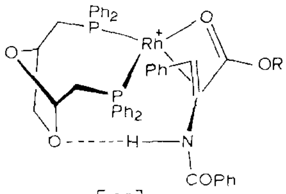
[136]

a X = Ph, Y = H
b X = H, Y = Ph

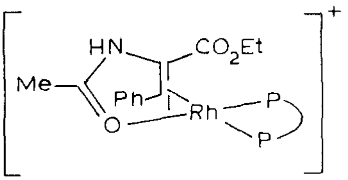
observed by ^{31}P NMR when the hydride is reacted with (Z)-α-benzamidocinnamic acid (Scheme LXV). Presence of triethylamine is necessary for high optical yields in this system, presumably via formation of the tridentate substrate-rhodium complex shown in the lower right of Scheme LXV, but the rate is unaffected. The stereoselectivity is suggested to possibly have its origin in a rate-determining transition state such as [137] where the substrate can hydrogen bond to the ligand (ref. 515). The CD spectra of $[Rh(CHIRAPHOS)(EAC)]ClO_4$ (EAC = ethyl-(Z)-α-acetamidocinnamate) in solution and in the solid state are very similar confirming that the isolated species is also the major species in solution ([138]). Since the prevailing chirality of the hydrogenation product is opposite from that expected from [138], these results further support the proposal that the reactive species in solution is the minor diastereomer, [139] (ref. 516). The reaction of $[Rh(NBD)Cl]_2$



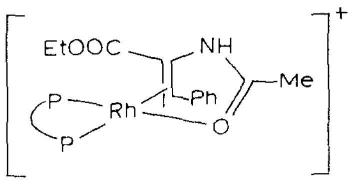
Scheme LXV



[137]



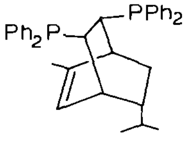
[138]



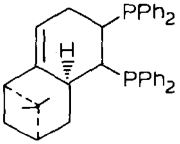
[139]

and (R,R)-1,2-bis(diphenylphosphinomethyl)cyclobutane(L_2) *in the* presence of perchlorate ion gives $[Rh(NBD)(L_2)]ClO_4$ which on hydrogenation in benzene/THF yields $[(\eta^6-C_6H_6)Rh(L_2)]ClO_4$. This is proposed as a model for the "resting state" of this type of catalyst system in instances where strongly coordinating anions are absent. However the system gives only about 65% optical yields from prochiral olefins (ref. 517). The structure of $[RhH((+)\text{-DIOP})_2]$ ((+)-DIOP = (4R,5R)-bis-(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane) has been determined and described as a severely distorted trigonal bipyramid with the hydride ligand in an equatorial site. It is fluxional even at -60° C. The complex is a good catalyst for styrene hydrogenation with olefin coordination occurring prior to the oxidative addition of hydrogen. An intermediate containing a monodentate DIOP ligand is postulated. Since the catalyst is inhibited by excess DIOP but not triphenylphosphine, the inhibition is thought to be due to the formation of an oligomer with bridging DIOP ligands (ref. 518). The solution structures of a number of asymmetric rhodium catalysts have been examined by the extended x-ray absorption fine structure (EXAFS) technique. For $[Rh(L_2)L']^+$ (L_2 = diphos, DIPAMP (DIPAMP = (R,R)-1,2-bis(o-anisylphenylphosphino)ethane); L' = COD, α-(acylamino)cinnamic acid) the results on the solids are in good agreement with the x-ray structural data. In solution the results are similar but with somewhat longer Rh-P, -O and -C distances indicating a possible relaxation of the coordination sphere. The results for the hydrogenation product of $[Rh(COD)(DIPAMP)]^+$ in methanol are most consistent with it being $[Rh(DIPAMP)(MeOH)_2]^+$ (ref. 519). Finally, the ligands (2S,4S)bis(diphenylphosphino)pentane(SKEWPHOS) and (S)-1,3-bis(diphenylphosphino)butane(CHAIRPHOS) have been used with rhodium-diene complexes to generate hydrogenation catalysts. With (Z)-(N-acylamido)-acrylic acids as substrates, high optical yields are obtained with SKEWPHOS complexes but not with those of CHAIRPHOS. This is attributed to the skew conformation of the SKEWPHOS ligand placing the phenyl groups on phosphorus in a chiral arrangement like that described for (S,S)-CHIRAPHOS while the favored chair conformation of CHAIRPHOS does not give such an arrangement. The conformations of the products are predominantly R implying that the reaction proceeds through the minor disastereomer of the possible catalyst-substrate complexes as described above (ref. 516). The oxidative addition of hydrogen is considered to be the slowest step and therefore the optical yield will be determined by the stereochemistry of the hydride species which is most rapidly formed (ref. 520).

High optical yields in the hydrogenation of N-acetyl-α-aminoacrylic acids are realized with rhodium complexes of [140]((S,S)-PHELLANPHOS) and [141]((R,R)-NOPAPHOS)) but their effectiveness is poor with other substrates (ref. 521). Other effective catalysts for the hydrogenation of α-(acetamido)cinnamic and -acrylic



[140]

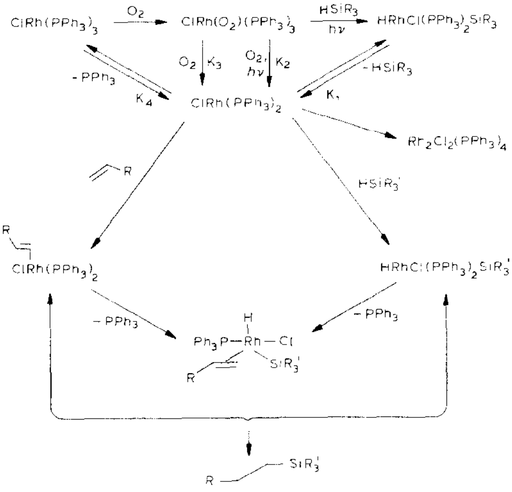


[141]

acids are derived from (+)- or (-)-NORPHOS and the closely related ligands (+)- and (-)-2,3-bis(diphenylphosphinomethyl)norbornene (refs. 522, 523). Other systems giving low to moderately good optical yields with related substrates are rhodium complexes using (R,R)- and (S,S)-2,4-bis[(diphenylphosphinyl)oxy]pentane (BDPOP), DIOXOP, (-)-BPPM and (1R,2R)-bis(diphenylphosphino)cyclohexane. The DIOXOP systems has been used to hydrogenate optically active dehydropeptides to give a new center of S configuration regardless of that for the existing center while the last two systems have been used to obtain optically active dipeptides from 2-(acetylamino-acetylamino)-2-alkenoic acids (refs. 524-527). A comparison has been made between the stereoselectivity of rhodium complexes of BPPM and its polymer-anchored analog, prepared by the copolymerization of N-acryloyl-(2S,4S)-R-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidine with hydroxymethylmethacrylate or N,N-dimethylacrylamide, in the catalysis of the hydrogenation of α-acetamidocinnamic acids. Both give comparable optical yields (ca. 90%) but the supported catalyst is reusable (ref. 528). With the same substrate, the rates of hydrogenation using rhodium complexes of polymer-supported DIOP-type ligands are lower than for the homogeneous analogs but the optical yields are higher. As hydroformylation catalysts for styrene they give lower optical yields and higher amounts of branched-chain aldehydes than the homogeneous analogs (ref. 529). By contrast, the copolymerization of 1-methyl-2-hydroxypropyl acrylate with ethylenedimethacrylate and acryloyl-functionalized BPPM and DIOP gives ligands forming rhodium complexes which catalyze the hydrogenation of α-acetamidoacrylic acid in very poor optical yields. Evidence is presented that the pendant hydroxyl groups affect the active site (ref. 530). Another supported catalyst giving rather poor optical yields was prepared from a copolymer of (R)-cyclohexylmethyl-p-styrylphosphine, hydroxyethylmethyl methacrylate and ethylene dimethacrylate (ref. 531). In ethanol, a rhodium-DIOP moiety supported on cross-linked Amberlite resin catalyzes the hydrogenation of prochiral ketones to the corresponding alcohols in high chemical but very low optical yield (ref. 532). Polystyrene-anchored 1,2-bis(N-diphenylphosphino-N-(1-phenylethyl)amino)ethane together with (1R)-phenyl-1-diphenylphosphino-(2S)-N-methylaminopropane and 1,4-bis(diphenylphosphino)-2,5-dibenzylpiperazine have been used to form rhodium catalysts for the asymmetric hydrogenation of α-acetamido-cinnamic acid. Only the second system gave favorable optical yields (ref. 533). Vinyl esters have been hydroformylated to 2-(acyloxy)propanals in moderate optical yields using rhodium complexes of DIOP-type ligands. The best employed a ligand with 2,2'-biphenyl substitutents on phosphorus (ref. 534). Related catalysts were effective in the asymmetric hydroformylation and hydrosilylation of N-(α-ketoacyl)-α-amino esters to provide synthons for chiral depsipeptides (ref. 535). Other catalyst systems described include rhodium complexes of phosphinites derived from glucose or camphoric acid for the hydrosilylation of acyl benzenes by $PhSiH_2R$ (R = Ph, 1-naphthyl) (ref. 536), of (+)-neomenthyldiphenylphosphine, (S)-(-)-(p-$MeC_6H_4SO_2$)NHCH(Et)CH_2PPh_2 and (2R,3R)-(-)-2,3-o-cyclohexylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane for the hydrogenation of α-acetamidocinnamic acid (ref. 537), of $Ph_2PCHMeR$ (R = Et, Pr^i) for the hydrogenation of acrylic acid derivatives (ref. 538), of chiral, mono(diphenylphosphino) derivatives of 5- and 6-membered ring sugars for the hydrogenation of tiglic acid (ref. 539) and of phosphites derived from galactopyranose and glucofuranose for the hydrogenation of α-acetylaminocinnamic acids (ref. 540). In all cases, the optical yields were modest at best.

In the hydrogenation of methoxymethyl- and alkyl-2-acetamidoacrylic acid esters, rhodium complexes of ligands containing achiral phosphorus atoms linked by a four-carbon chiral unit give higher optical yields from E substrates than from those of Z configuration. The reverse is true when a two-carbon chiral linkage is present. Better optical yields are obtained when the chirality resides at phosphorus as in DIPAMP (ref. 541). Catalytic hydrosilylation of poly(isopropenylmethyl ketone) with diphenylsilane and chiral rhodium phosphine complexes has been used to prepare optically active poly(3-methyl-3-buten-2-ol) (ref. 542). Reaction of styrene with bromotrichloromethane in ethanol-benzene in the presence of a rhodium complex of (-)-DIOP gives a 32% optical yield of (S)-(-)-1-bromo-1-phenyl-3,3,3-trichloropropane. This is the first example of the generation of a chiral center via carbon-bromine bond formation in a reaction catalyzed by a chiral catalyst (ref. 543).

Complexes of the type $[Rh(NBD)L_n]ClO_4$ (L = PEt_3, PPh_3; n = 2. L = PMe_3; n = 3. L_n = diphos) function as catalysts for the hydrogenation of styrene oxide and ketones, RC(O)Me (R = Me, Et, Pr^n, $MeOCH_2$, Ph, $PhCH_2$, $PhCH_2CH_2$, Ph_2CH, CH_2=CH). For the first system, the alkyl phosphines produce $PhCH_2CH_2OH$ and a moderate yield of oligomers while the triphenylphosphine catalyst gives mainly $PhCH_2CHO$ and much more oligomer. The oligomers are mainly dimers. In the latter system the rate depends on the ligand as well as the ketone structure with the best catalyst being formed with triethylphosphine (refs. 544, 545). Aminoarenes and aliphatic aldehydes in the presence of the corresponding nitroarenes and $[Rh(NBD)Cl]_2$ are converted into 2-alkyl- and 2,3-dialkylquinolines in good yield (ref. 546). Olefins and acetylenes can be hydrogenated and hydroformylated in the presence of $[Rh(COD)_2]ClO_4$ or $[Rh(COD)_n(stilbenediamine)]ClO_4$ (n = 1,2) (ref. 547). Of the various factors affecting the rate and stereochemistry of the hydrogenation of 4-tert-butylmethylene cyclohexane catalyzed by $[HRh(PPh_3)_4]$, the most significant is the hydrogen pressure. The results are interpreted in terms of changes in the nature of the rate-determining step (ref. 548). The reaction of syn-tetramethyldisiloxane with 1,3-divinyltetramethyldisiloxane is catalyzed by $[RhCl(PPh_3)_3]$ or mixtures of rhodium(III) chloride and PBu^n_3 or $P(OBu^n)_3$. The rate is significantly enhanced by photolysis in the presence of oxygen or organic hydroperoxides and for the Rh(I) system, photocatalysis is observed. The intermediacy of silylrhodium hydrides is indicated by the fact that $[RhHCl(SiMe_2Cl)(PPh_3)_2]$ gives a more active catalyst system than does $[RhCl(PPh_3)_3]$. The proposed mechanism is detailed in Scheme LXVI (ref. 549). $[RhCl(PPh_3)_3]$ has also been used to catalyze the hydrosilylation of



Scheme LXVI

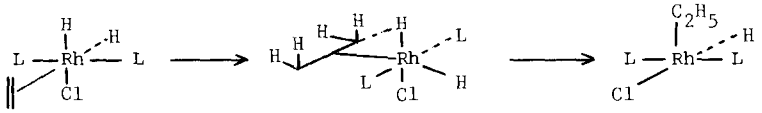
divinyl sulfide by diethylsilane. The major products are 2-diethylsilylethyl vinyl sulfide and 1-diethylsilylethyl ethyl sulfide. Small quantities of cyclic products also were seen. With diallyl sulfide however the only product was 3-diethylsilylpropyl allyl sulfide (ref. 550). The Rh(II) complexes $[RhCl_2L_2]$ [L = P(o-tolyl)$_3$, P(cyclohexyl)$_3$) catalyze the hydrosilylation of oct-1-ene with $HSiR_3$ (R_3 = Et_3, Me_2Ph, $(OEt)_3$, $Me(OEt)_2$) to give n-octylsilanes in high yield. With 2,3-dimethylbutadiene the products are $Me_2C{=}C(Me)CH_2SiR_3$ and $H_2C{=}C(Me)CH_2SiR_3$ (R = Et, OEt) while with hex-1-yne comparable amounts of cis and trans $Bu^nCH{=}CHSiR_3$ (R = Et, OEt) are produced (ref. 551).

Olefin hydrogenation catalyzed by $[RhCl(PPh_3)_3]$ is photostimulated. However the reasons for the rate enhancement on irradiation were not given (ref. 552). This catalyst has also been used with deuterium and tritium to prepare specifically labelled compounds, for example $CH_3(CH_2)_3(CX_2)_2(CHD)_2(CH_2)_7CO_2CH_3$ (X= H,D) from $CH_3(CH_2)_3(CX_2)_2CH{=}CH(CH_2)_7CO_2CH_3$ and predominantly (2SR,3SR,4RS)-[4-$^3H^2H$]-N-acetylvaline from 2-(RS)-(E)-[4-^2H]-2-acetylamino-3-methylbuten-3-oic acid (refs. 553, 554). The complexes $[M_2Cl_2(TDDX)]$ (M = Rh, Ir; TDDX = p-$[(Ph_2PCH_2CH_2)_2PCH_2]_2C_6H_4$) are olefin hydrogenation catalysts and appear to operate by a mechanism analogous to that for $[RhCl(PPh_3)_3]$ with the two metal centers functioning independently (ref. 555).

A number of supported analogs of $[RhCl(PPh_3)_3]$ have been investigated as hydrogenation catalysts. Complexes of formula $[RhClL_2]$ (L_2 = PPh_2R

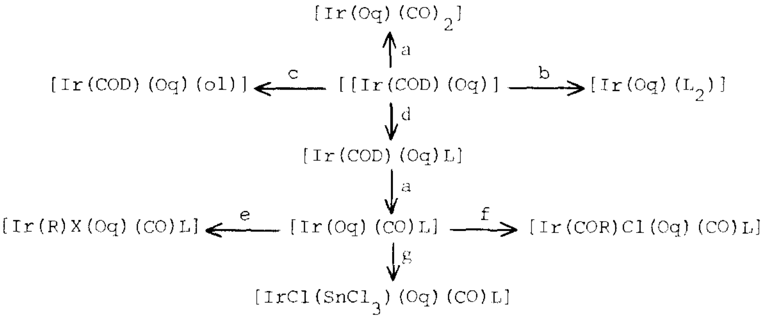
(R = $(CH_2)_nSi(OEt)_3$, n = 1,6; $CH_2SiMe_{3-m}(OEt)_m$, (m = 1-3)) were prepared in situ and their activities compared with those of the same species anchored by reaction of the siloxy functions with a silica surface. Both are deactivated by dimer formation which occurs to varying extents depending on the chain-length of the anchoring group (ref. 556). Silica functionalized with pendant tertiary amines has been used to support $[RhCl(PPh_3)_3]$ for olefin hydrosilylation while related phosphine complexes have been attached to a variety of supports to form olefin hydrogenation catalysts. In the latter case, only linear polystyrene proved to be a satisfactory system since severe leaching problems were encountered with the other supports used (refs. 557, 558). The complex $[Rh(NBD)(diphos)]^+$ has been supported by intercalation into hectorite and catalyzes the 1,2 and 1,4 addition of hydrogen to butadiene, isoprene and 2,3-dimethylbutadiene. The rates are generally much slower than for the homogeneous system but the proportion of 1,2 addition obtained is more than twice as great. The supported system increases in activity as the ability of the solvent used to cause swelling of the support increases indicating that swelling is necessary to provide facile access to the catalyst (ref. 559). The activity of $[RhCl(PPh_3)_3]$ as an olefin hydrogenation catalyst is increased in the presence of silver polystyrene sulfonate which adsorbs the triphenylphosphine lost by the catalyst following hydrogen activation (ref. 560). Rhodium complexes of phosphines bearing substituents having surfactant structure can be heterogenized in a two-phase liquid system in the presence of surfactants. The catalyst remains bound to the aqueous phase with catalysis occurring in the micelles (ref. 561).

Further results of theoretical studies on the $[RhC(PPh_3)_3]$-catalyzed hydrogenation of olefins have appeared. Using the model complex $[RhH_2Cl(C_2H_4)(PH_3)_2]$, the process involved in the transfer of the first hydrogen atom to the olefin is considered to be that shown in Scheme LXVII. Up to the transition state the process is described as an insertion of the olefin into the Rh-H bond with the necessary rearrangement of the other ligands occurring simultaneously. The process is favored by π-donor ligands trans to the site of insertion (ref. 562).



Scheme LXVII

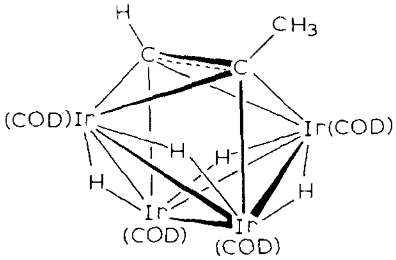
Reaction of $[Ir(COD)Cl]_2$ with sodium 8-hydroxyquinolinate (NaOq) in methanol yields [Ir(COD)(Oq)] which decomposed on attempted recrystallization. The chemistry of this complex is summarized in Scheme LXVIII. The reaction of [Ir(Oq)(CO)L] with chlorine gives the corresponding dichloro complex together with complete chlorination of the quinolinate ligand (ref. 563). Treatment of



a) CO in CH_2Cl_2. b) L_2 = diphos, cis-$Ph_2PCH{=}CHPPh_2$, DPM, DPPB in ether. c) ol = TCNE, maleic anhydride. d) L = PPh_3, $P(OPh)_3$, PEt_3, $PBu^n{}_3$, PMe_2Ph, $P(OMe)_3$ in ether. e) RX = MeI, allyl bromide. f) RCOCl (R = Me, Et). g) $SnCl_4$.

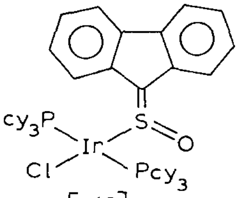
Scheme LXVIII

$[Ir(COD)Cl]_2$ with $RN(PPh_2)_2$ (R = Me, Ph, p-tolyl) in benzene, THF or methanol gives solvated $[Ir(RN(PPh_2)_2)_2]Cl$ species but metathesis with sodium tetraphenylborate gives the corresponding unsolvated salt. The carbonyl derivative $[Ir(CO)(RN(PPh_2)_2)_2]Cl$ (R = Me, p-tolyl) can be prepared from the appropriate ligand and $[Ir(CO)_2Cl(p\text{-toluidine})]$ or $[Ir(CO)Cl(PPh_3)_2]$ respectively (ref. 564). The Schiff base complexes [Ir(COD)(SB)] (SB = N-(RC_6H_4)-salicylaldimino (R = H, o-Me, m-Me, p-Ph)) are obtained from $[Ir(OMe)(COD)]_2$ and the corresponding neutral ligand (ref. 565). Reaction of $[IrCl(COD)]_2$ with isopropylmagnesium bromide in ether at -50° C followed by photolysis at room temperature produces the air- and heat-stable butterfly cluster [142] (ref. 566). The first example of an Ir(I) sulfine complex,



[142]

formulated as [143], results from the reaction of $[IrCl(COD)]_2$ with four equivalents of tricyclohexylphosphine and fluorene-9-ylidene-sulfine. However, attempts to prepare analogs from RSC(X)SO (R = aryl, alkyl; X = aryl, S-aryl) were unsuccessful (ref. 567).



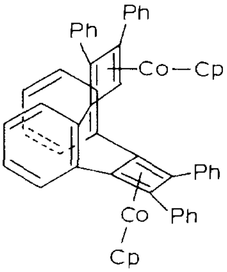
[143]

Complexes of the formula $[Ir(COD)L_2]^+$ (L_2 = $(PPh_3)_2$, $(PMePh_2)_2$, diphos, *o*-phenanthroline, substituted *o*-phenanthroline) function as precursors for water-gas-shift catalysts in aqueous dioxane. Presumably the carbon monoxide present displaces COD to give carbonyl complexes which are the active species. They are reported to be more active than $[Rh(CO)_2I_2]^-$ but not as good as those based on $[Ru_3(CO)_{12}]$ (ref. 568). Catalysts for the reduction of cyclohexanones and benzylidene aniline by hydrogen transfer from isopropanol in the presence of base are prepared from $[Ir(cyclooctene)_2Cl]_2$, ethylene and bipyridyl, *o*-phenanthroline and derivatives thereof. The initial complexes are formulated as $[Ir(C_2H_4)_2(L_2)Cl]$ (L_2 = bipy, etc.) (ref. 569). The complex $[Ir(COD)(py)(P(cyclohexyl)_3)]PF_6$ is reported to be a more effective catalyst than $[RhCl(PPh_3)_3]$ under mild conditions for the hydrogenation of Δ^4-3-ketosteroids to 5-α-3-ketosteroids (ref. 570). The related complex $[Ir(COD)(PMePh_2)_2]PF_6$ when activated by hydrogen catalyzes the conversion of allyl ethers to their vinyl isomers without reduction to propyl compounds as occurs with $[RhCl(PPh_3)_3]$. They are thus more useful in procedures used to remove allyl protecting groups in oligosaccharide syntheses (ref. 571).

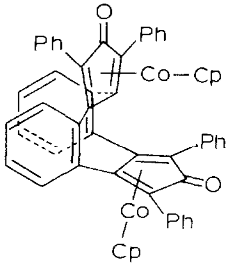
The ^{29}Si NMR spectra of $[Rh(acac)(CH_2{=}CHR)_2]$ (R = $SiMe_3$, $SiMe_2(OEt)$, $Si(OEt)_3$, CH_2SiMe_3), $[cpRh(CH_2{=}CHSiMe_3)_2]$ and $[Co_2(CO)_6L]$ (L = $Me_3SiC{\equiv}CSiMe_3$, $Me_3SiC_4SiMe_3$, $Me_2ClSiC{\equiv}CSiClMe_2$) have been measured. Where the silicon atom is bound to a coordinated carbon the silicon chemical shift is 6-11 ppm downfield of that for the free ligand. This effect is additive so that with two metals involved the shift is roughly twice as great. A slight upfield shift is seen if the silicon atom is remote from the coordinated carbon atom. Rhodium-silicon coupling was also observed in some instances (ref. 572).

Metal Alkyne Compounds

The reaction of $[cpCo(CO)_2]$ with alkynes continues to receive considerable attention. With 1,2-bis(phenylethynyl)benzene in refluxing xylene a variety of products are obtained including [144] - [147] and the organic compound [148]. With

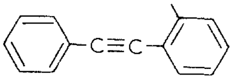


[144]

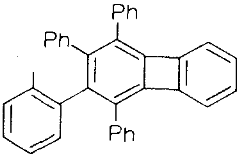


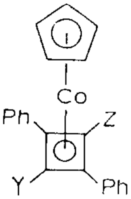
[145]

Y =

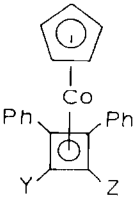


Z =

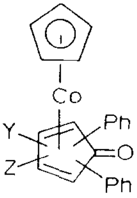




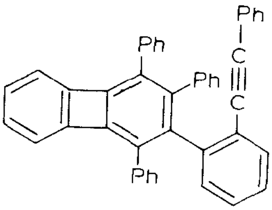
[146 a]



[146 b]

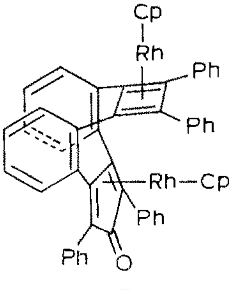


[147]



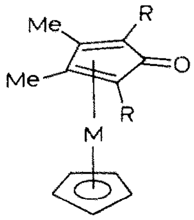
[148]

[cpRh(CO)$_2$] several products also were formed including [149] and [cp$_3$Rh$_3$(CO)$_3$] [ref. 573]. With MeC≡CR(R = Bu^n, Pr^i) all possible isomers of the cyclopentadienone complexes [cpCo(η^4-C$_4$Me$_2$R$_2$CO)] were formed together with small quantities

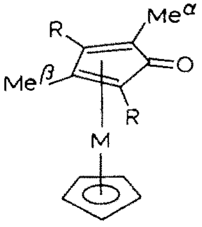


[149]

of both isomers of the p-benzoquinone complexes [cpCo(η^4-C$_4$Me$_2$R$_2$(CO)$_2$)]. For R = Bu^t only the cyclopentadienone complexes [150] were formed. All three acetylenes



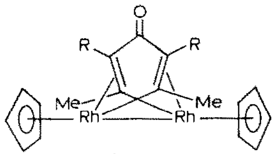
[150 a]



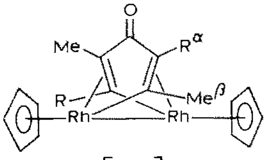
[150 b]

M = Co
R = Bu^t

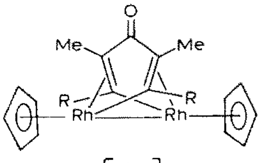
with [cpRh(CO)$_2$] produced all possible isomers of the corresponding cyclopentadienone and quinone complexes together with the isomeric mixture [151]. As the



[151a]

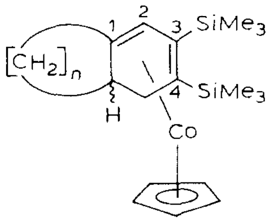


[151b]

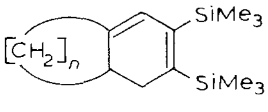


[151c]

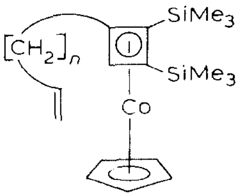
size of the group R increases, the yield of products decreases (ref. 574). In the 1980 Survey, the use of [cpCo(CO)$_2$] to effect the cocyclization of acetylenes and α, ω enynes with bis(trimethylsilyl)acetylene (BTMSA) was reported in some detail. Further work in this area has now appeared. With HC≡C(CH$_2$)$_n$CH=CH$_2$ (n = 2-4) and BTMSA, [152] - [154] are the products with n = 4 giving [152] as a diastereomeric mixture while n = 2 gives only the endo-H isomer. The same enynes (n = 3,4) cocyclize with CH$_3$(CH$_2$)$_4$C≡CSiMe$_3$ under comparable conditions to give [155] via [156] as a postulated intermediate (ref. 575). The cocyclization of BTMSA with CH$_3$CHRC≡CH (R = OH, OMe, Ph) gave a mixture of the diastereomers [157a] and [157b] which were separated by liquid chromatography. Flash vacuum pyrolysis of either



[152]



[153]



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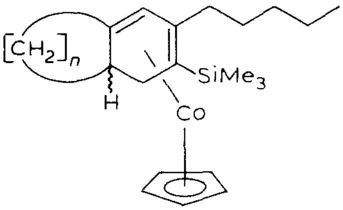

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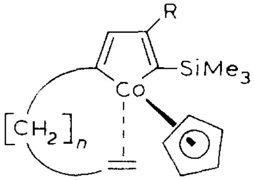

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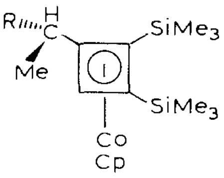
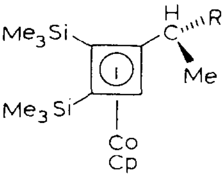
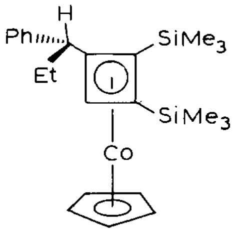


[157a]

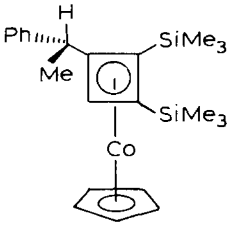


[157b]

diastereomer produced extensive equilibration. Further, the copyrolysis of [158] and [159] gave diastereomeric mixtures of each complex but no crossover indicating

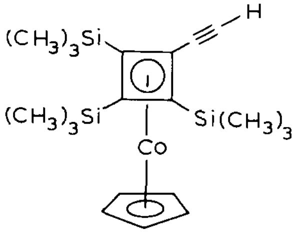


[158]



[159]

that the interconversion of diastereomers occurs by retrocyclization via a bis-(acetylene) complex (ref. 576). The use of liquid chromatography in the separation of the often complex product mixtures of these and related reactions is described in two additional papers. Cocyclization of BTMSA with 1-trimethylsilyl-3-phenylbut-1-yne yielded [160] - [162] while with 5-hexen-1-yne the complexes [163] and [164]



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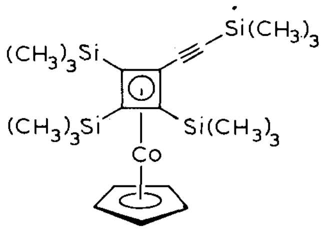

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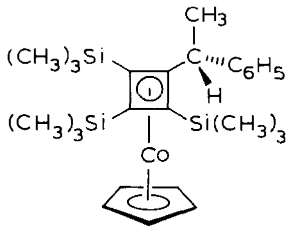

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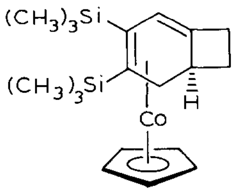
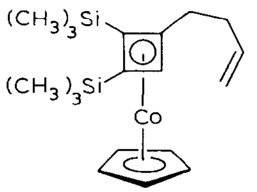
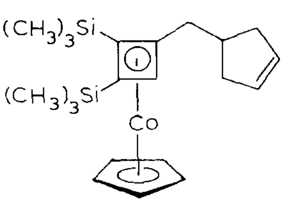


[163]



[164]

were isolated. Finally, with 3-(2-propynyl)cyclopentene the five complexes [165] - [169] were obtained and separated. The origin of the methyl group on the cyclopentadienyl ring of [168] is unknown (ref. 577). In the second paper, slow addition of [cpCo(CO)$_2$] and 1,6-bis(trimethylsilyl)-1,5-hexadiyne to refluxing *o*-xylene under irradiation gave a complex mixture of products from which sixteen complexes ([170] - [185]) could be separated and characterized. The yields are



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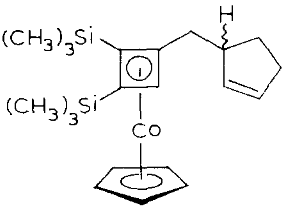
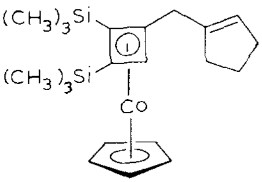


[166]



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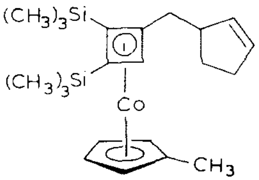

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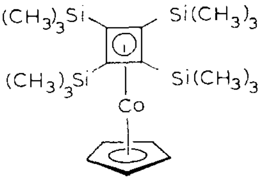
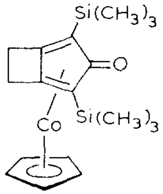


[169]



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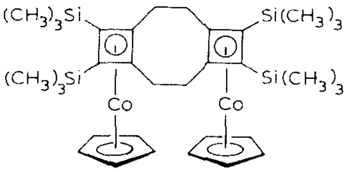
[170]



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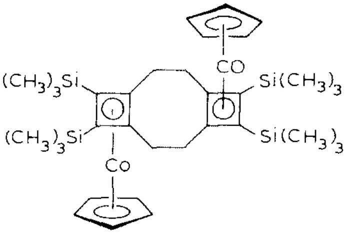
[171]



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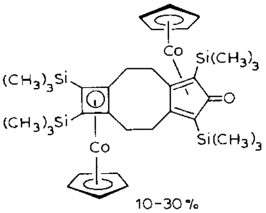
[172]



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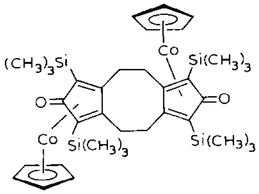
[173]



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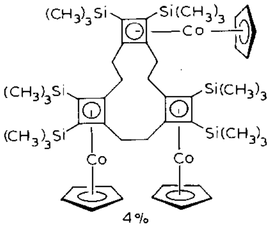

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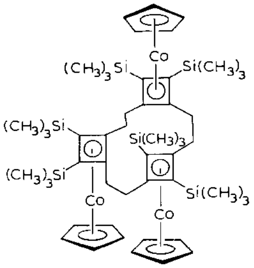
[175]



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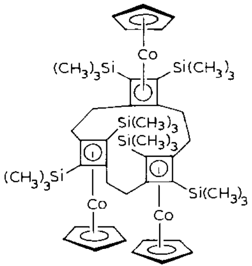

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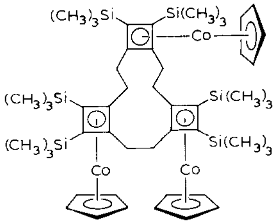
[176b]



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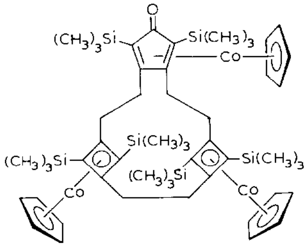
[177]



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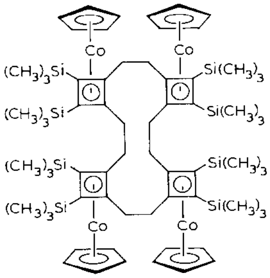
[178]



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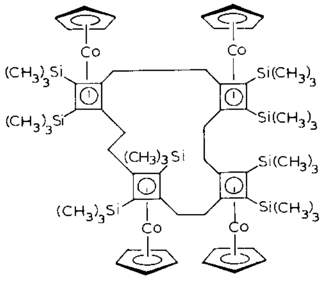
[179]



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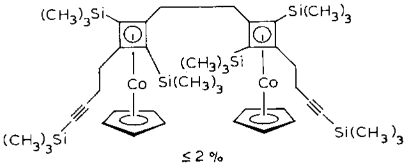
[180]



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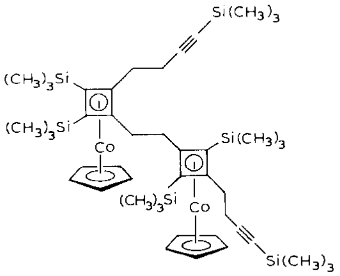
[181]



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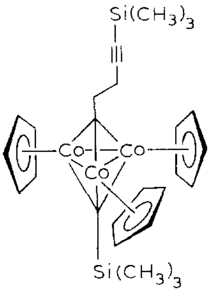
[182]



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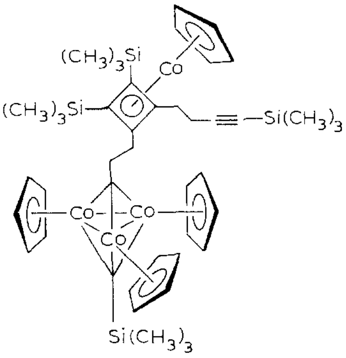
[183]



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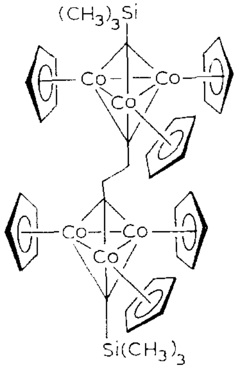
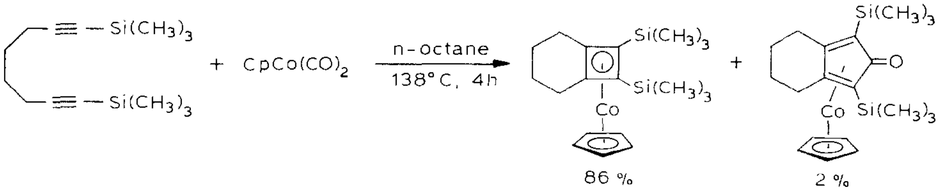
[184]



8 %

[185]

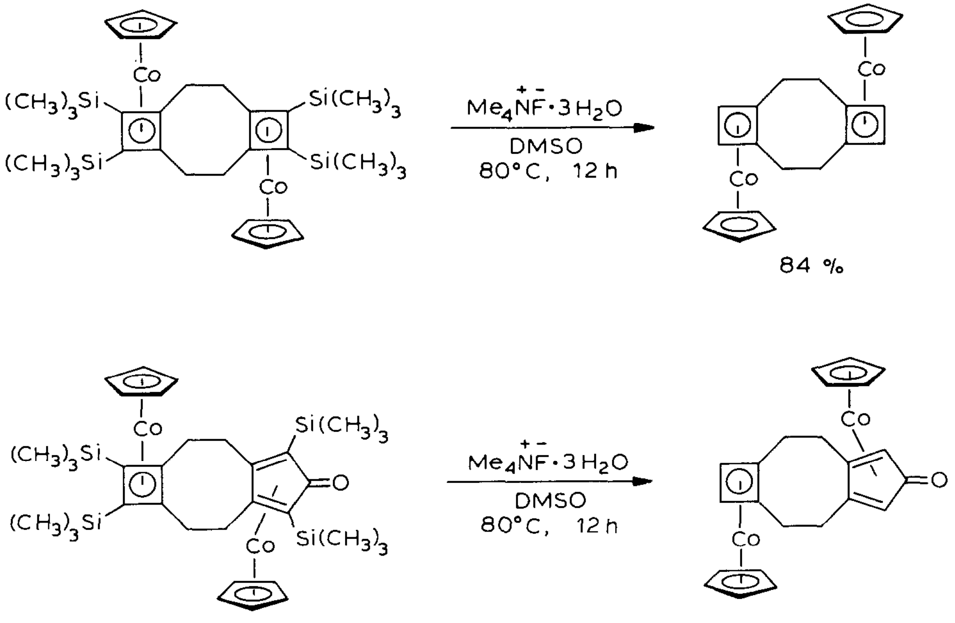
given below each figure. Two additional tetramers besides [179] and [180] were found but in insufficient amounts to be fully characterized. Interestingly the same reaction in refluxing n-decane using an excess of the cobalt complex gave [183] - [185] and [172] as the only identifiable products. In n-octane, [cpCo(CO)$_2$] and 1,8-bis(trimethylsilyl)-1,7-octadiyne react according to Scheme LXIX while



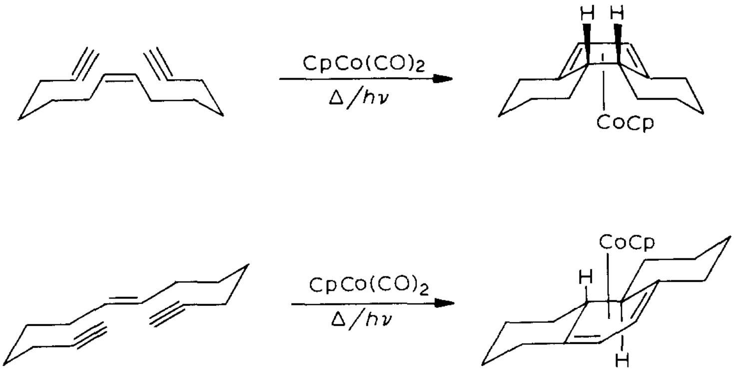
Scheme LXIX

removal of the trimethylsilyl groups from [172] and [173] can be accomplished as shown in Scheme LXX (ref. 578). A final example of the use of [cpCo(CO)$_2$] is its ability to mediate the stereospecific [2+2+2] intramolecular cycloaddition of endiynes. Two examples are depicted in Scheme LXXI (ref. 579).

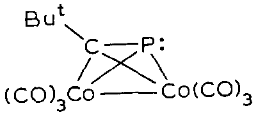
In the area of alkyne complexes derived from [Co$_2$(CO)$_8$] it is found first that the phospha-alkyne $Bu^tC{\equiv}P$: reacts as an alkyne to give [186] as an air- and moisture-sensitive red oil (ref. 580). A further report on the reactions of the cobalt-complexed propargyl cations, [Co$_2$(CO)$_6$(HC$_2$CRR')]BF$_4$ (R = R' = H, Me. R = Me, Ph; R' = H) has appeared. Reaction with a variety of methylating agents (e.g. MeMgI, Me$_2$Cd, Me$_2$Hg, Me$_4$Si, Me$_4$Sn) yields dimers [Co$_2$(CO)$_6$(HC$_2$CRR'CRR'C$_2$H)Co$_2$(CO)$_6$] rather than effecting methylation of the propargyl group. Some of the desired



Scheme LXX

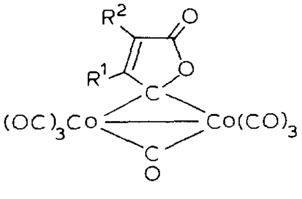


Scheme LXXI

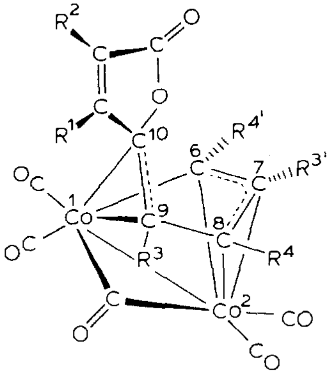


[186]

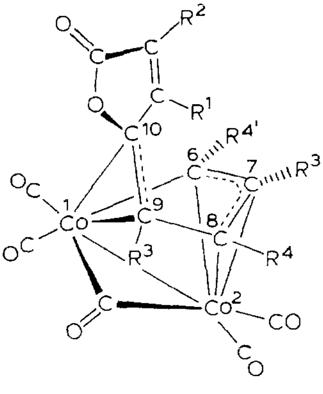
$[\mathrm{Co_2(CO)_6(HC_2CRR'Me)}]$ is produced using $[\mathrm{cpFe(CO)_2Me}]$ or trimethylaluminum but the best system is $[\mathrm{Co_2(CO)_6(HC_2CRR'O_2CMe)}]$ and trimethylaluminum at -78° C (ref. 581). The standard $[\mathrm{Co_2(CO)_6(ROC_2OR)}]$ complexes ($\mathrm{R = Pr^i, Bu^t}$) are formed from $[\mathrm{Co_2(CO)_8}]$ and the corresponding acetylenic diethers (ref. 582). Analogous complexes of the optically active acetylenes $\mathrm{PhC_2CO_2CH_2CHPhR}$ (R = Me, Et) are fluxional and no low temperature limiting ^{13}C NMR spectra could be obtained. Reaction with trimethylphosphite or methyldiphenylphosphine (L) gives $[\mathrm{Co_2(CO)_5L(acetylene)}]$ or $[\mathrm{Co_2(CO)_4\text{-}L_2(acetylene)}]$. The diastereomers of the former complex were separated (ref. 583). At room temperature methyl propiolate and $[\mathrm{Co_2(CO)_8}]$ form $[\mathrm{Co_2(CO)_6(HC_2CO_2Me)}]$ which reacts with carbon monoxide at elevated temperatures to give $[\mathrm{MeO_2CCH_2CCo_3\text{-}(CO)_9}]$. The same product can be generated directly from $[\mathrm{Co_2(CO)_8}]$ and the acetylene under carbon monoxide pressure at 120° C. It is also formed as the minor product from the same reaction with dimethylacetylene dicarboxylate (DMAD). The major product here is $[\mathrm{(MeO_2C)_2CHCCo_3(CO)_9}]$. However if $[\mathrm{Co_2(CO)_6(DMAD)}]$ is refluxed in n-decane under one atmosphere of carbon monoxide, the product is $[\mathrm{Co_4\text{-}(CO)_{10}(DMAD)}]$ (ref. 584). Oct-7-en-1-yne is cyclized by prolonged heating in the presence of $[\mathrm{Co_2(CO)_8}]$ at 95° C to bicyclo[4.3.0]non-1-en-8-one in moderate yield. The reaction proceeds through initial formation of the $[\mathrm{Co_2(CO)_6(acetylene)}]$ complex since if run at room temperature, this complex is isolated and on heating it at 95° C under carbon monoxide the bicyclic ketone is produced. In an analogous fashion, bicyclo-[3.3.0]oct-1-en-3-one can be got from hept-6-en-1-yne (ref. 585). Reaction of [187] either the acetylenes $\mathrm{R^3C_2R^4}$ ($\mathrm{R^3 = H; R^4 = Me, Pr^n, Bu^n, Ph, CH_2OMe}$) gives $[\mathrm{Co_2(CO)_6(R^3C_2R^4)}]$ and the isomers [188a] and [188b] ($\mathrm{R^1 = R^2 = R^3 = H; R^4 = Pr^n, Ph, CH_2OMe.\ R^1 = R_3 = H; R^2 = Ph, R^4 = Me, Bu^n, CH_2OMe}$). With internal alkynes, the corresponding products are obtained together with several others (ref. 586). The reaction of a variety of aliphatic internal alkynes with



[187]



(188a)

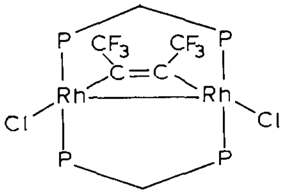


(188b)

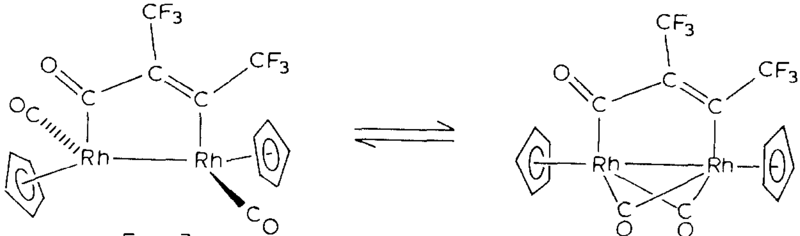
$[HFeCo_3(CO)_{12}]$ or with a mixture of $[Fe(CO)_5]$ and $[Co_2(CO)_8]$ yields a variety of products including two binuclear cobalt-carbonyl-alkyne complexes containing oxygenated substituents attached to the carbon α to the coordinated triple bond (ref. 587).

Electrochemical reduction of $[Co_2(CO)_6(Ph_2C_2)]$ and $[YCCo_3(CO)_9]$ (Y = Cl, Ph) in the presence of PPh_3, $PBu^n{}_3$ or $P(OMe)_3$ leads to facile substitution of one carbonyl ligand which is proposed to occur <u>via</u> the reductive cleavage of a Co-Co bond to give a labile 17-electron species which undergoes substitution followed by reoxidation to neutral product (ref. 588). The ultraviolet PES spectra of $[Co_2(CO)_6\text{-}(R_2C_2)]$ (R = H, Me) have been measured and interpreted to indicate that the HOMO is a mixture of metal and acetylene orbitals (ref. 589). A variety of torsional modes of $[Co_2(CO)_6(C_2H_2)]$ have been assigned using data from inelastic neutron scattering measurements (ref. 590).

Reaction of $[Rh(COD)Cl]_2$ with DPM in the presence of hexafluorobut-2-yne (HFB) produces the A-frame-type complex [189] in which the metal-metal distance is 2.7447(9) A. The metal-metal bond is cleaved on reaction with carbon monoxide at the open face to give $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-HFB})(DPM)_2]$ (ref. 591). On the other hand HFB reacts with $[Rh(CO)_2Cl]_2$ followed by treatment with thallium cyclopentadienide to give <u>cis</u>- and <u>trans</u>-$[cp_2Rh_2(CO)_2HFB]$ and [190] which is fluxional as depicted in Scheme LXXII. Decarbonylation of [190] with trimethylamine oxide yields [191] and [192] (ref. 592). The acetylenes $RO_2CC_2CO_2R$ (R = H, Me) are cyclotrimerized by $[Rh(CO)_2(PPh_3)_2]_2$ in refluxing benzene under carbon monoxide but no reaction is observed if the acetylene does not bear electronegative substituents. For R = Me, complex [193] was also isolated and the mechanism of Scheme LXXIII was proposed. Reaction of [193] with $P(OCH_2)_3CEt$ yields [194] (ref. 593). Condensation of α-olefins with RC_2R' (R = R' = Ph, Me; R = Ph, R' = Me) is catalyzed by $[Rh_4(CO)_{12}]$ at 180° C in the presence of carbon monoxide to yield the furanones [195] and [196]. For R' = H, the yield is good but for R" = alkyl it is rather low. Other effective catalyst presursors are $[Rh_6(CO)_{16}]$ and $[Rh(CO)Cl(PPh_3)_2]$ (ref. 594).

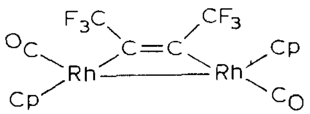


[189]

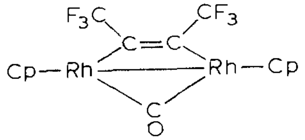


[190]

Scheme LXXII

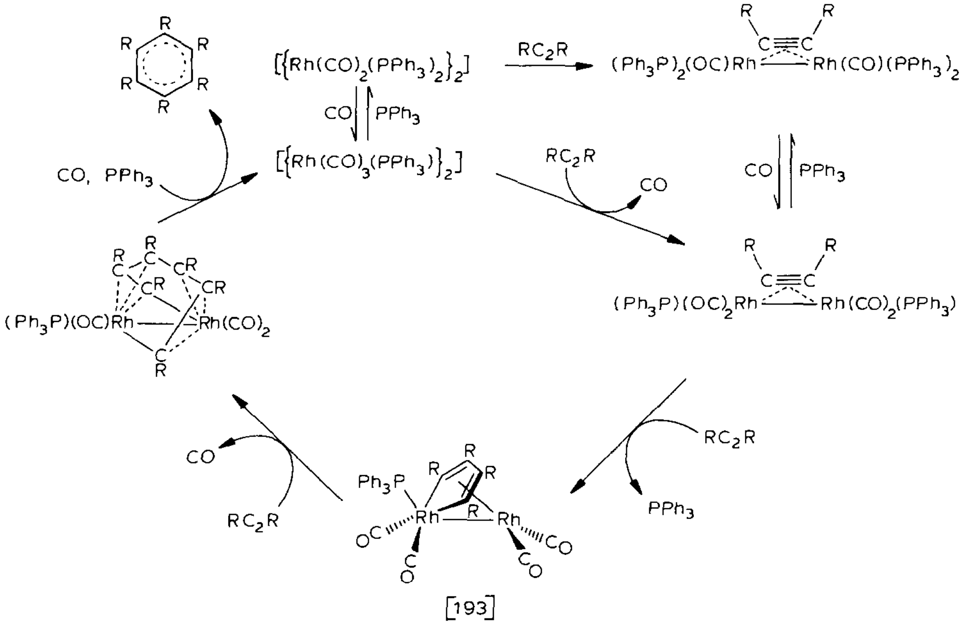


[191]



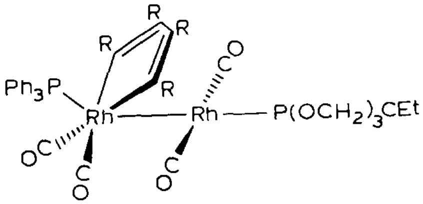
[192]

Catalysts prepared in situ from [Rh(cyclooctene)$_2$Cl]$_2$ and triphenylphosphine effect the hydrosilylation of pent-1-yne by triethylsilane to give cis- and trans-1-triethylsilylpent-1-ene in a ca 2:1 ratio. With stronger donor phosphines, the proportion of the cis-olefin decreases implying that the silane adds to the acetylene in a cis-fashion with the observed isomer mixture arising from isomerization of the intermediate vinyl rhodium complex (ref. 595). A variety of Rh(I) complexes (e.g. [RhCl(PPh$_3$)$_3$], [RhCl(SbPh$_3$)$_3$] and [Rh(CO)ClL$_2$] (L = PPh$_3$, AsPh$_3$)) catalyze the hydrosilylation of $HC{\equiv}CCH_2NR_2$ (R_2 = Me$_2$, Et$_2$, $(CH_2)_n$ (n = 4-6)) by triethylsilane. The addition is not stereospecific but is regioselective with the cis- and trans-olefinic products being formed according to Farmer's rule. In the hydrosilylation of phenylacetylene, the catalyst activity increases with increased donor strength of the phosphine ligand while with increased ligand bulk, the regioselectivity is increased (refs. 596, 597).



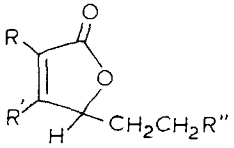
R = CO_2Me

Scheme LXXIII

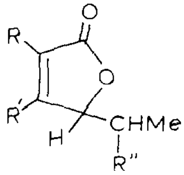


[194]

R = CO_2Me

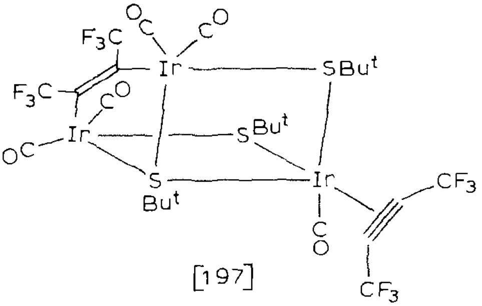


[195]

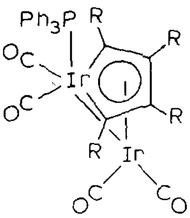


[196]

Reaction of $[Ir_3(\mu\text{-}SBu^t)_3(\mu\text{-}HFB)(CO)_6]$ with additional HFB yields [197] (ref. 598). With $[Ir(CO)_3(PPh_3)]_2$, diethylacetylene dicarboxylate yields [198] in refluxing benzene while phenylacetylene in refluxing dichloromethane yields [199] (refs. 599,600).

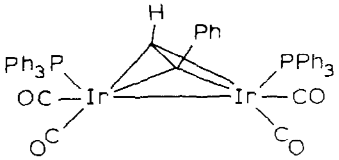


[197]



[198]

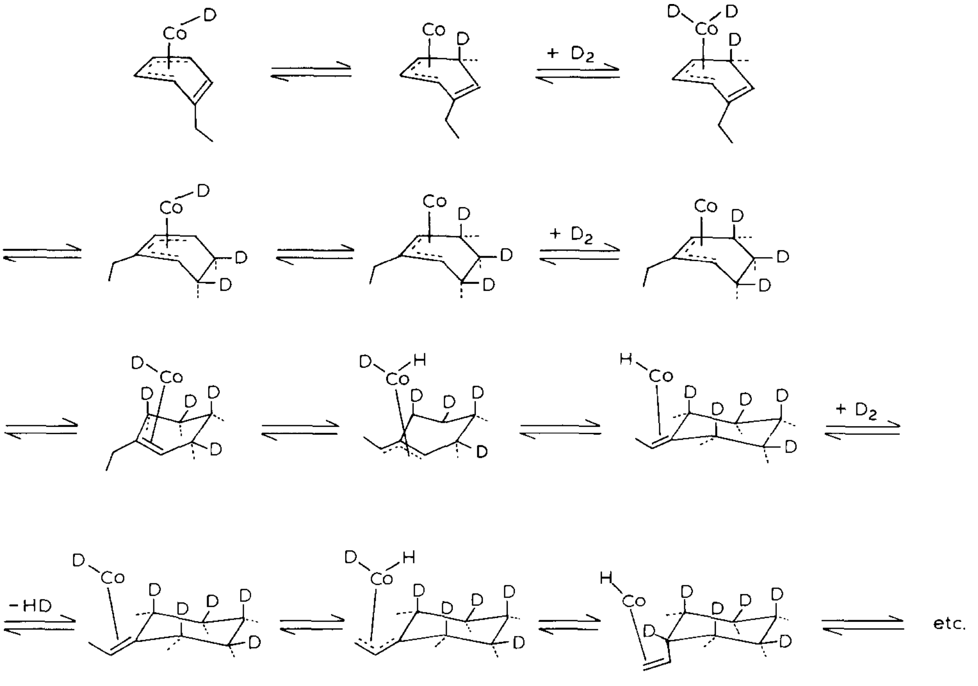
R = CO_2Et



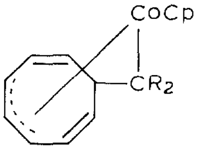
[199]

Metal π-allyl Compounds

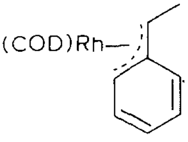
Phosphites displace COD from $[(\eta^3\text{-}C_8H_{13})Co(COD)]$ to give $[(\eta^3\text{-}C_8H_{13})CoL_3]$ (L = $P(OR)_3$ (R = Me, Et, Pr^i)) which catalyze the hydrogenation of benzene to cyclohexane in modest yields. The mechanism of the reaction has been studied in detail for L = $P(OMe)_3$ and cis-addition of hydrogen to the ring carbon atoms occurs as determined by labelling studies. Deuterogenation of alkyl benzenes also results in deuterium incorporation into the alkyl group provided that each carbon in it originally bears at least one hydrogen atom. The active catalyst is thought to be $[CoHL_2]$ and since arene hydrogenation in the presence of olefins gives some cyclohexenes instead of only cyclohexanes it appears that displacement of catalyst-bound cyclohexene occurs prior to the final hydrogenation step. The proposed mechanism is shown in Scheme LXXIV (refs. 601, 602). Photolysis of $[cpCo(CO)_2]$ and bicyclo[6.1.0]nonatriene gives [200] (R = H, D) as the first example of a σ-π complex formed in a metal-assisted ring opening (ref. 603). Reaction of $[Rh(COD)Cl]_2$ with isopropylmagnesium bromide in the presence of styrene yields [201] which reacts further with allylbenzene to give [202] and



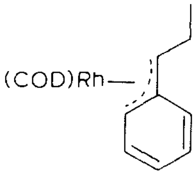
Scheme LXXIV



[200]

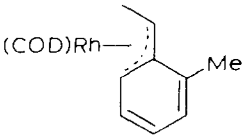


[201]



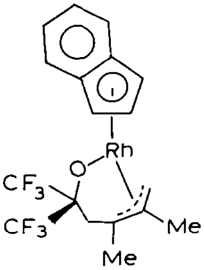
[202]

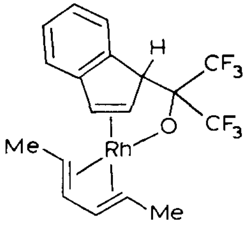
trans-β-methylstyrene. Complex [202] can be got directly if *trans*-β-methylstyrene is used in the original reaction. By the same route, *o*-methylstyrene gives [203] (ref. 604). Hexafluoroacetone and $[(\eta^5\text{-}C_9H_7)Rh(\eta^4\text{-isoprene})]$ react to give [204] and [205]. An analogous product is formed from the corresponding 2,3-dimethylbutadiene complex. In an attempt to determine which face of the olefin is attacked



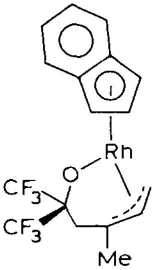
[203]

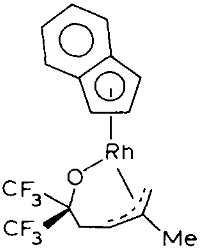
by the hexafluoroacetone, the same reaction with the 2,4-hexadiene analog was performed but instead the product was the isomeric mixture [206] (ref. 605). Coupling of an allyl group with diphenylacetylene occurs when $[cpRh(\eta\text{-}Ph_2C_5H_3)]BF_4$ is formed from $[cpRh(\eta^3\text{-}C_3H_5)]$ and the acetylene in the presence of $AgBF_4$ (ref. 606). Addition of DPM to a dichloromethane solution of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Rh(COD)]$ yields [207] together with the isomer in which the allyl groups are both rotated by 180° from that shown (ref. 607). Rhodium allyl hydride species supported on silica are effective catalysts for the hydrogenation of benzene to cyclohexane however with naphthalene the activity falls with time and propene is evolved. An


[204]

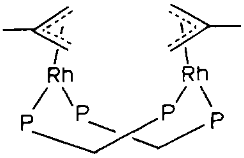

[205]

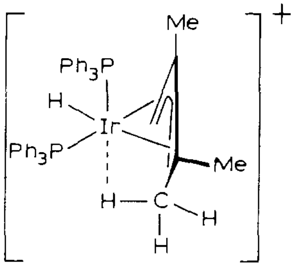
exchange of the original allyl ligand for an allylic species derived from naphthalene is proposed. Addition of phosphine quenches the catalyst. A heterolytic activation of hydrogen is proposed (ref. 608).


[206a]


[206b]

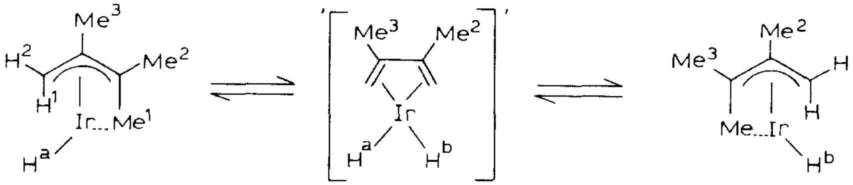
Reaction of 2,3-dimethylbutadiene with $[IrH_2(PPh_3)_2(acetone)_2]^+$ yields [208] in which the iridium-methyl hydrogen interaction is proposed to be significant from


[207]



[208]

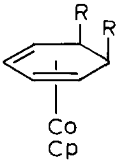
NMR evidence. Further NMR studies indicate the operation of the fluxional process depicted in Scheme LXXV (ref. 609).

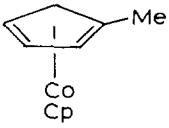


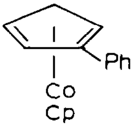
Scheme LXXV

Metal Carbocyclic Compounds

Attempts to prepare π-complexes of the penta(carboxymethyl)cyclopentadienyl group gave species such as $[Co(C_5(CO_2Me)_5)_2]$ but as they dissolve in water to give $[Co(H_2O)_6]^{2+}$ they are best considered as ionic cyclopentadienides. However, refluxing $[Rh_2(O_2CMe)_4]$ with this cyclopentadiene derivative in methanol gave $[(\eta^5\text{-}C_5H_2(CO_2Me)_3)_2Rh][C_5(CO_2Me)_5]$as the first example of a rhodacinium salt which has been structurally characterized (refs. 610, 611). The monocarboxymethylcyclopentadienyl group does bind as expected and the electrochemistry of $[cpCo(\eta^5\text{-}C_5H_4CO_2Me)]^+$ has been studied in aqueous ethanol. A reversible one-electron reduction step is observed but further reduction is irreversible unless done in basic or nonaqueous media. Electrolysis at -1.4 v at pH 4 converts it to $[cpCo(\eta^5\text{-}C_5H_4CH_2OH)]^+$ (ref. 612). Alkylation of the cobalticinium ion with alkyllithium occurs in an exo fashion to give $[cpCo(\eta^4\text{-}C_5H_5R)]$ (R = Me, Ph) which can be converted to $[cpCo(\eta^5\text{-}C_5H_4R)]BF_4$ with triphenylmethyl tetrafluoroborate. This sequence is thought to represent the first example of a substitution reaction of the cobalticinium ion (ref. 613). Successive reactions of cobalt(II) bromide with pentamethylcyclopentadienyllithium, ferric chloride and hexafluorophosphate ion yields $[cp'_2Co]PF_6$ which can be reduced to $[cp'_2Co]$ with potassium amalgam. Reaction of the neutral metallocene with alkyl iodides results in exo attack on one ring to give $[cp'Co(\eta^4\text{-}C_5Me_5R)]$ (R = Me, Ph, CH_2Cl, CHClOMe, CHClMe). When R = CH_2Cl, CHClMe, ring-expansion occurs in methanol solution to yield $[cp'Co(\eta^5\text{-}C_6Me_5\text{-}HR')]Cl$ (R' = H, Me) which can be oxidized by nitric acid to the arene complex $[cp'Co(\eta^6\text{-}C_6Me_5R')]^{2+}$ (ref. 614). An improved synthesis of $[Co(P(OR)_3)_3Br]$ (R = Et, Pr^i) employs the reduction of cobalt(II) bromide with zinc in THF in the presence of the phosphite. Reaction with NaR' (R' = indenyl, fluorenyl) gives $[(\eta^5\text{-}R')Co(P(OR)_3)_2]$ in which one phosphite can be replaced by carbon monoxide. In the fluorenyl complex, the exceptionally high-field resonance seen for the proton on C-9 is interpreted to indicate a contribution of a $\sigma + \pi$ component to the bonding of the organic ligand (ref. 615). In attempts to effect double nucleophilic additions to arene ligands, the 1,3-cyclohexadiene complex, $[cpCo(\eta^4\text{-}C_6H_8)]$ was synthesized from the diene and $[cpCo(CO)_2]$ in refluxing nonane and converted to $[cpCo(\eta^6\text{-}C_6H_6)](BF_4)_2$ with triphenylmethyl tetrafluoroborate. Reaction with NaR (R = OMe, cp) gave the unstable complexes [209]. For R = cp, other isomers and $[cp_2Co]BF_4$ were also produced. Complex [209] (R = OMe) was also synthesized from $[cpCo(\eta^4\text{-}C_6H_7OMe)]$ by successive reaction with triphenylmethyl tetrafluoroborate and sodium methoxide. Reaction of $[cp_2Co]BF_4$ with sodium cyclopentadienide gave two isomers of $[cpCo(\eta^4\text{-}C_5H_5C_5H_5)]$. The reaction of $[cpCo(\eta^6\text{-}C_6H_6)](BF_4)_2$ with methyllithium, methylmagnesium bromide, lithium diisopropylamide, sodium borohydride or a variety of carbon nucleophiles gave benzene and uncharacterized cobalt-containing products (ref. 616). Heating $[cpCo(\eta^4\text{-}C_5H_5R)]$ (R = exo-Me, exo-Ph) above 100° C yields the rearranged species [210] and [211]

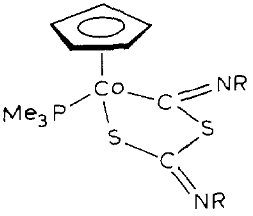

[209]


[210]


[211]

respectively which on hydride abstraction yield [cpCo(η^5-C_5H_4R)]$^+$. With DMAD, [cpCo(η^4-C_5H_6)] gives the *cis*- and *trans*-isomers of [cpCo(η^4-$C_5H_5C(CO_2Me)=CHCO_2Me$)] (ref. 616).

One and two equivalents of cyanide ion react with [cpCo(PMe_3)$_3$](PF_6)$_2$ in refluxing THF to give [cpCo(CN)(PMe_3)$_2$]PF_6 and [cpCo(CN)$_2$$PMe_3$] respectively. With [cpCo(CO)I_2] and triethylphosphine one obtains [cpCo(PEt_3)I_2] or [cpCo(PEt_3)$_2$I]I or [Co(PEt_3)$_2$$I_2$] plus [Co($PEt_3$)$_2(CO)_2$] and [cpCo($PEt_3$)$_3$]I respectively using one, two or three equivalents of phosphine (ref. 618). Reaction of isothiocyanates with [cpCo(PMe_3)$_2$] yields [cpCo(PMe_3)CNR] (R = Me, Bu^t, Ph) together with small amounts of [212]. Reaction of [cpCo(PMe_3)CNPh] with methyl iodide in acetone gives [cpCo(PMe_3)I(C(Me)=NPh)] while the others react in pentane to yield [cpCo(PMe_3)-Me(CNR)]I (R = Me, Bu^t). These are converted in acetone solution into [213] and [214]. Acylation of [cpCo(PMe_3)CNR] to give [cpCo(PMe_3)(C(O)Me)CNR]PF_6 (R = Me, Bu^t, Ph) can be effected by reaction with acetyl chloride followed by metathesis with ammonium hexafluorophosphate. The same product is formed from [cpCo(CO)Me-(PMe_3)]PF_6 and the appropriate isocyanide. Reduction with sodium hydride yields a



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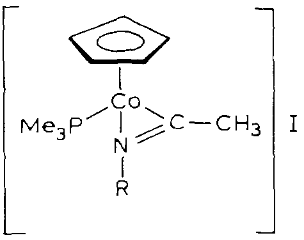

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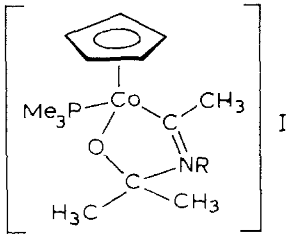
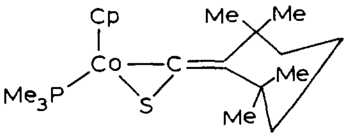


[214]

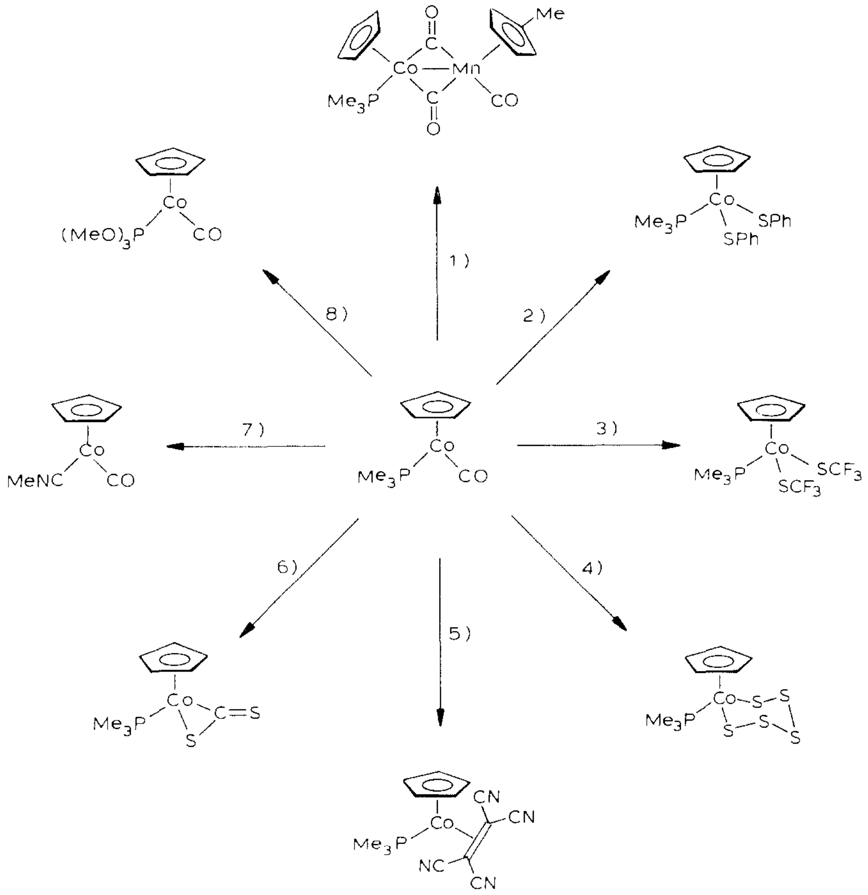
60:40 mixture of [cpCo(PMe$_3$)CNR] and [cpCo(CO)PMe$_3$] and similar proportions of acetaldehyde and methane. The rhodium analog (R = Bu^t) gives exclusively [cpRh(PMe$_3$)CNBu^t] and acetaldehyde while [cpRh(PMe$_3$)(C(O)Me)CNMe]PF$_6$ gives exclusively [cpRh(CO)PMe$_3$] and methane. The analogous complexes [cpM(PMe$_3$)$_2$(C(O)Me)]$^+$ (M = Co, Rh) on reduction with sodium hydride give [cpCo(PMe$_3$)CO] plus methane and [cpRh(PMe$_3$)$_2$] plus acetaldehyde respectively (ref. 619). The action of alkyl bromides on [cpCo(PMe$_3$)$_2$] at -78° C causes ring-alkylation and the formation of [(η^5-C$_5$H$_4$R)CoH(PMe$_3$)$_2$]Br (R = Pr^i, Bu^t, CMe$_2$Et) which can be reduced with sodium hydride to give [(η^5-C$_5$H$_4$R)Co(PMe$_3$)$_2$]. These in turn react with methyl iodide to give [(η^5-C$_5$H$_4$R)CoMe(PMe$_3$)$_2$]I but with alkyl bromides to give [(η^5-C$_5$H$_3$RR')CoH(PMe$_3$)$_2$]Br (R' = Pr^i, Bu^t) where R' is in the 3-position relative to R. Further treatment of these last complexes with sodium hydride gives [(η^5-C$_5$H$_3$RR')Co(PMe$_3$)$_2$] which react with methyl iodide to give [(η^5-C$_5$H$_3$RR')CoMe(PMe$_3$)$_2$]. Also [cpCo(PMe$_3$)$_2$] reacts with trimethylsilyltrifluoromethylsulfonate and ammonium hexafluorophosphate to give [(η^5-C$_5$H$_4$SiMe$_3$)CoH(PMe$_3$)$_2$]PF$_6$. As before, reduction and further alkylation can be performed and with two bulky substituents the rotation of the cyclopentadienyl ring becomes quite hindered (ref. 620). Some thioketenes also react with [cpCo(PMe$_3$)$_2$] and one product was shown to be [215]. A rhodium analog was also prepared from [cpRh(PMe$_3$)(C$_2$H$_4$)] (ref. 621). In related work,



[215]

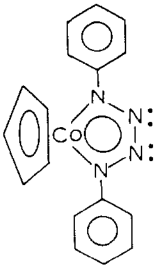
[cpCo(CO)(PMe$_3$)] was found to undergo the wide range of reactions shown in Scheme LXXVI. The cobalt-manganese complex reacts with tetraphenylbiphosphine to give [cp$_2$Co$_2$(μ-PPh$_2$)$_2$] and with diphenyldisulfide to yield [cpCo(PMe$_3$)(SPh)$_2$](ref. 622). Finally, [cp$_2$Co$_2$(μ-PMe$_2$)$_2$] reacts with elemental sulfur to produce [cp$_2$Co$_2$(μ-S)-(μ-PMe$_2$)$_2$]. Analogs with bridging selenium, tellurium and sulfur dioxide were prepared as well and all but the last are protonated by trifluoroacetic acid yielding [cp$_2$Co$_2$(μ-EH)(μ-PMe$_2$)$_2$] (E = S, Se, Te) (ref. 623).

The cobalt tetraazadiene complex [216] can be prepared from phenyl azide and [cpCo(CO)$_2$] and on photolysis yields [217]. Alternate routes to [217] involve reaction of [cpCo(CO)$_2$] with azobenzene at 160° C or with N-phenyl-*o*-phenylenediamine followed by oxygenation. The failure to intercept an intermediate in the conversion of [216] to [217] suggested an intramolecular rearrangement which on extrusion of dinitrogen forms a coordinated nitrene which then inserts into an *o*-C-H bond (ref. 624). The structure of the pentafluorophenyl analog of [216] has



1) $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(THF)]$. 2) Ph_2S_2. 3) $N(SCF_3)_3$. 4) S_8. 5) TCNE. 6) CS_2. 7) SCNMe. 8) $P(OMe)_3$.

Scheme LXXVI



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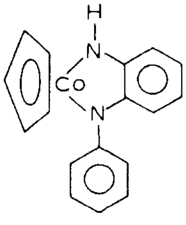
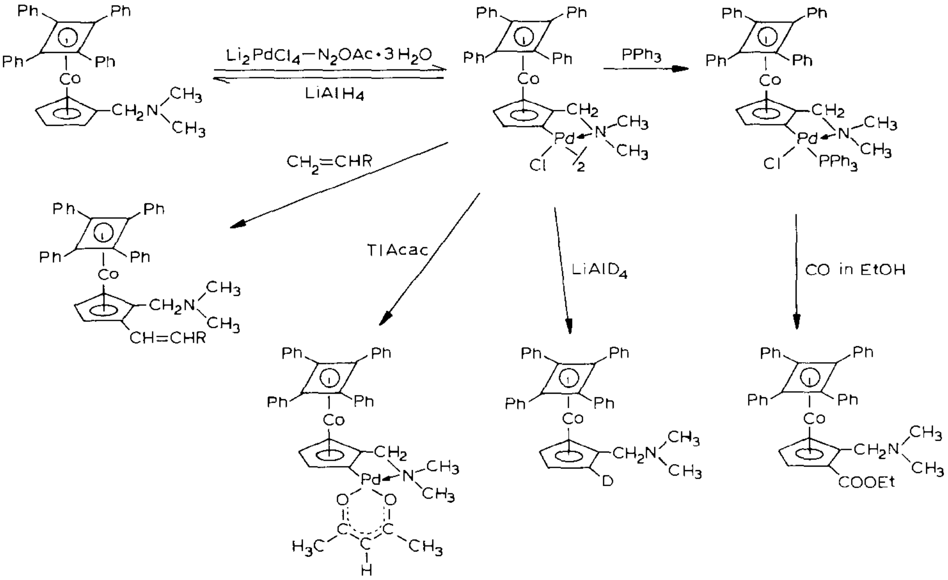


[217]

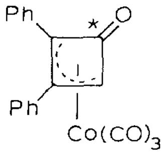
been determined and the results together with molecular orbital calculations support the electronic structure shown which includes considerable Co-N π-bonding (ref. 625). Reaction of $[(\eta^5\text{-}C_5H_4CH_2NMe_2)Co(\eta^4\text{-}C_4Ph_4)]$ with lithium tetrachloropalladate occurs according to Scheme LXXVII which also depicts the chemistry of the bimetallic complex formed (ref. 626).



(R = H, Ph, COMe, COPh, cpFe(η^5-C_5H_4), (η^5-C_5H_4)Co(η^4-C_4Ph_4))

Scheme LXXVII

Electrochemical studies on [cpCoL] (L = η^4-C_6H_8, η^4-1H-benzo[b]cycloheptane, COD, η^4-C_5H_5Ph, η^4-C_4R_4 (R = H, Me, Ph), η^5-1-phenyl-4,5-dihydro-1H-borepine) show that all undergo a one-electron oxidation to a monocation but further oxidation leads to decomposition. For all but the last this first oxidation is reversible. A minor sideproduct was $[cp_2Co]^+$ (ref. 627). Electrolysis of a THF solution of cyclopentadiene and tetrabutylammonium bromide at a cobalt anode gives $[cp_2Co]$ while if performed under carbon monoxide, $[cpCo(CO)_2]$ is the product (ref. 628). The complexes [218] and [219] have been prepared with ^{13}C enrichment at the designated ligand carbon atom. The coupling of this carbon to the adjacent unsubstituted carbon atom is 40.8±1.2 Hz which is the lowest value yet seen between formally sp^2 carbon atoms. This is interpreted to indicate considerable p character in this carbon-carbon bond (ref. 629).



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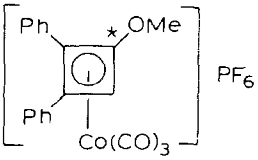
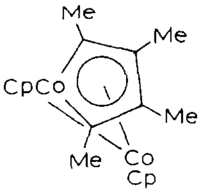
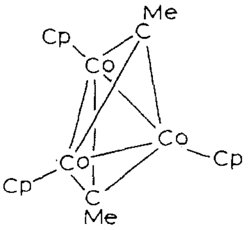


[219]

Reaction of $Na[C_5H_4COR]$ (R = Me, OMe) with cobalt(II) chloride in THF yields $[(\eta^5\text{-}C_5H_4COR)_2Co]$ while from $[Rh(CO)_2Cl]_2$ is obtained $[(\eta^5\text{-}C_5H_4COR)Rh(CO)_2]$. From $Na[C_5H_4COR]$ (R = H, Me), $[Co_2(CO)_8]$ and iodine, $[(\eta^5\text{-}C_5H_4COR)Co(CO)_2]$ is obtained which reacts further with $Ph_3P{=}CH_2$ to form $[(\eta^5\text{-}C_5H_4C(R){=}CH_2)Co(CO)_2]$ and with sodium borohydride followed by acryloyl chloride to give $[(\eta^5\text{-}C_5H_4CHRO_2CCH{=}CH_2)\text{-}Co(CO)_2]$. These last two complexes have been used as monomers for the formulation of polymer-supported catalysts (ref. 630). Reaction of $[(\eta^5\text{-}C_5Me_4Et)Co(CO)_2]$ with cyanogen halides gives $[(\eta^5\text{-}C_5Me_4Et)Co(CO)(CN)X]$ (X = Br, I) (ref. 631). Substituted cyclopentadienones convert $[cp_2Co]$ into $[cpCo(\eta^4\text{-}C_5R_4O)]$ (R = p-XC_6H_4 (X = H, Me, MeO, Cl)) while $[Co_2(CO)_8]$ and NBD react at elevated temperature to give $[(NBD)Co(CO)_2]_2$. This last complex on reaction with sodium tetraphenylborate gives $[(NBD)Co(\eta\text{-}C_6H_5BPh_3)]$ (refs. 632, 633). Reduction of $[cpCoI_2]_2$ with sodium amalgam in the presence of dienes yields [cpCo(diolef)] (diolef = COD, butadiene, hexa-1,3-diene) while in the presence of but-2-yne the products are [220] plus a small amount of [221]. The same reaction using diphenylacetylene yields

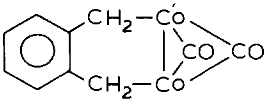


[220]

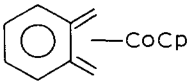


[221]

$[cpCo(\eta^4\text{-}C_4Ph_4)]$ and the phenyl analog of [221]. The reduction is proposed to proceed through $[cp_2Co_2(\mu\text{-}I)_2]$ which is solvolyzed to yield a reactive solvated {cpCo} fragment (ref. 634). Photolysis of $[cpCo(CO)_2]$ in aromatic solvents yields a variety of polynuclear complexes and low yields of [cpCo(arene)] and [cpCo(arene)$_2$] (arene = benzene, toluene, mesitylene). The complexes are proposed to contain η^4- and η^2-arene moieties respectively although the presence of an η^3-cyclopentadienyl group cannot be excluded. Unfortunately NMR spectra could not be obtained. Heating [cpCo(benzene)] with but-2-yne in refluxing toluene gave [cpCo-(hexamethylbenzene)] but no free C_6Me_6 leading to the conclusion that these arene complexes are not intermediates in related cobalt-catalyzed cyclotrimerizations (ref. 635). The kinetics of the substitution of [cpCo(PPh$_3$)$_2$] by trimethylphosphine at -60° C show the reaction to be first order in complex, zero order in trimethylphosphine and to be strongly inhibited by added triphenylphosphine implying that the slow step is dissociation of triphenylphosphine from the starting complex (ref. 636). Reaction of the radical anion $[cp_2Co_2(\mu\text{-}CO)_2]^{\dot{-}}$ with $\underline{o}$-$(BrCH_2)C_6H_4$ at low temperature gives thermally unstable [222] which decomposes at room temperature in THF solution to [223]. Carbonylation of [223] at 70° C yields indan-2-one while at

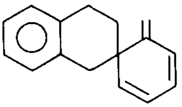


[222]

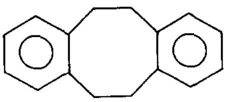


[223]

room temperature reaction with various ligands gives [cpCo(CO)L] (L = PMePh$_2$, PMe$_2$Ph, PPh$_3$, PEt$_3$, CO) and [224] plus [225]. In the reaction with phosphines



[224]

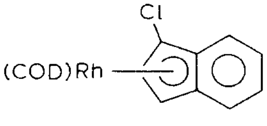


[225]

infrared evidence for [cp(L)Co(μ-CO)$_2$Cocp] is obtained. These complexes can also be synthesized from [cp$_2$Co$_2$(μ-CO)$_2$] and one equivalent of phosphine (ref. 637).

An equilibrium mixture of [cpCo(1,3-COT)] and [cpCo(1,5-COT)] undergoes a one-electron reduction to give the corresponding radical anions with the 1,5-COT species rapidly and irreversibly isomerizing to the 1,3-COT species. This can be reduced to a dianion which on protonation gives the corresponding cyclooctatriene complex. A one-electron reduction of [cpCo(1,5-COD)] is also seen but it is complete and reversible only in DMF. In other solvents, bulk reduction and subsequent reoxidation gave [cpCo(1,3-COD)]. The ESR spectrum of $[cpCo(1,3\text{-COT})]^{\dot{-}}$ shows the odd electron to reside in the uncoordinated portion of the COT molecule while for the two isomeric COD radical anions it is largely metal-centered. The results are supported by molecular orbital calculations (refs. 638, 639). Electrochemical studies on $[cp_3Co_3(\mu_3\text{-S})(\mu_3\text{-R})]$ (R = S, CS) show the former to undergo one reversible one-electron reduction and two one-electron oxidation steps while the latter has a single one-electron reduction. Its first oxidation occurs irreversibly and leads to cluster decomposition (ref. 640). Ion-cyclotron resonance studies on $[cpM(CO)_2]$ (M = Co, Rh) have produced some conflicting results for the gas-phase proton affinities of the cobalt complex. From one, M-H bond energies of 73 and 80±5 kcal/mol were determined while the other concluded that protonation occurred on the cyclopentadienyl ring. Clearly these results warrant further study. The latter paper also reported an order of ligand binding energies for $[cpCo]^+$ of $C_6H_6 > MeCN \sim NH_3 > THF \sim acetone > C_3H_6 \sim MeCHO \sim Me_2O \sim NO > MeOH > CO$ with a similar sequence for $[cpCo(CO)]^+$ (refs. 641, 642). Finally, the stability constants for the complexes $[ML]^{(n-1)+}$ and $[ML_2]^{(n-2)+}$ ($L = [cpCo(P(O)(OEt)_2)_3]^-$; M= Li^+, Na^+, K^+, Mg^{2+}, Co^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^+ and Lu^{3+}) have been determined. For the alkali and alkaline earth complexes, the stability constant increases with decreasing cation radius as expected for a predominantly ionic interaction. Also the sodium complex appears more stable than sodium-crown ether complexes (ref. 643).

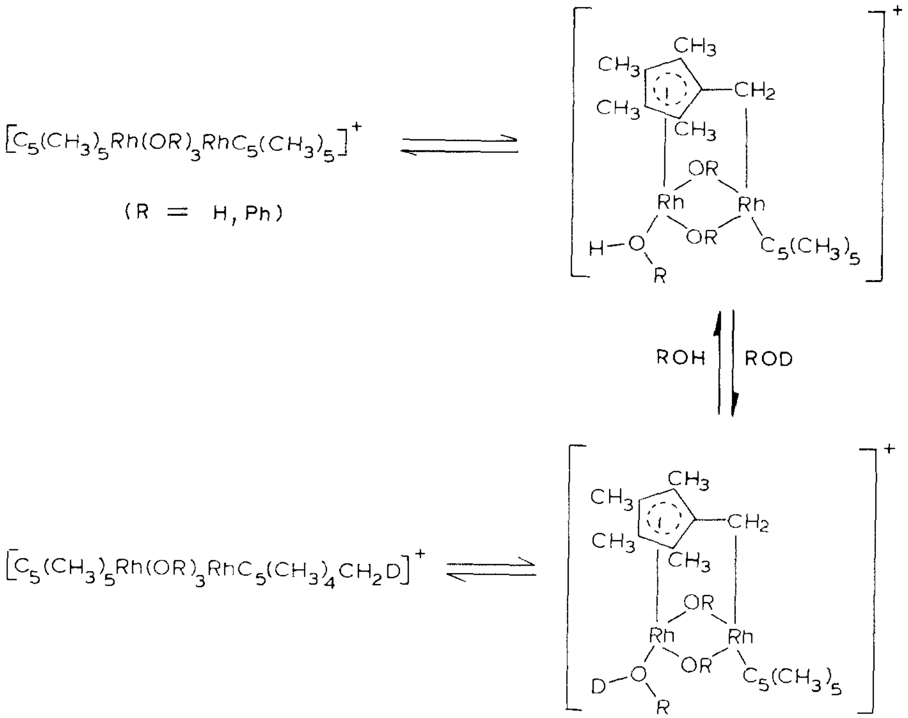
Rhodium(III) chloride reacts with an excess of cyclopentene to give $[cpRhCl_2]_n$ (n probably 2) while with a lower olefin/metal ratio $[(\eta^3\text{-}C_5H_7)RhHCl_3]$ is also obtained (ref. 644). Insertion of the carbene produced from diazoindene into a rhodium-chlorine bond occurs in $[Rh(COD)Cl]_2$ to give [226]. The same reaction with $[Rh(CO)_2Cl]_2$ or $[Rh(CO)Cl(PPh_3)_2]$ did not give any characterizable products (ref. 645). In refluxing benzene, DPPB and $[cpRh(CO)_2]$ yield $[cp_2Rh_2(CO)_2(\mu\text{-DPPB})]$ and



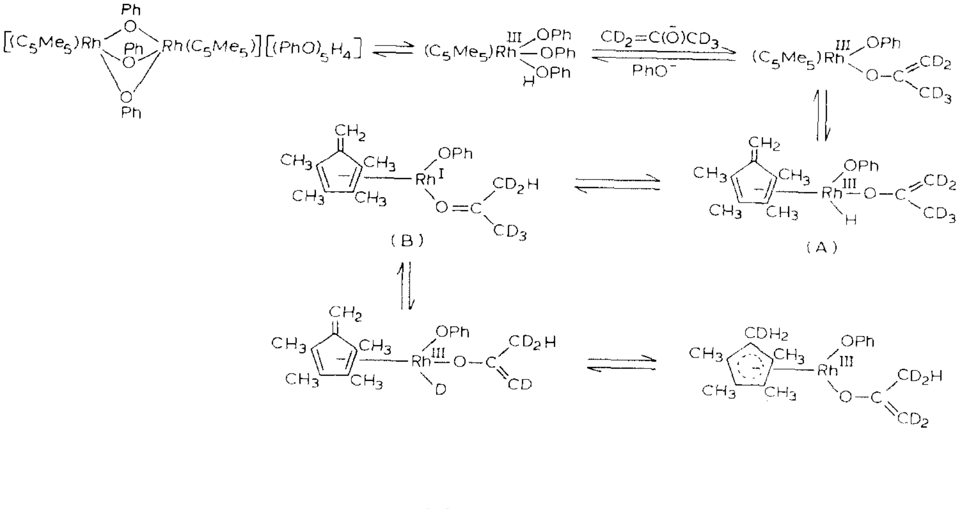
[226]

other uncharacterized products. The dimer reacts with halogens or methyl iodide to give $[cp_2Rh_2(CO)_2X_2(\mu\text{-DPPB})]X_2$ (X = Cl, Br, I) and $[cp_2Rh_2(COMe)_2I_2(\mu\text{-DPPB})]$ respectively. With nitrosyl hexafluorophosphate, the product is $[cp_2Rh_2(NO)_2(\mu\text{-DPPB})](PF_6)_2$ while with Me_3OBF_4, $[cp_2Rh_2Me_2(CO)_2(\mu\text{-DPPB})](BF_4)_2$ is formed which surprisingly does not convert to the acetyl complex even in the presence of triphenylphosphine. The original complex also reacts with chloroacetonitrile or mercury(II) chloride to give $[cp_2Rh_2(CO)_2(CH_2CN)_2(\mu\text{-DPPB})]Cl_2$ and $[cp_2Rh_2(CO)_2(HgCl_2)_2(\mu\text{-DPPB})]$ respectively (ref. 646).

The chemistry of $[cp'_2M_2(\mu\text{-OH})_3]PF_6$ (M = Rh, Ir) has been extensively described. Heating the rhodium complex for three days in isopropanol at 50° C gives $[cp'_3Rh_3(\mu\text{-H})_3(\mu_3\text{-O})]PF_6$, which is not fluxional, and acetone. Reaction at 60° C for 16 hrs in aqueous isopropanol gives the same complex plus a black precipitate. However the same reaction run for 80 hrs gives $[cp'_4Rh_4H_4]PF_6$ and the black precipitate. Interestingly, the trinuclear species did not convert into the tetranuclear one on further heating. With primary alcohols, RCH_2OH, the reaction initially gives $[cp'_2Rh_2(\mu\text{-H})_2(\mu\text{-O}_2CR)]^+$ (R = Me, Et, Pr^n, Pr^i) plus water and subsequently $[cp'_2Rh_2(\mu\text{-H})(\mu\text{-O}_2CR)_2]^+$ plus hydrogen. Reaction of $[cp'_2Ir_2(\mu\text{-OH})_3]OH$ with aqueous ethanol and precipitation with ammonium hexafluorophosphate gave $[cp'_2Ir_2(\mu\text{-H})_3]PF_6$. Since the trinuclear rhodium complex is not seen in any appreciable quantities in the early stages of the reaction with alcohols, it is thought that alkoxy-complexes such as $[cp'_2Rh_2(\mu\text{-OR})_3]^+$ may be the initial species formed. This is supported by the isolation of such a species (R = Ph) from the reaction of $[cp'_2Rh_2(\mu\text{-OH})_3]PF_6$ with aqueous phenol. If the chloride or hydroxide salt of the starting complex is used, the product is isolated with $[(PhO)_5H_4]^-$ as the anion and in d_6-acetone a rapid H/D exchange occurs between solvent and the methyl groups of the pentamethylcyclopentadiene ligands as shown in Schemes LXXVIII and LXXIX. The corresponding iridium complex reacted with phenol to give a mixture of products (refs. 647, 648). Further chemistry of $[cp'_2Rh_2(\mu\text{-OH})_3]Cl$ is detailed in Scheme LXXX. The sulfate complex on recrystallization gives a species thought to be a polymer although in aqueous solution it may initially exist as $[cp'Rh(OH)_2)_3]^{2+}$. Aqueous solutions of $[cp'Ir(O_2CMe)_2(H_2O)]$ on heating at 60° C give $[cp'_2Ir_2(\mu\text{-OH})_3]O_2CMe\cdot 14H_2O$ while the iridium complexes $[cp'_2Ir(\mu\text{-OH})_3]OH$ and $[cp'_2Ir_2(\mu\text{-OH})_2(\mu\text{-PhNH})]PF_6$ are got by the routes given above for their rhodium analogs. By contrast with aniline, primary aliphatic amines react with $[cp'_2Rh_2(\mu\text{-OH})_3]OH$ to give what is thought to be the monomers $[cp'Rh(RNH_2)_3](PF_6)_2$ (R = Pr^n, $PhCH_2$) although they decompose in solution (refs. 649, 650). The dimers $[cp'_2M_2Cl_4]$ (M = Rh, Ir) are cleaved by trimethylphosphine in dichloromethane to give $[cp'M(PMe_3)Cl_2]$ which on treatment with silver acetate in benzene is converted to $[cp'M(PMe_3)(O_2CMe)_2]$ containing monodentate acetate ligands. Reaction with aqueous potassium hexafluorophosphate gave the bidentate acetate complex $[cp'M(PMe_3)(O_2CMe)]PF_6$. Reduction of $[cp'IrCl_2(PMe_3)]$ with sodium borohydride in isopropanol

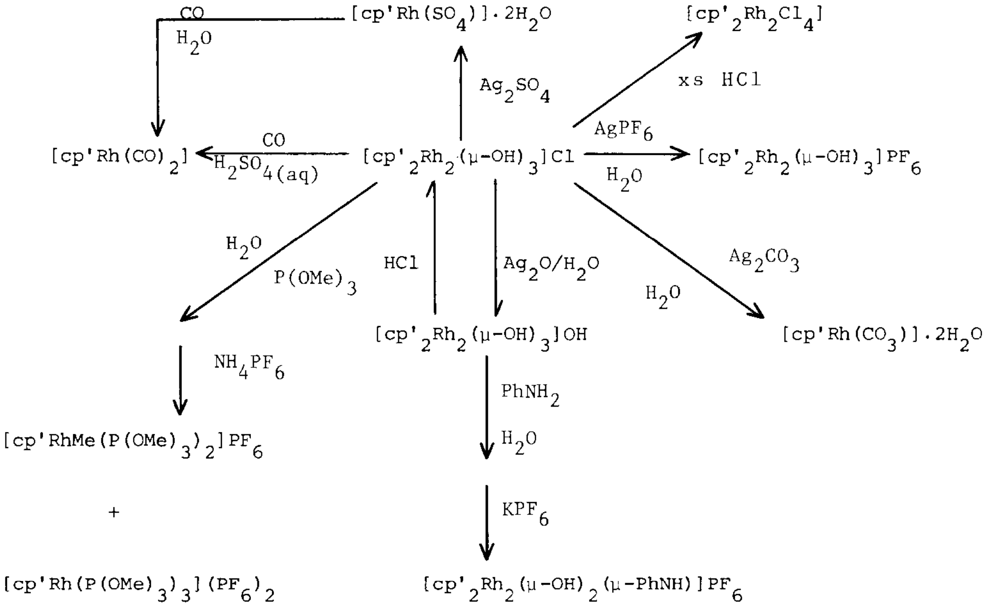


Scheme LXXVIII



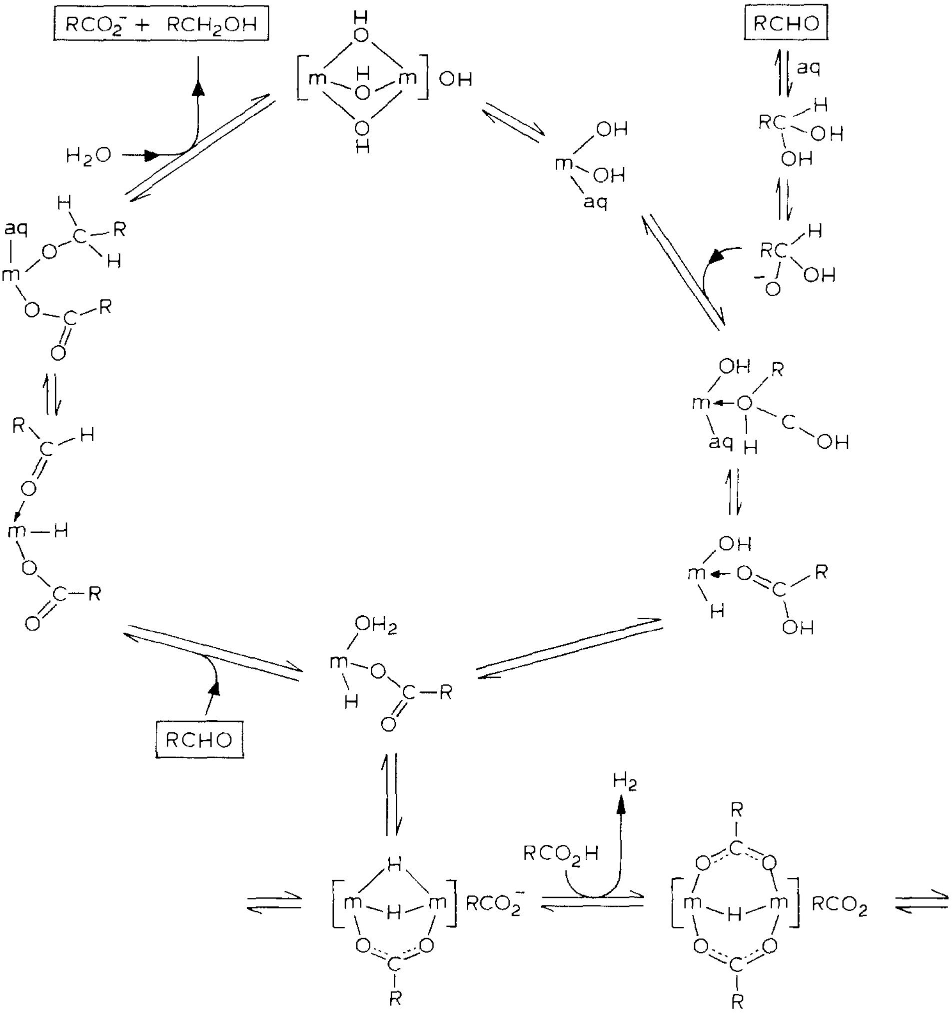
Scheme LXXIX

can be carried through [cp'IrHCl(PMe_3)] to [cp'IrH_2(PMe_3)] and the rhodium analog of the latter was also formed but detected in solution only. A better route to the dihydrides is reduction with $NaAlH_2(OCH_2CH_2OMe)_2$ in benzene. While the iridium dihydride in stable to oxygen, the monohydride is converted to [cp'$_2$$Ir_2$(μ-OH)$_3$]OH on oxygenation in benzene. On the other hand the rhodium dihydride reacts with oxygen but the only product identified was trimethylphosphine oxide (ref. 651). Several of these pentamethylcyclopentadienyl complexes are catalytically active. The disproportion of aldehydes to primary alcohols and acids is catalyzed by [cp'$_2$$Rh_2$(μ-OH)$_3$]Cl in water and in the presence of base at a $pH > 12.8$, the rate is four orders of magnitude greater than under neutral conditions. What is now a metal-catalyzed Cannizzaro reaction evidently competes very well with the aldol condensation as only small amounts of products from the latter reaction are seen. If the system catalyzing acetaldehyde disproportionation is quenched with



Scheme LXXX

hexafluorophosphate, [cp'$_2$$Rh_2$$H_x$($O_2CMe$)$_y$]$PF_6$ ($x = 1$, $y = 2$; $x = 2$, $y = 1$) are formed suggesting the process depicted in Scheme LXXXI (refs. 652, 653). The oxygenation of THF to γ-butyrolactone is catalyzed by [cp'$_2$$Rh_2$(μ-OH)$_3$]Cl in aqueous isopropanol. The system also catalyzes the oxidation of triphenylphosphine to its oxide but triethylphosphite is not oxidized. From studies using hydrogen peroxide

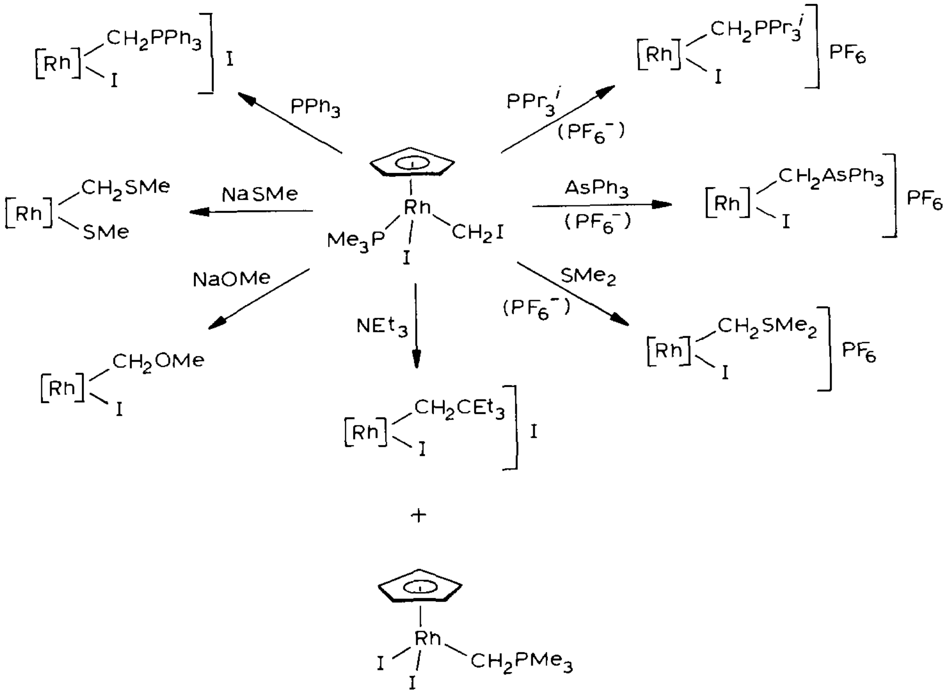


$m = Rh(C_5Me_5), Ir(C_5Me_5)$; $aq = xH_2O$

Scheme LXXXI

intermediates such as [cp'Rh(O$_2$)Cl] were suggested to be formed (ref. 654). Hydrosilylation of hex-1-ene by triethylsilane is catalyzed by [cp'$_2$Rh$_2$Cl$_4$]. The products are *n*-hexyltriethylsilane, (E)-hex-1-enyltriethylsilane and (E)-hex-2-enyltriethylsilane together with *n*-hexane and internal hexene isomers indicating that hydrogen transfer reactions compete with the hydrosilylation. As the olefin/silane ratio increases, more of the unsaturated silanes are seen suggesting that the reaction involves olefin coordination of a silyl-rhodium species (ref. 655).

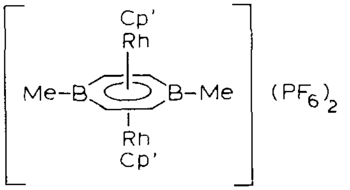
Attempts to oxidize [cpRh(CO)(PPh$_3$)] with silver hexafluorophosphate in toluene gave [(cpRh(CO)(PPh$_3$))$_2$(μ-Ag)]PF$_6$ which is considered to be a stable source of the radical cation [cpRh(CO)PPh$_3$]$^+$. Thus the silver complex reacts with nitric oxide to give elemental silver, [cpRh(CO)(PPh$_3$)] and [cpRh(NO)(PPh$_3$)]PF$_6$ (ref. 656). Oxidative addition of diiodomethane to [cpRh(PMe$_3$)L] (L = CO, C$_2$H$_4$) gives [cpRh(CH$_2$I)I(PMe$_3$)] which reacts further as depicted in Scheme LXXXII (ref. 657). In a study of the nucleophilicity of [cp'Rh(CO)L] (L = PMe$_3$, P$_2$Me$_4$), the desired complexes were prepared from [cp'Rh(CO)$_2$] and the ligand in refluxing benzene. For



[Rh] = [cpRh(PMe$_3$)]

Scheme LXXXII

L = P_2Me_4, some [$cp'_2Rh_2(CO)_2(\mu\text{-}P_2Me_4)$] was also produced. The first reacted with acids and alkyl iodides to give [$cp'RhH(CO)PMe_3$]X (X = BF_4^-, $CF_3SO_3^-$) and [$cp'Rh(COR)I(PMe_3)$] (R = Me, Et) respectively while the second reacted with stoichiometric or excess quantities of methyl iodide to give [$cp'Rh(COMe)I(P_2Me_4)$] or [$cp'Rh(COMe)I(PMe_2PMe_3)$]I. The first of these products is converted into the second by reaction with methyl iodide. Also reaction of either [$cp'Rh(CO)P_2Me_4$] with [Me_3O]BF_4 or of [$cp'Rh(COMe)I(P_2Me_4)$] with $AgBF_4$ produced [$cp'Rh(CO)Me(P_2Me_4)$]BF_4. All of these reactions are consistent with electrophilic attack at the metal indicating that the metal is more basic than a PMe_2 group (ref. 658). The "triple-decker" sandwich complex [227] can be synthesized by treating [$cp'RhCl_2$]$_2$ with aluminum trichloride followed by [228] or by protonation of [228] with trifluoroacetic acid at -80° C (ref. 659). Triphenylphosphonium cyclopentadienylide reacts with [RhL_2Cl]$_2$ and hexafluorophosphate to yield [$RhL_2(\eta^5\text{-}C_5H_4\text{-}PPh_3)$]$PF_6$ (L_2 = $(CO)_2$, COD, NBD) while with [$cp'Rh(acetone)_3$]$(PF_6)_2$, [$cp'Rh(\eta^5\text{-}C_5H_4PPh_3)$]$(PF_6)_2$ is obtained (ref. 660).



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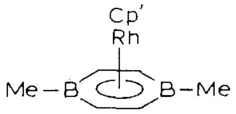
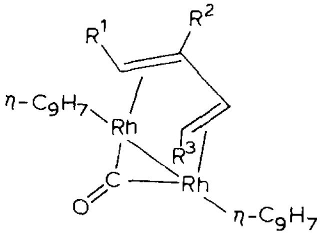


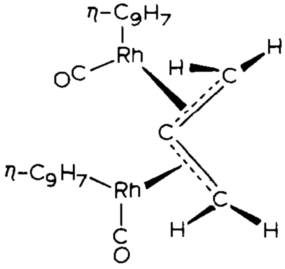
[228]

Sulfur dioxide replaces the bridging carbonyl ligand in [$cp_2Rh_2(CO)_2(\mu\text{-}CO)$] to give [$cp_2Rh_2(CO)_2(\mu\text{-}SO_2)$] which has been structurally characterized. The same conversion can be effected with methylfluorosulfonate (ref. 661). At 60° C in toluene solution a variety of dienes react with [$(\eta^5\text{-}C_9H_7)_3Rh_3(CO)_3$] to give [229]



[229]

($R^2 = R^3 = H$, $R^1 = H$, Me; $R^1 = R^3 = H$, $R^2 = Me$; $R^1 = R^3 = Me$, $R^2 = H$). Analogous diene complexes were also obtained with cyclopentadiene and cyclohexa-1,3-diene while with allene the initial product is [230] which on protonation with tetrafluoroboric acid yields [231]. Presumably the presence of two metals bound to the allene moiety prevents attack of the proton at the central carbon as frequently occurs in mononuclear allene complexes (refs. 662, 663). The coordinatively unsaturated complex $[cp'_2Rh_2(CO)_2]$ reacts with $[Pt(C_2H_4)_3]$ in toluene at 0° C to yield [232]. The related complex $[cp'_2Rh_2(\mu\text{-}CO)_2Pt(CO)(PPh_3)]$ reported in the



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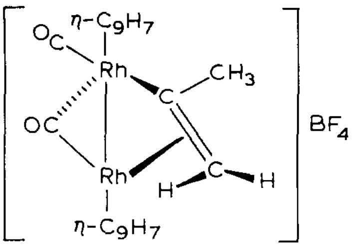
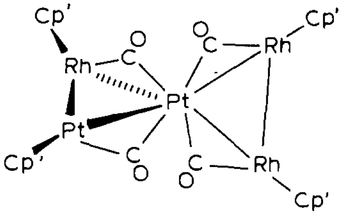


[231]



[232]

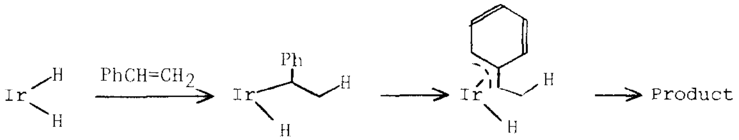
1980 Survey protonates across a Pt-Rh bond to give $[cp'_2Rh_2(\mu\text{-}CO)_2(\mu\text{-}H)\text{-}Pt(CO)(PPh_3)]BF_4$ (ref. 664).

Styrene-divinylbenzene copolymers functionalized with cyclopentadienyl groups have been used to support $\{RhCl_2\}$ and $\{M(CO)_2\}$ (M = Co, Rh) moieties. In the presence of triethylamine, the former catalyzes the hydrogenation of olefins and arenes while it its absence it catalyzes the isomerization of allyl benzene to styrene. Under hydroformylation conditions, the $RhCl_2$ moiety is converted to the corresponding dicarbonyl species and is a hydroformylation catalyst (refs. 665, 666).

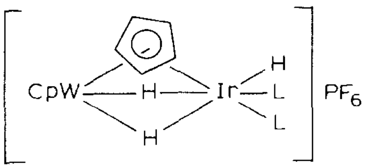
The $^{13}C\{^1H, ^{103}Rh\}$, $^{17}O\{^{103}Rh\}$, $^1H\{^{103}Rh\}$ and $^{103}Rh\{^1H\}$ NMR spectra of $[cpRh(CO)_2]$ have all been observed directly and the various coupling constants obtained, among them $^2J_{Rh\text{-}O} = 7.2Hz$ (ref. 667).

Treatment of $[Ir(COD)Cl]_2$ with isopropylmagnesium bromide followed by the fulvenes C_5H_4CRR' yields $[(\eta^5\text{-}C_5H_4CRR'Pr^i)Ir(COD)]$ (R = R' = Me; R = Me, R' = Et) while the use of methyllithium in place of the Grignard reagent yields $[(\eta^5\text{-}C_5H_4C\text{-}(Me){=}CH_2)Ir(COD)]$ (R = R' = Me) or a mixture of $[(\eta^5\text{-}C_5H_4C(Et){=}CH_2)Ir(COD)]$ and

$[(\eta^5\text{-}C_5H_4C(Me)=CHMe)Ir(COD)]$ (R = Me, R' = Et) (ref. 668). The formation of $[cpIrH(PPh_3)_2]BF_4$ from cyclopentane and $[IrH_2S_2(PPh_3)_2]BF_4$ (S = H_2O, acetone) in the presence of an olefin as a hydrogen acceptor does not occur if the olefin contains an aromatic substitutent (e.g. styrene) this is attributed to the formation of the arene complex $[(\eta^6\text{-}C_6H_5Et)Ir(PPh_3)_2]BF_4$ which has now been isolated. The failure to replace the arene moiety with benzene and the absence of the arene complex when the original reaction is performed in the presence of ethyl benzene indicates the formation of the arene complex by an intramolecular process such as that of Scheme LXXXIII (ref. 669). The arene exchange reaction of $[(\eta^6\text{-arene})Ir(COD)]X$ (X = BF_4, CF_3SO_3) in acetone or chloroform has been studied the rate is independent of the concentration of added arene and the extent of its ring-substitution but is dependent on the extent of substitution on the arene originally coordinated. Steric effects were observed only when more than three methyl groups were present on the arene. The rate is slower in chloroform than in acetone and is dependent on the nature of the counterion indicating possible coordination of the counterion. Evidently a good donor solvent aids in the displacement of the original arene since the rate of the reaction is increased in the presence of acetonitrile. Unfortunately no evidence concerning the hapticity of the arenes in the course of the reaction could be obtained. When the added arene was allylbenzene or cis-propenylbenzene, considerable trans-propenylbenzene was found indicating isomerization of these arenes by a component of the reaction mixture presumably via an allyl hydride mechanism (ref. 670). Reduction of $[(\eta^6\text{-}C_6H_6)Ir(COD)]BF_4$ with lithium triethylborohydride gives $[(\eta^5\text{-}C_6H_7)Ir(COD)]$. A direct exo attack on the arene is proposed and rationalized on the basis that the COD ligand is a relatively good π-acid as well as a poor σ-donor thus enhancing the positive charge on the arene and rendering it more susceptible than the COD ligand to nucleophilic attack (ref. 671). Reaction of $[cp_2WH_2]$ with $[IrH_2L_2(EtOH)_2]PF_6$ yields [233] (L = PPh_3, PMe_2Ph, PEt_3) possibly via the initial formation of $[cp_2W(\mu\text{-}H)_2IrL_2]PF_6$ (ref. 672).



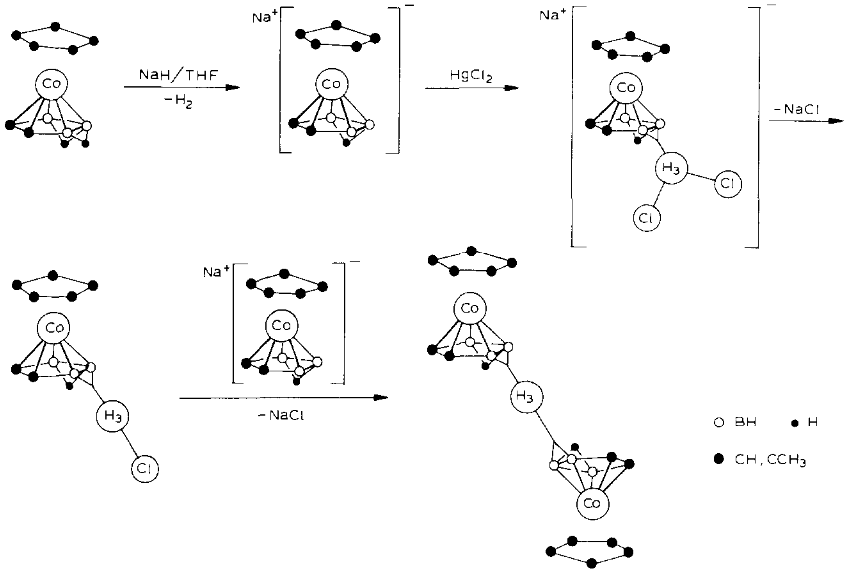
Scheme LXXXIII



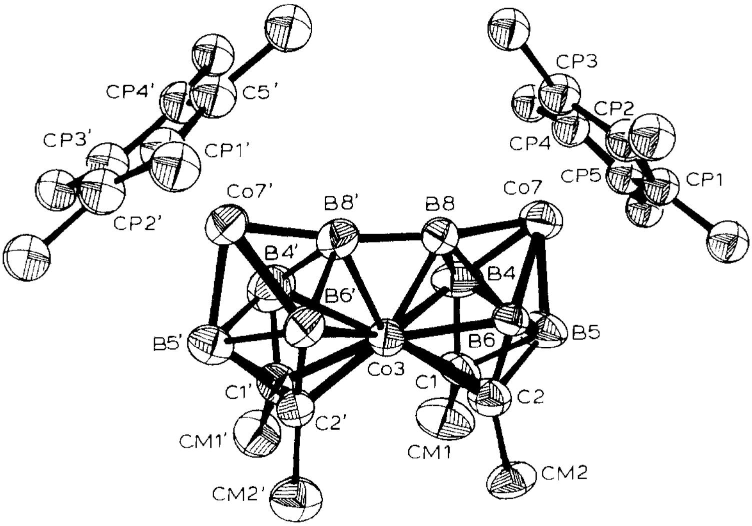
[233]

Metal Carbaborane Compounds

The *closo* species [2-H-2,2-(PEt$_3$)$_2$-1,6,2-C$_2$CoB$_7$H$_9$] is prepared from [Co(PEt$_3$)$_4$] and *arachno*-1,3-C$_2$B$_7$H$_{13}$. An analogous rhodium complex can be got using [(η^3-C$_3$H$_5$)-Rh(PEt$_3$)$_2$] but from structural studies is a rotational isomer of the cobalt complex (ref. 673). Related *closo* species [6,6-(PEt$_3$)$_2$-1,2,6-C$_2$CoB$_7$H$_9$] and [1,1-(PEt$_3$)$_2$-1,2,4-CoC$_2$B$_8$H$_{10}$] are prepared from [Co(PEt$_3$)$_4$] and *nido*-4,5-C$_2$B$_7$H$_{11}$ and *nido*-5,6-C$_2$B$_8$H$_{12}$ respectively. These have been structurally characterized as well (ref. 674). Some chemistry of [cpCo(R$_2$C$_2$B$_3$H$_5$)] (R = H, Me) is shown in Scheme LXXXIV. The initial HgCl$_2$ adduct is unstable and rapidly loses chloride. Interestingly, the proton NMR signal for bridging hydrogen shows ^{199}Hg satellites (ref. 675). The reaction of pentamethylcyclopentadienyllithium, cobalt(III) chloride and Na[Me$_2$C$_2$B$_4$H$_5$] in THF at 0° C gives a mixture of *closo*-[1,2,3-cp'CoMe$_2$C$_2$B$_4$H$_4$], *closo*-[1,7,2,3-cp'$_2$Co$_2$Me$_2$C$_2$B$_3$H$_3$] and [234]. Notable in the last is the direct boron-boron bond between the two carbaborane moieties. The "extra" hydrogen atom is proposed to be associated with the cobalt atom, the two directly bonded boron atoms and the boron atoms B$_6$ and B$_6$'. In solution only terminal B-H units are seem by NMR suggesting fission of the B-B bond and the presence of a tautomeric exchange of the "extra" hydrogen between these two borons (ref. 676). Gamma-irradiation of [1,2-dicarbollylCo(III)] in bromoform/nitrobenzene solution gives a mixture of mono- and dibromo derivatives of the complex (ref. 677). Codeposition of cobalt atoms, cyclopentadiene, B$_5$H$_9$ and sulfur gives [6,8,7,9-cp$_2$Co$_2$S$_2$B$_5$H$_5$] and *nido*-[2,3,6-cp$_2$Co$_2$SB$_5$H$_7$] while under similar conditions with B$_6$H$_{10}$ and



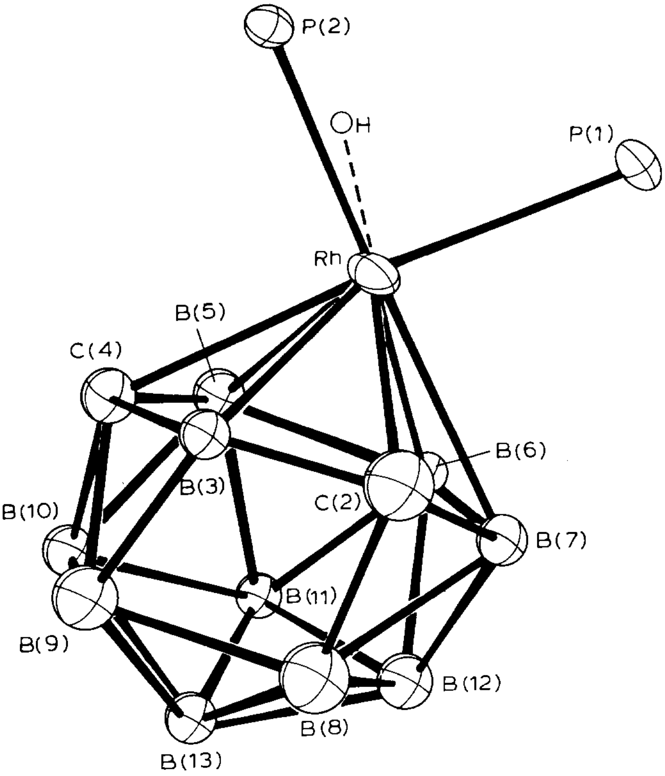
Scheme LXXXIV



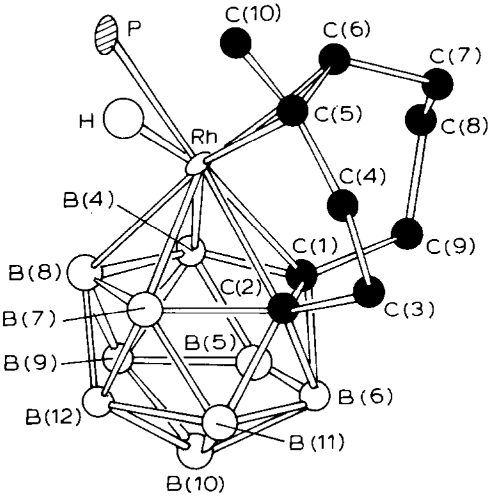
[234]

cyclohexene-episulfide, arachno-[7,6,8-cpCo$S_2B_6H_8$] is the product (ref. 678). Molecular orbital calculations on models for [$cp_3Co_3B_4H_4$] indicate that its non-conformity to the skeletal electron pair theory for the observed dodecahedral geometry is a consequence of the preference of the cpCo units for occupying sites of high connectivity. This occurs because these units are relatively electronegative and the high-connectivity sites are relatively electron-rich. This arrangement gives only eight low-lying skeletal molecular orbitals which is just sufficient to accommodate the available electrons (ref. 679).

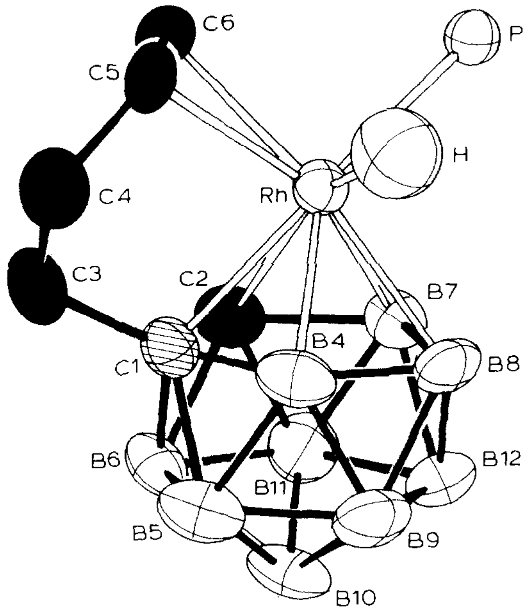
Only the unstable isomer of [$C_2B_{10}H_{13}$]$^-$ (provisionally the 9,11 isomer) reacts with [RhCl(PPh_3)$_3$] to give a metallacarbaborane. This has been shown to be [235] which is not fluxional but is unusual in that the carbaborane cage has an open face due to the lack of a bond between B_3 and B_8 (ref. 680). Related complexes closo-[6,6-(L)$_2$-6-H-6,2,3-Rh$C_2B_7H_7$] (L = PPh_3, P(p-tolyl)$_3$) are prepared from [RhL_3Cl] or [RhL_2Cl]$_2$ and Na[1,3-$C_2B_7H_{12}$]. The iridium analogs closo-[2,3-(R)$_2$-6,6-(L)$_2$-6-H-6,2,3-Ir$C_2B_7H_7$] (R = H, Me) were also synthesized. The rhodium complexes are moderately active catalysts for the hydrogenation of vinyltrimethylsilane (ref. 681). From [RhCl(PPh_3)$_3$] and Cs[7,8-bis(butenyl)-7,8-$C_2B_9H_{10}$] in refluxing ethanol [236] is obtained. This complex is a moderately effective hydrogenation catalyst but the double bond in the ligand is not hydrogenated (ref. 682). This is in contrast to what is observed with the mono-butenyl derivative [237] where the olefinic side chain is hydrogenated and the resulting species in the presence of one equivalent of triphenylphosphine shows high catalytic activity for olefin hydrogenation. In the absence of added phosphine, hydrogenation yields an isomeric mixture of dimers which may involve a process such as that shown in Scheme LXXXV


P(2)
H
P(1)
Rh
B(5)
C(4)
B(6)
B(3)
C(2)
B(10)
B(7)
B(11)
B(9)
B(12)
B(8)
B(13)

[235]

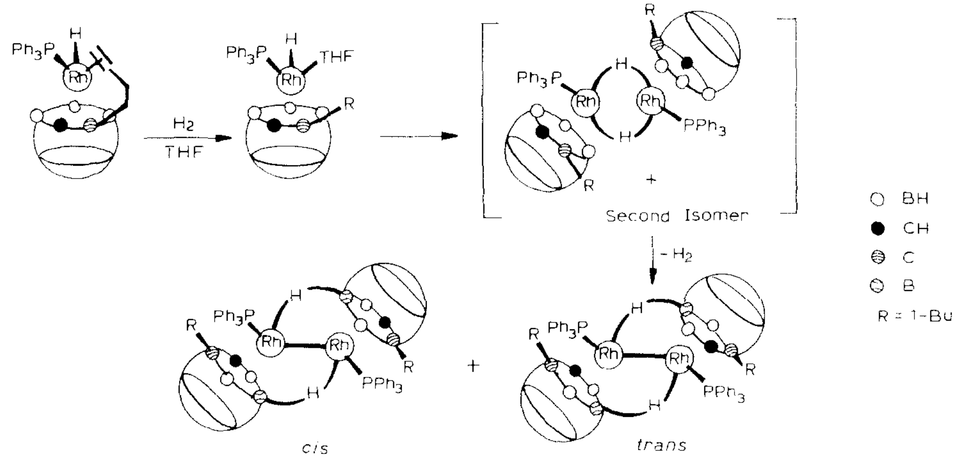

P
C(10)
C(6)
C(7)
H
C(5)
C(8)
Rh
C(4)
B(4)
C(9)
C(1)
B(8)
C(2)
C(3)
B(7)
B(5)
B(9)
B(6)
B(12)
B(11)
B(10)

[236]



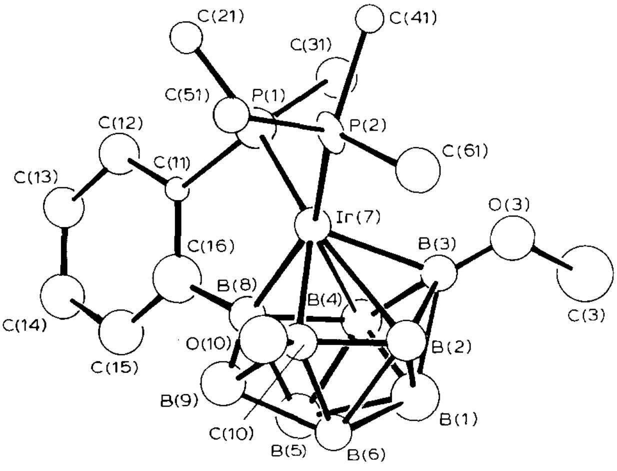
[237]

(ref. 683). A full report has now appeared on NMR studies of fluxional rhodium and iridium carbaboranes wherein the {ML$_2$H} (L = tertiary phosphine) unit rotates about the face of the [C$_2$B$_9$H$_{11}$]$^{2-}$ cage moiety to which it is bound. As predicted from theoretical studies the rotational barrier is greatest when the cage is the



Scheme LXXXV

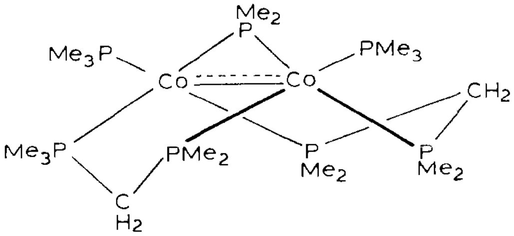
$[7,9\text{-}C_2B_9H_{11}]^{2-}$ isomer (ref. 684). Reaction of $[Ir(CO)Cl(PPh_3)_2]$ and $(Et_3NH)_2$-$[B_{10}H_{10}]$ in refluxing methanol yields a mixture of products one of which has been characterized as the iso-nido, ten-vertex metallocarbaborane [238]. Unusual features are the o-cycloboronation of a phenyl group from a ligand and the clustoboronation of the carbonyl group (ref. 685).



[238]

Miscellaneous Compounds

Although not as strictly organometallic in nature as the compounds discussed up to this point, the complexes covered in this section are sufficiently related to the subject of this Survey to warrant inclusion. Further work on complexes of the cyclo-triphosphorus ligand has appeared. Reaction of $[(triphos)Co(P_3)]$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) with $[Fe(H_2O)_6]^{2+}$ and 1,1,1-tris-(diethylphosphinomethyl)ethane(etriphos) followed by addition of ammonium hexafluorophosphate gives $[(triphos)Co(\mu\text{-}P_3)Fe(etriphos)](PF_6)_2$. Analogs with Co(II) and Ni(II) were also prepared. The size of the coordination polyhedron $(M(\mu\text{-}P_3)M')$ increases with the number of electrons in the bimetallic unit in agreement with the proposal that if more than thirty electrons are present, the excess occupies M-P antibonding orbitals. Syntheses of $[(triphos)M(\mu\text{-}P_3)Rh(triphos)]X_2$ (M = Co, Ni, Rh; X = BF_4,BPh_4) and $[(triphos)Co(\mu\text{-}P_3)Ir(triphos)](BF_4)_2$ have also appeared (refs. 686, 687). Heating $[Co(DMPM)_2(PMe_3)]Cl$ (DMPM = bis(dimethylphosphino)methane) at 40° C in THF yields [239] in which the cobalt is said to have a formal oxidation state of +0.5 (ref. 688). The complex $[CoCl(PPh_3)_3]$ is a mild and effective agent for the coupling of benzylic halides. A radical process involving a 1,2 hydrogen shift is proposed (ref. 689). $[CoH(N_2)(PPh_3)_3]$ catalyzes the isomerization of 4-methylpent-1-ene to a mixture of cis-and trans-4-methylpent-2-ene under nitrogen at



[239]

room temperature in benzene solution. The observation of small amounts of pent-1-ene and 2-methylpent-1-ene in the products suggested the occurrence of cleavage reactions as well (ref. 690). Methyl vinyl ketone is hydrodimerized to 2,7-octanedione by $[CoX(bipy)_2]$ (X = Cl, Br, I) prepared in situ (ref. 691).

Reduction of $[RhCl(PPh_3)_3]$ or rhodium(III) chloride and triphenylphosphine gives $[Rh(PPh_3)_4]$. Similarly $[Co(L_2)_2Cl_2]$ is converted to $[Co(L_2)_2]$ (L_2 = cis-$Ph_2PCH{=}CHPPh_2$) (ref. 692). The carbonylation of dimethylamine under hydroformylation conditions conditions is catalyzed by $[RhCl(PPh_3)_3]$. A mechanism involving $[RhH_2(MeNCO_2H)L_n]$ (L = PPh_3) as an intermediate is postulated (ref. 693). The coupling of R_3SnH with R'SH to give R_3SnSR' (R = Bu^n, Ph; R' = Pr^i, Bu^n, Bu^t, Ph, $PhCH_2$) is also catalyzed by $[RhCl(PPh_3)_3]$ (ref. 694). Reaction of $[RhX(PPh_3)_3]$ with stilbene episulfoxide yields $[Rh(SO)X(PPh_3)]_2$ (X = Cl, Br) together with stilbene, triphenylphosphine oxide and triphenylphosphine sulfide (ref. 695). Under photolytic conditions, $[RhCl(PPh_3)_3]$ catalyzes the dehydrogenation of isopropanol (ref. 696) while the same complex supported on various phosphinated polystyrenes followed by treatment with hydrogen is proposed to give Rh(II) species. These have been compared to the homogeneous system and to silica-supported analogs for olefin hydrogenation and isomerization. The activity of the polymer supported species is much less than those on the silica support however if the polymer support is rigid polystyrene beads, a reasonable activity is seen (ref. 697). The hydrosilylation of ketones and aldehydes by $(R''O)_3SiH$ (R" = Me, Et) is catalyzed by $[RhCl(PPh_3)_3]$ and the products are $RR'CHOSi(OR'')_3$ (R = alkyl, H) (ref. 698). $[Rh_2(O_2CMe)_4]$ supported on phosphinated silica is also a catalyst for dehydrogenation of isopropanol (ref. 699).

The emission spectra of $[M(cis\text{-}Ph_2PCH{=}CHPPh_2)_2]ClO_4$ (M = Rh, Ir) have been studied and interpreted in terms of a two-level emitting manifold with the splitting arising from spin-orbit coupling (ref. 700).

The complex $[Ir(L_2)_2]Cl$ (L_2 = $(Ph_2P)_2N$(p-tolyl)) reacts with hydrogen to give cis-$[IrH_2(L_2)_2]Cl$ which on heating in dichloromethane converts to the trans isomer.

Oxidative addition of hydrogen chloride gives trans-$[IrHCl(L_2)]^+$ which was isolated as the tetraphenylborate salt (ref. 701). The chemistry of $[IrCl_4(PMe_2Ph)_2]$ as a one-electron oxidizing agent has been explored. With $[cp_2M]$ (M = Fe, Ni), $[cp_2M]$-$[IrCl_4(PMe_2Ph)_2]$ is obtained while with $[Pt(C_2H_4)(PPh_3)_2]$ and $[PdCl_2(AsMe_3)_2]$ the products are $[IrCl_2(PMe_2Ph)_2(\mu\text{-}Cl)_2Pt(PPh_3)_2][IrCl_4(PMe_2Ph)_2]$ and $[IrCl_2(PMe_2Ph)_2$-$(\mu\text{-}Cl)_2PdCl(AsMe_3)]$ plus $[Me_3AsH][IrCl_4(PMe_2Ph)_2]$ respectively (ref. 702). Ketones are catalytically hydrogenated in the presence of $[IrH_3(PPh_3)_3]$ or $[IrH_5(PPh_3)_2]$ and trifluoroacetic acid. A hydride transfer from iridium to the protonated ketone is proposed. With α-β unsaturated ketones, nonselective hydrogenation is observed (ref. 703). Also $[IrH_nCl_{3-n}(PPh_3)_3]$ (n = 1-3) and $[IrH_5(PPh_3)_2]$ reduce triarylcarbenium ions to R_3CH (R = Ph, p-tolyl, p-$MeOC_6H_4$). ESR evidence for the presence of iridium radical cations was found (ref. 704). Addition of triphenylphosphine to $[M(SnCl_3)_5Cl]^{3-}$ (M = Rh, Ir) in ethanol containing hydrochloric acid gives $[Ph_3PH]_3[M(SnCl_3)_5Cl]$ which on heating in the presence of oxygen yields either $[Rh(SnCl_2OPPh_3)_4(SnCl_3)Cl]Cl$ or $[Ir(SnCl_2OPPh_3)_5Cl]Cl_2$. The same species can be got directly by reaction of triphenylphosphine oxide with $[M(SnCl_3)_5Cl]^{3-}$ (ref. 705).

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