COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1985*

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

CONTENTS

Introduction

As was the case last year the majority of papers appearing in 1985 report continuing studies rather than the breaking of new ground. Two developing areas that continue to attract attention are the activation of carbon-hydrogen bonds by rhodium and iridium complexes and the gas phase

---

*No reprints available. Previous Survey, J. Organometal. Chem., 305(1986)1.

reactions of mono- and polynuclear metal cations and organometallic fragments with a variety of hydrocarbons and their derivatives. Other highlights of the year include the isolation of the first complex of sulfur monoxide, the synthesis of some binuclear rhodium and iridium complexes which act as clathrochelates, the demonstration of the stereospecific oxidative addition of dihydrogen to unsymmetrical iridium phosphine complexes, the direct, intramolecular transfer of dihydrogen from rhenium to iridium and the isolation of an iridium complex of molecular hydrogen. A monograph covering aspects of homogeneous catalysis by rhodium and iridium complexes has been published this year (ref. 1). It appears to be a useful review of the area but is a bit dated as the literature coverage ends with 1982.

Reviews have appeared on labile oxidized forms of organo-cobalt and -rhodium compounds (ref. 2), the oxidation of organometallic compounds (ref. 3), the photochemistry of transition metal alkyl complexes (ref. 4) and the activation of carbon-hydrogen bonds by homogeneous (refs. 5, 6) and supported (ref. 7) rhodium and iridium systems. Two reviews covering organocobaloximes (ref. 8) and -cobalamins (ref. 9) are also available.

Accounts of the effects of ion-pairing on the chemistry and physical properties of transition metal carbonylate anions (ref. 10), the occurrence of associative substitution reactions of metal carbonyl compounds (ref. 11), the photochemically induced disproportionation of dicobalt octacarbonyl and related complexes (ref. 12) and novel reactions of metal carbonyl clusters (ref. 13) have appeared. Other reviews in this area include those on electron transfer reactions of bimetallic and cluster complexes (ref. 14), on the metal-catalyzed hydrogen transfer reduction of organic compounds (ref. 15), on $[Rh_6(CO)_{16}]$ as a catalyst for the WGSR (ref. 16) on selective metal-ligand interactions in heterometallic clusters (ref. 17) and on germanium-containing cobalt carbonyl clusters (ref. 18). Three more reviews on aspects of metal carbonyl complexes cover ligand substitution reactions of square planar complexes (ref. 19), metal carbonyl complexes containing porphyrin, nucleoside and amino acid ligands (ref. 20) and thiocarbonyl complexes (ref. 21).

An extensive review of nitrosyl and nitrido cluster complexes includes examples from the cobalt group (ref. 22) as does one on metal pentadienyl compounds (ref. 23) and one on alkoxide complexes (ref. 24). Two further reviews cover aspects of asymmetric hydrogenation catalyzed by chiral rhodium phosphine complexes (refs. 25, 26). Cobalt compounds containing allene, alkyne and acetylide ligands are reviewed (ref. 27) as is recent work using $[cpCo(CO)_2]$ and related cobalt compounds to mediate cyclization reactions leading to heterocyclic and steroidal molecules (refs. 28, 29).

Included in a review of homogeneous catalyst systems for the hydrogenation of aromatic compounds are ones based on $[Co_2(CO)_8]$, $[cp'RhCl_2]_2$ and $[(\eta^3\text{-}C_3H_5)Co(P(OMe)_3)_3]$ (ref. 30). Also some complexes of the cobalt group appear in a review of electrochemical reactions of organometallic complexes which are accompanied by structural changes in the molecule (ref. 31) and in a review of multilayer sandwich complexes containing diborolene ligands (ref. 32).

Three final reviews cover the photochemical behavior of charge transfer complexes of bis(fulvalene)dicobalt cations (ref. 33), evidence for metal-mediated phosphorus-carbon bond cleavage in phosphine ligands as a mechanism for the deactivation of homogeneous hydrogenation and hydroformylation catalysts (ref. 34) and polyhydride complexes of transition metals including those of the cobalt group (ref. 35).

Dissertations

Over forty dissertations containing material of relevance to this survey were abstracted this year and readers of previous surveys will find much familiar material in them. Those dealing with metal-carbon σ-bonded compounds include one on the synthesis and reactivity of alkyl-bridged rhodium and iridium dimers (ref. 36) and two dealing with the synthesis and reactivity of alkylcobalamins and related species (refs. 37, 38). Two further dissertations report on the chemistry and electrochemistry of binuclear rhodium complexes containing either bridging diisocyanides (ref. 39) or monodentate isocyanides and bridging DPM or DAM ligands (ref. 40).

A sizeable number deal with metal carbonyl complexes including ones on new syntheses of $[M_6N(CO)_{15}]^-$ (M = Co, Rh) (ref. 41) and a black form of $[Ir_6(CO)_{16}]$ (ref. 42), the reduction of $[Ir_4(CO)_{12}]$ to $[Ir_4(CO)_{11}]^{2-}$ and $[Ir_4(CO)_{10}]^{4-}$ (ref. 43), studies of various cobalt carbonyl clusters on oxide supports as Fischer-Tropsch catalysts (ref. 44) and the reaction of $[Co(CO)_4]^-$ with the carbene complexes $[cpM(C(SMe)_2)(CO)(MeCN)]PF_6$ (M = Fe, Ru) to form $[cpM(CO)(\mu\text{-}CO)(\mu\text{-}C(SMe)_2)Co(CO)_2]$ (ref. 45). Others include reports of the syntheses of $[cp'_3Co_3(\mu\text{-}CO)_2]$ and related heterometallic complexes (ref. 46), the novel complexes $[(cp'_2Yb)_2(\mu_3\text{-}OC)_4M_3cp]$ (M = Co, Rh) (ref. 47), the heterometallic cluster anions $[CoFe_2Ru(CO)_{13}]^-$ and $[CoFeRu_2(CO)_{13}]^-$ (ref. 48) and of the study of $[cpMoIr_3(CO)_{11}]$ and $[cp_2Mo_2Ir_2(CO)_{10}]$ supported on alumina as bimetallic catalyst precursors (ref. 49).

Other dissertations report on the chemistry of binuclear cobalt and rhodium complexes containing bridging di-tert-butylphosphide ligands (refs. 50, 51), the synthesis of rhodium complexes of the dimethylbis(pyrazolyl)gallate ion (ref. 52), the synthesis and chemistry of $[Ir(CO)_2(Tcbiim)]^-$

(ref. 53), the photochemical oxidation of 2,6-dimethylphenylisocyanide catalyzed by $[Co(NO)L_3]$ (L = 2,6-dimethylphenylisocyanide) (ref. 54), and the synthesis of cobalt phosphine complexes containing both nitrosyl and nitrite ligands (ref. 55).

Further topics covered include reactions of heterobimetallic complexes of tungsten and cobalt or rhodium with $[Rh_4(COD)_4(\mu_4\text{-}PPh)_2]$ (ref. 56), the synthesis and catalytic activity of binuclear rhodium and iridium complexes of 3,5-bis(diphenylphosphinomethyl)pyrazole (ref. 57), the formation of acetylene adducts of $[M_2(COD)_2(\mu\text{-}PPh_2)_2]$ (M = Rh, Ir) (ref. 58) and the study of alkyne addition reactions promoted by $[Co_2(CO)_6(RC_2R')]$ for the synthesis of organoboranes and -silanes (ref. 59).

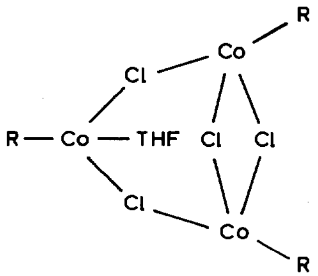
The $[cpCo(CO)_2]$-mediated [2+2+2] cycloaddition reactions of polyenynes (ref. 60), the synthesis of rhodium complexes of bis(trimethylsilyl)methylphosphines (ref. 61), the mechanism of the Arbusov-type reactions of $[cpCo(DPPE)(P(OMe)_3)]BF_4$ in the presence of halide ions (ref. 62), the reactions of $[cp'Co(CO)_2]$ with trimethylsilyl azide to form bicapped tricobalt clusters (ref. 63) and studies of extrusion of sulfur dioxide from $[cpCo(\eta^4\text{-thiophene-1,1-dioxide})]$ (ref. 64) are covered in other dissertations.

Also described are cobalt NQR studies on complexes containing one cyclopentadienyl-type ligand (ref. 65), the substitution reactions of $[cpRh(CO)_2]$ and its pentamethylcyclopentadienyl and indenyl analogs (ref. 66), the synthesis of metallaphosphazines containing {cpM} (M = Co, Rh) moieties (ref. 67) and the preparation of $[cp'RhSiW_9Nb_3O_{40}]^{5-}$ (ref. 68). An additional three dissertations cover the synthesis, chemistry and catalytic activity of a variety of rhodacarbaboranes (refs. 69-71).

Of the final six dissertations covered, two are concerned with gas phase, ion molecule reactions between cobalt ions and various organic molecules (refs. 72, 73), two more report on the chemistry of $[IrH_2(PPh_3)_2(acetone)_2]PF_6$ and related species with particular focus on their ability to cleave carbon-hydrogen bonds in alkanes (refs. 74, 75) and the final two cover coinage metal adducts of iridium hydride complexes (refs. 76, 77).

Metal-Carbon σ-bonded Complexes

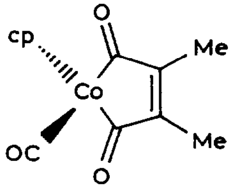
Anhydrous cobalt(II) bromide can be converted to $[Co(O_2CCF_3)_2]\cdot Et_2O$ by silver trifluoroacetate in diethyl ether. Subsequent reaction with pentafluorophenylmagnesium bromide forms $[Co(C_6F_5)_2\cdot Et_2O]$ from which the ether molecule can be removed by boron trifluoride in toluene to give $[(\eta^6\text{-}C_6H_5Me)Co(C_6F_5)_2]$. Pentachlorophenyl and 2,3,5,6-tetrafluorophenyl analogs were also prepared (ref. 78). At low temperature, $Li[C(SiMe_3)_3]$ reacts with anhydrous cobalt(II) chloride to form [1] (R = $C(SiMe_3)_3$) (ref.



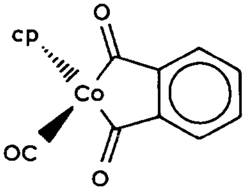
[1]

79). The methyl cobalt complexes [CoMe(PPh$_3$)$_3$], [CoMe(PPh$_3$)$_2$], [CoMe(acac)-(PMe$_2$Ph)] and [CoMe(DPPE)$_2$] are formed from [Co(acac)$_3$] and [Me$_4$Al$_2$O·Et$_2$O] in the presence of the phosphine ligand (ref. 80) while [CoCl$_2$(bipy)] reacts with Li$_2$[1,1'-bis(*o*-carboranyl)SiMe$_2$] to form [Co(1,1'-bis(*o*-carboranyl)SiMe$_2$)(bipy)] (*o*-carboranyl = *o*-C$_2$B$_{10}$H$_{10}$) (ref. 81). Oxidation of *cis*-[CoR$_2$(bipy)$_2$]ClO$_4$ (R = Me, Et) by one-electron oxidants like TCNE or TCNQ causes coupling of the alkyl groups. With weaker oxidants like *p*-benzoquinone the reaction can be catalyzed by magnesium perchlorate and in the case of the dimethyl complex a charge transfer complex with TCNE can be observed initially (refs. 82, 83).

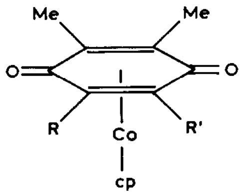
The synthesis of [(η^5-C$_5$H$_2$Me$_3$)CoMe$_2$(PPh$_3$)] and [(η^5-C$_5$H$_4$CO$_2$Me)CoMe$_2$-(PPh$_3$)], presumably by standard routes, has been reported (ref. 84). In refluxing xylene [cpCo(CO)$_2$] reacts with dimethylcyclobutenedione or benzocyclobutanedione to form the maleoyl complexes [2] and [3] respectively. Photolysis of [2] in the presence of hex-1-yne forms [4] (R = R' = Et) while in the presence of diethyl sulfide substitution of carbonyl by diethyl sulfide occurs. This latter complex reacts thermally with a variety of acetylenes to give other examples of [4] (R = Et; R' = Et, COMe,



[2]

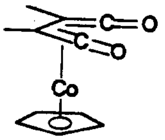


[3]

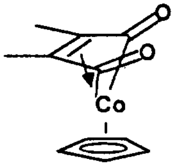


[4]

OEt. R = H; R' = Bu^n, CH_2Cl, CH_2NHCH_2Ph, CH_2OH. R = Me; R' = $CMe{=}CH_2$, CH_2OEt). Photolysis of [2] in the absence of potential ligands afforded a new species characterized as a bisketene complex whose structure indicates should be described as intermediate between the limiting forms [5a] and [5b]. Despite its ready reaction with acetylenes to give [4] (R = Me; R' = CH_2Cl, CO_2Et. R = $SiMe_3$; R' = H) suggesting its intermediacy in the synthesis of [4] described above, it also is readily converted to [2] by carbon monoxide making it also possible that quinone formation proceeds directly from the maleoyl complex (refs. 85, 86).



[5a]



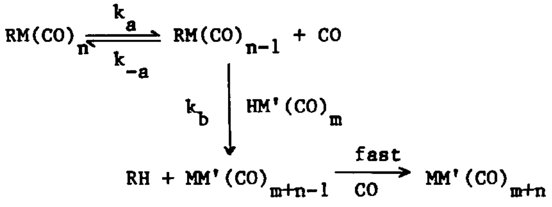
[5b]

Among several papers which explore aspects of cobalt-catalyzed carbonyl reactions is one which reports a relatively facile route to alkoxycarbonyl cobalt tetracarbonyls, a species thought to be an intermediate in some of these processes. Thus the reaction of $[ICo(CO)_4]$ with crown ether-solubilized potassium alkoxides in hexane at low temperature yields $[ROC(O)Co(CO)_4]$ (R = Me, Et, Pr^i, Bu^t, $\underline{n}$-C_5H_{11}, $\underline{n}$-$C_{12}H_{25}$, cy, bz, $PhCHMeCH_2$, Ph, $\underline{o}$-tolyl, $\underline{p}$-RC_6H_4 (R = Bu^t, OMe, Br, MeC(O)), $\underline{1}$-naphthyl, $\underline{2}$-naphthyl). In the instances when R = Me or Ph, $[Co(CO)_4]^-$ and other anionic species, as yet unidentified, were detected during the reaction leading to the suggestion that the effect of iodide promoters in cobalt-catalyzed carbonylations is to form anionic species (ref. 87). The incorporation of labelled carbon monoxide into $[EtO_2CCH_2Co(CO)_4]$ (no acyl species form) was found to follow first order kinetics. This together with the kinetic data on the reaction of this complex with hydrogen, triphenylphosphine and $[HCo(CO)_4]$ suggested the processes of Scheme I (R = EtO_2CCH_2) (ref. 88). In a

$$\begin{tikzcd}
 & {[RCo(CO)_3(PPh_3)]} & \\
{[RCo(CO)_4]} \arrow[r, leftrightharpoons] & {[RCo(CO)_3] + CO} \arrow[u, "PPh_3"'] \arrow[dl, "H_2"'] \arrow[dr, "HCo(CO)_4"] & \\
RH + [HCo(CO)_4] \arrow[rr, "RCo(CO)_3 + CO"] & & RH + [Co_2(CO)_8]
\end{tikzcd}$$

Scheme I

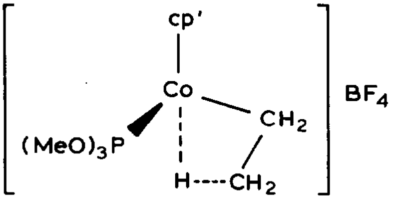
related study to explore the occurrence of binuclear reductive elimination processes in these systems, the reactions of Scheme II (M or M' = Co; n or m = 4. M or M' = Mn; n or m = 5. R = EtO_2C, EtO_2CCH_2) were performed.



Scheme II

For M = Mn, K_a was only 5-10% of that for M = Co while k_b/k_{-a} was much larger for M = Mn and M' = Co than for either reverse combination or for both homometallic systems (ref 89). Other binuclear reductive elimination reactions studied were those between $[Me(CH_2)_4C(O)Co(CO)_4]$ and $[HM(CO)_4]^{n-}$ (M = Co, n = 0; M = Ru, n = 1) where aldehyde formation occurred more rapidly with the ruthenium complex. Further work showed that $[HRu_3(CO)_{11}]^-$, $[H_2Ru_4(CO)_{12}]^{2-}$, $[HRuCo_3(CO)_{12}]$ and $[HFeCo_3(CO)_{12}]$ were less reactive hydride sources (ref. 90).

The protonation of $[cp'Co(P(OMe)_3)(C_2H_4)]$ with tetrafluoroboric acid etherate at low temperature produces an "ethylene hydride" complex which has been shown by NMR spectroscopy to contain an agostic ethyl group ([6]).

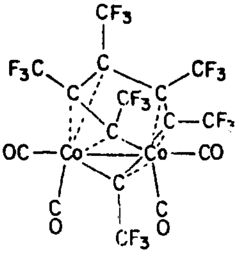


[6]

Two fluxional processes were identified; one involving a hindered rotation of the methyl group which equilibrates three protons of the ethyl group and the other involving equilibration with an ethylene hydride species accompanied by olefin rotation which equilibrates all five protons. Reaction of [6] with trimethylphosphite forms $[cp'Co(P(OMe)_3)_2Et]BF_4$ while with ethylene a catalytic formation of linear polyethylene ensues. A Ziegler-Natta type mechanism involving a stepwise coordination-insertion sequence is proposed. Monitoring of the reaction by proton NMR indicated the presence of several analogs of [6] containing alkyl groups of various lengths. This conclusion was bolstered by the observation of very similar NMR spectra when [cp'Co(P(OMe)$_3$)(CH$_2$=CHR)] (R = Me, Et) was protonated under the same conditions used to form [6]. The fact that no alkyl olefin species could be observed - only species containing an agostic alkyl group were detected - suggested that the latter should be considered as the resting state of the catalyst (ref. 91).

Some reports which can be briefly mentioned include the use of finely divided cobalt powders prepared in ether or hydrocarbon media by the alkali metal reduction of cobalt salts for the synthesis of various σ- and π-bonded organometallic complexes (ref. 92), the presumed intermediacy of cobalt alkyls in the formation of C_2D_6 from cobalt(II) chloride and CD_3Li or CD_3MgBr (ref. 93) and the use of [Co(Et)(bipy)$_2$] as a catalyst for the hydrogenation of buta-1,3-diene to predominately *cis*-but-2-ene and for the conversion of NBD to nortricyclene (ref. 94).

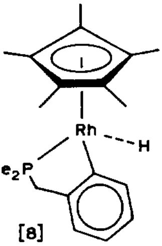
The charge transfer spectra of [Co(C$_6$Cl$_5$)$_2$(PPh$_2$R)$_2$] (R = Me, Et, Pr^n, Bu^n) have been interpreted to suggest that two hydrogens from the phosphine ligands approach the metal sufficiently closely to make it appear six coordinate (ref. 95). EPR studies on [(η^6-C$_6$H$_5$Me)Co(C$_6$F$_5$)$_2$] indicate that the odd electron occupies an orbital of predominantly d_{yz} character (ref. 96) while EXAFS measurements on Na[Co(CH$_2$CN)(CO$_2$Me)(CO)$_3$] indicate the presence of two distinct cobalt-carbon distances and therefore a trigonal bipyramidal structure. However it was not possible to identify the axial ligands (ref. 97). The electrochemical behavior of the "flyover" complexes [R$_6$C$_6$Co$_2$(CO)$_4$] (R = CF$_3$([7]); R$_6$ = (CF$_3$)$_5$H, (CF$_3$)$_4$H$_2$, (CF$_3$)$_3$H$_3$, Bu$_3^t$H$_3$)



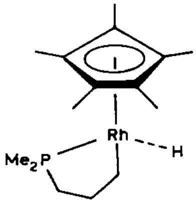
[7]

has been investigated. All five complexes undergo a reversible, one-electron reduction to a radical anion whose stability and subsequent chemistry is quite solvent-dependent. The first eliminates hexakis-(trifluoromethyl)benzene upon reduction in acetone or dichloromethane but the radical anion is stable in THF. In acetonitrile substitution of one carbonyl group on each cobalt by solvent occurs. The last two show the same behavior as the first in acetone and THF, while the fourth (R$_6$ = (CF$_3$)$_3$H$_3$) shows no substitution reactions upon reduction in acetonitrile during the cyclic voltammetric experiment but does so when subjected to bulk electrolysis (ref. 98). An analysis of the solid state conformations of the metallacycles $[(PPh_3)(R)MLL']$ (R = cp; M = Co; L,L' = $(CH_2)_4$, $C_4(C_6F_5)_4$, C_4PhH_3, $C_4Ph(CO_2Me)_3$. R = cp'; M = Rh, Ir; L,L' = $(CH_2)_4$) and of related acylic species (R = η^5-C_5Me_4Et; M = Co; L = L' = Cl. R = cp'; M = Rh; L = L' = NO_3) suggests that intramolecular contacts between the metallacycle and the phosphine ligand are the major determinants of conformation (ref. 99). A computational modelling of the cycloreversion reactions of $[L_n\overline{MCH_2CH_2O-O}]$ (M = Mo, Rh) using an adiabatic ground state surface failed to explain why the molybdenum complex yields the epoxide while the rhodium complex forms the aldehyde. A nonconcerted ring-opening was suggested for the rhodium complex (ref. 100).

Reduction of [cp'Rh(Ph)(L)Br] with $Li[AlH_2(OCH_2CH_2OMe)_2]$ yields [cp'Rh(H)(Ph)L] (L = PMe_2bz, PMe_2Pr) which reversibly eliminates benzene on heating and reversibly metallates the ligand to yield [8] and [9] respectively. Conversion of these hydrides to the corresponding bromides with

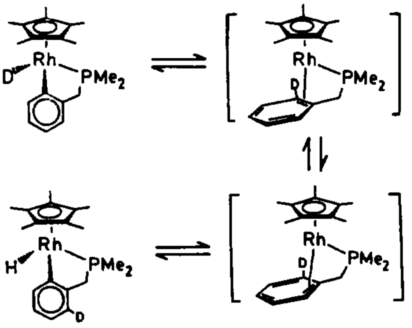


[8]



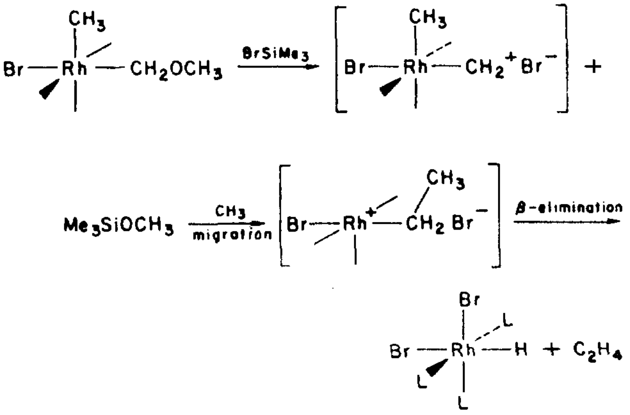
[9]

bromoform permitted isolation of the metallated species. Reduction of $[cp'Rh(PMe_2Pr)Br_2]$ with the aluminum reagent formed $[cp'RhH_2(PMe_2Pr)]$ which on photolysis in liquid propane gave $[cp'RhH(Pr^n)(PMe_2Pr)]$. This on warming eliminated propane and also formed [9]. The reversibility of the ligand metallation process leading to [8] and the apparent intermediacy of an η^2-arene intermediate was further demonstrated using the deuteride analog of [8] whereupon deuterium incorporation into the aromatic ring occurred as outlined in Scheme III. Although, as expected, there is a



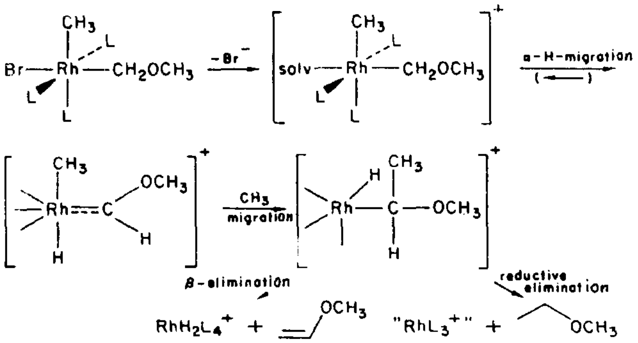
Scheme III

thermodynamic preference for intramolecular vs intermolecular C-H activation by the {cp'RhL} intermediate in these systems when the solvent used is a competing reactant (as demonstrated by the formation of the propyl complex in liquid propane), a kinetic selectivity favors the intermolecular process (ref. 101). Oxidative addition of bromomethyl methyl ether to $[RhMe(PMe_3)_4]$ forms mer-$[RhBr(Me)(CH_2OMe)(PMe_3)_3]$ which reacts with bromotrimethylsilane to form methoxytrimethylsilane, ethylene and $[RhHBr_2(PMe_3)_3]$ by a route proposed to be that of Scheme IV (L = PMe_3). Abstraction of bromide from



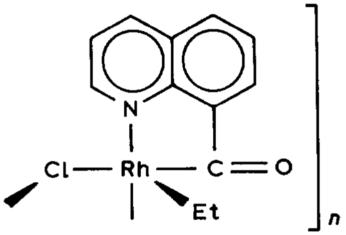
Scheme IV

$[RhBr(Me)(CH_2OMe)(PMe_3)_3]$ in acetonitrile yields the reasonably stable solvated complex mer-$[Rh(MeCN)(Me)(CH_2OMe)(PMe_3)_3]^+$ but in non-coordinating solvents, decomposition occurs to form both methyl vinyl ether and methyl ethyl ether. Scheme V (L = PMe_3) is proposed with the key step being the α-hydrogen migration from the methoxymethyl group to the metal (ref. 102).



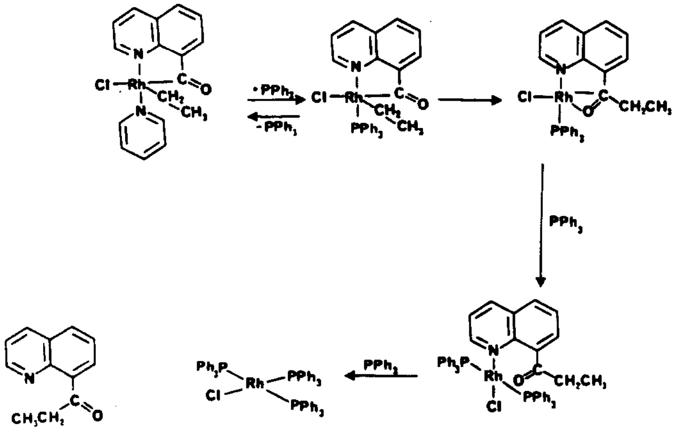
Scheme V

Reaction of 8-formylquinoline with $[RhCl(C_2H_4)_2]_2$ initially forms an insoluble product thought to be [10]. This can be solubilized on addition of pyridine and the resulting pyridine adduct is induced to undergo



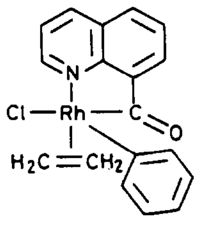
[10]

reductive elimination by triphenylphosphine as depicted in Scheme VI. The same pyridine adduct, shown at the top left of Scheme VI is formed when

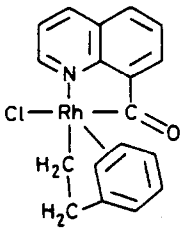


Scheme VI

$[RhCl(C_2H_4)_2]_2$ reacts with several 8-acylquinolines in refluxing benzene followed by treatment with pyridine. The reaction is thought to proceed via oxidative addition of the R-C(O) (R = Et, Bu^n, CHMePh, CMe_2Ph, cy) bond to the metal, decomposition of the resulting alkyl complex by β-elimination and trapping of the hydride species thus formed by ethylene. Heating the system to 100°C under ethylene pressure affords a catalytic conversion of the starting quinolines to 8-propionylquinoline. By contrast when $[RhCl(C_2H_4)_2]_2$ is reacted with 8-benzoylquinoline a catalytic production of styrene and 8-propionylquinoline is observed. This is proposed to involve [11] and [12] as intermediates with the difference from the previous

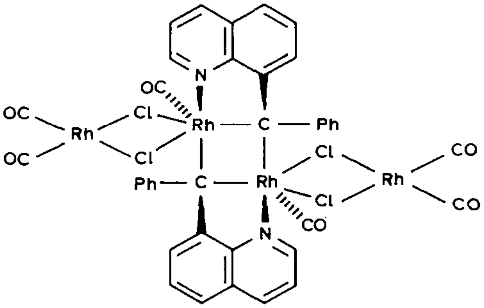


[11]



[12]

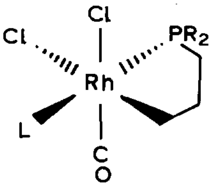
systems resulting from the ability of the aryl group to interact in an η^2 fashion with the metal as proposed in [12] (refs. 103, 104). By contrast, the reaction of 8-benzoylquinoline with $[RhCl(CO)_2]_2$ forms [13] and carbon



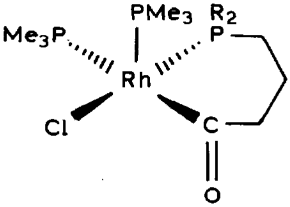
[13]

dioxide. Interestingly, both quinoline moieties are attached to the same side of and are approximately perpendicular to the dimetallacyclobutane ring. An acyl species (as yet not isolated) appears to be an intermediate and it is proposed that transfer of the oxygen atom from this acyl group to a coordinated carbon monoxide gives rise to the carbon dioxide produced (ref. 105).

Another example of a chelate-assisted oxidative addition of a carbon-chlorine bond occurs when $[Rh(CO)ClL_2]$ (L = $R_2P(CH_2)_3Cl$ (R = Ph, cy)) is refluxed in benzene and [14] forms. This reacts with excess trimethylphosphine to give the CO-insertion product [15] (ref. 106). Other examples of

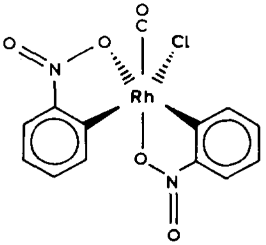


[14]



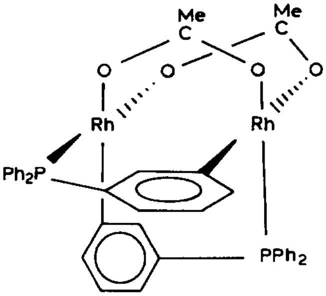
[15]

metallations include the first example of a cyclometallated o-nitrophenyl group in [16], prepared from $[RhCl(CO)_2]_2$ and bis(o-nitrophenyl)mercury



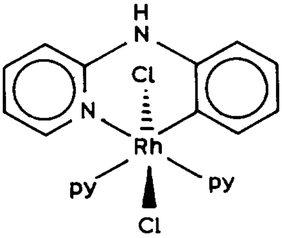
[16]

(ref. 107) and [17] which results from reaction of $[Rh_2(O_2CMe)_4(MeOH)_2]$ with triphenylphosphine in refluxing glacial acetic acid followed by



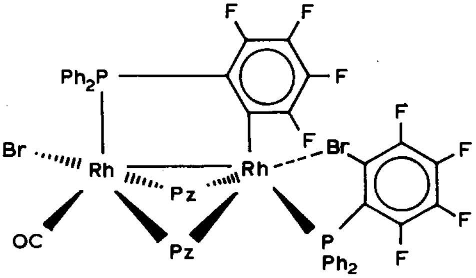
[17]

recrystallization in the presence of pyridine (ref. 108). What is proposed to be the first example of a rhodium(III) complex containing a six-membered ring involving an o-metallated phenyl ring occurs in [18] which forms when



[18]

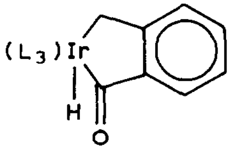
hydrated rhodium(III) chloride and 2-anilinopyridine are refluxed in ethanol followed by reaction with pyridine. No indication of mechanism was given (ref. 109). Among the products formed when $[Rh(CO)(L)(\mu\text{-}pz)]_2$ (L = $Ph_2P(\underline{o}\text{-}BrC_6F_4)$) is thermolyzed in toluene is [19] (ref. 110).



[19]

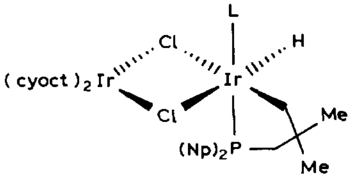
A bimolecular reductive elimination of methane (together with some acetaldehyde) occurs when cis-$[OsH_2(CO)_4]$ reacts with $Bu_4N[Rh(C(O)Me)(CO)I_3]$. The possibility that methane formation occurs via proton transfer from osmium was ruled out by the observation that no methane is evolved when the rhodium complex is treated with trifluoroacetic acid. One equivalent of methane is also evolved when the osmium complex reacts with $[IrCl_2(Me)(CO)_2(AsPh_3)]$ and the intermediate formation of $[Ir(C(O)Me)Cl_2(CO)(AsPh_3)]$ was detected. The evident feasibility of this bimolecular reductive elimination of methane from a preformed acyl species is taken as support for the acyl intermediate proposed several years ago in the reaction of $[OsH_2(CO)_4]$ with $[OsMe_2(CO)_4]$ which forms methane and $[Os_2H(Me)(CO)_8]$ (ref. 111). At room temperature several acyl chlorides oxidatively add to $[RhCl(PPh_3)_3]$ to form $[Rh(C(O)R)Cl(PPh_3)_3]$ (R = Ph, *p*-anisyl, $CH_3(CH_2)_{14}$, *p*-$CH_3(CH_2)_{14}OC_6H_4$). Raising the temperature to 80°C converts this to $[Rh(R)Cl_2(CO)(PPh_3)_2]$ and on heating to 110°C $[Rh(R)Cl_2(PPh_3)_2]$ forms. At each stage of the reaction, a polystyrene coated aluminum chip was dipped into the solution, vacuum dried and the surface analyzed by ESCA. The appropriate species was identified by this technique in each instance leading to the proposal that this method holds promise for the isolation and identification of intermediates in homogeneously catalyzed systems (ref. 112). While mainly discussing literature results bearing on the role of alkyl rhodium compounds in olefin hydrogenation and isomerization processes, one further paper also reports the synthesis of $[RhH(X)Cl(PPh_3)_3]$ and $[Rh_2H_2Cl_4(PPh_3)_4]$ from $[RhX(PPh_3)_3]$ ($X = Cl^-$, $SnCl_3^-$) and hydrogen chloride. These hydrides reacted further with ethylene and hex-1-ene to form unstable complexes formulated as $[Rh(R)Cl_2(PPh_3)_2]$ (R = Et, *n*-C_6H_{13}) (ref. 113).

Five-coordinate, fluxional complexes of formula [MR(CO)(triphos)] (M = Ir; R = Me, Ph, Np, CH_2SiMe_3. M = Rh; R = CH_2SiMe_3) are formed straightforwardly from [MCl(CO)(triphos)] and the appropriate lithium reagent. By contrast, an attempt to prepare [Ir(*o*-tolyl)(CO)(triphos)] from $[Ir(o\text{-tolyl})(CO)(PPh_3)_2]$ and triphos produced [20] (L_3 = triphos) instead.

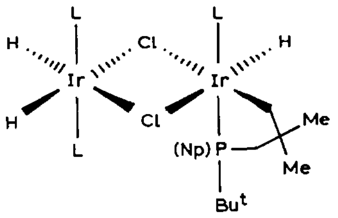


[20]

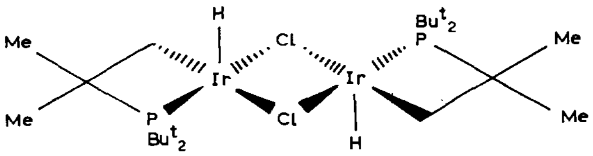
Analogs with $RP((CH_2)_nPPh_2)_2$ (n = 2; R = Ph. n = 3; R = Ph, Me) were prepared in like fashion as were some related species derived from the corresponding mesityl and 2,6-dimethylphenyl iridium(I) complexes. In related work, metallation of bulky tertiary phosphines by iridium was noted. Thus $[IrCl(cyoct)_2]_2$ and tris(neopentyl)phosphine in refluxing toluene forms only [21] (L = $P(Np)_3$) while tert-butylbis(neopentyl)phosphine and di-tert-butyl(neopentyl)phosphine form [22] (L = $P(Np)_2Bu^t$) and [23] (L = $P(Np)Bu^t_2$) respectively together with $[IrH_2ClL_2]$. No metallation



[21]

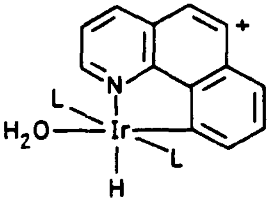


[22]



[23]

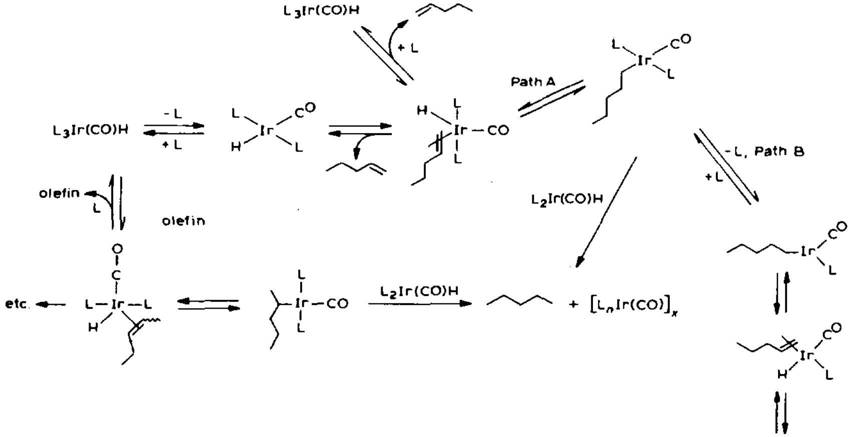
was seen when triisopropylphosphine was used (refs. 114-117). Metallation of 7,8-benzoquinoline by iridium occurs when it is reacted with $[Ir(COD)(PPh_3)_2]^+$ in moist dichloromethane under hydrogen. The product, [24], reacts with trialkylborohydride ion to replace the water molecule with a



[24]

hydride ligand but with dihydrogen, the "trihydride" which forms reversibly by replacement of the water molecule is considered to be a complex of undissociated molecular hydrogen rather than a classical trihydride. This latter species is however proposed as an intermediate in the dynamic process which operates to exchange the hydrogen of the Ir-H and $Ir(H_2)$ moieties (ref. 118). Hydrated iridium(III) chloride reacts with 2-phenylpyridine to give a mixture of $[Ir_2(\mu\text{-}Cl)_2(\overset{\frown}{N\,C})_4]$ and fac-$[Ir(\overset{\frown}{N\,C})_3]$ ($\overset{\frown}{N\,C}$ = o-metallated 2-phenylpyridine). The electronic absorption and emission spectra were measured and a strongly reducing photoexcited state was characterized (ref. 119).

Hydrogenolysis of [Ir(R)(CO)$(PPh_3)_2$] (R = Me, Np, Ph, CH_2SiMe_3) for brief periods yields fac-[IrH_3(CO)$(PPh_3)_2$] but over longer times a mixture of both mer isomers forms (ref. 120). Alkylation of [IrCl(CO)$(PPh_3)_2$] with n-octyllithium and n-octyl- or n-pentylmagnesium bromide gives thermally unstable species formulated as [Ir(R)(CO)$(PPh_3)_2$] (R = n-octyl, n-pentyl). A study of their decomposition which produces the corresponding alkane and an isomeric mixture of olefins suggested the processes of Scheme VII (ref. 121). The corresponding methyl complex is prepared similarly from methyllithium and in contrast to an earlier report is found to be quite stable. The previously reported instability is attributed to either the presence of a methyllithium adduct in the earlier preparation or to a reaction with methoxide ion arising from the methanol used to quench the original reaction. Some chemistry of the complex is outlined in Scheme VII (L = PPh_3)



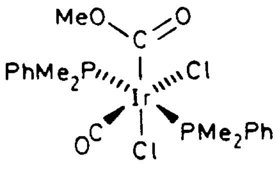
Scheme VII

$$\begin{tikzcd}
{[IrMe_2(CO)(I)L_2]} & {[IrMe(L')(CO)L_2]} & {[IrMe(CO)_2L_2]} \arrow[dl, bend left, "e"] \\
{[IrMe(O_2)(CO)L_2]} & {[IrMe(CO)L_2]} \arrow[ul, "b"] \arrow[l, "a"'] \arrow[u, "c"] \arrow[ur, "d"] \arrow[r, shift left, "f"] \arrow[d, "g"'] \arrow[dr, "i"] & {[Ir(C(O)Me)(CO)_2L_2]} \arrow[l, shift left, "e"] \\
{[IrH_3(CO)L_2]} & {[IrMeH_2(CO)L_2]} \arrow[l, "h"'] & {[IrH(CO)_2L_2]}
\end{tikzcd}$$

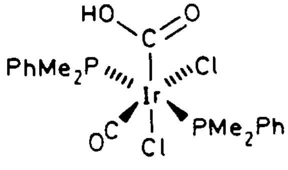
a) O_2. b) MeI. c) L' (= MeO_2CCH=$CHCO_2Me$, DMAD). d) CO, THF, -78°C. e) 25°C. f) CO (1000 psi), hexane, 70°C. g) H_2, -78°C. h) H_2, -40°C. i) paraformaldehyde.

Scheme VIII

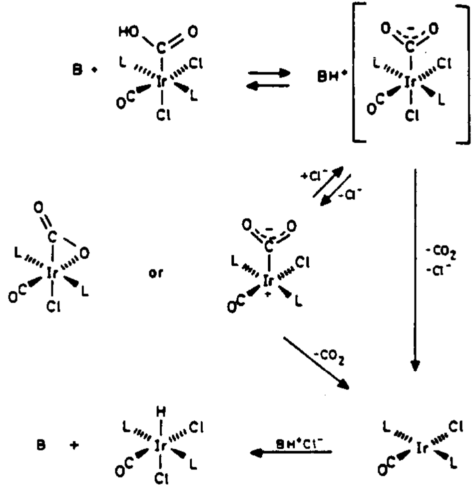
(ref. 122). Oxidative addition of methyl chloroformate to [Ir(CO)Cl-(PMe$_2$Ph)$_2$] yields [25] which can by hydrolyzed to [26] by several treatments with hydrogen chloride in chloroform followed by washing with moist ether. Complex [26] undergoes a facile base-catalyzed decarboxylation to [IrHCl$_2$(CO)(PMe$_2$Ph)$_2$] possibly according to Scheme IX (L = PMe$_2$Ph; B = bz$_3$N, Et$_3$N). It also reacts with acid to give [27] *via* either [28] or [29] (ref. 123). [IrH$_5$(PPr$^i_3$)$_2$] catalyzes H-D exchange between deuterobenzene and *tert*-butylethylene. In the initial stages a specific deuterium incorporation into the olefin *trans* to the *tert*-butyl group is seen although after longer reaction times D$_2$C=CHBu^t is also detected. The initial C$_6$D$_5$H seen is considered to arise from hydrogen transferred to the deuterobenzene



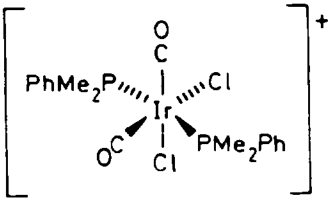
[25]



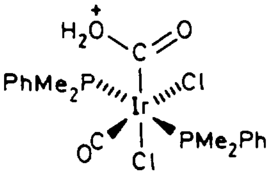
[26]



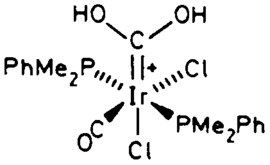
Scheme IX



[27]

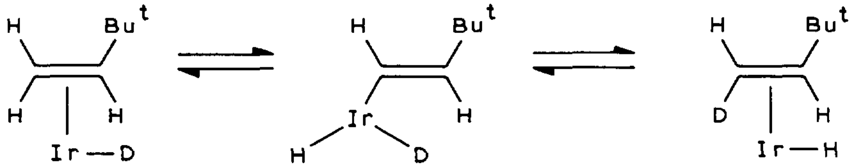


[28]



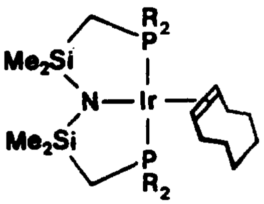
[29]

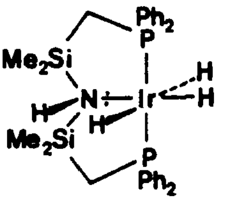
from the phosphine ligand *via* an intermediate metallated species. In this process, deuterium is transferred to the metal and as the olefin used is incapable of forming the usual allyl hydride complex, the mechanism of Scheme X is proposed. It is concluded that the proposed σ-vinyl intermediate may be more prevalent in metal-catalyzed olefin reactions than has been previously thought (ref. 124).



Scheme X

The recent observation that [30] (R = Ph) reacts with hydrogen to form [31] suggested the possibility that a ligand-assisted heterolytic activation of hydrogen (by addition across the metal-amide bond) had occurred.

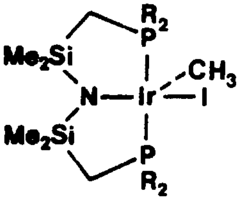


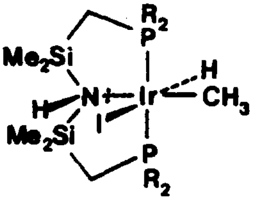


[30]

[31]

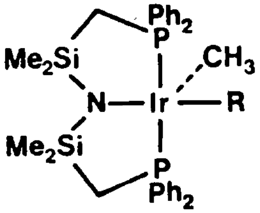
To further probe this reaction [30] (R = Ph, Pr^i) was reacted with methyl iodide to give [32] which added hydrogen to form [33]. The stereochemistry of [33] was determined from an X-ray crystal structure study and is such that a concerted heterolytic activation of hydrogen appears unlikely. Complex [32] (R = Ph) can be alkylated by alkyllithium reagents in toluene solution to give [34] (R = Np, CH_2SiMe_3), the first examples of five-coordinate dialkyls of iridium. Although thermally stable, the neopentyl complex is readily photolyzed to afford a 55:45 mixture of [35] and [36] plus





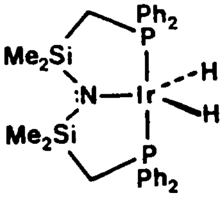
[32]

[33]

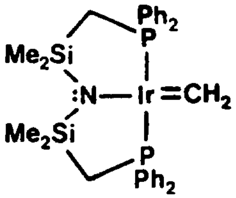


[34]

tert-butylethylene and neopentane in the same proportions. An α-hydrogen abstraction process is proposed to explain the results (refs. 125, 126).

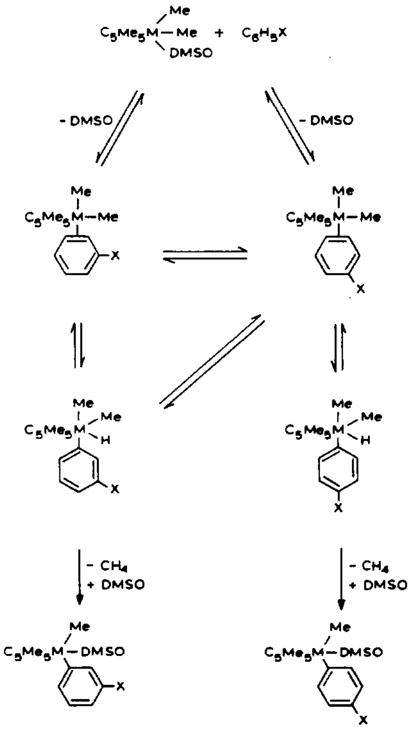


[35]



[36]

Scheme XI (M = Rh; X = H. M = Ir; X = H, Cl, Br, I, COMe, CO_2Me, NO_2,



Scheme XI

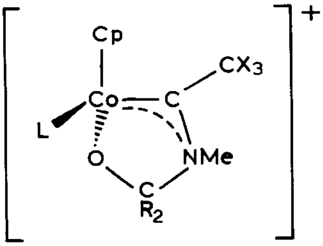
CF_3, CN, NH_2) outlines the proposed mechanism for the reaction of [cp'MMe_2(DMSO)] with various benzene derivatives. With X = H, Cl, or I, the iridium system also forms [cp'$Ir(C_6H_4X)_2$(DMSO)] when run at elevated temperature. Treatment of [cp'$IrMe_2$(DMSO)] with hydrogen halides or cerium(IV) salts generates mainly methane but with silver tetrafluoroborate, ethane is the exclusive hydrocarbon product. By contrast, treatment of [cp'$IrMe(C_6H_4X)$(DMSO)] (X = Cl, Br, I, NO_2) with silver tetrafluoroborate does not cause coupling of the organic ligands (C_6H_5X forms instead) although this can be accomplished using the hexachloroiridate(IV) ion to give the corresponding substituted toluenes. In refluxing cyclohexane, [cp'MMe_2(DMSO)] reacts with aldehydes to yield [cp'M(R)Me(CO)] (M = Rh, Ir; R = Me, Et, Ph, o-tolyl, m-tolyl, p-tolyl) plus methane. Similarly, [cp'Ir(Me)(Ph)(DMSO)] reacts with p-XC_6H_4CHO (X = H, Me) to form a mixture of [cp'Ir(Me)(CO)(p-XC_6H_4)] and [cp'Ir(Ph)(CO)(p-XC_6H_4)] while [cp'$IrPh_2$(DMSO)] and p-tolualdehyde forms [cp'IrPh(p-tolyl)(CO)]. These reactions are inhibited by the presence of excess DMSO suggesting that dissociation of this ligand is the initial step. As tests for radicals proved negative a mechanism involving η^2-coordination of the aldehyde followed by oxidative addition of the C-H bond was favored (refs. 127, 128). In a further study of the activation of carbon-hydrogen bonds by iridium complexes, [cp'IrH(cyclo-C_6H_{11})(PMe_3)] was reacted with ethylene at 130-160°C in perdeuterocyclohexane to yield one equivalent of cyclohexane (undeuterated) and a 2:1 ratio of [cp'IrH(CH=CH_2)(PMe_3)] and [cp'$Ir(C_2H_4)$(PMe_3)]. This ratio of products remains constant throughout the reaction indicating that the ethylene complex is not a precursor to the vinyl complex (in fact the vinyl complex converts to the ethylene complex at somewhat higher temperature). The results suggest that π-coordination of the olefin to the metal is not a prerequisite to C-H bond activation (ref. 129). Cyclic voltammetric studies on [IrR(CO)$(PPh_3)_2$] (R = Me, Ph, CH_2CN) show the presence of a two-electron irreversible oxidation process but when excess phosphine is present the behavior can be explained by the processes of Scheme XII (L =

$$[IrR(CO)L_2] \underset{-L}{\overset{+L}{\rightleftharpoons}} [IrR(CO)L_3] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [IrR(CO)L_3]^+$$

Scheme XII

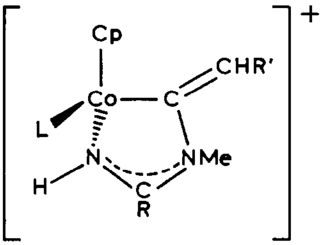
PPh_3). When R = Ph the Ir(II) cation is stable for days in solution but the others decompose in a matter of hours with the cyanomethyl complex yielding $[Ir(CO)L_3]^+$ and $[Ir(CH_2CN)_2(CO)L_2]^+$ (ref. 130).

A large number of five-membered cobaltaheterocycles have been prepared in continuing studies on the [3+2] cycloaddition reactions of imidoyl and carbonyl compounds. Reaction of [cpCo(CNMe)L] (L = PMe_3) with methyl iodide or its perdeutero analog in acetone forms the cationic complex [37]

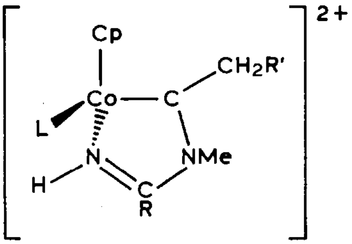


[37]

(X = H, D; R = CH_3) while in a non-polar solvent [cpCoMe(CNMe)L]I is the product. This converts to [37] on dissolution in acetone suggesting it is an intermediate in the original reaction. The cycloaddition reaction is evidently reversible since dissolution of [37] (R = CH_3; X = H) in deuteroacetone yields the analog with R = CD_3 and X = H, while with nitriles, [38] (R = Me, Ph, CH=CH_2, CH=CHMe, CMe=CH_2, cyclo-C_3H_5, NH_2, NMe_2, SMe; R' = H) forms. Complexes [38] (R' = H) can also be formed directly from [cpCoMe(CNMe)L] and the appropriate nitrile and are reversibly protonated with TFA to form [39] (R' = H). Another example of [38] (R = R' = Me) is prepared

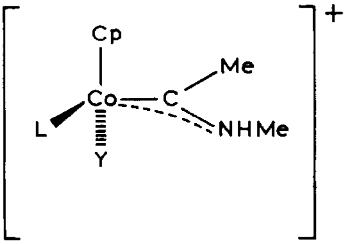


[38]

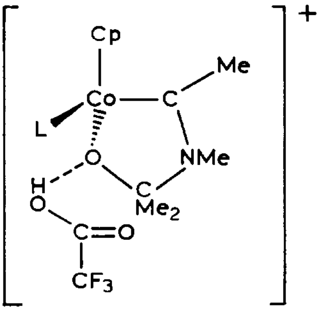


[39]

from [cpCo(CNMe)L], ethyl iodide and acetonitrile. It also is reversibly protonated to give [39] (R = R' = Me). Protonation of [37] (R = Me; X = H) with TFA yields [40] (Y = CF_3CO_2) possibly via initial formation of [41]. Addition of iodide ion to [40] (Y = CF_3CO_2) yields the analog with Y = I. Complex [37] (R = Me; X = H) reacts with trimethyloxonium tetrafluoroborate to yield [42] (R = Me) which could not be converted to [40] (Y = I) with TFA and iodide ion. However protonation of [37] (R = Me; X = H) with tetrafluoroboric acid gave [42] (R = H) which did form [40] (X = I) on further treatment with TFA and iodide ion. Protonation of [cpCo(C(Me)=NPh)(I)L] (L = PMe_3) affords [43] while reaction with trimethylphosphine

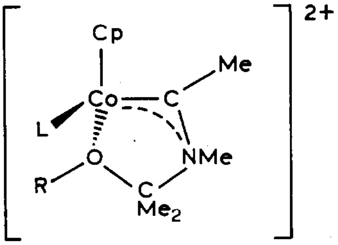


[40]



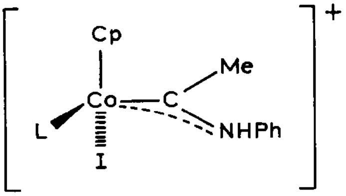
[41]

yields [44] (R = Ph). Analogs of [44] with R = Me, Bu^t are formed from [37] (R = Me; X = H) and [cpCo(C(Me)=NBu^t)(L)] (L = Me_3P) respectively on

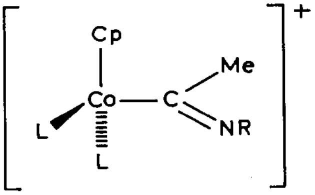


[42]

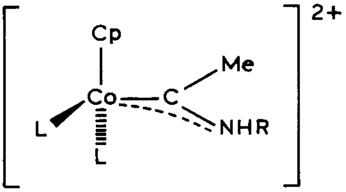
treatment with one equivalent of trimethylphosphine. All three complexes can be protonated with TFA to form [45] (R = Me, Bu^t, Ph). In refluxing



[43]

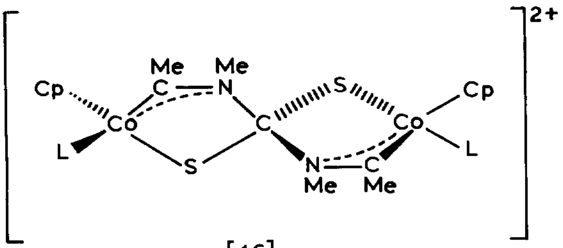


[44]

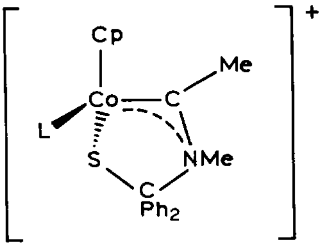


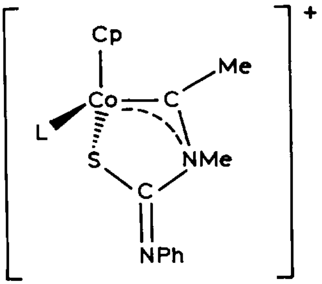
[45]

acetone, [37] (R = Me; X = H) reacts with carbon disulfide to form [46] but under the same conditions [cpCo(C(Me)=NPh)(PMe$_3$)] forms [43]. Thiobenzophenone and phenylisothiocyanate replace acetone in [37] (R = Me; X = H) to



[46]

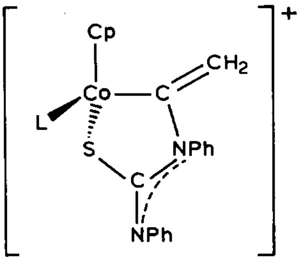


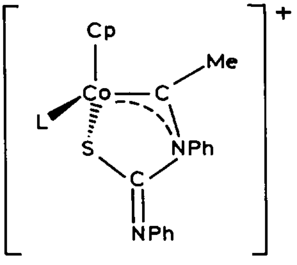


[47]

[48]

give [47] and [48] respectively while [cpCo(C(Me)=NPh)I(PMe$_3$)] and phenylisothiocyanate yield an equilibrium mixture of [49] and [50] (L = PMe$_3$).

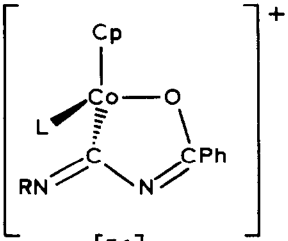




[49]

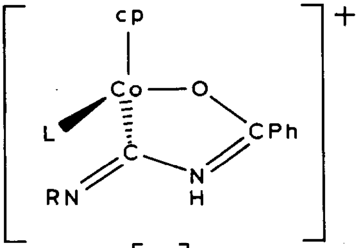
[50]

Analogs of [48] - [50] with methyl, tert-butyl- and cyclohexylisothiocyanate were also prepared. Finally, benzoyl azide reacts with [cpCo(CNR)L] (R = Me, Ph; L = PMe$_3$) to form [51] which on treatment with TFA or

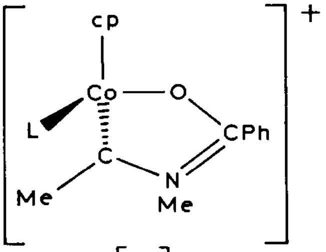


[51]

trimethyloxonium tetrafluoroborate yields [52] and [53] respectively (refs. 131-135).

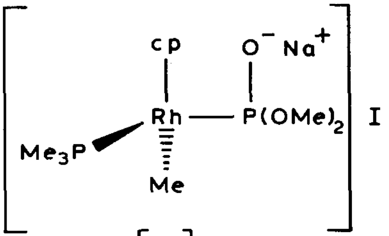


[52]

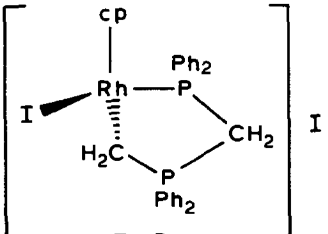


[53]

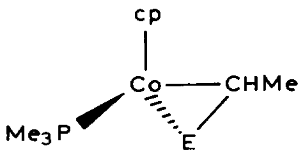
The synthesis and reactivity of complexes containing the $\{RhCH_2X\}$ (X = halogen) moiety which can serve as precursors to carbenoid species continue to be extensively studied. Successive additions of two equivalents of two different phosphorus ligands and sodium cyclopentadienide to $[RhCl(cyoct)_2]_2$ yields $[cpRhL(L')]$ (L = PMe_3; L' = PMe_2Ph, $PMePh_2$, PPh_3, $P(OR)_3$ (R = Me, Et, Pr^i, Ph). L = PEt_3, PPr^i_3, PMe_2Ph, $PMePh_2$; L' = $P(OMe)_3$). Similarly, the addition of four equivalents of an isocyanide followed by sodium cyclopentadienide forms $[cpRh(CNR)_2]$ (R = Me, Bu^t) while from $[RhCl(C_2H_4)_2]$, $[cpRh(C_2H_4)L]$ (L = $P(OMe)_3$, SMe_2) can be synthesized. Reaction of diiodomethane with $[cpRhL(L')]$ followed by metathesis with hexafluorophosphate ion yields $[cpRh(CH_2I)L(L')]PF_6$ (L = PMe_3; L' = PMe_2Ph, $PMePh_2$, $P(OR)_3$ (R = Me, Pr^i). L = PEt_3, PMe_2Ph, $PMePh_2$; L' = $P(OMe)_3$. L = L' = CNMe, $CNBu^t$, $P(OEt)_3$) but for L = PMe_3 and L' = PPh_3, $P(OPh)_3$ the product is $[cpRh(CH_2I)I(L)]$. This latter product (L = $P(OMe)_3$) also forms when diiodomethane reacts with $[cpRh(C_2H_4)(P(OMe)_3)]$. In a study of the reactivity of other dihalomethanes in these systems it was found that $[cpRh(PMe_3)_2]$ and dichloro- or chloroiodomethane, followed by metathesis with hexafluorophosphate, formed $[cpRh(CH_2Cl)(PMe_3)_2]PF_6$ but dibromomethane initially gave a mixture of $[cpRh(CH_2Br)(PMe_3)_2]Br$ and $[cpRh(CH_2PMe_3)Br(PMe_3)]Br$. Metathesis of the mixture with hexafluorophosphate ion followed by addition of triethylamine formed $[cpRh(CH_2PMe_3)Br(PMe_3)]PF_6$ as the sole product. With $[cpRh(PMe_3)(P(OMe)_3)]$, dibromo- and chloroiodomethane gave, following metathesis, $[cpRh(CH_2X)(PMe_3)(P(OMe)_3)]PF_6$ (X = Br and Cl respectively) but dichloromethane evidently induces an Arbusov-type reaction as the product is $[cpRhMe(P(O)(OMe)_2)(PMe_3)]$. This was further supported by the observation that $[cpRh(PMe_3)(P(OMe)_3)]$ reacts with sodium iodide to form [54]. In further variations on this theme, $[cpRh(C_2H_4)(PMe_3)]$ and CH_2XX' (X = X' = Br, I. X = Cl, CN; X' = I) form $[cpRh(CH_2X)(X')(PMe_3)]$ while with CHX_3 (X = Br, I) the products are $[cpRh(CHX_2)(X)(PMe_3)]$.


[54]

Related reactions with [cp'Rh(CO)$_2$] and [cp'Rh(CO)L] (L = PMe$_3$, PMe$_2$Ph, P(OMe)$_3$) yielded [cp'Rh(CHX$_2$)(X)(CO)] (X = Br, I) and [cp'Rh(CH$_2$X)(I)(CO)] (X = Cl, I, CN) or [cp'Rh(CHBr$_2$)(Br)(L)] and [cp'Rh(CHX$_2$)(I)L] (X = Cl; L = PMe$_3$. X = I; L = PMe$_3$, PMe$_2$Ph, P(OMe)$_3$) respectively. The nucleophilic reactivity of various examples of these halomethylrhodium complexes has been investigated. Addition of iodide ion to [cpRh(CH$_2$I)L(L')]$^+$ (L = L' = P(OEt)$_3$. L = PMe$_3$; L' = P(OMe)$_3$) gives the Arbusov product [cpRh(CH$_2$I)-(P(O)(OR)$_2$)L] (R = Me, Et) without affecting the halomethyl group but when L = L' = PMe$_3$ reaction with trimethylphosphine gives [cpRh(CH$_2$PMe$_3$)L$_2$]$^{2+}$ while various Bronsted bases (B) convert it to [cpRh(CH$_2$PMe$_3$)(I)(L)]$^+$ (B = NEt$_3$, OMe$^-$, acac) or to a mixture of [cpRh(CH$_2$PMe$_3$)(SMe)(L)]$^+$ and [cpRh-(CH$_2$SMe)L$_2$]$^+$ (B = SMe$^-$). Heating [cpRh(CH$_2$I)(L)(L')]PF$_6$(L = P(OMe)$_3$; L' = PMe$_3$, PMe$_2$Ph, PMePh$_2$. L = P(OEt)$_3$; L' = PMe$_3$) forms [cpRh(CH$_2$L')(I)(L)]PF$_6$ but whether this occurs intramolecularly or *via* initial dissociation of L' is not clear. A sizeable number of other neutral and anionic nucleophiles were also found to displace iodide from the iodomethyl group in [cpRh-(CH$_2$I)(I)(PMe$_3$)] to give analogous products. An exception is [cp'Rh(CH$_2$I)-(CO)I] which reacts with triphenylphosphine to give [cp'Rh(PPh$_3$)I$_2$], with sodium methoxide to give [cp'$_2$Rh$_2$(μ-CO)$_2$] and with DPM to form [55] (refs. 136-138).

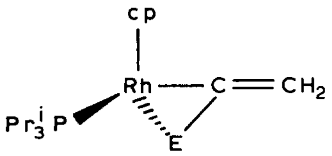

[55]

In related work, [cpCo(CO)(PMe$_3$)] reacts with 1,1-dibromoethane to yield [cpCo(CHBrMe)Br(PMe$_3$)]. This with sodium hydrogen sulfide or selenide forms [56] (E = S, Se). The vinylidene complex [cpRh(=C=CH$_2$)L] (L = PPr$^i{}_3$)



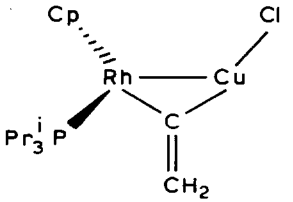
[56]

reacts with hydrogen chloride in a stepwise manner to form [cpRh(CH=CH$_2$)Cl(L)] and then [cpRh(CHClCH$_3$)Cl(L)]. The last step can be reversed by treatment with sodium hydrogen sulfide. The vinylidene complex also reacts with elemental sulfur or selenium to form [57] (E = S, Se) which can be catalytically hydrogenated in the presence of [RhCl(PPh$_3$)$_3$] to give an

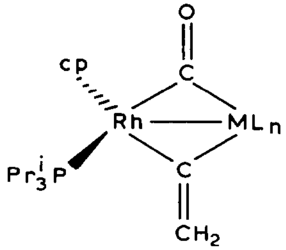


[57]

analog of [56] (ref. 139). Further reactions of the vinylidene complex are with copper(I) chloride to form [58] and with [Fe$_2$(CO)$_9$], [(η^6-C$_6$H$_6$)Cr(CO)$_3$] or [cpMn(CO)$_3$] to form [59] (ML$_n$ = Fe(CO)$_3$, (η^6-C$_6$H$_6$)Cr(CO), cpMn respectively) (ref. 140).

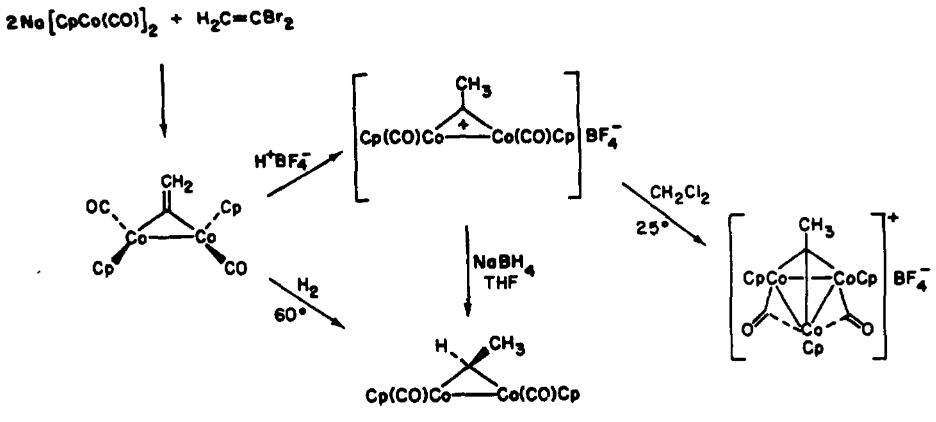


[58]



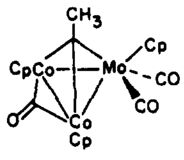
[59]

Scheme XIII outlines the synthesis and some reactions of a vinylidene-bridged dicobalt complex. Other reactions of this complex include those with [cpMo(CO)$_2$(L)H] (L = CO, PPh$_3$, PMe$_3$) and with [HMn(CO)$_5$] to form [60] and [61] respectively. In each case [cp$_2$Co$_2$(CO$_2$)(μ-CHMe)] also forms. The formation of [60] is thought to proceed via a non-chain radical process as outlined in Scheme XIV (ref. 141). A new, one-pot synthesis of [cp'$_2$M$_2$(CO)$_2$(μ-C=CR$_2$)] (M = Co, Rh; R = Me; R$_2$ = (CH$_2$)$_5$) has been reported which

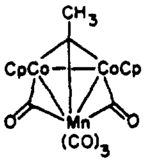


Scheme XIII

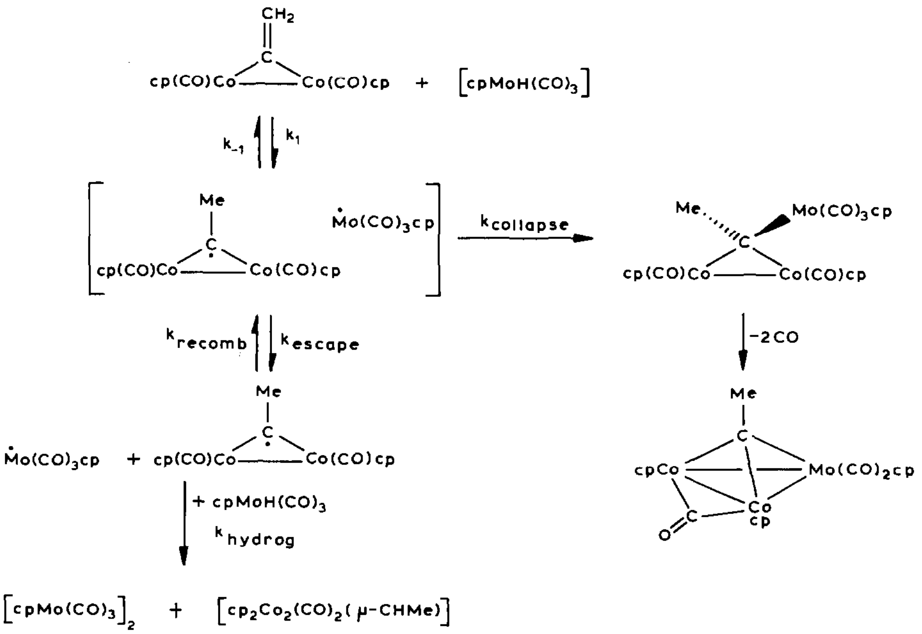
involves treatment of $[cp'_2M_2(\mu\text{-}CO)_2]$ with the appropriate cyclic N-nitrosourethane in a THF/methanol solvent containing lithium ethoxide (refs.



[60]

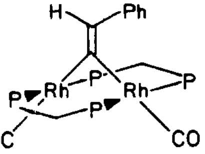


[61]

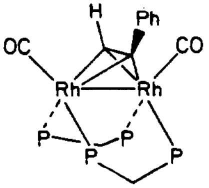


Scheme XIV

142, 143). At room temperature, $[Rh_2(CO)_3(DPM)_2]$ reacts slowly with excess phenylacetylene in benzene to form [62] while at reflux the reaction is



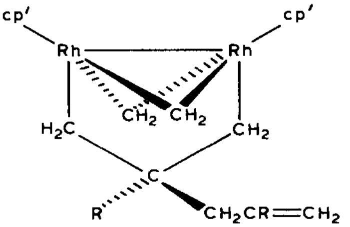
[62]



[63]

considerably faster and a 30:70 mixture of [62] and [63] is produced. In acetone only [63] forms. Although [63] slowly converts to [62] in refluxing benzene, the rate of this process is too slow to account for the rapid appearance of [62] in the second reaction. Also, the formation of only [63] is inhibited by the presence of carbon monoxide indicating that the two products form by separate pathways. These are considered to involve an initial activation of the acetylenic carbon-hydrogen bond by rhodium in $[Rh_2(CO)_3(DPM)_2]$ for [62] and acetylene addition to $[Rh_2(CO)_2(DPM)_2]$ for [63] (ref. 144).

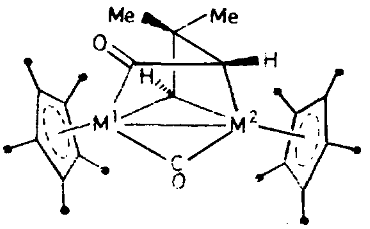
In an extension of earlier work on cobalt systems, the radical anion $[cp'_2Rh_2(\mu\text{-}CO)_2]^{\dot{-}}$ was prepared by reduction of $[cp'_2Rh_2(\mu\text{-}CO)_2]$ with sodium-potassium alloy and here, further reduction to $[cp'_2Rh_2(CO)_2]^{2-}$ also was achieved. Reaction of either anion with dichloromethane gave equal quantities of $[cp'_2Rh_2(CO)_2(\mu\text{-}CH_2)]$ and $[cp'_2Rh_2(\mu\text{-}CO)_2]$ in low yield while methyl iodide formed traces of cis- and trans-$[cp'_2Rh_2(CO)_2Me_2]$ and 1,3-bis[p-tolylsulfonyloxy]propane yielded $[cp'_2Rh_2(CO)_2(\mu\text{-}(CH_2)_3)]$. Alkylation of $[cp'_2Rh_2(\mu\text{-}CO)_2]$ with methyllithium forms $Li[cp'MeRh(\mu\text{-}CO)_2Rhcp']$ which was identified in solution. This anion reacts with methyl iodide or p-tolylsulfonylethane to form single isomers of $[cp'_2Rh_2(CO)_2Me_2]$ and $[cp'Et(CO)RhRhcp'(CO)Me]$. Direct reaction of $[cp'_2Rh_2(\mu\text{-}CO)_2]$ with p-tolylsulfonylethane forms a single isomer of $[cp'_2Rh_2Et_2(CO)_2]$. All three dialkyl complexes slowly form a mixture of cis- and trans-isomers on standing in benzene solution (ref. 145). Allylic Grignard reagents react with trans-$[cp'_2Rh_2Cl_2(\mu\text{-}CH_2)_2]$ to afford [64] (R = H, Me) which is thought



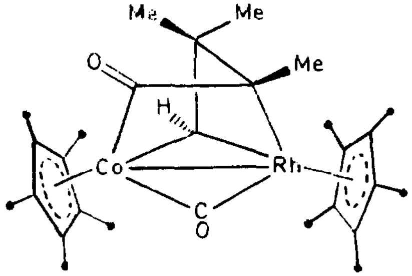
[64]

to form *via* a bis(η^1-allyl) complex followed by cyclization. A direct measurement of $^{1}J_{Rh-Rh}$ showed it to be *ca* 12 Hz. Also reported in this paper was the reaction of *trans*-$[cp'_2Rh_2(MeCN)_2(\mu\text{-}CH_2)_2]^{2+}$ with DPM or DPPE (L_2) to form $[cp'_2Rh_2(\mu\text{-}L_2)(\mu\text{-}CH_2)_2]^{2+}$ (ref. 146).

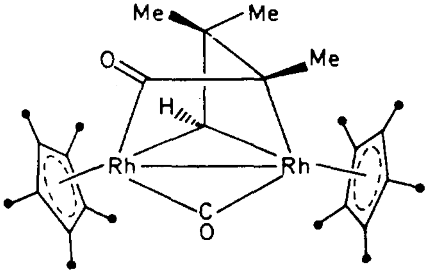
Cleavage of the carbon-carbon double bond occurs when 3,3-dimethylcyclopropene reacts with $[cp'_2M^1M^2(\mu\text{-}CO)_2]$ to give [65] ($M^1 = M^2 =$ Co, Rh. $M^1 =$ Co; $M^2 =$ Rh, Ir. $M^1 =$ Ir, $M^2 =$ Rh). The reactivity follows the order CoRh > Rh_2 > RhIr > CoIr > Co_2. Only the CoRh and Rh_2 dimers reacted with 2,3,3-trimethylcyclopropene and here the products were [66] and [67] plus [68] respectively. Protonation of [65] ($M^1 = M^2 =$ Rh) with TFA formed [69] while [67] produced [70]. By contrast, [67] and triflic acid gave [71] (ref. 147). Organic azides (RN_3; R = Ph, PhC(O), *p*-$MeOC_6H_4SO_3$) react readily with [72] to form [73]. Complex [73] also forms when [72] is heated with isocyanates (RNCO: R = Me, Bu^t, *p*-tolyl) or when it is treated with carbodiimides (RNCNR: R = Pr^i, cy). A second product from the former



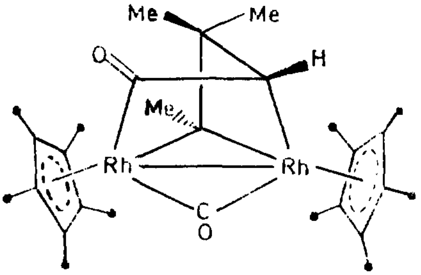
[65]



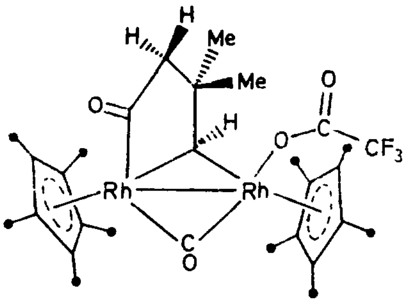
[66]



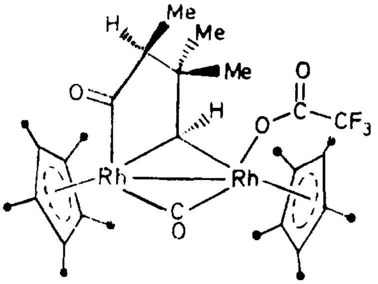
[67]



[68]

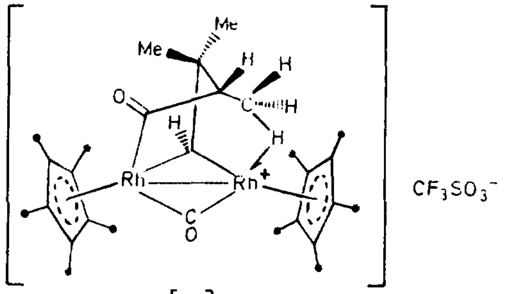


[69]

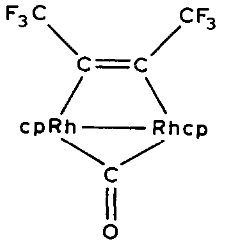


[70]

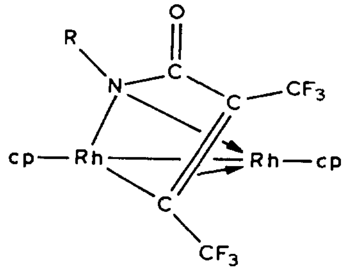
reaction is $[cp_2Rh_2(CO)_2(\mu\text{-}F_3CC{=}CCF_3)]$ while the latter also forms $[cp_2Rh_2\text{-}(CO)(CNR)(\mu\text{-}F_3CC{=}CCF_3)]$. In all instances, [72] is considered to function as a trap for a nitrene produced by fragmentation of the organic reagent used although the carbodiimide is thought to coordinate prior to fragmentation.



[71]

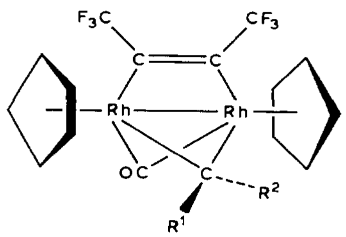


[72]



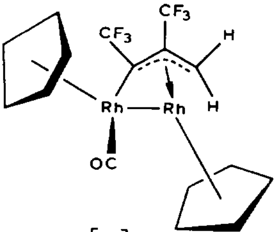
[73]

Methylene-bridged derivatives of [72] ([74] $R^1 = R^2 = H$, CO_2Et) result when it is treated with the appropriate diazo compound.

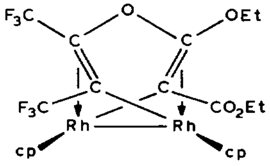


[74]

Both complexes undergo alkylidene to alkyne migration reactions, the first more readily than the second, but the products [75] and [76] are quite



[75]



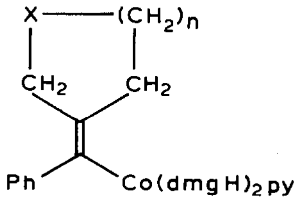
[76]

different (refs. 148, 149). An original rationale for the study of the alkylidene-bridged binuclear complexes $[cp_2MM'(CO)_2(\mu\text{-}CRR')]$ (M = M' = Co, Rh. M = Co; M' = Rh, Ir. R,R' = various combinations of H and alkyl) and their pentamethylcyclopentadienyl analogs was the hope that they could serve as models for possible surface intermediates in the Fischer-Tropsch reaction. Now an extensive report on thermolysis reactions of these species has appeared. Despite the formation of complex mixtures in most instances, a few significant reaction paths were discerned. One is elimination of the bridging moiety as a carbene which then abstracts two hydrogen atoms from the cyclopentadienyl ligands to form a hydrocarbon with the same number of carbon atoms or, for those where R and/or R' is an alkyl group, which may undergo rearrangements following release from the complex. Another is coupling of two carbene moieties to form an olefin, a process which is particularly prevalent in analogs containing two bridging alkylidene moieties. In those instances where the alkylidene fragment is a carbocycle, both ring-opening and isomerization to give a cyclic olefin occurred (ref. 150).

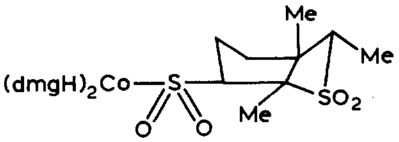
A new series of methylene-bridged iridium dimers has been synthesized from $[Ir_2(CO)_2L_2(\mu\text{-}SBu^t)_2]$ and diiodo- or dibromomethane and formulated as $[Ir_2X_2(CO)_2L_2(\mu\text{-}CH_2)]$ (X = I; L = CO, $P(OMe)_3$, PMe_3, $PMePh_2$, PPh_3. X = Br; L = PPh_3). The trimethylphosphine and trimethylphosphite complexes were formed as mixtures of two isomers. Each isomer was fluxional but no interconversion between isomers was detected. Stepwise removal of iodide from several of these complexes could be accomplished with silver perchlorate or hexafluorophosphate and additional neutral ligands (CO, phosphines or phosphites) coordinated (ref. 151).

Although some groups continue to study alkylcobaloxime complexes as possible models for reactions mediated by vitamin B_{12}, there appears to be a growing opinion that these may not be the best model compounds. The work in this area has, however, shown that cobaloxime systems may be useful in other areas of organic synthesis. Hydrogenation of a mixture of

$[\mathrm{Co(dmgH)_2py}]$ and the enol ester of methyl pyruvate in methanol yields $[\mathrm{(Me(MeC(O)O)(CO_2Me)C)Co(dmgH)_2py}]$ as the first example of an organocobaloxime with an acetoxy substituent on a tertiary α-carbon (ref. 152). Also a sugar derivative, $[\mathrm{RCo(dmgH)_2py}]$ (R = 1,2:3,4-diisopropylidene-6-deoxy-6-yl-α-D-galactopyranose), has been prepared from $[\mathrm{Co(dmgH)_2py}]^-$ and the iodo derivative of the sugar (ref. 153). Radical pathways are involved in the reactions of $[\mathrm{(alkenyl)Co(dmgH)_2py}]$ with arenesulfonyl iodides and with polyhalomethanes. In the first instance aryl alkenyl sulfonates are formed while in the latter trihaloalkanes result which may be acyclic or cyclic depending on the concentration of the polyhalomethane used (refs. 154, 155). Photolysis of $[\mathrm{(PhC{\equiv}CCH_2X(CH_2)_n)Co(dmgH)_2py}]$ ($n = 2,3$; X = $\mathrm{CH_2O}$) forms [77] ($n = 1,2$) while $[\mathrm{(H_2C{=}CH(CH_2)_3CHMe)Co(dmgH)_2py}]$ forms $[\mathrm{(2\text{-}methylcyclopropylmethyl)Co(dmgH)_2py}]$. If carbon tetrachloride is present, no cyclization occurs and the products observed are those derived from reaction of carbon tetrachloride with the radicals produced by cobalt-carbon bond homolysis (ref. 156). Racemization occurs when optically active $[\mathrm{(MeCHDCHPh)Co(dmgH)_2}]$ reacts with sulfur dioxide to form $[\mathrm{(MeCHD\text{-}CHPhS(O)_2)Co(dmgH)_2}]$ while $[\mathrm{(Me_2C{=}CH(CH_2)_2CH(Me))Co(dmgH)_2}]$ and sulfur dioxide form [78]. Both results suggest that the insertion proceeds *via* a non-chain radical process (ref. 157). Photolytic oxygenation of $[\mathrm{RCo(dmgH)_2py}]$ (R = $\mathrm{CH(CO_2Et)CH_2CH{=}CH_2}$, $\mathrm{CH_2CH(CO_2Et)CH{=}CH_2}$, $\mathrm{CH_2CH_2CH{=}CHCO_2Et}$) yields the same peroxo species, $[\mathrm{(EtO_2CCH{=}CHCH(Me)O\text{-}O)Co(dmgH)_2py}]$ in each case. This is proposed to indicate a process where photolytic homolysis of the cobalt-carbon occurs initially followed by rearrangement of the organic radical to its most stable form before reaction with oxygen (ref. 158).



[77]

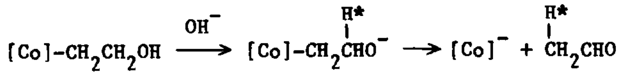


[78]

This contrasts with a second study of the oxygenation of [(MeCHPh)Co(dmgH)$_2$-py] where some degree of stereospecificity in the reaction is claimed. Although not clear from the abstract, it may be that this reaction did not involve photolysis which could account for the different result (ref. 159).

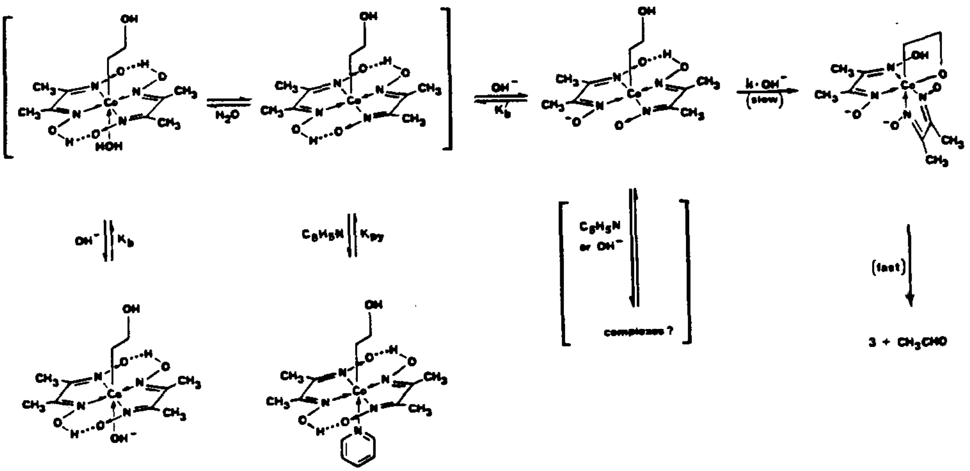
Several extensive studies of the rates of replacement of nitrogen bases by trimethylphosphite in organocobaloximes indicate that the rate increases as the trans-influence of the organic group increases. This was determined from the observation that the ^{31}P coordination chemical shift for the phosphite ligand in the product decreased as the rate of replacement increased indicating a weaker binding of the axial base. Indeed the cobalt-phosphorus bond in [(adamantyl)Co(dmgH)$_2$(P(OMe)$_3$)], which is the species showing the fastest rate, is extremely long. In a similar comparison of base-exchange reactions between [RCo(dmgH)$_2$B] and [RCo(saloph)B] using trimethylphosphite it was found that in addition to the trans effect noted above there is apparently a cis effect since the saloph complex showed much taster rates. The results of these studies suggest that when the axial R group is a good σ-donor there should be a significant concentration of the five-coordinate base-off form in solution and that where the axial base is weakly coordinated, cobalt-carbon bond cleavage should be facile (refs. 160-162). This conclusion concerning the effect of the σ-donor capacity of the organic group on the lability of the axial base was also reached in a thermogravimetric study of the decomposition of [RCo(salen)py] (R = alkyl) in which pyridine loss occurs initially (ref. 163). The complexes [RCo((DO)(DOH)pn)(H$_2$O)]ClO$_4$ (R = Et, Pr^i, CH$_2$CF$_3$, Np) can be prepared from [Co((DO)(DOH)pn)]Cl$_2$ by successive reaction with aqueous alkali, the appropriate alkyl halide, sodium borohydride, silver nitrate and sodium perchlorate. For R = CH$_2$CO$_2$Me, CH$_2$SiMe$_3$, bz it was necessary to modify the reaction sequence by adding methanol, nitric acid and then sodium perchlorate following the borohydride reduction. The kinetics of replacement of water by pyridine were measured and it was concluded that these species may be better models for vitamin B$_{12}$ chemistry than the analogous cobaloximes (ref. 164). A similar conclusion that cobaloximes are poor models for B$_{12}$ when steric effects and hydrogen bonding are important in the biological systems was reached in a study comparing the replacement of water in [MeCo(dmgH)$_2$(H$_2$O)] and aquocobalamin by neutral sulfur ligands such as thioureas, thioacetamide and thiosemicarbazide (ref. 165). Standard methods were used to prepare [(CF$_3$CH$_2$)Co(dmgH)$_2$(L)] (L = PPh$_3$, P(OMe)$_3$, 4-CNpy) and the structures were determined. Variations in the C-C-F and F-C-F angles were proposed to reflect differences in the carbanionic character of the alkyl group (ref. 166). Approximate ab initio calculations have been performed on $[Co(NH_3)_5Me]^{2+}$ to analyze the properties of the cobalt-carbon bond. The biggest effect on the bond strength appeared to be the extent of angular distortion of the alkyl group rather than any puckering of the equatorial ligands or the nature of the trans ligand. The results were taken to suggest, in contrast to some earlier conclusions, that in vitamin B_{12} systems any steric interactions which cause an angular distortion in the alkyl group will be the major factor promoting cobalt-carbon bond homolysis (ref. 167).

The base-free dimers $[RCo(dmgH)_2]_2$ (R = Me, CH_2Cl) form the ligand-bridged dimers $[RCo(dmgH)_2(\mu\text{-}L)(dmgH)_2CoR]$ (L = dth, pyz, 4,4'-bipyridyl, DPPE). Analogous behavior is noted for related BAE and salen species (ref. 168). The complexes $[(XCH_2CH_2)Co(dmgH)_2py]$ (X = CN, CO_2Me) rearrange to $[(MeCHX)Co(dmgH)_2py]$ upon photolysis. Presumably cobalt-carbon bond homolysis occurs with the alkyl radical formed undergoing rearrangement (ref. 169). In aqueous acid, $[(ROCH_2CH_2)Co(dmgH)_2(H_2O)]$ (R = H, Et, Ph) decomposes to form ethylene. A kinetic study revealed the presence of a common intermediate in all three systems whose decomposition is the rate-limiting step irrespective of the acidity of the medium and which is seen to accumulate at high acid concentration. It is proposed to be a σ-bonded ethylcarbonium ion possibly stabilized by σ-π hyperconjugation (ref. 170). In related work, the pK_a's of carboxymethyl- and 2-carboxyethylcobalamin and -cobinamide have been determined and compared with those for the corresponding cobaloximes. The results were interpreted to suggest a significantly greater degree of hyperconjugation in the cobalt-alkyl interaction in the former two species (ref. 171). In contrast to the acid-induced decomposition of $[(HOCH_2CH_2)Co(dmgH)_2(H_2O)]$ just discussed, the hydroxide-induced decomposition of the pyridine analog yields acetaldehyde in a reaction which occurs much more readily than for many other cobaloxime complexes. Similar results were obtained with analogs in which the alkyl group was $CH_2CH(OH)Me$, cis-or trans-2-hydroxycyclohexyl, trans-2-hydroxycyclopentyl or exo-2-hydroxynorborn-endo-6-ylmethyl and decomposition formed the appropriate ketones. In contrast to results reported previously by Schrauzer, the hydroxide dependence of the rates was not uniformly first order but instead was second order in hydroxide at very low hydroxide concentration, became first order at larger concentrations and tended towards zeroth order at concentrations greater than 0.5 N. Also, the 2-hydroxypropyl complex showed a very small deuterium isotope effect in contrast to earlier reports and the decomposition was inhibited by excess pyridine. The results are thus incompatible with Schrauzer's mechanism (Scheme XV) and that of Scheme XVI (3 = $[Co(dmgH)_2py]^-$ is proposed.



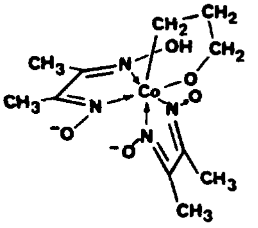
$$[Co]-CH_2CH_2OH \xrightarrow{OH^-} [Co]-CH_2\overset{H*}{\overset{|}{C}}HO^- \longrightarrow [Co]^- + \overset{H*}{\overset{|}{C}}H_2CHO$$

Scheme XV



Scheme XVI

Support for the cyclic intermediate was provided by the observation that while $[(HO(CH_2)_3)Co(dmgH)_2py]$ is reasonably stable in aqueous base, addition of two equivalents of sodium deuteroxide to a DMSO solution of the complex formed a species characterized as [79] (ref. 172). The electrochemical behavior of $[RCo(dmgH)_2(H_2O)]$ (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i,

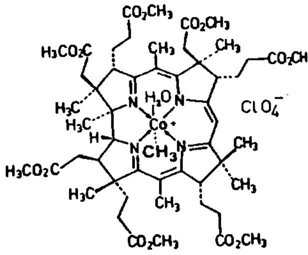


[79]

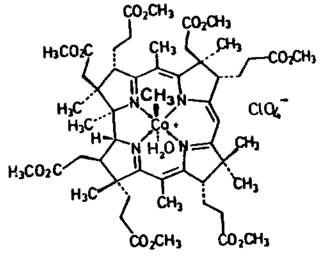
Ph, bz, CH_2CF_3) was examined by cyclic voltammetry in DMF, DMSO and acetonitrile solutions. Two reduction steps were observed, the first of which was quasi-reversible and the other reversible. The first step is considered to form the radical anion of the intact complex in which a reversible homolysis of the cobalt-carbon bond competes with the second electron transfer step. The stability of the radical anion is dependent upon both the solvent on the the nature of the alkyl group (ref. 173).

Kinetic studies of the acid-induced decomposition of $[RCo(7\text{-}Mesalen)(en)]^+$ (R = Me, Et, Bu^n) suggest that at low concentrations of acid a reversible formation of $[RCo(7\text{-}Mesalen)(H_2O)_2]^+$ occurs. At higher acidities, formation of this species is followed by cobalt-carbon bond homolysis. The replacement of ethylenediamine by various mono- and bidentate N- and O-donor ligands was also studied (refs. 174, 175). [Co(salen)] functions as an electrocatalyst for the carboxylation of allylic and benzylic halides by carbon dioxide and for the reduction of a variety of organic halides. Alkyl-cobalt intermediates are proposed to be formed (refs. 176, 177). Acidification of [RCo(TPP)] and [RCo(OEP)] (R = Me, Et, Ph, *p*-tolyl, *p*-anisyl, *p*-BrC_6H_4, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$, C(Ph)=CHMe, C(*p*-$NO_2C_6H_4$)=CH_2) with TFA results in migration of R to the porphyrin ring followed by demetallation (ref. 178). A similar migration-demetallation process occurs when [(*p*-RC_6H_4)Co(TPP)] (R = MeO, Me, H, Br, Cl, NO_2) is allowed to react with oxygen in the presence of trichloroacetic acid or with tris(4-bromophenyl)-aminium hexachloroantimonate. In both instances the aryl migration is the rate-limiting step. Cyclic voltammetric studies show the presence of two oxidation steps attributable to oxidations of the porphyrin π-system (ref. 179). EPR studies of the photolysis products of [RCo(acacen)] (R = Me, Pr^n, Bu^n, Bu^i) have been reported (ref. 180) as have electrochemical experiments on *trans*-$[Me_2Co(TIM)]ClO_4$ (ref. 181). The latter complex methylates Pb(II) to $[PbMe]^+$ and partially to $[PbMe_2]$ as well as converting both $[PbMe_2]^{2+}$ and $[PbMe_3]^+$ to $[PbMe_4]$ (ref. 182).

In aqueous solution iodine reacts with methylcobalamin to give aquocobalamin and methyl iodide while in the presence of chloride ion the product is methyl chloride. It is proposed that the initial step is electron transfer from the cobalamin to iodine to form the radical cation of the methylcobalamin which subsequently undergoes a nucleophile-induced heterolytic cleavage of the cobalt-carbon bond (ref. 183). However in the oxidative decomposition of benzylcobalamin by oxygen, 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy or iron(III) the first two processes appear to involve a rate-determining cobalt-carbon bond homolysis. The last does appear to proceed *via* a slow electron transfer in an adduct of the iron with the cobalamin (ref. 184). From proton NMR spectra, a monomer-dimer equilibrium exists for methylcobalamin in neutral aqueous solution. The analogous ethylcobalamin shows a lesser tendency to dimerize but when the alkyl group is *n*-propyl or 5'-deoxyadenosyl, no dimerization is detected. The major interaction in the dimer is thought to be that between the π-systems of the corrin rings (ref. 185). The proton and phosphorus-31 NMR spectra of a series of alkyl cobalamins (alkyl = CH_2CN, CH_2CF_3, Me, Et, Pr^n, Bu^s), as well as aquo- and cyanocobalamin, containing phosphorus ligands have been measured and the suggestion is made that trends in the chemical shifts observed may be useful in assessing conformational and structural changes in these species as has been done in model compounds (ref. 186). Rate data for the dealkylation of alkylcobinamides (alkyl = Et, Np, cy) in both base-on and base-off forms suggest that all involve an initial cobalt-carbon bond homolysis step whether or not the net reaction appears to result in β-elimination (ref. 187). Equilibrium constants have been determined for the substitution of water in aquocobalamin and diaquocobinamide by the malonitrile anion. This is the first example of the measurement of this quantity for the coordination of a tetrahedral carbanion to a transition metal and the data suggest that the affinity of Co(III) for this species is similar to that of $[HgMe]^+$ (ref. 188). Model studies to explore the hydrogen abstraction step in the methylmalonyl-SCoA/succinyl-SCoA system revealed no evidence for hydrogen abstraction from an unactivated carbon atom (ref. 189). Methyl tosylate selectively converts heptamethylcob(I)yrinate to [80] while methyl iodide yields 7% of [80] and 73% of [81]. A radical process is proposed for the latter reaction (ref. 190).

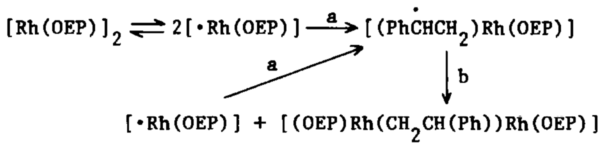


[80]



[81]

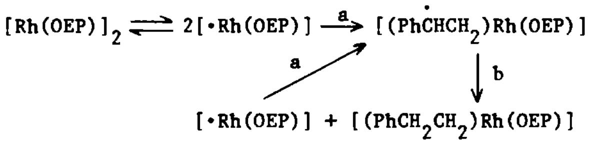
At elevated temperatures, $[Rh(OEP)]_2$ reacts with toluene derivatives to form $[(RC_6H_4)Rh(OEP)]$ (R = H, p-Me, m-Me) and [RhH(OEP)]. The latter tends to lose hydrogen under reaction conditions to reform the starting dimer. Similar behavior is noted with ethylbenzene where [(Ph(Me)CH)Rh(OEP)] forms initially although at higher temperature some $[(PhCH_2CH_2)Rh(OEP)]$ is also seen. With n-propyl- and isopropylbenzene the products are [(Ph(Et)CH)Rh(OEP)] and $[(Ph(Me)CHCH_2)Rh(OEP)]$ respectively. In the former reaction, small quantities of the isomers $[(PhCH_2CH(Me))Rh(OEP)]$ and $[(Ph(CH_2)_3)Rh(OEP)]$ also form while after long reaction times the latter system decomposes to $[Rh(OEP)]_2$ and α-methylstyrene. Thermolysis of [(Ph(Et)CH)Rh(OEP)] and $[(Ph(CH_2)_3)Rh(OEP)]$ gives $[Rh(OEP)]_2$, n-propylbenzene and cis-β-methylstyrene in both instances. The results suggest that activation of carbon-hydrogen bonds in alkylaromatics by $[Rh(OEP)]_2$ generally gives benzylic products if possible. The contrary results of the isopropylbenzene system were explained by a labelling study which showed that initial attack at the benzylic position did in fact occur but that the initial species then rearranged to give the observed product. The alkylation reactions are proposed to occur by a metallo radical process which does not involve free radicals while the thermal decomposition proceeds via initial formation of a geminate radical pair. Thermolysis of [$(PhCH_2)$Rh(OEP)] and [(Ph(Me)CH)Rh(OEP)] in the presence of oxygen yields benzaldehyde and acetophenone respectively (ref. 191). In apparent contrast to these results are those of the reaction of $[Rh(OEP)]_2$ with styrene (which proceeds under considerably milder conditions) to form [(OEP)Rh(CH_2CH(Ph))-Rh(OEP)] which is proposed to involve a free radical chain mechanism as outlined in Scheme XVII. The reaction of styrene with [RhH(OEP)] was found



a) $PhCH{=}CH_2$. b) $[Rh(OEP)]_2$

Scheme XVII

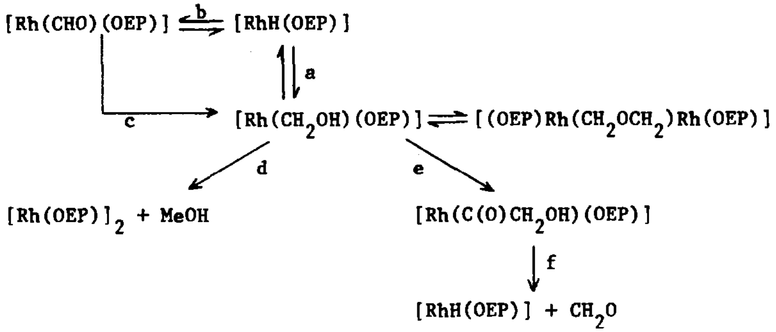
to be catalyzed by $[Rh(OEP)]_2$, again suggesting a radical path as depicted in Scheme XVIII. An analogous radical chain mechanism is also proposed to accomodate the kinetics observed for the reaction of carbon monoxide with



a)$PhCH{=}CH_2$. b) [HRh(OEP)].

Scheme XVIII

[HRh(OEP)] to form [Rh(CHO)(OEP)] which has previously been thought by some to be an example of the elusive carbon monoxide insertion into a metal-hydrogen bond (ref. 192). Other chemistry of [RhH(OEP)] is outlined in Scheme XIX (ref. 193). Acetone can be metallated by $[Rh(OEP)]^+$, generated by chloride abstraction from [RhCl(OEP)] by silver perchlorate in refluxing acetone, to form [Rh(CH_2C(O)Me)(OEP)]. Acetylacetone and ethylacetoacetate can be similarly metallated (ref. 194). The photolytic cleavage of the rhodium-methyl bond in [RhMe(OEP)] has been studied and the reactive excited state determined (refs. 195, 196). [RhI(TPP)] catalyzes the



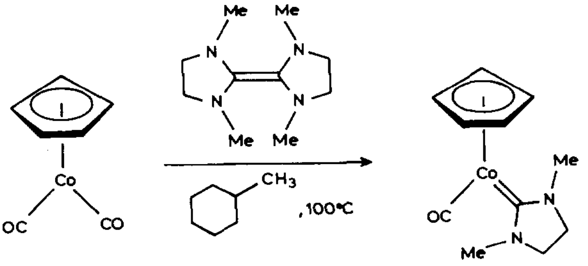
a) CH_2O, C_6D_6. b) CO. c) 1. $AlHBu^i_2$; 2. H_2O. d) Δ, C_6H_6.
e) hν, CO. f) hν.

Scheme XIX

decomposition of diazoesters providing a ready source of ethoxycarbonylcarbene which can insert into aliphatic carbon-hydrogen bonds (ref. 197). The electrochemical or chemical reduction of $[Rh(salen)py_2]PF_6$ produces a mixture of three species, all thought to contain Rh(I), which reacts with phenylacetylene to form $[(PhC{\equiv}C)Rh(salen)py]$. The same mixture failed to react with hex-1-yne and with 3,3,3-trifluoropropyne gave an uncharacterizable tar. By contrast, $[Co(salen)]^-$, prepared <u>in situ</u>, gave a high yield of $[(CF_3{\equiv}C)Co(salen)py]$ but only a low yield of the phenyl acetylide analog (ref. 198).

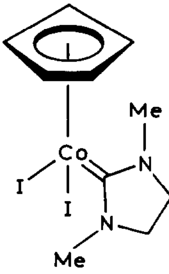
Metal Carbene Complexes

The first example of a mononuclear cobalt carbene complex has been synthesized as depicted in Scheme XX. It reacts with iodine in diethyl

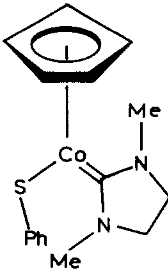


Scheme XX

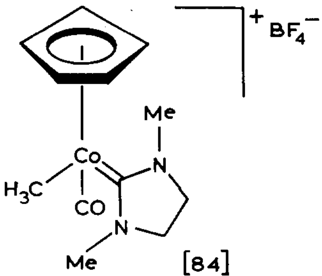
ether, with diphenyldisulfide in toluene or with methyl iodide and silver tetrafluoroborate in methanol to form [82] - [84] respectively (ref. 199). Oxidation of a mixture of hydrated cobalt(II) or rhodium(III) chloride and 2-hydroxyethylisocyanide forms $[M(\overline{{=}COCH_2CH_2NH})_6]Cl_3$ (M = Co, Rh) (ref. 200). The electron-rich olefins [85] (R = Me, Et, Ph, p-tolyl, p-anisyl,



[82]

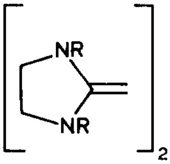


[83]

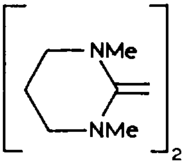


[84]

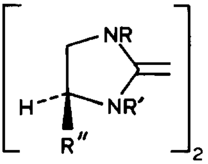
o-anisyl), [86], [87] (R = R' = R" = Me. R" = Bu^i; R = R' = Me, Et; R =



[85]

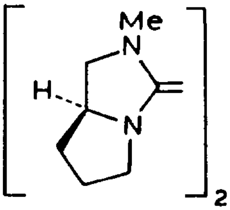


[86]

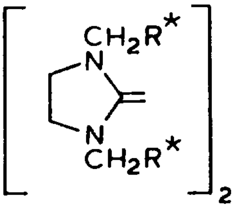


[87]

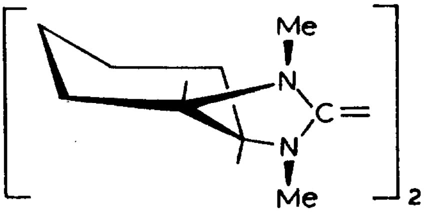
Me, R' = Et), [88], [89] (R* = (+)- and (−)-3-pinene) and [90] have been used to form a large number of rhodium carbene complexes. These are



[88]

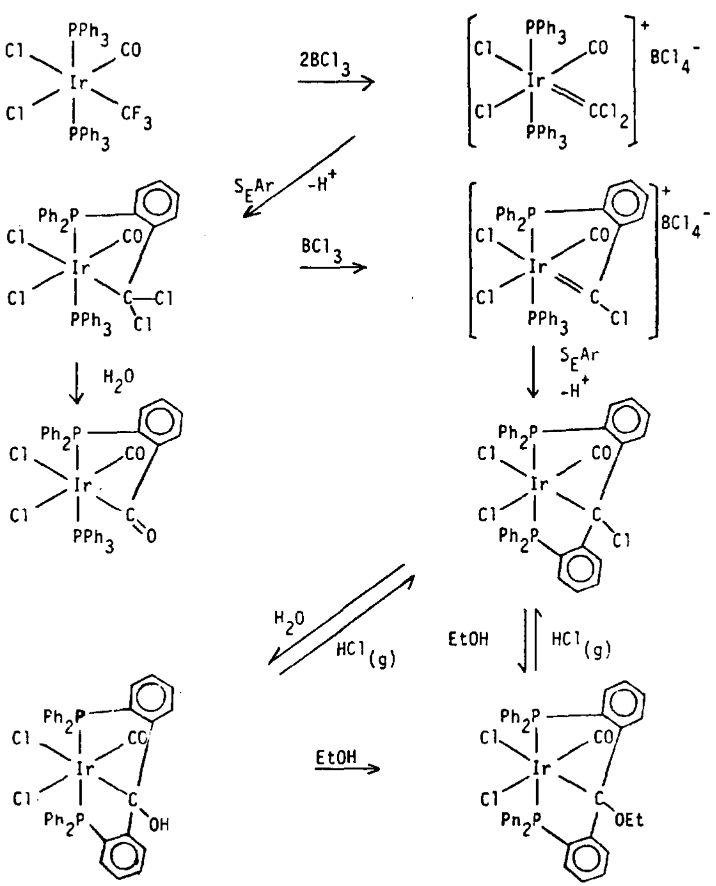


[89]



[90]

generally formed by replacement of one phosphine ligand in [Rh(CO)Cl-(PPh$_3$)$_2$] or [RhCl(PPh$_3$)$_3$] or by cleavage of the chlorine bridge in [RhCl-(COD)]$_2$ by the carbene ligand. In one instance, [87] (R = R' = R" = Me) reacted with [Co(NO)(CO)$_3$] and triphenylphosphine to form [Co(carbene)-(CO)(NO)(PPh$_3$)] (refs. 201, 202). Reaction of [Ir(CF$_3$)Cl$_2$(CO)(PPh$_3$)$_2$] with boron trichloride is proposed to form the dichlorocarbene complex shown in the top right of Scheme XXI although this was not isolated as it rapidly converted to the metallacycle shown in the left hand column. Further chemistry of this latter species is also depicted (ref. 203).

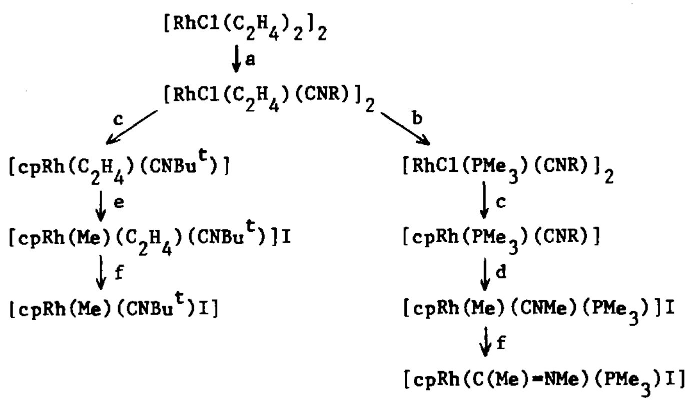


[Scheme XXI]

Metal Isocyanide Complexes

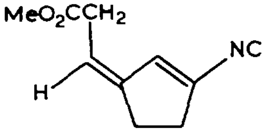
Equilibrium constants for the disproportionation of [Co(CNR)$_4$L]$^+$ (R = 2,6-Me$_2$C$_6$H$_3$; L = PPh$_3$, P(OPh)$_3$, P(*p*-ClC$_6$H$_4$)$_3$. R = *o*-tolyl; L = P(OPh)$_3$, P(*p*-ClC$_6$H$_4$)$_3$. R = mesityl, 2,6-Et$_2$C$_6$H$_3$; L = PPh$_3$) to [Co(CNR)$_3$L$_2$]$^+$ plus [Co(CNR)$_5$]$^+$ have been determined. As expected, these get smaller as the size of the isocyanide substituent increases (ref. 204). In contrast to the reaction described in ref. 200, reaction of 2-hydroxyethyl isocyanide with [CoCl$_2$(PPh$_3$)$_2$] in ethanol forms [Co(CN(CH$_2$)$_2$OH)$_3$(PPh$_3$)$_2$]$^+$ which was isolated as its hexafluorophosphate salt. The analogous rhodium complex as its chloride salt was prepared from [RhCl(PPh$_3$)$_3$] in dichloromethane. Oxidation with iodine formed [RhCl(CN(CH$_2$)$_2$OH)$_3$(PPh$_3$)$_2$](I$_3$)$_2$ (ref. 205).

In work related to that described in ref. 136, the reactions of Scheme XXII were carried out (ref. 206). The isocyanide [91] (L) reacts with [cp'$_2$Rh$_2$X$_4$] (X = Cl, SCN) to form [cp'RhX$_2$(L)] which tends to lose the isocyanide ligand in solution (ref. 207).



a) CNR (R = Me, Bu^t). b) PMe_3. c)Tlcp. d) MeI (R = Me)
e) MeI (R = Bu^t). f) Δ, acetone.

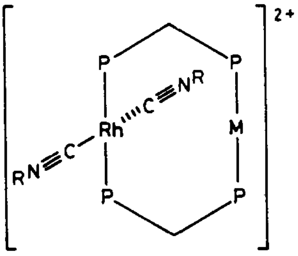
Scheme XXII



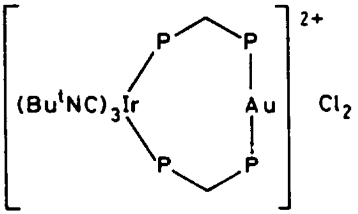
[91]

Iodine oxidatively adds to $[Rh(CNR)_4]^+(TCNQ)^{\dot{-}}$ (R = *p*-tolyl, *p*-anisyl, mesityl, 2,6-$Me_2C_6H_3$) and $[Rh(CNPh)_4]^+(TCNQ)_{0.67}^{\dot{-}}(ClO_4)_{0.33}$ plus TCNQ to form $[RhI_2(CNR)_4]^+(TCNQ)^{\dot{-}}$ and $[Rh(CNPh)_4I_2]^+(TCNQ)_2^{\dot{-}}$ respectively. Both products show semiconductor behavior (ref. 208). The effect of various substituted pyridines (B) on the electrochemical oxidation of $[Rh_2(CNBu^n)_4(DPM)_2]^{2+}$ has been studied. The final products are $[Rh_2B_2(CNBu^n)_4(DPM)_2]^{4+}$ and the ease of oxidation parallels the base strength of B suggesting that the role of the base is to stabilize the oxidized product. Coordination of the base during the second oxidation step is proposed (ref. 209). Vibrational and electronic spectra of $[Rh_2br_4L_2]^{n+}$, $[Rh_2(TMB)_4L_2]^{n+}$ (n = 4; L = H_2O, MeCN. n = 2; L = Cl^-, Br^-, I^-, N_3^- NCS^-) and $[Ir_2(TMB)_4X_2]^{2+}$ (X = Cl, Br, I) have been measured and assigned. Three vibrations appear associated with the $\{LM_2L\}$ unit and although some mixing occurs, the ν_2 vibration appears to be largely ν_{M-M}. The electronic spectra are dominated by an intense $d_\sigma \rightarrow d_{\sigma*}$ transition which is mixed with a ligand-to-metal charge transfer transition. The temperature dependence of this transition suggests a large excited state distortion along the metal-metal stretching coordinate analogous to that in $[Mn_2(CO)_{10}]$ (ref. 210). The photophysics of $[Rh_2L_4]^{2+}$ (L = br, TMB) have been studied but the decay mechanisms associated with the excited states have not yet been fully elucidated (refs. 211, 212).

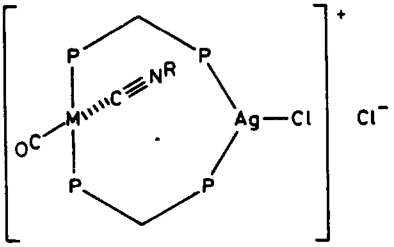
Reaction of $[M_2(CNBu^t)_4(DPM)_2]^{2+}$ with DPM in dichloromethane yields $[M(CNBu^t)_2(DPM)_3]^+$ (M = Rh, Ir) containing monodentate DPM. A trigonal bipyramidal structure with axial isocyanides is proposed. Reaction of the rhodium complex with silver(I) or gold(I) complexes produced [92] (M = Ag, Au). When halide counterions are present, one of these may be coordinated to the coinage metal. Successive treatment of $[IrCl(cyoct)_2]_2$ with four equivalents of DPM, six equivalents of tert-butylisocyanide and $[AuCl(PPh_3)]$ yields [93]. Again, it is possible that chloride coordination to gold occurs. Finally, the complexes [94] (M = Rh, Ir; R = Bu^t, p-tolyl. M = Ir; R = Me) can be prepared from $[Ir(CO)(DPM)_2]Cl$, silver chloride and



[92]



[93]



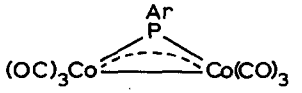
[94]

one equivalent of the isocyanide or from $[Rh(CO)_2Cl]_2$ and DPM under a carbon monoxide atmosphere followed by addition of [AgCl(CNR)]. Here evidence for chloride coordination to the silver was more definite (ref. 213).

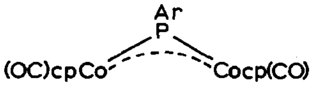
Metal Carbonyl Complexes and Related Compounds

a) Homonuclear Carbonyl Compounds

Recent interest in phosphinidene chemistry has spurred investigations into the reactions of $[Co(CO)_4]^-$ with organophosphorus dichlorides. In THF, $K[Co(CO)_4]$ and $(Me_3Si)_2CHPCl_2$ react to form $[Co_4(\mu_4\text{-}PCH(SiMe_3)_2)(\mu_4\text{-}PCH_2SiMe_3)(\mu\text{-}CO)_2(CO)_8]$ and $[Co_3(\mu_3\text{-}PCH(SiMe_3)_2)(CO)_9]$, both of which are analogous to products formed from dichlorophenylphosphine. However with $2,4,6\text{-}Bu^t{}_3C_6H_2PCl_2$ at low temperature the phosphinidene complex [95] $(Ar = 2,4,6\text{-}Bu^t{}_3C_6H_2)$ was isolated. The "open" analog, [96] was prepared

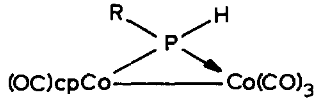


[95]



[96]

similarly from $Na[cp_2Co_2(\mu\text{-}CO)_2]$ while this binuclear radical anion with $(Me_3Si)_2CHPCl_2$ formed [97] $(R = CH(SiMe_3)_2)$. The mechanism of this last

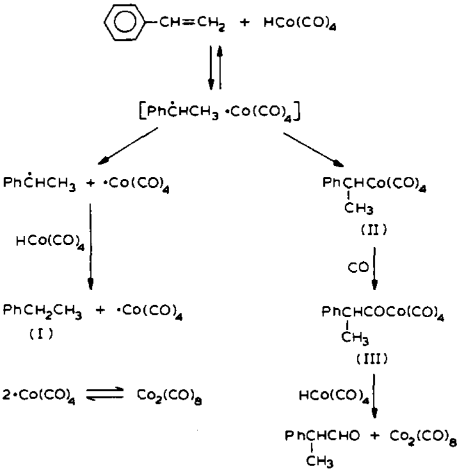


[97]

reaction is unknown but the $\{Co(CO)_3\}$ moiety is thought to derive from $[Co(CO)_4]^-$, present as an impurity in the $Na[cp_2Co_2(\mu\text{-}CO)_2]$ solution. It appears from this work that an extremely bulky substituent on phosphorus is necessary in order to obtain phosphinidene complexes (refs. 214-216). In related work, the phosphorane $(\underline{o}\text{-}\overline{OC_6H_4O)_2P}Cl$ reacts with $Na[\overline{Co(CO)_3}(PPh_3)]$ at low temperature to form the metallophosphorane $[(\underline{o}\text{-}\overline{OC_6H_4O)_2P})Co(CO)_3\text{-}(PPh_3)]$ (ref. 217). The first example of an η^3-1,3-diphosphaallyl complex, $[(\eta^3\text{-}RPCHPR)Co(CO)_3)]$, $(R = 2,4,6\text{-}Bu^t{}_3C_6H_2)$ is formed from $Na[Co(CO)_4]$ and $RP{=}CHPClR$. This is proposed to involve initial formation of $[(RP{=}CHP(R))\text{-}Co(CO)_4]$ but this species was not detected (ref. 218).

In an attempt to prepare a metal-metal bonded cobalt-ruthenium complex, $[cpRu(PPh_3)_2Cl]$ was reacted with $Tl[Co(CO)_4]$ but only the ionic species

$[cpRu(CO)(PPh_3)_2][Co(CO)_4]$ was formed in low yield (ref. 219). Oxidation of a mixture of $[Co_2(CO)_8]$ and triphenylphosphine with ferricinium tetrafluoroborate afforded trans-$[Co(CO)_3(PPh_3)_2]BF_4$ (ref. 220) while electrochemical reduction of $[Co_2(CO)_2(MeN(PF_2)_2)_3]$ forms the binuclear radical anion in which the unpaired electron is delocalized over both metal atoms (ref. 221). The photolysis of $[Co_2(CO)_6(PBu^n{}_3)_2]$ in toluene containing various quinones and phenothiazine has been studied. With ortho-quinones, EPR spectra indicate the formation of a spin adduct formulated as $[(PBu^n{}_3)(CO)_3Co(quinone)]$ and containing a chelated quinone while with para-quinones only the formation of the p-semiquinone radical could be detected (ref. 222). Following work demonstrating that $[Co_2(CO)_8]$ disproportionates in THF solution only when water is present (J. Organomet. Chem., 275(1984)-C25), a new study explored the effects of adding hex-1-ene to a wet THF solution of $[Co_2(CO)_8]$ which had been equilibrated with CO/H_2. Initially a rapid gas uptake, primarily carbon monoxide, was observed followed by a slower uptake of carbon monoxide and hydrogen in equimolar quantities. Under these conditions the initial species formed upon olefin addition is $[C_6H_{13}C(O)Co(CO)_4]$ which is why carbon monoxide is preferentially absorbed at first. On the other hand, if the system is strictly anhydrous or if too much water is present, no hydroformylation occurs under ambient conditions suggesting that the ion pairs $\{[Co(L)_n]^{2+}, 2[Co(CO)_4]^-\}$ (L = CO, THF, H_2O) are somehow involved in the generation of the active catalyst (ref. 223). An earlier report of the involvement of radicals in the reaction of $[HCo(CO)_4]$ with styrene under carbon monoxide has been confirmed by the observation of CIDNP during the reaction and Scheme XXIII is proposed (ref. 224). A comparison has been made of the hydroformylation of dodec-1-ene

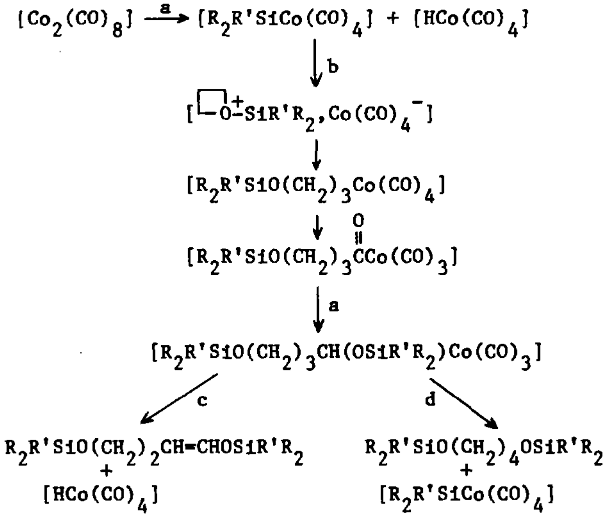


[Scheme XXIII]

catalyzed by $[Co_2(CO)_8]$ plus the bulky phosphines cyclohexyl(1,5-cyclooctandiyl)phosphine and bis(1,5-cyclooctandiyl)biphosphine to determine if such ligands would favor formation of the straight-chain aldehyde. Up to ca 50% conversion, the selectivity was quite high but then a significant drop in the straight-/branched-chain ratio was observed suggesting a decomposition of the ligand had occurred (ref. 225). The possibility of the reversibility of the cobalt-catalyzed hydroformylation has been explored in a study of the reactions of 3-phenyl- and 3,3-diphenylpropan-1-ol with $[Co_2(CO)_8]$ under standard hydroformylation conditions. The appropriate propanols and small amounts of the corresponding olefins were found to form. It was proposed that dehydrogenation of the alcohol to the aldehyde occurred via a radical process followed by decarbonylation and β-hydride elimination to give the parent olefin. Thus the reaction is reversible but the measured rates were so slow that in practice the reverse reactions should not be significant (ref. 226). Another model for cobalt-catalyzed hydroformylation involving two cycles, one using $[Co_2(CO)_8]$ and the other $[HCo(CO)_4]$ as important intermediates, has been proposed (ref. 227).

Two studies of methanol homologation under hydroformylation conditions have appeared. The first uses $[Co_2(CO)_8]$, triphenylphosphine and methyl iodide and the kinetic data suggest the rate-limiting step is the oxidative addition of methyl iodide to a cobalt carbonyl species although oxidative addition of hydrogen as the slow step could not be ruled out (ref. 228). The second uses ruthenium(III) chloride in place of the phosphine and under reaction conditions both $[Co(CO)_4]^-$ and a ruthenium carbonyl iodide of unspecified composition were detected. It is proposed that cobalt complexes catalyze the formation of acetaldehyde which is then hydrogenated in a subsequent step catalyzed by a ruthenium complex (ref. 229). Mixtures of $[Co_2(CO)_8]$ or $[cpCo(CO)_2]$ and its pentamethylcyclopentadienyl analog with diphenylsulfide or -selenide, bromotriphenylgermane or tributyltin chloride catalyze the conversion of methanol or butanol plus acetaldehyde to glycol monoalkyl ethers (ref. 230).

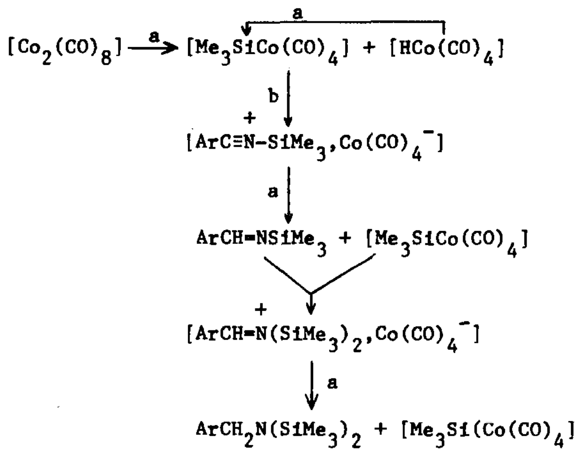
Cobalt carbonyls and derivatives continue to be extensively used to catalyze a variety of organic reactions but in most cases, no mechanistic information has been sought. A mixture of $[Co_2(CO)_8]$ with $[RhH(CO)(PPh_3)_3]$ or $[RhCl(PPh_3)_3]$ forms a moderately active catalyst system for the amidocarbonylation of allylic and homoallylic alcohols but not oxiranes. It is thought that the allylic alcohol is isomerized to the vinylic alcohol by the rhodium complex followed by further reaction on a cobalt center (ref. 231). The course of the reaction of trialkylsilanes with THF in the presence of carbon monoxide and catalytic amounts of $[Co_2(CO)_8]$ is solvent-dependent while with oxetanes it depends on the substituents on silicon. Thus methyldiethylsilane and THF in benzene forms the corresponding 1,5-disiloxypentane while in acetonitrile moderate yields of 1,5-disiloxypent-1-ene are obtained. On the other hand while oxetane reacts with triethylsilane under the same conditions to give 1,4-bis(triethylsiloxy)butane, with tert-butyldimethylsilane a mixture of (Z)- and (E)-1,4-bis(tert-butyldimethylsiloxy)but-1-ene forms. Scheme XXIV is proposed in which the



a) $R_2R'SiH$. b) oxetane. c) β-hydride abstraction, then CO.
d) $R_2R'SiH$ then CO.

Scheme XXIV

$[Co(CO)_4]^-$ formed in step b) attacks a carbon-oxygen bond in the oxetane ring. Aliphatic epoxides and trialkylsilanes are similarly converted into the silyl ethers of 1,3-diols but styrene oxide under the same conditions does not incorporate carbon monoxide into the products which are $Ph(CH_2)_2$-$OSiR'R_2$ and (Z)- plus (E)-$PhCH{=}CHOSiR'R_2$ (R = R' = Et. R = Me, R' = Bu^t). As before, however, with triethylsilane the saturated product predominates while with tert-butyldimethylsilane the olefin mixture is the major product (refs. 232-234). Two other cobalt-catalyzed hydrosilylation systems are those using $[Co_2(CO)_8]$ plus triphenylphosphine to homologate propionaldehyde and carbon monoxide with methyldiethylsilane to 2-(methyldiethylsiloxy)butyraldehyde (ref. 235) and $[Co_2(CO)_8]$ alone to catalyze the reduction of nitriles to disilylamines by trimethylsilane. Scheme XXV is

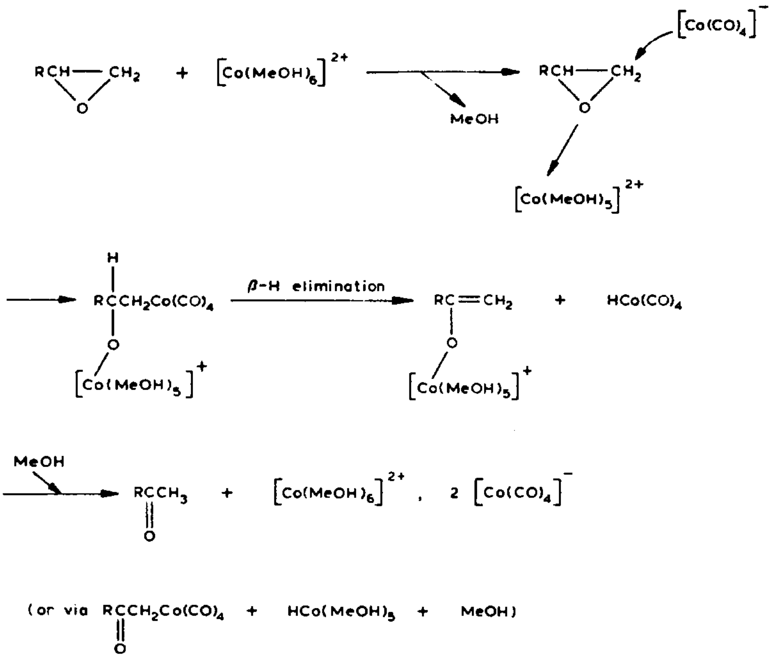


a) $HSiMe_3$. b) ArCN.

Scheme XXV

proposed for the latter system (Ar = RC_6H_4 (R = H, o-Me, m-Me, p-Me, p-MeO, p-Cl, p-Me_2N, p-MeOC(O))) (ref. 236).

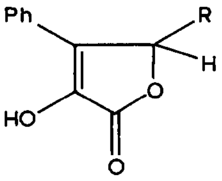
Under rather strenuous conditions (190°C, 900 psi), $[Co_2(CO)_8]$ in the presence of carbon monoxide effects the desulfurization of aromatic and benzylic thiols to the corresponding hydrocarbons and the conversion of analogous disulfides to moderate yields of monosulfides and/or monothioesters (refs. 237, 238). Other systems using $[Co_2(CO)_8]$ as a catalyst precursor include one which converts 1,4-pentadienes to substituted cyclopentanones in refluxing aqueous acetone under carbon monoxide (ref. 239), another for the conversion of 3-cyanopropionaldehyde and methanol to the corresponding dimethylacetal (ref. 240) and a third which effects the hydroesterification of formaldehyde dialkylacetals in dioxane solution containing pyridine under hydroformylation conditions. The key step in this last system is thought to be the reaction of $[HCo(CO)_4]$ with the acetal to give the corresponding alkoxymethylcobalt tetracarbonyl and alcohol (ref. 241). The oxidation of solutions of 3-cyanopropionaldehyde containing $[Co_2(CO)_8]$ forms cobalt(II) complexes of the aldehyde (refs. 242, 243). The epoxidation of styrene and 3-chlorostyrene by 3-chloroperoxybenzoic acid is inhibited to a modest extent by $[Co_2(CO)_8]$ and $[RhCl(CO)(PPh_3)_2]$ (ref. 244) and while no mention is made of further reactions another report shows that $[Co_2(CO)_8]$ is an effective catalyst for the rearrangement of terminal epoxides to methyl ketones in methanol. As $[Co_2(CO)_8]$ reacts with methanol to form $[Co(MeOH)_6]^{2+}$ and $[Co(CO)_4]^-$, the process of Scheme XXVI is proposed with the reaction being initiated by the interaction of $[Co(MeOH)_6]^{2+}$ with the epoxide oxygen (ref. 245).



[Scheme XXVI]

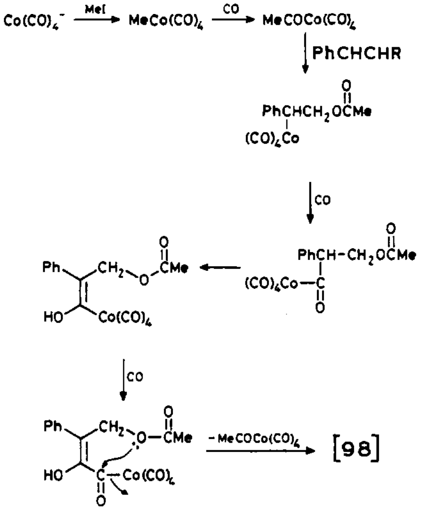
Dicobalt octacarbonyl reacts with carboxydithioates and thiocarboxamides containing polymerizable substituents to give derivatized cobalt carbonyl clusters which can be copolymerized with styrene or methylmethacrylate to give supported clusters (ref. 246). Complexes of the formula $[Co_2(CO)_6L_2]$ (L = neomenthyldiphenylphosphine, diphenylphosphino-6-deoxo-1,2:3,4-diisopropylidene-D-galactose) catalyze the asymmetric hydrogenation of prochiral ketones but optical yields were very low (refs. 247, 248). When L = PPh_3 one has a catalyst for the formylation of iodobenzene to benzaldehyde by carbon monoxide in the presence of a hydrogen donor such as poly(methylhydrosiloxane) (ref. 249). Benzylic halides, ArCH(R)X (Ar = Ph, *p*-ClC_6H_4; R = Me, Ph; X = Cl, Br) are converted to the corresponding carboxylates by carbon monoxide in ethanolic sodium hydroxide containing catalytic quantities of $[Co(CO)_4]^-$. In related work, aryl halides can be carboxylated to esters by $[(ECH_2)Co(CO)_4]$ (E = CO_2Me, CO_2Et, F, CN), carbon monoxide and methanol in the presence of base or by a mixture of an alkyl halide and $[Co(CO)_4]^-$ under the same conditions (refs. 250, 251).

Under phase transfer conditions, $[Co(CO)_4]^-$ catalyzes the carbonylation of chloromethylated polystyrene (ref. 252). Another phase transfer system, $CO/MeI/NaOH/H_2O/C_6H_6/CTAB/[Co_2(CO)_8]$, is effective for the double carbonylation of styrene oxide and its β-methyl analog to form [98] (R = H, Me) for which Scheme XXVII is proposed. The enolization step may be the critical one for the success of this system since α-methylstyrene which is unable to



[98]

enolize after ring-opening does not react under these conditions (ref. 253). In model studies for the catalysis of coal hydrogenation, it was found that cobalt carbonyl hydrides showed a high regioselectivity as catalysts for the hydrogenation of the heterocyclic ring in species such as quinoline, acridine and benzo(h)quinoline (see also ref. 813) (ref. 254).



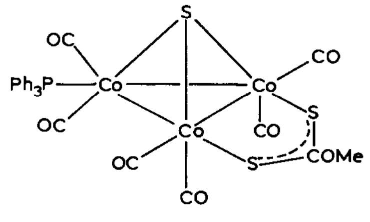
a)PhCHCHR.

Scheme XXVII

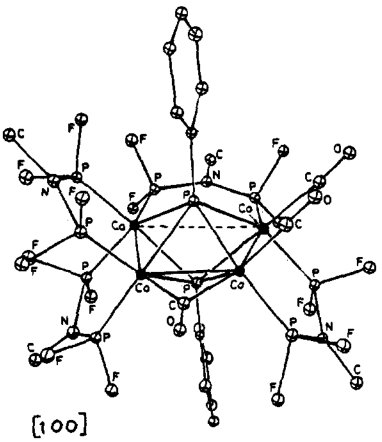
Two theoretical papers concerned with cobalt carbonyls discuss Hartree-Fock-Slater calculations on the protonation energies of $\{Co(CO)_5{}^+\}$ and $[M(CO)_4]^-$ (M = Co, Rh, Ir), among others, as an approach to determining a scale of nucleophilicity for such species (ref. 255) and ab initio, configuration interaction calculations on $[HCo(CO)_4]$ to explore the potential energy surface for the photolytic cleavage of the cobalt-hydrogen bond. The latter authors propose that the initial photoexcited singlet state undergoes intersystem crossing either to a $^3A_1$ state from which Co-H dissociation occurs or to a lower energy ^3E state from which loss of a carbonyl ligand occurs (ref. 256).

Fast pyrolysis of $[Co_2(CO)_8]$ supported on silica containing small amounts of titanium dioxide affords a finely dispersed cobalt catalyst which was used for carbon monoxide hydrogenation. The presence of titanium appears to enhance the affinity of the support for $[Co_2(CO)_8]$ and in the products of carbon monoxide hydrogenation, more light hydrocarbons and alcohols, particularly ethanol, are seen than is the case when titanium is absent (refs. 257, 258). Addition of $[Co_2(CO)_8]$ to HY, CaY and LaY zeolites results in conversion to supported $[Co_4(CO)_{12}]$ while with NaY infrared evidence for $[Co(CO)_4]^-$ and $[Co_6(CO)_{15}]^{2-}$ was also obtained. Thermal decarbonylation of the supported clusters formed Co^{2+} ions on the acidic zeolites and metallic cobalt in the supercages of the others (ref. 259). Pyrolysis of $[H_3SiCo(CO)_4]$ in a flow system forms cobalt silicide and is proposed as a convenient means of depositing films of this material (ref. 260).

The face-capped cluster $[Co_4(CO)_9(TPM)]$ undergoes substitution of one apical carbonyl group by phosphorus ligands ($P(OMe)_3$, PMe_3, $PBu^n{}_3$) at a rate considerably faster than is considered possible were a dissociative process to occur and an I_a mechanism is proposed. With trimethylphosphine the kinetic product is $[Co_4(CO)_7(TPM)(PMe_3)_2]$ with both substitutions occurring at the apical metal atom but subsequent rearrangement occurs to place one trimethylphosphine ligand in a basal site. An analog of this latter species, $[Co_4(CO)_7(DPM)(TPM)]$, shows a stereoselective exchange of carbon monoxide at the apical site (ref. 261). One and two equivalents of $EtN(P(OR)_2)_2$ (L_2: R = Me, Pr^i, Ph) react with $[Co_4(CO)_{12}]$ to form $[Co_4(CO)_7(\mu\text{-}CO)_3(\mu\text{-}L_2)]$ and $[Co_4(CO)_5(\mu\text{-}CO)_3(\mu\text{-}L_2)_2]$ respectively. The structure of the former (R = Ph) was determined which showed the ligand to be bound in axial sites on two basal cobalt atoms (ref. 262). Cobalt(II) chloride and potassium methylxanthate in the presence of carbon monoxide yield $[Co_3(CO)_7(\mu\text{-}S_2COMe)(\mu_3\text{-}S)]$ which forms the triphenylphosphine derivative [99] (ref. 263). While $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ reacts with trimethylphosphite (L) to form $[Co_4(CO)_{8-n}L_n(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ or with one equivalent of DPM or DPPE (L_2) to give $[Co_4(CO)_6(L_2)(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ in which all four cobalt-cobalt bonds remain intact, with an excess of $MeN(PF_2)_2$ the product is [100] in which one metal-metal bond is cleaved. This does not appear to occur with an excess of DPM or DPPE; instead oligomeric products are formed (ref. 264). Other examples of $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PR)_2]$



[99]

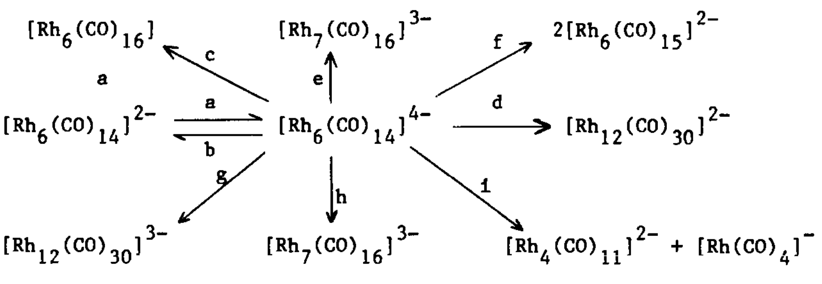


[100]

(R = NEt_2, OBu, p-$Me_2NC_6H_4$) form together with $[Co_3(CO)_9(\mu_3\text{-PR})]$ in the reaction of $[Co_2(CO)_8]$ with the appropriate dichlorophosphine. Addition of $[Fe(CO)_4]^{2-}$ to $[Co_3(CO)_9(\mu_3\text{-PNEt}_2)]$ forms $[Co_2Fe(CO)_9(\mu_3\text{-PNEt}_2)]$ (ref. 265). The cluster $[MeCCo_3(CO)_7(DPM)]$, prepared from DPM and $[MeCCo_3(CO)_9]$ in warm benzene is a modest catalyst for hex-1-ene hydroformylation. At temperatures below 110°C the majority of the cluster can be recovered intact suggesting that this may be an example of cluster catalysis (ref. 266). A slight excess of $Na[Co(CO)_4]$ reacts with $[ClCCo_3(CO)_9]$ in warm diisopropyl ether to form $Na_2[Co_6C(CO)_{15}]$. This air-sensitive cluster can also be synthesized directly from $Na[Co(CO)_4]$ and chloroform but in poorer yield. It reacts with carbon monoxide in THF to yield $[Co_6C(CO)_{14}]^-$, $[Co_2(CO)_8]$, $[Co(CO)_4]^-$ and traces of $[HCCo_3(CO)_9]$, $[OC(CCo_3(CO)_9)_2]$ and $[Co_5(CO)_{15}(C_3H)]$. A better synthesis of $[Co_6C(CO)_{14}]^-$ is the oxidation of $[Co_6C(CO)_{15}]^{2-}$ with iron(III) in acetone. An improved synthesis of $Na_2[Co_8C(CO)_{18}]$ was also developed which involves reaction of $[ClCCo_3(CO)_9]$ with three equivalents of $Na[Co(CO)_4]$ and one half an equivalent of $[Co_4(CO)_{12}]$ in warm diisopropyl ether. The first step is thought to involve oxidation of the initially formed $[Co_6C(CO)_{15}]^{2-}$ to $[Co_6C(CO)_{14}]^-$ and $[Co(CO)_4]^-$ by $[Co_4(CO)_{12}]$. Carbonylation of $[Co_8C(CO)_{18}]^{2-}$ in THF yields $[Co_6C(CO)_{14}]^-$, $[Co(CO)_4]^-$, $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ (ref. 267). Oxidation of $[Co_{13}C_2(CO)_{24}]^{4-}$ with iodine in acetonitrile forms $[Co_{13}C_2(CO)_{12}(\mu\text{-CO})_{12}]^{3-}$ which is rather easily oxidized further, can be reduced back to the tetraanion with zinc and slowly reacts with carbon monoxide to form $[Co(CO)_4]^-$, alkylidyne nonacarbonyltricobalt species and other, as yet unidentified, clusters. The trianionic cluster is isostructural with its tetraanionic parent but the cobalt-carbide distances are somewhat shorter in the former suggesting that the odd electron in the paramagnetic tetraanion is delocalized in a manner which expands the prismatic cavities occupied by the carbides (ref. 268).

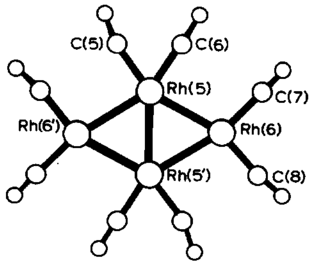
The magnetic properties of the clusters $\{Co_4\}$, $\{Co_4(\mu\text{-}CO)_3\}$ and $\{Co_4(CO)_3(\mu\text{-}CO)_3\}$ have been calculated to assess the effect of the presence of ligands on the magnitude of the paramagnetism of the metal core. Even with six carbonyl ligands, a significant paramagnetism is predicted although it is less than in the bare metal cluster (ref. 269). The clusters $[M_4(CO)_9(TPM)]$ (M = Co, Rh, Ir) have been attached to various solid supports by reaction with phosphinated polystyrene-divinylbenzene or silica but in trial catalytic runs significant leaching of the cluster from the support occurred (ref. 270). Some of these same clusters (M_4 = Co_4, Rh_4, Co_2Rh_2) have been the subject of electrochemical studies. The two cobalt-containing clusters show a quasi-reversible, one-electron reduction and then a second irreversible reduction at very negative potentials which leads to fragmentation. The tetracobalt cluster exhibits an electrocatalytic substitution of a carbonyl ligand on the unsubstituted vertex by phosphines (PMe_3, PMe_2Ph, $PMePh_2$). Rapid loss of a carbonyl ligand from the radical anion is proposed and although there is no requirement that this system behave as does the neutral precursor (see ref. 261) it would have been helpful had the two studies been more closely comparable so that mechanistic comparisons could be possible. The tetrarhodium complex shows irreversible, one-electron reduction and oxidation steps for which a greater degree of reversibility is seen when carbon monoxide is present (ref. 271).

Details have now appeared concerning the nature of the system formed when $[RhCl(CO)(PPh_3)_2]$ is reduced with sodium amalgam under carbon monoxide pressure. Contrary to the original report of Collman, et al., the reaction initially produces a mixture of $[Rh(CO)_4]^-$ and free phosphine. Only when the solution is held under a dynamic vacuum for some time is phosphine coordination seen. The structure of the species isolated, $Na(18\text{-crown-}6)[Rh(CO)_3(PPh_3)]$ shows a tetrahedrally coordinated metal with one carbonyl group interacting with the cation <u>via</u> its oxygen atom. Analogs with trimethylphosphine, dimethylphenylphosphine and methyldiphenylphosphine were also prepared. Reaction of $Na[Rh(CO)_4]$ with DPPE initially forms $Na[Rh(CO)_3(DPPE)]$ in which DPPE is monodentate. Only after standing in solution under nitrogen for several weeks does the chelated complex $[Na(THF)_2][Rh(CO)_2(DPPE)]$ form. In contrast to the triphenylphosphine system, reduction of a mixture of $[RhCl(CO)_2]_2$ and triphenylphosphite with potassium amalgam under carbon monoxide forms a mixture of $[Rh(CO)_4]^-$ and $[Rh(CO)_3(P(OPh)_3)]^-$ (ref. 272). Scheme XXVIII outlines some chemistry of rhodium carbonyl cluster anions (ref. 273). Treatment of $[Rh_{12}C_2(CO)_{24}]^{2-}$ with an excess of potassium hydroxide in methanol yields $[Rh_{12}C_2(CO)_{23}]^{4-}$. The same cluster can be produced by refluxing $[Rh_6C(CO)_{15}]^{2-}$ in diglyme but here other clusters also form. Reaction of the tetraanion with water in acetontrile or acetone gives $[Rh_{12}C_2(CO)_{23}]^{3-}$ among other cluster products. The main difference between $[Rh_{12}C_2(CO)_{24}]^{2-}$ and $[Rh_{12}C_2(CO)_{23}]^{4-}$ is a formal loss of one carbonyl group from the central layer of rhodium atoms and rearrangement of some of the others. The central layers of the di- and tetraanions are shown as [101] and [102] respectively. In the latter, the rhodium-carbon bonds are generally shorter and the carbon oxygen bonds longer than in the former suggesting a delocalization of the increased negative charge over the cluster (ref. 274). Protonation of $[Rh_{14}(CO)_{25}]^{4-}$ with TFA in dichloromethane containing [PPN]Cl under carbon monoxide forms $[Rh_6(CO)_{16}]$ and $[Rh_{12}H_2(CO)_{25}]$ ([103]). The hydrogen atoms were not located but an analysis of the metal-metal distances suggested that one may be within the central octahedron of metal atoms (Rh(4)-Rh(9)) while the other may cap the Rh(10)-Rh(12) face, an arrangement consistent with the observation that one hydrogen is lost as a proton in THF solution (ref. 275). At low temperature, $[RhCl(CO)_2]_2$ reacts with two equivalents of lithium di-tert-butylarsenide to give moderate yields of $[Rh_2(CO)_4(\mu$-As-

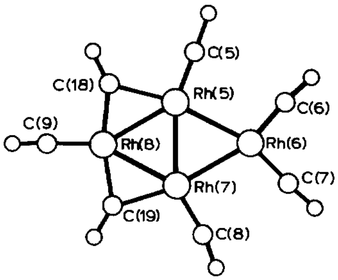


a) 25-30% KOH, H_2O. b) p-tolylSO$_3$H, MeCN. c) xs p-tolylSO$_3$H.
d) MeCO$_2$H. e) $[Rh(CO)_2(MeCN)_2]^+$. f) $1[Rh_6(CO)_{16}]$. g) $3[Rh_6(CO)_{16}]$.
h) $[Rh_6(CO)_{15}]^{2-}$. i) CO.

Scheme XXVIII



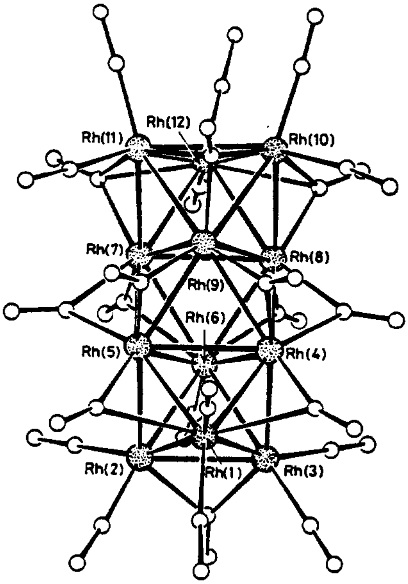
[101]



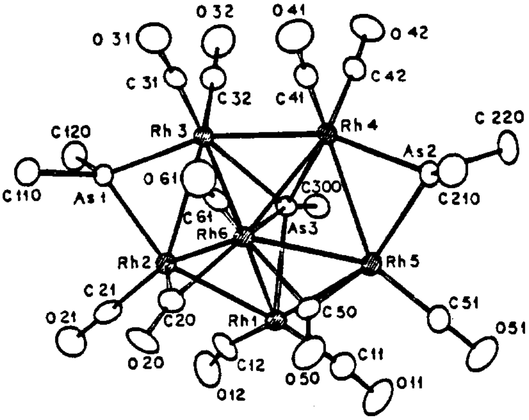
[102]

Bu$^t{}_2)_2$] and the cluster [$Rh_6(CO)_9(\mu\text{-}CO)_2(\mu\text{-}AsBu^t{}_2)_2(\mu_4\text{-}AsBu^t)$] ([104], methyl groups omitted). An unusual feature of this structure is the nearly planar group of five rhodium atoms (ref. 276).

Thermodynamic parameters for the equilibrium between [$Rh_2(CO)_8$] and [$Rh_4(CO)_{12}$] have been recalculated and the new values considered to be more accurate than those determined previously (J. Organometal. Chem., 246(1983) 309) (ref. 277). From a non-empirical, SCF-CI calculation it appears that the π-backbonding component is the major bonding interaction in the linear {Rh(CO)} moiety. In fact this model indicates that the carbon lone pair/Rh 5s σ-interaction is repulsive (ref. 278). EHMO calculations have been performed on [$Rh_2(CO)_4(\mu\text{-}PH_2)_2$], a model for di-tert-butylphosphido-bridged dimers of this sort, to explore the bonding and possible pathways for the interconversions between isomers in which the coordination geometry at both metals is planar (PP), is tetrahedral (TT) or in which one is tetrahedral and the other planar (PT). The relative energies of the three isomers are rather close and increase in the order PP<PT<TT. The PP→PT conversion is symmetry-forbidden if the {Rh_2P_2} core remains planar but is allowed if it is hinged along the phosphorus-phosphorus axis. The PT→TT conversion is



[103]

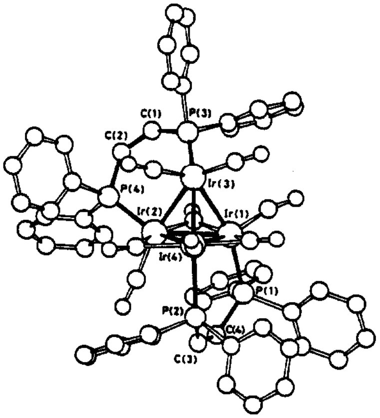


[104]

symmetry-allowed if the least motion path is followed (ref. 279). Several papers have appeared describing various computational efforts aimed at obtaining satisfactory electronic structures for metal clusters including carbonyl clusters of the cobalt group. The first two analyze prior efforts with particular emphasis on octahedral clusters, the role of d electrons in metal-metal bonding and the validity of the isolobal analogy between {BH} and $\{M(CO)_3\}$ fragments. The author concludes that the generality and utility of Wade's rules and the isolobality principle are due to their basis in symmetry arguments. However it is felt that the energetics and details of electronic structure cannot be treated with similar generality but require specific calculations appropriate to the system under consideration (refs. 280, 281). Two further papers discuss a justification of the topological electron counting theory for clusters and a scheme for determining the preferred number of metal atoms in a variety of symmetric close-packed polygons and polyhedra with several high-nuclearity cobalt and rhodium carbonyl clusters used as illustrations (ref. 282, 283). A further series reports on molecular orbital calculations, particularly on high nuclearity rhodium carbonyl clusters, and indicates that the bonding within the cluster involves primarily radial interactions between the surface and the interstitial metal atoms (refs. 284-286). Two final papers propose a simple notation for metal and ligand polyhedra in carbonyl and carbonyl hydride clusters based on a modified Flöppl notation (ref. 287) and a tensor surface harmonic method to obtain cluster bonding orbitals in tetrahedral and octahedral clusters which is said to be a simple means of qualitatively identifying the HOMO and LUMO (ref. 288).

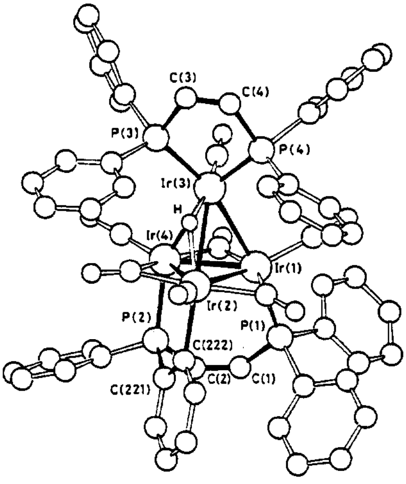
Both $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ are catalyst precursors for olefin hydroformylation with the former converting to the latter under reaction conditions. Although the rates appear to be the same as when $[RhCl(CO)(PPh_3)_2]$ is used, it is suggested that catalysis occurs with intact $[Rh_6(CO)_{16}]$ (ref. 289). Another report claims, however, that under hydroformylation conditions small rhodium carbonyl clusters declusterify, presumably to form the active species, while large clusters, if formed, do so irreversibly. As the large clusters are apparently inactive, their formation results in catalyst deactivation (ref. 290). Either $[Rh_4(CO)_{12}]$ or $[RhCl(CO)_2]_2$ plus six equivalents of triphenylphosphine forms a catalyst for the hydroformylation of vinyl ethers (ref. 291) while $[Rh_6(CO)_{16}]$ mediates the selective hydrogenation of cycloocta- or hexa-1,5-diene to the monoene by hydrogen transfer from isopropanol (ref. 292). A number of rhodium carbonyl clusters catalyze the selective reduction of nitropropane to propionitrile under water-gas-shift conditions (ref. 293) while large clusters such as $[Rh_7(CO)_{16}]^{3-}$ or $[Rh_{12}(CO)_{30}]^{2-}$ provide systems effecting the reduction of nitroarenes to the corresponding anilines in aqueous methanol. Another active system is $[RhCl(CO)_2]_2$ and carbon monoxide contained in benzene together with 5M sodium hydroxide. No phase transfer agent appears necessary in either system and in fact the latter is totally inactivated by addition of tetraalkylammonium halides, presumably because the rhodium clusters associate with the tetraalkylammonium cations and are extracted into the organic phase from which they then precipitate. This can be overcome by the addition of $[Co_2(CO)_8]$ which forms $[Co(CO)_4]^-$ and apparently preferentially associates with the cations thereby forcing the rhodium clusters back into the aqueous phase (ref. 294). Two further applications of $[Rh_4(CO)_{12}]$ are for the carbonylation of mixtures of acetylenes and ethylene to form ethylfuranones and of benzene and ethylene to form styrene. In the former system the addition of alcohols results in formation of alkoxyfuranones while the presence of hydrogen directs the products to α,β-unsaturated ketones (refs. 295, 296).

Reaction of $[Ir_4(CO)_{12}]$ with cis-vdiphos (L_2) in THF at room temperature forms a mixture of $[Ir_4(CO)_7(\mu\text{-}CO)_3(L_2)]$ and [105]. The former product was a mixture of isomers containing chelated and bridging cis-vdiphos ligands. At reflux temperature, the products were [105] and [106] (ref. 297).



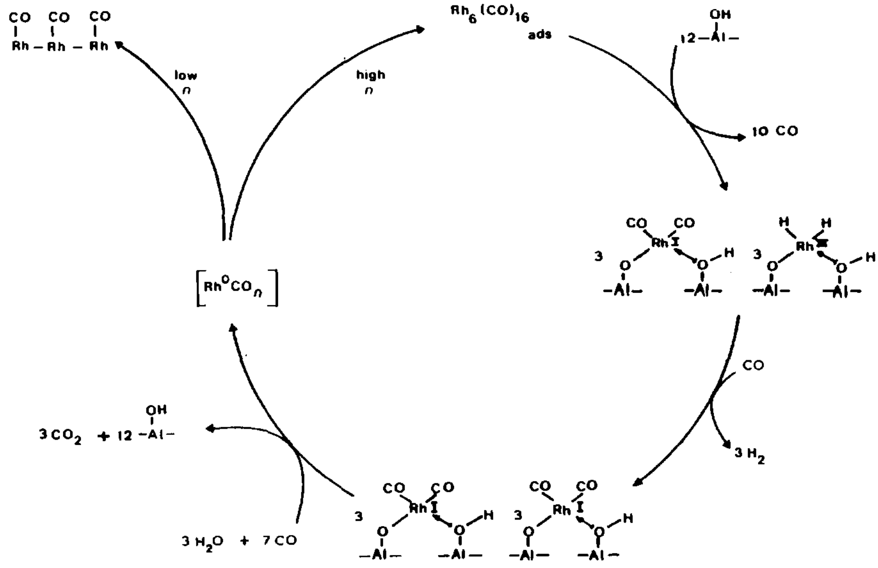
[105]

Sulfur dioxide replaces the olefin ligand in $[Ir_4(CO)_{11}(\text{norborn-2-ene})]$ to form $[Ir_4(CO)_9(\mu\text{-}CO)_2(\mu\text{-}SO_2)]$ which is further converted to $[Ir_4(CO)_8(\mu\text{-}CO)_3(SO_2OMe)]^-$ by methoxide ion. The sulfur dioxide ligand in the initial product can be replaced by phosphines and arsines (ref. 298). Another catalyst system for the reduction of nitrobenzene to aniline is formed from $[Ir_4(CO)_{12}]$ and o-phenanthroline operating under water-gas-shift conditions (ref. 299).



[106]

Laser raman, FTIR and photoacoustic FTIR spectra have been measured for the species formed when $[Co_2(CO)_8]$ and $[RhCl(CO)_2]_2$ are reacted with phosphinated alumina or magnesium oxide or aminated silica. The data suggest that binuclear rhodium species are retained when long, flexible attachments to the surface are used but only mononuclear moieties are seen when the attachment is short and stiff (refs. 300, 301). An in situ raman spectroscopic study of propylene hydroformylation catalyzed by $[Co_2(CO)_6(PPh_3)_2]$ in homogeneous solution or supported on alumina or silica suggests that different intermediates are present in each system (ref. 302). Support of alkylidyne nonacarbonyltricobalt clusters on silica or a NaY zeolite has been accomplished using the $[(EtO)_3SiCH_2CH_2CCo_3(CO)_9]$ derivative while $[PhCCo_3(CO)_9]$ has been supported on silica/alumina by impregnation from pentane solution and by dry mixing. Considerable cluster decomposition occurred during grinding in the latter method so only the former was studied with respect to reactions with hydrogen or carbon monoxide or both. The results suggest that the preference for carbon-carbon over carbon-cobalt bond hydrogenolysis in the cluster is greater in the mixed gas than in hydrogen alone (refs. 303, 304). Small rhodium particles form when $[Rh_6(CO)_{16}]$ is deposited on silica, alumina, titanium dioxide or carbon. These are suggested to form from individual clusters and agglomerate when heated under hydrogen. The smallest particles are less active than the larger ones for ethane hydrogenolysis (ref. 305). The WGSR is catalyzed by $[Rh_6(CO)_{16}]$ and $[RhCl(CO)_2]_2$ on alumina or by $[RhCl(CO)_2]_2$ in NaY or HY zeolites. The zeolite-supported catalysts were much less active and the two alumina-supported systems and seem to give a common catalytic cycle as depicted in Scheme XXIX (ref. 306). Alumina-supported rhodium and iridium adsorb carbon monoxide to give only terminal carbonyl groups. The heat of adsorption was measured (ref. 307). In another study an ultra-dispersed rhodium-on-alumina system was characterized by EXAFS, XPS and EPR before and after treatment with carbon monoxide. Initially three-dimensional metallic crystallites were seen but treatment with carbon monoxide disrupted the metal-metal bonds to give $\{Rh(CO)_2^+\}$ moieties attached to three oxygen atoms of the support (ref. 308). Addition of dimethylphenylphosphine to a carbonylated sample of rhodium supported on NaY zeolite used to catalyze propylene hydroformylation increased the proportion of linear aldehyde in the product. In some instances a shift in the selectivity towards alcohols and ketones was noted (ref. 309).

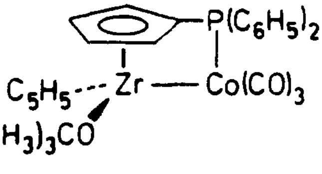


Scheme XXIX

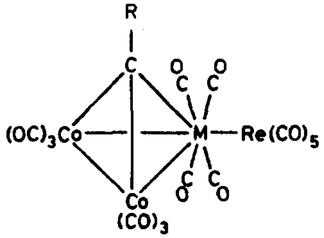
Carbonylation of iridium supported on NaY zeolite forms $\{Ir(CO)_3^+\}$ moieties which are converted to $[Ir_4(CO)_{12}]$ by heating under water-gas-shift conditions. The presence of bridging carbonyl ligands was noted and attributed to a strong interaction of the cluster with the support (ref. 310). In a related study, $[Ir_4(CO)_{12}]$ on dehydrated alumina reacts with residual surface hydroxyl groups on heating to form aluminum-bound formate moieties and dispersed iridium species containing terminal carbonyl groups (ref. 311). Reaction of $[Ir_4(CO)_{12}]$ with 2-diphenylphosphinoethyldiphenylbenzylphosphonium tetrafluoroborate ($[P\text{-}P^+]BF_4$) forms $[Ir_4(CO)_9(P\text{-}P^+)_3](BF_4)_3$ which could be intercalated into hectorite (ref. 312).

b) Heteronuclear Metal-metal Bonded Compounds

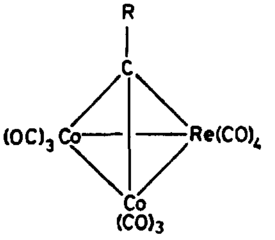
Irradiation of a THF solution of $[Co(CO)_4]^-$ and $[(\eta^5-C_5H_4PPh_2)Zr(cp)-(OBu^t)Cl]$ forms [107] (ref. 313). Standard methods were used to prepare $[cp(\eta^5-C_5H_4CH(Me)Ph)Nb(CO)(Co(CO)_4)]$ which contains a chiral niobium center. The stereostability is not high however because the niobium-cobalt bond is readily cleaved (ref. 314). The metal carbyne moiety in $[(OC)_5-ReM(\equiv CR)(CO)_4]$ (M = Cr, Mo, W; R = p-tolyl) behaves like an alkyne towards $[Co_2(CO)_8]$ and [108] is readily formed. Thermolysis in toluene forms $[M(CO)_6]$ and [109]. An additional product for M = W is [110] (ref. 315). One or both carbonyl groups on cobalt in $[cp'_2Cr_2Co_2(CO)_2(\mu_3-S)_4]$ can be replaced by triphenylphosphine or trimethylphosphite in warm toluene (ref. 316). Related complexes ([111] (X = P, As)) are formed from [112] and $[Co_2(CO)_8]$ (ref. 317) while the cobalt carbonyl also reacts with $[Mo_2S_4-(S_2CNEt_2)_2]$ in acetonitrile to give $[(MeCN)_2(Et_2NCS_2)_2Mo_2Co_2(CO)_4(\mu_3-S)_4]$



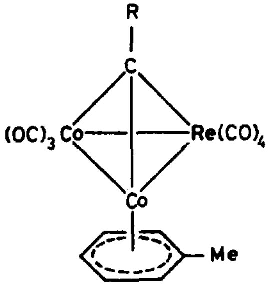
[107]



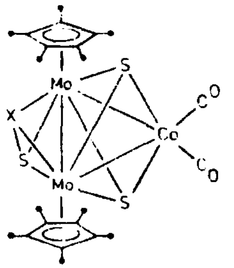
[108]



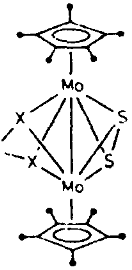
[109]



[110]



[111]



[112]

of similar structure (ref. 318). Transfer of a $\{P_2\}$ fragment occurs when $[Co_2(CO)_6(\mu\text{-}P_2)]$ reacts with $[W_2(OPr^i)_6py_2]$ to form $[W_2(OPr^i)_6py(\mu\text{-}P_2)]$. The fate of the cobalt was not determined but it may have formed $[Co_4(CO)_{12}]$ (ref. 319). The same cobalt complex with $[Cr(CO)_4L(THF)]$ (L = CO, PPh_3, PBu^n_3) forms $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}P_2(Cr(CO)_4L)_n)]$ (n = 1,2) while $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}P_2(Cr(CO)_5))]$ reacts with $[W(CO)_5(THF)]$ to give $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}P_2(W(CO)_5)(Cr(CO)_5))]$ (ref. 320).

A number of facile routes to mixed iron-cobalt carbonyl anions have been reported. At room temperature in dichloromethane $(PPN)_2[Fe_2(CO)_8]$ and $[Co_2(CO)_8]$ form $PPN[FeCo(CO)_8]$ while from $[Fe_4(CO)_{13}]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$ and $[Fe_3W(CO)_{14}]^{2-}$ the product is $[Fe_3Co(\mu\text{-}CO)_3(CO)_{10}]^-$. Here, the bridging carbonyls are on the Fe-Co edges of the cluster. Additional products in all reactions are $[Fe(CO)_5]$ and $[Co(CO)_4]^-$ while the last reaction also forms $[W(CO)_6]$ and other unidentified species. Neither $[Fe_2(CO)_9]$ with $[Co(CO)_4]^-$ nor $[Fe_3(CO)_{11}]^{2-}$ with $[Co_2(CO)_8]$ proved to be a successful route to a Fe_2Co cluster. These syntheses are proposed to involve a radical process outlined in Scheme XXX (ref. 321). The iron-cobalt cluster

$$[Fe_x(CO)_y]^{2-} + [Co_2(CO)_8] \longrightarrow [Fe_x(CO)_y]^{\dot{-}} + [\cdot Co(CO)_4] + [Co(CO)_4]^-$$

$$[Fe_x(CO)_y]^{2-} + [\cdot Co(CO)_4] \longrightarrow [\cdot Fe_xCo(CO)_{y+4}]^{2-}$$

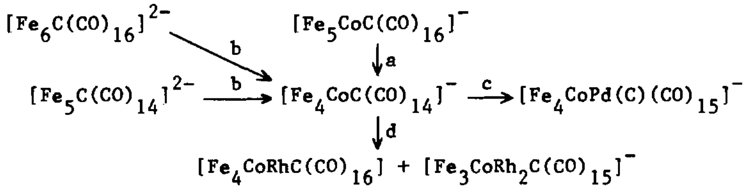
$$[\cdot Fe_xCo(CO)_{y+4}]^{2-} \longrightarrow [\cdot Fe_{x-1}Co(CO)_y]^{2-} + [Fe(CO)_4]$$

$$[\cdot Fe_{x-1}Co(CO)_y]^{2-} + [Co_2(CO)_8] \rightarrow [Fe_{x-1}Co(CO)_y]^- + [\cdot Co(CO)_4] + [Co(CO)_4]^-$$

Scheme XXX

$[Fe_5Co(C)(CO)_{16}]^-$ can be formed by reduction of $[Fe(CO)_5]$ with sodium amalgam followed by addition of $[Co_2(CO)_8]$ or by thermal decomposition of $[Fe_6C(CO)_{16}]^{2-}$ to $[Fe_5C(CO)_{14}]^{2-}$ and subsequent reaction with $[Co_2(CO)_8]$.

Further chemistry of the heterometallic cluster is outlined in Scheme XXXI (refs. 322, 323). Mercury(II) bromide reacts with $[MCo_3(CO)_{12}]^-$ (M = Fe,

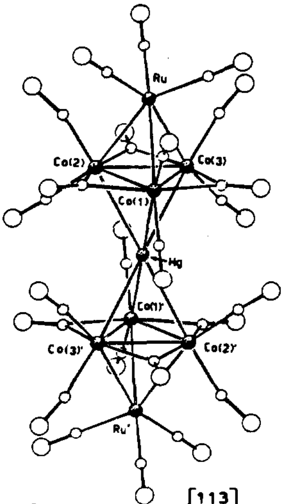


$$\begin{tikzcd}
{[Fe_6C(CO)_{16}]^{2-}} \arrow[dr, "b"] & {[Fe_5CoC(CO)_{16}]^-} \arrow[d, "a"] & \\
{[Fe_5C(CO)_{14}]^{2-}} \arrow[r, "b"] & {[Fe_4CoC(CO)_{14}]^-} \arrow[r, "c"] \arrow[d, "d"] & {[Fe_4CoPd(C)(CO)_{15}]^-} \\
 & {[Fe_4CoRhC(CO)_{16}] + [Fe_3CoRh_2C(CO)_{15}]^-} &
\end{tikzcd}$$

a) 100° C, diglyme. b) $[Co(H_2O)_6]Cl_2$. c) $[(\eta^3-C_3H_5)PdCl_2]$.
d) $[RhCl(CO)_2]_2$

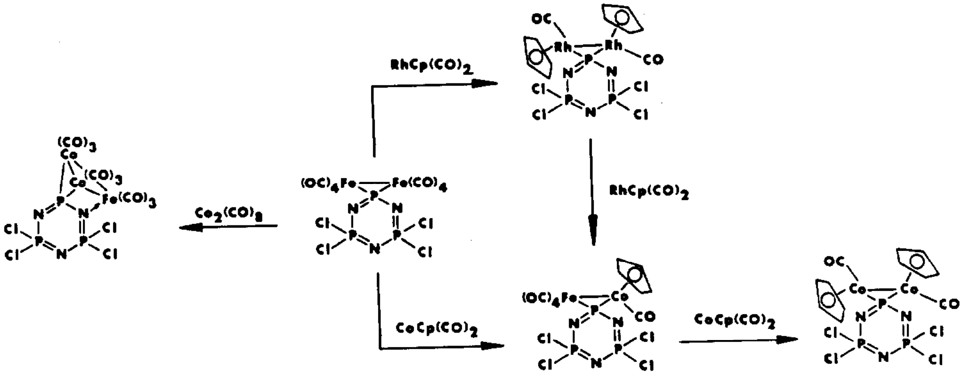
Scheme XXXI

Ru) to form [113]. The iron complex decomposes in refluxing toluene to



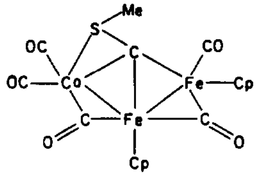
[113]

form metallic mercury, $[(\eta^6-C_6H_5Me)Co_4(CO)_9]$ and other unidentified products while with chloride ion, mercury(II) chloride and $[FeCo_3(CO)_{12}]$ form. Also explored was the reaction of $K[FeCo_3(CO)_{12}]$ with $Bu^n{}_4N[AuI_2]$ from which $Bu^n{}_4N[FeCo_3(\mu-CO)_3(CO)_9(\mu_3-AuCo(CO)_4)]$ was isolated (ref. 324). In THF solution $Na_2[Fe(CO)_4]$ reacts with $[Co_3(CO)_9(\mu_3-PR)]$ (R = Bu^t, Ph, NEt_2) to form $[Fe_2Co(CO)_9(\mu-H)(\mu_3-PR)]$ and with $[FeCo_2(CO)_9(\mu_3-Se)]$ to give $[Fe_2Co(CO)_9(\mu-H)(\mu_3-Se)]$. The hydride ligand appears to bridge the iron-iron bond in both clusters and in polar solvents, deprotonation occurs (ref. 325). Scheme XXXII outlines the synthesis of several metallaphosphazine complexes (ref. 326). Addition of $[Co(CO)_4]^-$ to the μ-thiocarbyne complex $[cp_2Fe_2(CO)_2(\mu-CO)(\mu-CSMe)]PF_6$ under photolytic conditions forms [114]

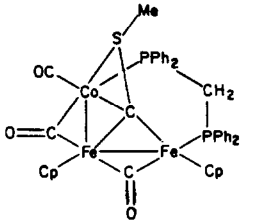


Scheme XXXII

which reacts further with DPM to give [115]. Substitution of one carbonyl ligand on cobalt occurs with several phosphines but no reaction occurs with

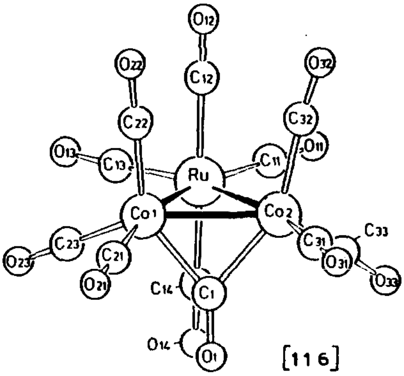


[114]



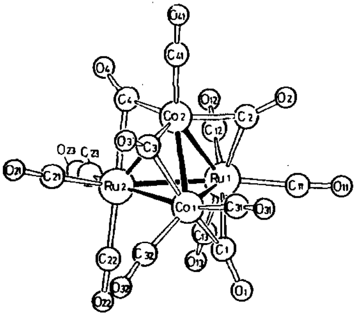
[115]

triphenylarsine or -stibine, pyridine, triethylamine, carbon monoxide, hydrogen, trimethylamine N-oxide or nitrite ion (ref. 327). A full paper has now appeared on the use of $[HFeCo_3(CO)_{12}]$ for the protonation of $[W(N_2)_2(DPPE)_2]$. In aqueous THF the product is $[W(OH)(NNH_2)(DPPE)_2]$-$[FeCo_3(CO)_{12}]$ while in dichloromethane at 5°C a species thought to be $[HW(N_2)_2(DPPE)_2][FeCo_3(CO)_{12}]$ forms although the location of the hydrogen is not certain. The latter reaction at room temperature gave $[WCl_2(DPPE)_2]$-$[FeCo_3(CO)_{12}]$ after two days (ref. 328). A Mössbauer study of $[Fe_2Co(CO)_9$-$(CCO)]^-$ and its triiron analog suggests a significant increase in the electronic symmetry at the iron atom towards which the ketenylidene ligand tilts as compared to the precursors $[Fe_3(CO)_{12}]$ and $[Fe_3(CO)_{10}H]^-$. It is proposed that the increased electronic symmetry resulting from the interaction of the ketenylidene ligand with this iron provides the driving force for the tilt of the ligand (ref. 329). A benzene suspension of $K[Co(CO)_4]$ and $[RuI_2(CO)_4]$ affords a low yield of [116] plus $[Co_4(CO)_{12}]$ and other products. Much better yields result when $K[Co(CO)_4]$ and $[RuCl_2(CO)_3]_2$ are



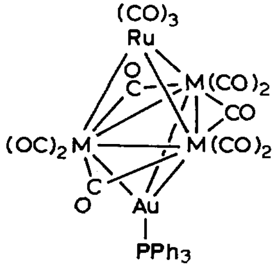
[116]

reacted in water. Heating [116] in hexane converts it to [117] (ref. 330).



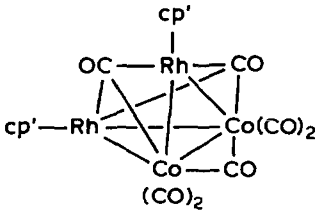
[117]

An inseparable mixture of the clusters $[HRuCo_{3-x}Rh_x(CO)_{12}]$ (x = 0-3) is formed in moderate yield from $[RuCo_2(CO)_{11}]$ and $[Rh(CO)_4]^-$ in THF after treatment with phosphoric acid. Deprotonation of the mixture with potassium hydride followed by addition of $[Au(PPh_3)Cl]$ gave $[(PPh_3)AuRuCo_{3-x}Rh_x(CO)_{12}]$ whose structure is [118] (M = Rh or Co). It was estimated from the



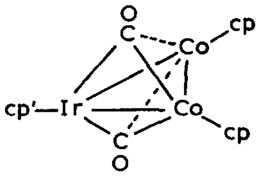
[118]

structural study that the average value of x was 1.4 suggesting that the same mixture of clusters (x = 0-3) was present (ref. 331). At low temperature, $Na[Co(CO)_4]$ reacts with $[cp'RhCl_2]_2$ to form [119] and $[cp'Rh(CO)_2]$ (ref. 332). A related rhodium-iridium complex has been reported previously



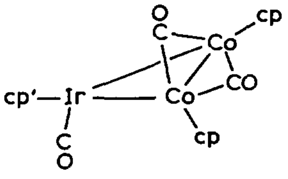
[119]

(J. Organometal. Chem., 278(1984)1, ref. 371). The paramagnetic cluster [120] is formed from [cp'Ir(μ-CO)$_2$Cocp] and [cpCo(C$_2$H$_4$)$_2$]. Despite the

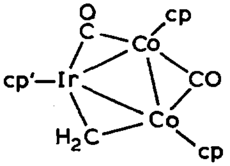


[120]

existence of semi-bridging carbonyl groups in the solid state, the two cyclopentadienyl groups appear equivalent by proton NMR in solution suggesting a "wagging" of these carbonyls between the cobalt atoms or formation of a species containing symmetrically bridging carbonyl groups. Complex [120] adds carbon monoxide to form [121] and reacts with diazomethane to yield [122]. With oxygen, ethylene or [cp'Ir(CO)$_2$], the starting iridium-cobalt dimer is regenerated (ref. 333).

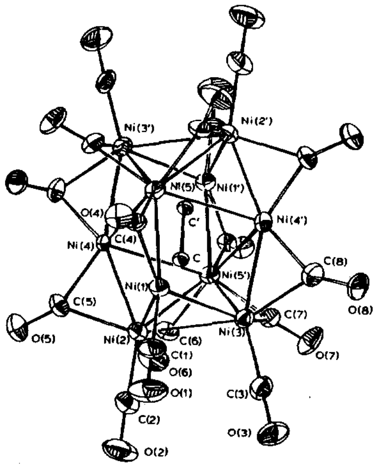


[121]



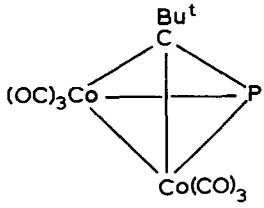
[122]

Another paramagnetic cluster, [123], is formed from [ClCCo$_3$(CO)$_9$] and [Ni$_9$C(CO)$_{17}$]$^{2-}$ in THF. Although it could not be successfully oxidized it was reversibly reduced to the corresponding trianion with sodium. Reaction of [123] with methanolic sodium hydroxide formed [Co$_3$Ni$_7$C$_2$(CO)$_{15}$]$^{3-}$ which

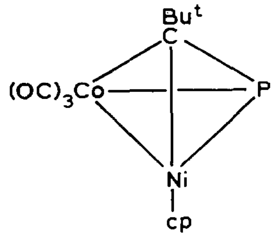


[123]

on acidification gave $[Co_6Ni_2C_2(CO)_{16}]^{2-}$, $[Ni(CO)_4]$ and other unidentified species. All three anions are air-sensitive and readily degrade to mononuclear species on reaction with carbon monoxide (ref. 334). Substitution of a {cpNi} moiety for a $\{Co(CO)_3\}$ unit in the phosphaalkyne complex [124] occurs on reaction with $[cpNi(CO)]_2$ to form [125]. This species can also



[124]

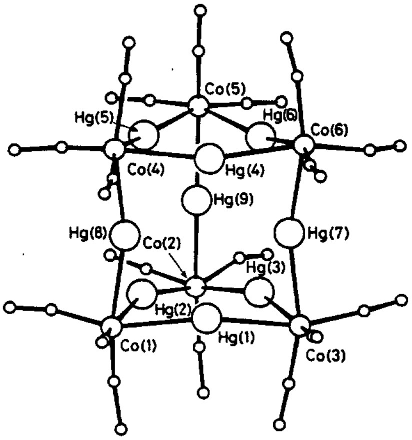


[125]

be prepared in low yield from $Bu^tC{\equiv}P$ and $[cpNi(\mu\text{-}CO)_2Co(CO)_3]$ but attempts to form it by displacement of an acetylene from $[cpNi(\mu\text{-acetylene})Co(CO)_3]$ by the phosphaalkyne failed. Coordination of $\{ML_n\}$ fragments (ML_n = $W(CO)_5$, $cpMn(CO)_2$) to phosphorus in [125] occurs on reaction with $[ML_n(THF)]$ (see also ref. 779). Attempts to form a cobalt-manganese analog of [125] from $[CoMn(CO)_9]$ and $Bu^tC{\equiv}P$ failed and only [124] and $[Mn_2(CO)_{10}]$ were obtained. Other efforts to prepare mixed-metal clusters of the phosphaalkyne from $[RhCo_2(CO)_{11}]$ or $[CoMn(CO)_9]$ and $[W(CO)_5(THF)]$ formed only the $\{W(CO)_5\}$ adduct of [124] and $[Ru_3(CO)_{12}]$ or $[Mn_2(CO)_{10}]$ respectively (ref. 335).

Two products from the reaction of copper(I) chloride with $Na[Co(CO)_4]$ are $[Cu_4(Co(CO)_4)_4]$ (see J. Organometal. Chem., 305(1986)1, ref. 321) and

$[Cu(Co(CO)_4)]_n$. The latter exists in the solid state as an infinite, zig-zag chain of metal atoms (ref. 336). In related work, addition of $Tl[Co(CO)_4]$ to [Cu(TMEDA)I] under carbon monoxide forms $[(TMEDA)Cu(\mu\text{-}CO)Co(CO)_3]$ in which the unique carbonyl group is semi-bridging and the metal-metal bond appears to have multiple bond character. The same reaction with $[L_2CuCl]$ (L_2 = DPPE, dmpe, DPM, DPPB; L = PPh_3, PPh_2Me, $PBu^n{}_3$) forms analogous $[L_2Cu(\mu\text{-}CO)Co(CO)_3]$ species (ref. 337). Removal of one carbonyl ligand from $[(Ph_3P)AuCo(CO)_4]$ with trimethylamine N-oxide in the presence of triphenylphosphine forms $[(Ph_3P)AuCo(CO)_3(PPh_3)]$ in which the {P-Au-Co-P} moiety is nearly linear (ref. 338). On heating, $[M(Co(CO)_4)_2]$ (M = Zn,Cd) converts to $[Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}M(Co(CO)_4)_2)]$. The latter complex (M = Zn) reacts with triphenyltin chloride in diethyl ether to form $[(Ph_3Sn)Co(CO)_4]$ but in dichloromethane an additional product is $[Co_2(CO)_7Zn_2Cl_2]_x$ (ref. 339). An unusual mercury-cobalt cluster, [126], is formed in low yield

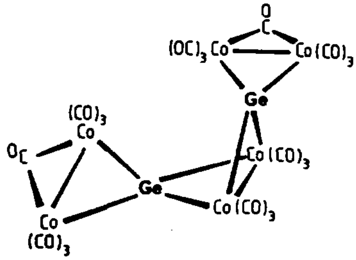


[126]

from a mixture of $[Hg(Co(CO)_4)_2]$ and mercury(II) cyanide in aqueous sodium hydroxide (ref. 340) while the complexes $[XHgCo(CO)_3L]$ (X = Cl, Br; L = $PBu^t{}_3$, $P(OMe)_3$, $P(OEt)_3$, $PEt(OEt)_2$, $PEt_2(OEt)$, PEt_2NEt_2, PEt_3, $PBu^n{}_3$, $PEt(NEt_2)_2$, $P(NEt_2)_3$) tend to dimerize. Carbonyl stretching frequencies and force constants were measured for the latter series (ref. 341).

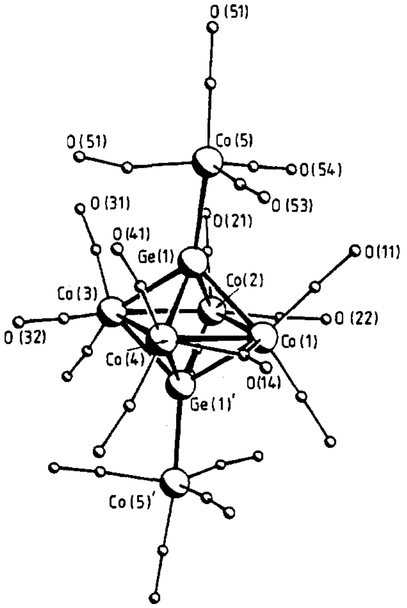
While the metal-metal bonded complex $[cp'_2Sm(THF)Co(CO)_4]$ can be obtained from $[cp'_2Sm(THF)]$ and $[Co_2(CO)_8]$ in pentane, reaction of the cobalt carbonyl with samarium(II) iodide or $[cp'Sm(THF)(\mu\text{-}I)]_2$ in THF forms only the ionic species $[SmI_2(THF)_5][Co(CO)_4]$ and $[cp'SmI(THF)_2][Co(CO)_4]$. The latter product could not be obtained pure and the structure proposed is only tentative. It reacted further in THF solution to form a mixture of the former species and $[cp'_2Sm(THF)Co(CO)_4]$ (ref. 342). Other ionic species, $[Ln(THF)_n][Co(CO)_4]_2$ (Ln = Sm, Eu, Yb; n = 3,4), are obtained from the corresponding lanthanide metal and $Hg[Co(CO)_4]_2$ or from the lanthanide diiodide and $Tl[Co(CO)_4]$ (ref. 343) while $[(\eta^5\text{-}C_5H_4R)M(CO)_2]$ (M = Co; R = H, Me, $SiMe_3$. M = Rh; R = H) and $[cp'_2Yb(OEt_2)]$ form $\{[cp'_2Yb]_2(\mu_3\text{-}OC)M_3\text{-}(\eta^5\text{-}C_5H_4R)_2\}$ (ref. 344).

After several days at room temperature, a hexane solution of $[Me_3EGeH_3]$ (E = Si, Ge) and $[Co_2(CO)_8]$ forms a mixture of $[Me_3ECo(CO)_4]$ and $[(Co_2\text{-}(CO)_6(\mu\text{-}CO))_2(\mu_4\text{-}Ge)]$. In the latter reaction a small amount of a species proposed to have the structure [127] and a trace of $[Co_4(CO)_{12}]$ also form.



[127]

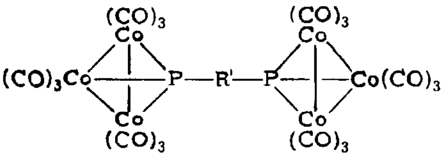
The reaction of $[Co_2(CO)_8]$ and $[Ge_2H_6]$ in a 3.3:1 ratio forms an equimolar mixture of $[(Co_2(CO)_6(\mu\text{-}CO))_2(\mu_4\text{-}Ge)]$ and [127] but an even better route to the latter is to use $[Me_2Si(GeH_3)_2]$ instead of $[Ge_2H_6]$. On heating in hexane, [127] loses one carbonyl group and rearranges to [128] (ref. 345).



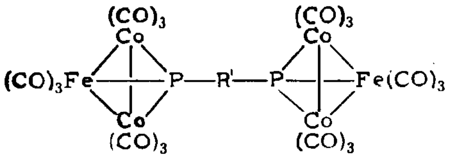
[128]

Both $Na[Co(CO)_4]$ and $[Co_2(CO)_8]$ react in THF with [(TPP)InCl] to form $[(TPP)InCo(CO)_4]$ while $[(TPP)SnCl_2]$ and $[Hg(Co(CO)_4)_2]$ in refluxing THF form the tetrametallic species $[(TPP)Sn(Co(CO)_3)HgCo(CO)_4]$ (ref. 346). Tetraphenylbibismuthine is cleaved by $[Co_2(CO)_8]$ to form $[Ph_2BiCo(CO)_4]$ while the corresponding arsenic and antimony species form the diphenylpnictide-bridged oligomers $[Co(CO)_n(\mu\text{-}EPh_2)]_x$ (E = As; n = 2. E = Sb; n = 3). The latter are cleaved to monomers (*trans*-$Co(CO)_3(PPh_3)(EPh_2)$) by triphenylphosphine (ref. 347). Cyclic voltammetric studies on $[Co_2(CO)_6$-$(\mu\text{-}CO)(\mu\text{-}Si(Ph)Co(CO)_4)]$ and $[PhSn(Co(CO)_4)_3]$ show that the radical anion formed initially soon decomposes to form $[Co(CO)_4]^-$ and other mononuclear products. In the former complex, the radical anion is sufficiently more stable, possibly due to the presence of the cobalt-cobalt bond, that the reoxidation can be observed if the scan is reversed sufficiently rapidly (ref. 348).

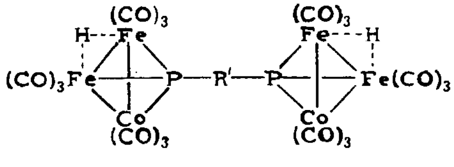
The Vahrenkamp group continues to explore synthetic routes to mixed-metal clusters and this year has been especially prolific. In an initial report, low yields of [129] and [130] (R' = *p*-C_6H_4, 4,4'-C_6H_4-C_6H_4) are obtained from reaction of $[Co_2(CO)_8]$ with $[Cl_2P\text{-}R'\text{-}PCl_2]$ and $[(OC)_4FePH_2R'\text{-}PH_2Fe(CO)_4]$ respectively. Complex [129] (R' = *p*-C_6H_4) can be converted to [130] by reaction with $[Fe(CO)_4]^{2-}$ while [130] (R' = *p*-C_6H_4) is also obtained from $K[Co(CO)_4]$ and $[(OC)_4FePCl_2\text{-}R'\text{-}PCl_2Fe(CO)_4]$, again in very low yield. Acidification of the residues from the last reaction with phosphoric acid gave a small amount of [131] (ref. 349). Also, $[Co_2(CO)_8]$ and



[129]



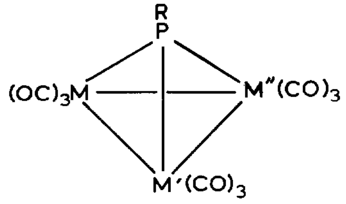
[130]



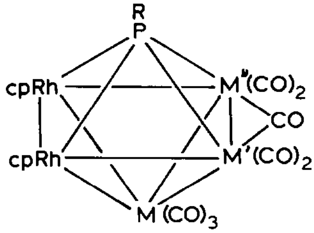
[131]

$[(H_3P)ML_n]$ or $[(RH_2P)ML_n]$ form $[Co_3(CO)_9(\mu_3\text{-}PML_n)]$ (ML_n = $M(CO)_5$ (M = Cr, Mo, W), $cpMn(CO)_2$) from the former and either $[Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}P(R)ML_n)]$ (R = Me, Ph; ML_n = $Cr(CO)_5$, $W(CO)_5$) or $[(OC)_3Co(\mu\text{-}PHR)ML_n]$ (R = Me, Ph; ML_n

= $cpMn(CO)_2$) from the latter (ref. 350). A comparison has been made of the ease of metal exchange reactions of $[Co_2Fe(CO)_9(\mu_3\text{-}PMe)]$ with that of its arsenic analog to test the proposition that metal-metal bond strengths in these clusters are primarily affected by steric factors. As predicted, the arsenic analogs did undergo the exchange reaction more readily but the greater reactivity also occasioned significantly greater decomposition (ref. 351). In some instances, cluster expansion occurs with these phosphorus-bridged clusters. Thus [132] (R = Me; M = Fe, M' = M" = Co; M = Ru; M' = FeH, RuH; M" = Co. R = Ph; M = Ru; M' = M" = Co. R = Bu^t; M = Ru; M' = FeH; M" = Co) reacts with $[cpRh(CO)_2]$ in refluxing toluene to form [133].

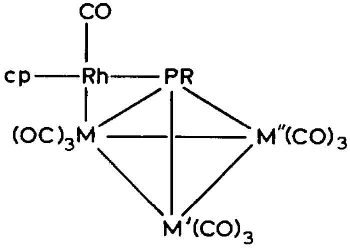


[132]



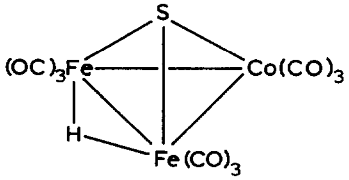
[133]

At lower temperatures an intermediate formulated as [134] (R = Me; M = Ru; M' = RuH, FeH; M" = Co. R = Ph; M = Ru; M' = M" = Co) could be isolated in

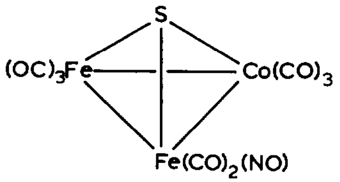


[134]

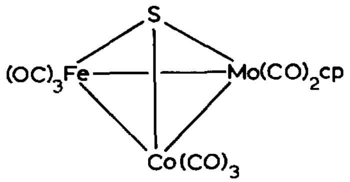
some instances (ref. 352). Reaction of $[FeCo_2(CO)_9(\mu_3\text{-}S)]$ with $[Fe(CO)_4]^{2-}$ forms [135] in which the hydride can be replaced by a $\{Ph_3PAu\}$ moiety while reaction with nitrous acid forms [136]. The same initial reaction with [137] forms [138] (ref. 353).



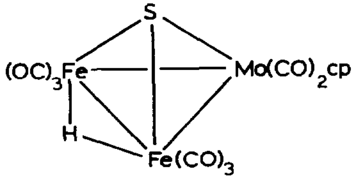
[135]



[136]

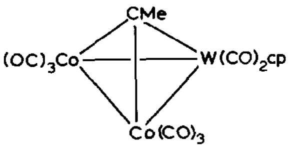


[137]

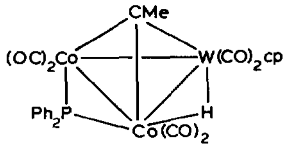


[138]

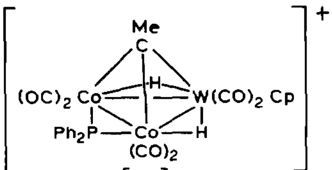
Turning now to capped triangular clusters where the capping group is an alkylidyne fragment or analogs with heavier Group IV elements the first report describes the thermal reaction of [139] with diphenylphosphine to form [140] and its protonation to give [141] (ref. 354). Scheme XXXIII (R = CO$_2$Pr^i) outlines routes to a number of tri- and tetrametallic clusters (ref. 355). While [RSiCo$_3$(CO)$_9$] (R = Me, Ph, *p*-tolyl) is too prone to decomposition to be a useful precursor to silicon-capped mixed-metal clusters using this method, it was found that reaction of [RSiH$_2$ML$_n$] (R = Me, Ph; ML$_n$ = cpMo(CO)$_3$, cpW(CO)$_3$, cpFe(CO)$_2$) with [Co$_2$(CO)$_8$] formed



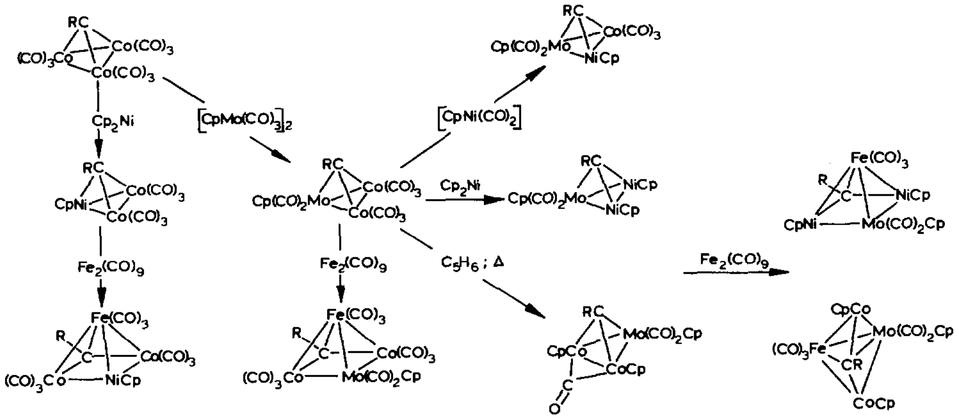
[139]



[140]

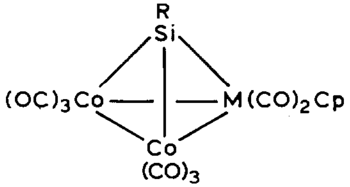


[141]

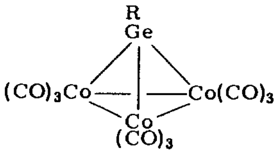


Scheme XXXIII

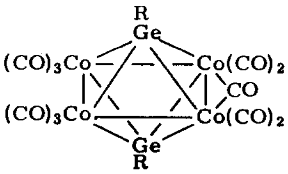
$[Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Si(R)ML_n)]$ which on heating (M = Mo, W) gave [142] (ref. 356). More success was had with related germanium-capped clusters. Thus reaction of $RGeX_3$ (R = Me, Bu^t; X = I. R = Ph; X = Cl) with a stoichiometric quantity of $K[Co(CO)_4]$ in refluxing cyclohexane afforded [143] and, for R = Me, [144]. Directed syntheses of [144] (R = Ph, Bu^t) used phenyltrichlorogermane or tert-butyltriiodogermane and two equivalents of $K[Co(CO)_4]$ in the presence of carbon monoxide. Other examples of [143] (R = $Co(CO)_4$, cpNi(CO), $cpFe(CO)_2$) were obtained from $[Co_2(CO)_8]$ and germanium (II) iodide in refluxing benzene and from $K[Co(CO)_4]$ and $[I_2GeR_2]$ (R = $Co(CO)_4$, cpNi(CO)) or from $[I_2Ge(Co(CO)_4)_2]$ and $K[cpFe(CO)_2]$ respectively. Also formed is $[Co_4(CO)_{12}]$ in the first reaction and $[cpFe(CO)_2Co(CO)_4]$ in the second. Complexes [143] proved useful for cluster substitution and expansion reactions. In refluxing benzene with $[cpM(CO)_3]_2$ (M = Mo, W), [145] (R = Me, Bu^t, Ph) forms while with $[cpNi(CO)]_2$ (R = Bu^t only) a mixture of [146] (ML_n = cpNi) and [147] are obtained. Complexes [145] (R = Bu^t) underwent further substitution on reaction with $[cpMo(CO)_3]_2$ to give [148] (M = Mo, W) and with $[cpNi(CO)]_2$ (M = Mo) to form [149]. Also, reaction of $Na_2[Fe(CO)_4]$ with [143] (R = Bu^t) or [145] (R = Bu^t; M = Mo) in



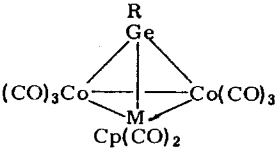
[142]



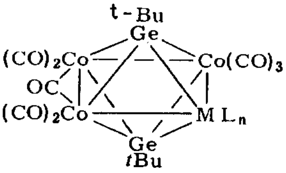
[143]



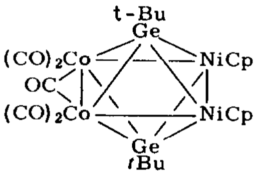
[144]



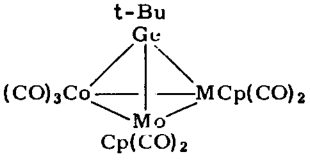
[145]



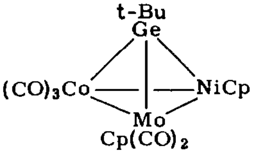
[146]



[147]

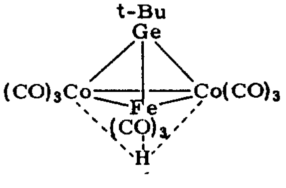


[148]

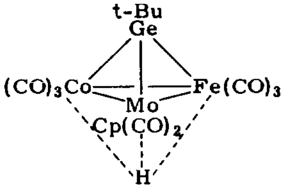


[149]

refluxing THF followed by acidification with phosphoric acid formed [150] and [151] respectively. Complex [143] (R = $cpFe(CO)_2$, $cpW(CO)_3$) with

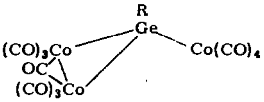


[150]

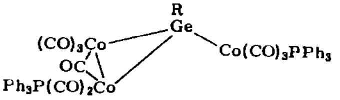


[151]

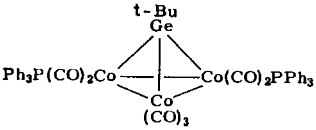
$[cpMo(CO)_3]_2$ in refluxing benzene yielded [145] (M = Mo; R = $cpFe(CO)_2$, $cpW(CO)_3$) but when R = $Co(CO)_4$ only substitution at germanium occurred to give [143] (R = $cpMo(CO)_3$). The same reaction when R = cpNi(CO) gave a mixture of [143] (R = $cpMo(CO)_3$) and [145] (M = Mo; R = $cpMo(CO)_3$). Other reactions of [143] (R = Me, Bu^t, Ph) include those with carbon monoxide in refluxing cyclohexane to form [152] (R = Me, Bu^t, Ph), with triphenylphosphine to give [153] (R = Me, Ph) or [154] and with $[cpM(CO)_3AsMe_2]$ (M = Cr,



[152]

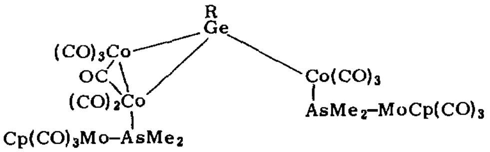


[153]

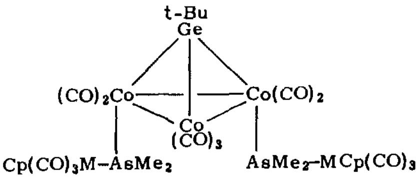


[154]

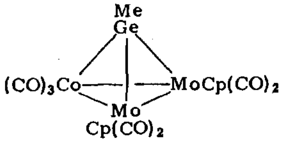
Mo, W) to yield [155] (R = Me, Ph) or [156] (M = Cr, Mo, W). Thermolysis of [155] (R = Me) in toluene formed a mixture of [145]; (M = Mo; R = Me, $cpMo(CO)_3$) and [157] while the analog with R = Ph gave only [145] (R = $cpMo(CO)_3$; M = Mo). In refluxing benzene, [156] (M = Mo, W) converted to [145] (R = Bu^t; M = Mo, W) (refs. 357-359).



[155]

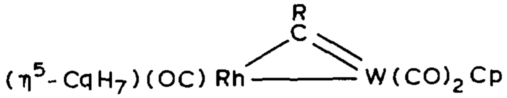


[156]

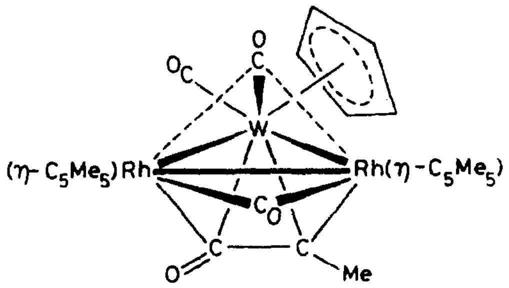


[157]

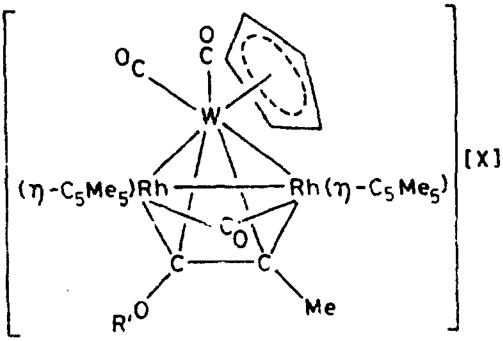
As part of a study of the coupling of carbon fragments bound to transition metals, [158] (R = *p*-tolyl) was reacted with [cp$_2$Ti(μ-Cl)(μ-CH$_2$)AlMe$_2$] but no characterizable products could be isolated (ref. 360). A ready reaction occurs between [cp'$_2$Rh$_2$(μ-CO)$_2$] and [cpW(≡CMe)(CO)$_2$] to form [159]. This can be protonated or alkylated to give [160] (R' = H; X =



[158]

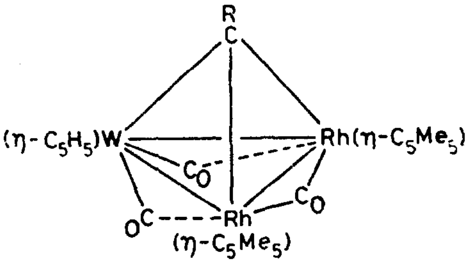


[159]

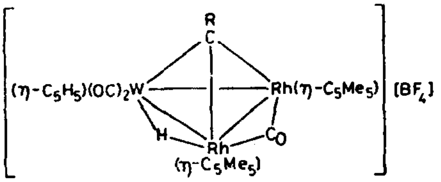


[160]

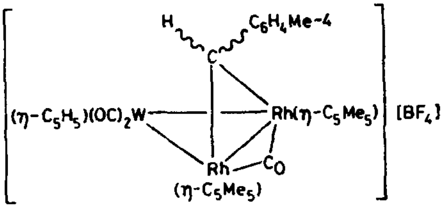
BF$_4$, CF$_3$CO$_2$. R' = Me; X = CF$_3$SO$_3$) and also decarbonylates to yield [161] (R = Me). Protonation of [161] (R = Me, p-tolyl) with tetrafluoroboric acid etherate forms [162] via [163] which was observed in one instance when the protonation was performed at low temperature. When [cpW(≡CMe)(CO)$_2$] reacts with [cp'Rh(μ-CO)$_2$Cocp'] the products are [164] and [165] (R = Me).



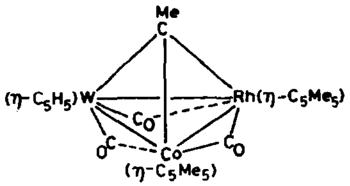
[161]



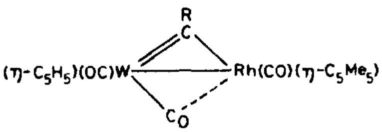
[162]



[163]

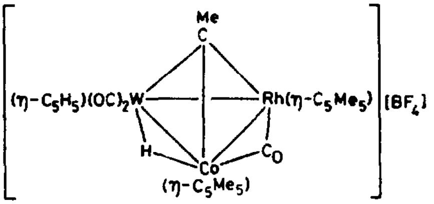


[164]

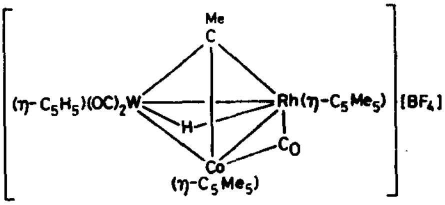


[165]

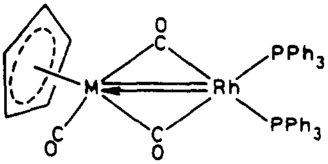
The formation of the latter species indicates that facile cleavage of the rhodium-cobalt double bond can occur. Protonation of [164] with tetrafluoroboric acid etherate yields a mixture of isomers proposed to be [166a] and [166b] (ref. 361). A ready reaction also occurs between [167] (M = Mo, W) and $[Fe_2(CO)_9]$ but the only iron-containing product identified was $[Fe(CO)_4(PPh_3)]$. Also isolated were $[cp_2M_2(CO)_6]$ and the unsaturated, 56-electron cluster [168] which could be reversibly carbonylated to give [169]. Complex [167] also reacted with $[Pt(C_2H_4)(PPh_3)_2]$ to yield a mixture of [170] and [171] (ref. 362). The alkylidyne-capped cluster



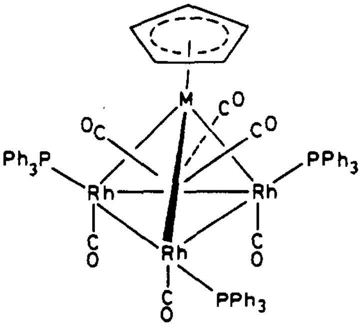
[166a]



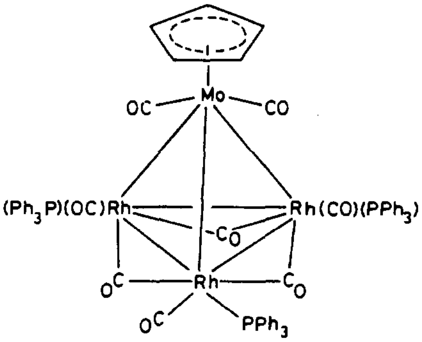
[166b]



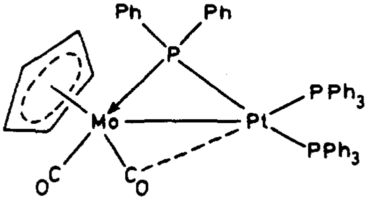
[167]



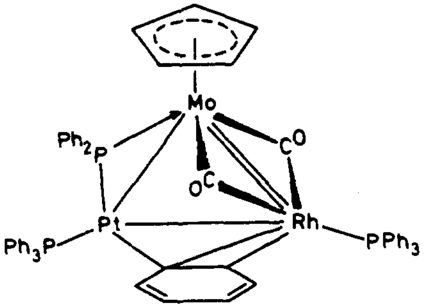
[168]



[169]

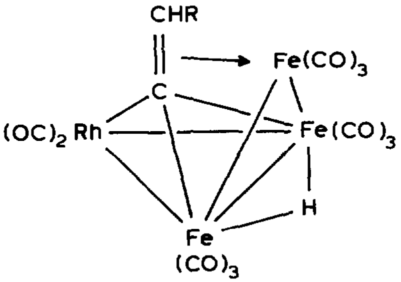


[170]

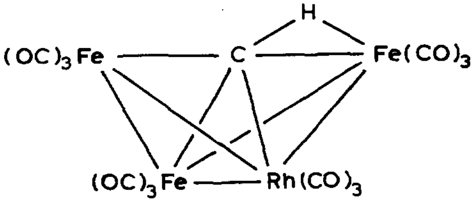


[171]

$[Fe_3(CO)_{10}(\mu_3\text{-CMe})]^-$ forms an apparently anionic cluster (which was not isolated) when treated with $[RhCl(CO)_2]_2$ and thallium tetrafluoroborate. Protonation of the resulting reaction mixture formed a species proposed to be [172] (R = H) in low yield. These can also be prepared, again in low yield, from $[RhCl(CO)_2]_2$ and $[HFe_3(CO)_9(\mu\text{-C=CHR})]^-$ (R = H, Ph) followed by acidification. Complex [172] (R = Ph) is a catalyst precursor for hex-1-ene hydroformylation but the active species appears to contain only rhodium as $[Rh_4(CO)_{12}]$ was recovered at the end of the reaction (ref. 363). In related work, the ketenylidene complex $(PPN)_2[Fe_3(CO)_9(CCO)]$ was treated with $[RhCl(CO)_2]_2$ and the products isolated were $PPN[RhCl_2(CO)_2]$ and $PPN\text{-}[RhFe_3C(CO)_{12}]$. Protonation of the latter with triflic acid at low temperature formed the unstable cluster [173]. Reaction of $(PPN)_2[Fe_4C(CO)_{12}]$

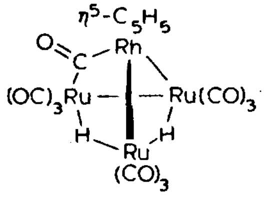


[172]



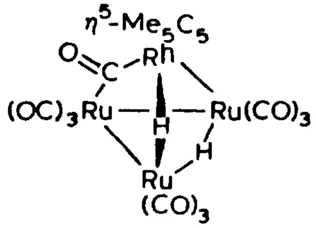
[173]

with $[Co_2(CO)_8]$ formed $PPN[Fe_4CoC(CO)_{14}]$ (ref. 364). In an atmosphere of hydrogen, $[Ru_3(CO)_{12}]$ and $[cpRh(CO)_2]$ react at elevated temperature to yield [174], a process which is reversed by treatment with carbon monoxide

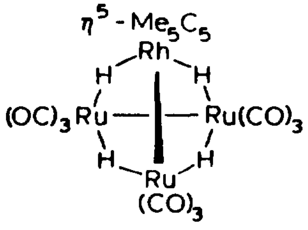


[174]

under ambient conditions. Interestingly, the same reaction using $[cp'Rh(CO)_2]$ forms [175] together with [176] and $[cp'_2Rh_2Ru_2(CO)_7]$. Complex



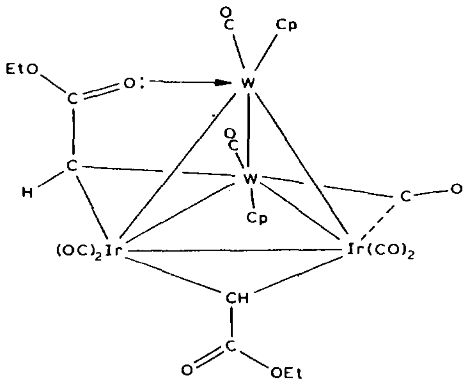
[175]



[176]

[175] can be slowly converted to [176] by hydrogen at room temperature and both react with carbon monoxide to regenerate $[Rh_3(CO)_{12}]$ and $[cp'Rh(CO)_2]$ (ref. 365). Reaction of $[RuCl_2(CO)_3]_2$ with $Na[Rh(CO)_4]$ in THF followed by solvent removal and acidification with dilute phosphoric acid affords an impure sample of $[(OC)_3Ru(H)Rh_3(CO)_6(\mu\text{-}CO)_3]$. Treatment with triphenylphosphine in the presence of a catylic amount of sodium benzophenone ketyl gave a bis(phosphine) derivative which was obtained pure and in which one carbonyl group on each of two rhodium atoms had been replaced by the phosphine. The hydride ligand was not located crystallographically but is thought to reside on the Rh_3 face of the cluster (ref. 366).

Ethyl diazoacetate and $[cp_2W_2Ir_2(CO)_{10}]$ react to form [177] (ref. 367) while $[W(CO)_5(THF)]$ and $[cp'Ir(CO)_2]$, initially at 77 K, form $[cp'(CO)_2IrW(CO)_5]$ on warming to room temperature. The latter complex is moderately stable in the solid state but soon decomposes in solution. A long and rather weak iridium-to-tungsten donor bond is proposed which is readily cleaved by addition of carbon monoxide or triphenylphosphine. The ^{13}C NMR spectrum in the carbonyl region shows dynamic behavior which is thought to be a bridge-terminal exchange process (ref. 368). The decomposition of



[177]

$[RuIr_4(CO)_{15}]^{2-}$ under nitrogen forms $[RuIr_3(CO)_{12}]^-$ and another cluster anion which has so far not been characterized. The former cluster has a structure analogous to that of $[Co_4(CO)_{12}]$ with the ruthenium atom in the basal plane (ref. 369).

A catalyst showing promise for applications in coal liquifaction was prepared from a mixture of $[Co_2(CO)_8]$ and $[Mo(CO)_6]$ supported on alumina but it was not determined if any heterometallic clusters were present (ref. 370). Only a slight amount of deprotonation of $[HFeCo_3(CO)_{12}]$ occurs when it is treated with silica in solution. In contrast, in the presence of alumina, a complete conversion to supported $[FeCo_3(CO)_{12}]^-$ occurs. Similar differences are noted when the neutral cluster is placed on the support by vapor deposition. With silica only physisorption occurs and the cluster decomposed on heating while with alumina partial decarbonylation occurs during the deposition (ref. 371). In catalysts derived from $[Rh_xCo_{4-x}(CO)_{12}]$ ($x = 0-2,4$) EXAFS studies indicate the presence of cobalt-oxygen bonds suggesting attachment of the cluster to oxygen atoms of the support (ref. 372). The cluster $[H_2RhOs_3(acac)(CO)_{10}]$ can be supported on a phosphinated styrene-divinyl benzene copolymer and the supported species like the free cluster, suffers loss of the rhodium moiety, possibly as $[Rh(acac)(CO)_2]$ on reaction with carbon monoxide. Loss of rhodium also occurs on heating in an atmosphere of hydrogen plus ethylene. The supported species shows no activity for olefin hydrogenation or isomerization at first and what is seen after the induction period is thought to be due to fragments of the original cluster (refs. 373, 374). The hydride species $[HCo(CO)_4]$, $[HRuCo_3(CO)_{12}]$ and $[HFeCo_3(CO)_{12}]$ form surface-bound ammonium salts of the corresponding anions when reacted with amine-modified silica gels. These can be decarbonylated to form highly dispersed, supported metal catalysts for carbon monoxide hydrogenation (ref. 375).

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

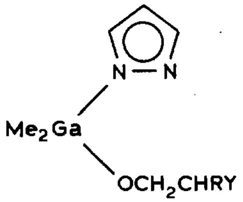
Reaction of $[CoR(np_3)]$ (R = H, Me) with formaldehyde in THF followed by crystallization from n-butanol forms $[Co(H)(CO)(np_3)]$ in both cases. If the recrystallization is done in the presence of tetraphenylborate ion, the product is $[Co(CO)(np_3)]BPh_4$. The formation of the hydridocarbonyl complex from the methyl precursor was interpreted to indicate that the hydride ligand originated with the formaldehyde. Initial formation of an unstable formyl complex was suggested and support for this proposal is the synthesis of $[Co(C(O)Me)(np_3)]$ from $[CoH(np_3)]$ and acetaldehyde. Chemistry of the acetyl complex is outlined in Scheme XXXIV (ref. 376). Addition of diphenylphosphine(L) to a methanol solution of cobalt(II) chloride forms a mixture of $[CoCl_2L_2]$ and $[CoClL_3]$ which on carbonylation first forms $[CoCl_2(CO)L_2]$ plus $[CoCl(CO)L_3]$ and ultimately only $[CoCl(CO)_2L_2]$. The reductant is proposed to be methanol. Deprotonation of one phosphine ligand in $[CoCl(CO)_2L_2]$ with sodium methoxide yields the known $[Co_2(CO)_2L_2(\mu\text{-}PPh_2)_2]$ (ref. 377). The hexadentate ligand bis(bis(2-diethylphosphinoethyl)phosphino)-methane (L_6) with cobalt(II) chloride forms $[Co_2Cl_4(L_6)]$ which converts to $[Co_2Cl_2(L_6)]Cl_2$ and on treatment with carbon monoxide and hydrogen in ethanol containing cobalt(II) chloride forms $[Co_2(CO)_4(\mu\text{-}L_6)]^{2+}$ which is initially isolated as the tetrachlorocobaltate(II) salt (ref. 378).

$$\begin{tikzcd}
 & {[CoH(np_3)] + [Co(CO)(np_3)]BPh_4} & \\
{[Co(np_3)]X} & {[Co(C(O)Me)(np_3)]} \arrow[l, "c"'] \arrow[u, "a"] \arrow[r, "b"] \arrow[d, "d"] & {[CoH(np_3)]} \\
 & {[CoMe(np_3)]} \arrow[r, "e"] & {[CoMe(np_3)]BPh_4}
\end{tikzcd}$$

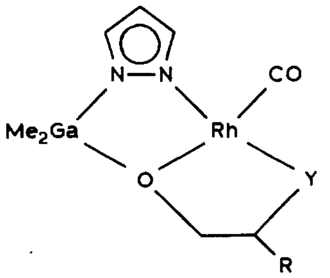
a) NaOMe, $NaBPh_4$. b) $LiBHEt_3$. c) HX (X = BF_4, O_2SOCF_3). d) MeLi.
e) $NaBPh_4$.

Scheme XXXIV

As usual, $[RhCl(CO)_2]_2$ has been extensively used for the synthesis of rhodium(I) carbonyl complexes. With sodium dimethylbis(3,5-dimethylpyrazolyl)gallate($Na[Me_2Ga(3,5\text{-}Me_2pz)_2]$) and triphenylphosphine at low temperature the square planar complex $[(Me_2Ga(3,5\text{-}Me_2pz)_2)Rh(CO)(PPh_3)]$ forms. The related ligand [178] (R = H; Y = NH_2, NMe_2, SMe, SPh. R = Me; Y = NH_2) gives [179] and when R = H and Y = NH_2 a five coordinate dicarbonyl species was detected in solution but could not be isolated. Complexes [179] (R = H; Y = NH_2, NMe_2) undergo oxidative addition with methyl iodide followed by migration of the methyl group to the carbonyl ligand to give

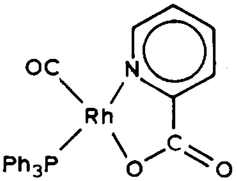


[178]



[179]

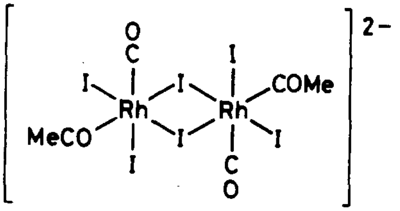
five-coordinate acetyl compounds. Both of these complexes suffer cleavage of the pyrazolylgallate ligand on reaction with triphenylphosphine and only $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}pz)_2]$ could be isolated (refs. 379, 380). Other derivatives of $[RhCl(CO)_2]_2$ include [180] prepared from picolinic acid in DMF



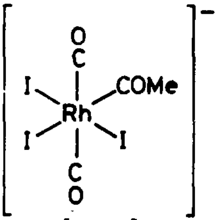
[180]

followed by treatment with the phosphine (ref. 381) and $[Rh(L_2)_2][Rh(CO)_2Cl_2]$ (L_2 = $RN(PPh_2)_2$ (R = Ph, *p*-tolyl)). The same ligands with $[RhCl(COD)]_2$ give $[Rh(L_2)_2]Cl$ which forms an unstable monocarbonyl adduct (ref. 382). With 1,2-bis(diphenylphosphino)-1,2-dicarbadodecaborane (L_2), $[RhCl(CO)_2]_2$ and $[RhCl(PPh_3)_3]$ form $[RhCl(CO)(L_2)]$ and $[RhCl(PPh_3)(L_2)]$ respectively. Both are moderately active hydrogenation and hydroformylation catalysts but in the latter system the selectivity is very low (ref. 383). Two equivalents of ligand (L = PBu^t_3, $AsBu^t_3$) with $[RhCl(CO)_2]_2$ forms *trans*-$[Rh_2(CO)_2L_2(\mu\text{-}Cl)_2]$ which with Me_3SiSR is converted to *cis*-$[Rh_2(CO)_2L_2(\mu\text{-}Cl)(\mu\text{-}SR)]$ (L = PBu^t_3; R = Pr^i, *p*-tolyl, *p*-ClC_6H_4. L = PBu^t_3, $AsBu^t_3$; R = Bu^t, $(EtO)_3Si(CH_2)_n$ (n = 2,3)). In homogeneous solution these catalyze olefin hydrogenation, isomerization, and hydroformylation and in the case of the phosphine complexes the dimeric structure appears to be maintained. The siloxy derivatives can be supported on a silica surface and while the phosphine species remain active and can be readily recycled, the arsine analogs are inactivated (refs. 384, 385). As noted in previous Annual Surveys, $[cpCo(P(O)R_2)_3]^-$ (R = OMe, OEt) is a cyclopentadienide ion analog and with $[RhCl(CO)_2]_2$ forms $[(cpCo(P(O)R_2)_3Rh)_2(\mu\text{-}CO)_3]$ *via* initial formation of $[cpCo(P(O)R_2)_3Rh(CO)_2]$. The latter reacts rapidly with phosphines to form $[cpCo(P(O)R_2)_3Rh(CO)(L)]$ (L = PEt_3, Pcy_3, PPh_3) which can also be obtained from the dimer and the phosphine in refluxing dichloromethane. The reaction of $[cpCo(P(O)R_2)_3Rh(CO)_2]$ with phosphines is much faster than that of $[cpRh(CO)_2]$ and is attributed to the fact that dissociation of one {P=O} moiety from rhodium in the former occurs more readily than slippage of the cyclopentadienyl ring in the latter (ref. 386). Also reported is a series of mono- and binuclear complexes of rhodium with 2-amino-1,2,3-dioxaphosphorinanes derived from $[RhCl(CO)_2]_2$ (refs. 387, 388).

Complex [181] is the only intermediate which has been isolated from the Monsanto catalyst system ($[Rh(CO)_2I_2]^-/I^-$) for the conversion of methanol to acetic acid. It is reversibly carbonylated to [182] and decomposes to $[Rh(CO)_2I_2]^-$ on standing. The lack of incorporation of ^{12}CO into the acetyl group of a $\{^{13}C(O)Me\}$-labelled sample of [181] was interpreted to indicate that deinsertion of this carbonyl group does not occur (ref. 389). In related work, methyl iodide was found to react with $[Rh(CO)_2I_2]^-$ in acetic acid to form [182]. Acceleration of this reaction by added anions, particularly iodide and acetate, was attributed to their coordination prior to oxidative addition which renders the metal more nucleophilic towards methyl iodide (ref. 390). Ligand redistribution occurs in mixtures of $[RhCl(CO)_2]_2$ and $[RhCl(CO)(PPh_3)_2]$; $[RhCl(CO)_2(PPh_3)]$, $[Rh(CO)(PPh_3)-(\mu-Cl)_2Rh(CO)_2]$ and $[Rh_2(CO)_2(PPh_3)_2(\mu-Cl)_2]$ were identified in the solution (ref. 391).

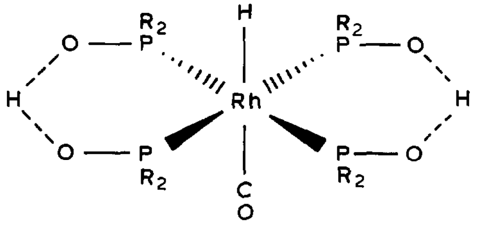


[181]



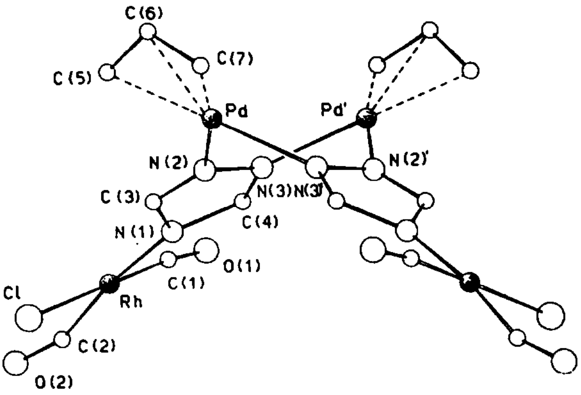
[182]

The acetylacetonate ligand in $[Rh(acac)(CO)_2]$ is removed on reaction with dimethyl- or diethylphosphonate to form [183] (R = OMe, OEt) (ref. 392) but with triphenylphosphite (L) the major products are $[Rh(acac)(CO)L]$ and $[Rh(acac)L_2]$. A very slow loss of the acetylacetonate ligand does



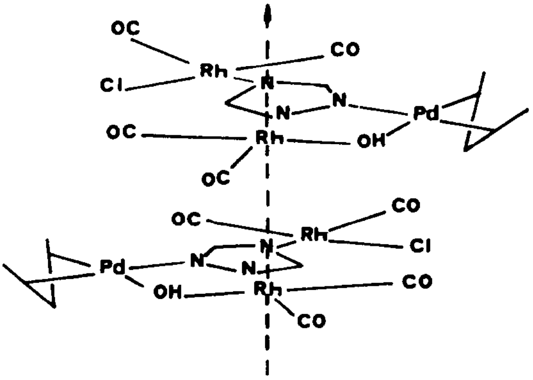
[183]

occur however and $[\mathrm{Rh}(\overset{\frown}{\mathrm{PO}})\mathrm{L}_3]$ ($\overset{\frown}{\mathrm{PO}}$ = o-metallated $\mathrm{P(OPh)_3}$) forms (ref. 393). Addition of $[\mathrm{Rh(acac)(CO)_2}]$ to a methanol solution of $[(\eta^3\text{-}\mathrm{C_3H_4R})_2\mathrm{Pd_2Cl_2}]$ (R = H, Me) and 1,2,4-triazole forms [184] (R = H) which reacts further



[184]

with $[\mathrm{RhCl(CO)_2}]_2$ in acetone to give a species proposed to be [185] on the basis of its deep blue color which is considered to be indicative of



[185]

metal-metal interaction (ref. 394).

The synthesis and chemistry of rhodium complexes of triphos are outlined in Scheme XXXV. It is proposed that the reaction of $[\mathrm{RhH_3(triphos)}]$ with carbon monoxide involves an initial dissociation of one arm of the triphos ligand (ref. 395). The complexes $[\mathrm{RhX(CO)(PPh_3)_2}]$ reversibly add carbon monoxide to give $[\mathrm{RhX(CO)_2(PPh_3)_2}]$ (X = Cl, Br, I) which is proposed to have a trigonal bypyramidal structure with axial carbonyl groups on the basis of infrared and NMR data. It was also proposed that species previously referred to as cis-$[\mathrm{RhCl(CO)L_2}]$ (L = phosphine) are more likely

$$\begin{tikzcd}
{[RhX(CO)(PPh_3)_2]} \arrow[dr, "a"] & {[Rh(CO)_2(triphos)]PF_6} \arrow[d, shift left, "c"] \arrow[dr, shift left, "d"] & {[Rh(CHMeCO_2Me)(CO)(triphos)]} \\
{[RhCl(CO)_2]_2} \arrow[r, "a"] & {[RhX(CO)(triphos)]} \arrow[u, shift left, "b"] \arrow[r, shift left, "d"] \arrow[d, "g"] & {[RhH(CO)(triphos)]} \arrow[l, shift left, "e"] \arrow[ul, shift left, "b"] \arrow[u, "f"] \\
RhCl_3 \cdot 3H_2O \arrow[r, "h"] & {[RhCl_3(triphos)]} \arrow[r, "i"] & {[RhH_3(triphos)]} \arrow[u, "j"]
\end{tikzcd}$$

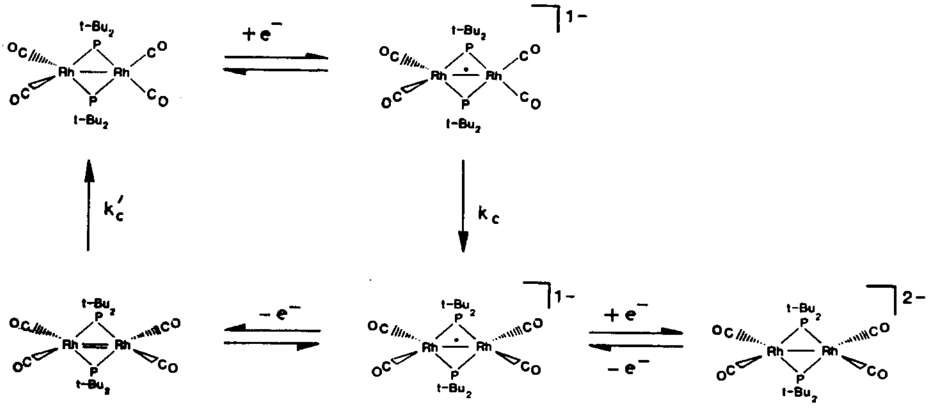
a) triphos, C_6H_6. b) CO, PF_6^-. c) X^- (=Cl^-). d) BH_4^-, MeOH.
e) RX (R = bz; X = Cl, Br. R = Me; X = I). f) CH_2=$CHCO_2Me$.
g) Cl_2. h) triphos. i) BH_4^-, $MeCN/H_2O$. j) CO.

Scheme XXXV

to be these dicarbonyls (ref. 396). At low temperature the five-coordinate adduct $[RhX(CO)L_2(PF_2X)]$ (X = Cl, Br; L = PEt_3) forms when the appropriate halodifluorophosphine is added to a toluene solution of $[RhX(CO)L_2]$. On warming, the bromo complex apparently rearranges to $[RhBr_2(PF_2)(CO)L_2]$ which rapidly decomposes while the chloro complex undergoes a more complicated sequence of reactions and $[RhCl_2(PFCl)(CO)L_2]$ forms. On standing this converts to a mixture of $[RhCl(CO)L_2]$, trifluorophosphine and $[RhCl_2(PCl_2)(CO)L_2]$, the last component of which can be formed directly from $[RhCl(CO)L_2]$ and phosphorus trichloride. With $[RhI(CO)L_2]$ and iododifluorophosphine only $[RhI_2(PF_2)(CO)L_2]$ could be seen even at low temperature (ref. 397). Equilibrium constants for the conversion of $[Rh(OClO_3)(CO)(PPh_3)_2]$ to $[Rh(CO)(L)(PPh_3)_2]ClO_4$ (L = CH_2=C(R)CN (R = H, Me), cis- or trans-MeCH=CHCN, CH_2=$CHCH_2CN$) have been measured and the nitrile is proposed to coordinate via the nitrogen atom (ref. 398). A reinvestigation of the reactions of trithiazyl trichloride ($N_3S_3Cl_3$) with rhodium complexes which was originally reported to give thionitrosyl complexes (J. Organometal. Chem 261(1984)103, ref. 495. Inorg. Chim. Acta, 48(1981)23) has shown these claims to be incorrect. The strong infrared absorption originally attributed to ν_{NS} is now shown to be due to the presence of $[Ph_3PNH_2]Cl$. Thus instead of $[RhCl_2(CO)(NS)(PPh_3)]_2$ and $[RhCl_2(CO)(NS)(PPh_3)_2]$, the products of the reaction of $[RhCl(CO)(PPh_3)_2]$ with trithiazyl trichloride are $[RhCl_3(CO)(PPh_3)_2]$, triphenylphosphine sulfide and $[Ph_3PNH_2]Cl$. Similarly $[RhCl(PPh_3)_3]$ and $[Rh(NO)(PPh_3)_3]$ form triphenylphosphine oxide and -sulfide plus $[Ph_3PNH_2]Cl$ and here no rhodium-phosphine products could be detected by ^{31}P NMR (ref. 399).

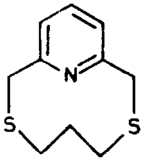
Addition of various imidazole derivatives (L) to $[RhCl(CO)(PPh_3)_2]$ in the presence of perchlorate ion yields $[Rh(CO)(L)(PPh_3)_2]ClO_4$ (ref. 400) while analogous species (L = 4-substituted pyridines, imidazole, benzimidazole) as hexafluorophosphate salts were formed from [$Rh(CO)_3(PPh_3)_2$]PF_6. In the latter series, a correlation was found between ν_{CO} and the pK_a of the conjugate acid of the nitrogen-donor ligand except where the conjugate acid contained more than one acidic proton (ref. 401). The complex [Rh(AA)-(CO)(PPh_3)] (AA = anthranilate) undergoes phosphine exchange with free triphenylphosphine (ref. 402). Flash photolysis of [$RhCl(CO)(PPh_3)_2$] forms a transient species believed to be [$RhCl(PPh_3)_2$] which is a key intermediate in [$RhCl(PPh_3)_3$]-catalyzed olefin hydrogenations. This species is absent when photolysis is carried out in the presence of carbon monoxide while in the presence of triphenylphosphine, hydrogen or ethylene species proposed to be [$RhCl(PPh_3)_3$], [$RhClH_2(PPh_3)_2$], and [$RhCl(C_2H_4)(PPh_3)_2$] respectively are detected (ref. 403). In methanol solution either [$Rh(CO)_2$-L_3]ClO_4 or [$Rh(CO)L_2(NO_3)$] (L = PPh_3) reacts with carbon disulfide and more phosphine to form [$Rh(CO)L_2(S_2CPPh_3)$]$^+$ which was isolated as the tetraphenylborate salt. The sulfur ligand can be replaced by pyridine or ammonia in acetone solution (ref. 404). At 100°C and 50 atm pressure of carbon dioxide or at room temperature in the presence of formic acid [$Rh(CO)(Pcy_3)_2$]BH_4 converts to the formate derivative, [$Rh(O_2CH)(CO)$-$(Pcy_3)_2$] (ref. 405). An aqueous ethanol solution of [$Rh(bipy)_2$]$^+$ functions as a catalyst for the WGSR and [$RhH(CO)(bipy)_2$]$^{2+}$ is proposed to be formed. At higher pH, more carbon monoxide can be absorbed but loss of the bipyridyl ligand occurs (ref. 406). Cocondensation of rhodium atoms with oxalyl chloride forms a very reactive product, probably a mixture, which is converted to [$RhCl(CO)(PPh_3)_2$] by triphenylphosphine and to [$RhCl(CO)_2$]$_2$ by carbon monoxide. The analogous reaction with iridium initially gave a rather insoluble orange material which was converted to [$IrCl_3(CO)_2(PPh_3)$] by triphenylphosphine (ref. 407). Photolysis of [$TPP(Rh(CO)_2)_2$] in benzene/carbon tetrachloride forms [RhCl(CO)(TPP)], [RhCl(TPP)] and [TPPH]Cl. The initial photoprocess is proposed to cause a disproportionation to generate [$Rh^{II}(TPP)(CO)_2$] plus {$Rh(CO)_2$} with the former abstracting chlorine from carbon tetrachloride (ref. 408).

The two-electron reduction of [$Rh_2(CO)_4(\mu\text{-}PBu^t{}_2)_2$] appears to occur by an ECE mechanism whereas the reoxidation is characterized as an EEC process as shown in Scheme XXXVI. It was proposed that the driving force for the isomerization which occurs upon reduction is a stabilization of the HOMO by this process (ref. 409). The ligands [186] - [189] react with [$RhCl(CO)_2$]$_2$ and hexafluorophosphate ion in methanol to form [Rh(CO)L]PF_6 (L = [188], [189]), [190] (M = Rh; X = CO) and [191]. The last is fluxional in solution and is thought to convert between the <u>trans</u>-isomer shown here and a

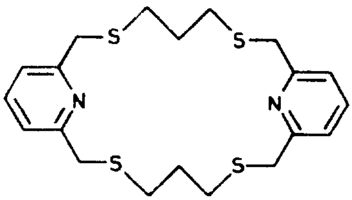


Scheme XXXVI

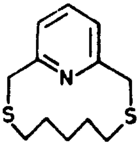
cis-isomer via an on/off exchange of the free and coordinated sulfur atoms (ref. 410). The coordination chemistry of three different ligands containing two phosphorus and two nitrogen atoms have been reported. The first is



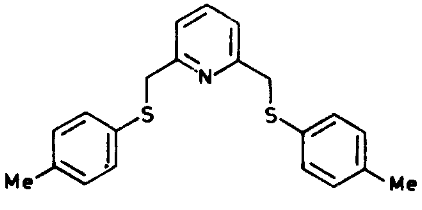
[186]



[187]

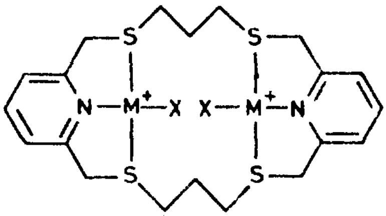


[188]

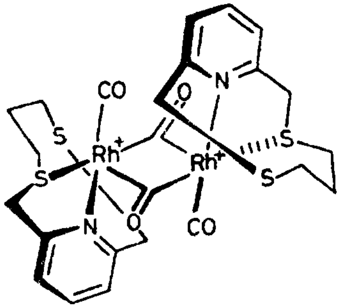


[189]

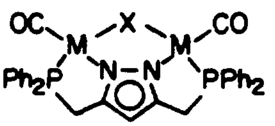
6,6'-bis(diphenylphosphino)-2,2'-bipyridyl (L_4) which reacts with $[Rh(L'_2)(acetone)_2]BF_4$ to form $[Rh_2(L'_2)_2(\mu\text{-}L_4)](BF_4)_2$ (L'_2 = COD, $(CO)_2$). Both of these species react with carbon monoxide to form $[Rh_2(CO)_6(\mu\text{-}L_4)](BF_4)_2$ and in all instances the ligand appears to coordinate only through phosphorus (ref. 411). The second ligand is PNNP which was purified as a nickel complex that reacted directly with $[RhCl(CO)_2]_2$ to form [192] (M = Rh; X = Cl). The free neutral ligand (PNNHP) reacted with $[M(diene)_2]BF_4$ (M = Rh,



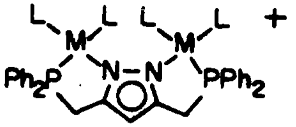
[190]



[191]

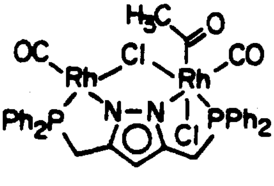


[192]

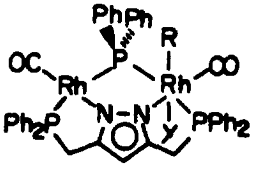


[193]

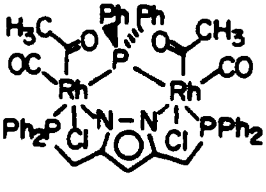
Ir; diene = COD. M = Rh; diene = NBD) in the presence of triethylamine to give [193] (M = Rh; Ir; 2L = COD. M = Rh; 2L = NBD). Treatment of [193] with carbon monoxide gave analogs with L = CO which reacted with the diphenylphosphide ion to form [192] (M = Rh, Ir; X = PPh$_2$). Complex [193] (M = Rh; L = CO) loses one carbonyl ligand from each metal in the absence of carbon monoxide and the tetrafluoroborate counterion is thought to coordinate. It reversibly adds acetyl chloride to form [194] and if X = PPh$_2$ the oxidative addition of acetyl chloride and methyl iodide to give [195] (R = C(O)Me; X = Cl. R = Me; Y = I) is irreversible but now a second equivalent of acetyl chloride adds reversibly to form [196]. Iridium analogs of [195] (R = C(O)Me; Y = Cl. R = Me; Y = I) and [196] both form irreversibly and here methyl iodide will also oxidatively add to both metal centers. The results of the oxidative addition experiments suggest that oxidative addition to one metal center deactivates the second metal somewhat towards further reaction. Complexes [193] (M = Rh; 2L = NBD. M = Ir;



[194]

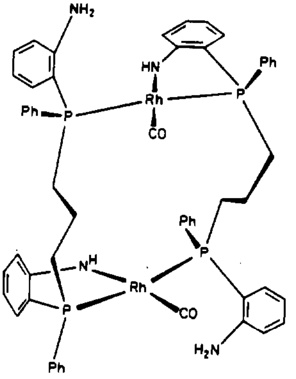


[195]



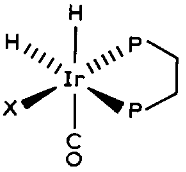
[196]

2L = COD) in methanol catalyze the hydrogenation of olefins and acetylenes. The rhodium complex also catalyzes the disproportionation of cyclohexa-1,3-diene to cyclohexane and benzene but the iridium complex gives primarily hydrogenation. At room temperature no hydrides could be detected although the diene ligands were hydrogenated. At low temperature however the complex $[(COD)H_2Ir(\mu\text{-PNNP})Ir(COD)]BF_4$ was seen (refs. 412, 413). The third ligand is 1,3-bis(phenyl(o-anilino)phosphino)propane which, as a mixture of rac and meso forms, reacts with $[Rh(CO)_2Cl_2]^-$ in the presence of base to form [197] (ref. 414).

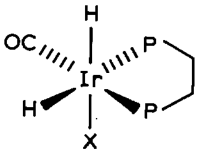


[197]

In an important series of papers, Eisenberg has demonstrated that a stereoselective, cis oxidative addition of hydrogen and triethylsilane occurs under kinetic control with cis-$[IrX(CO)L_2]$ (X = Cl, Br, I; L_2 = DPPE, CHIRAPHOS) which appears to be due to the electronic differences between the two monodentate ligands. Thus with [IrX(CO)(DPPE)] (X = Cl, Br, I) [198] is seen first and only slowly does it convert to the thermodynamically stable isomer [199]. This isomerization is accelerated by

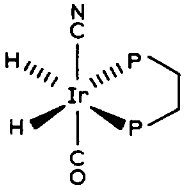


[198]



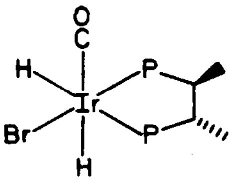
[199]

irradiation and in acetone is considered to involve reductive elimination of hydrogen and its re-oxidative addition. In benzene the isomerization occurs more rapidly, is inhibited by bromide ion and is accelerated by silver tetrafluoroborate. This faster process would seem to involve loss of halide with possible rearrangement of the resulting five-coordinate species without reductive elimination of hydrogen but the details have not yet been elucidated. A slower process, presumably the same as in acetone, is also seen. With [Ir(CO)$_{1,2}$(CN)(DPPE)], the reaction of hydrogen rapidly gives [198] (X = CN) followed by a slow equilibration forming [199] (X = CN) and also [200] in a final ratio of 89:5:6. Reaction of cyanide ion

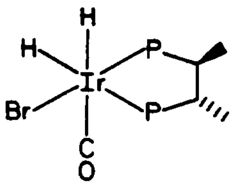


[200]

with [IrCl(CO)(DPPE)] and hydrogen forms <u>fac</u>-[IrH$_3$(CO)(DPPE)] and <u>all-cis</u>-[IrH$_2$(CN)$_2$(DPPE)]$^-$. Oxidative addition of hydrogen to [IrBr(CO)-(CHIRAPHOS)] at -25°C in acetone gives a 2:1 mixture of [201] and [202]

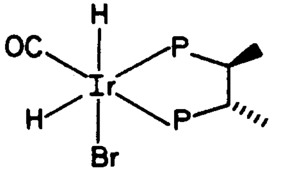


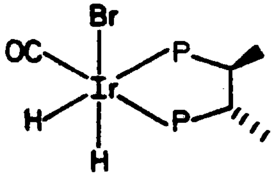
[201]



[202]

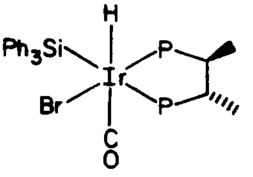
which on warming initially gives a 2.4:1 ratio of [203] and [204] but on standing this ratio drops to 1.3:1. Labelling experiments demonstrated that equilibration of [201] and [202] occurred prior to isomerization to [203] and [204] and all processes were proposed to occur <u>via</u> reformation of



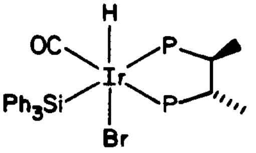


[203] [204]

[IrBr(CO)(CHIRAPHOS)]. In both sets of dihydrides a kinetic preference for the Δ isomer appeared to exist. Similarly, triphenylsilane adds to [IrBr-(CO)(CHIRAPHOS)] to initially form [205] and subsequently [206]. The results of this part of the study suggest a significant kinetic and thermodynamic differentiation of metal-centered chirality in the simple cis

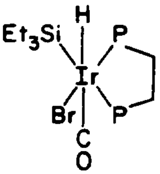


[205]

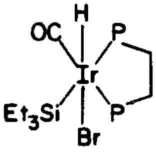


[206]

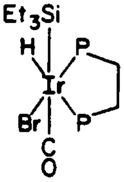
oxidative addition and a transition state for both reactions is proposed which is closer in appearance to reactants than to products in contrast to what has been suggested previously for reaction of hydrogen with [IrCl(CO)-$(PPh_3)_2$] (see also ref. 437). The final part of the study examined the reaction of [IrBr(CO)(DPPE)] with three equivalents of triethylsilane in benzene. Again a kinetic product, [207], is seen which subsequently converts to [208] via [IrBr(CO)(DPPE)] as a intermediate. A minor isomer, [209], is also seen which results from oxidative addition along the kinetically preferred P-Ir-CO axis but with the Si-H bond oriented in the opposite direction from that leading to [207]. Similar results were observed for reactions with triphenylsilane, triethoxysilane, dimethylchlorosilane and methyldichlorosilane except that the relative amounts of the isomers analogous to [207] - [209] varied. Also when electronegative substituents



[207]



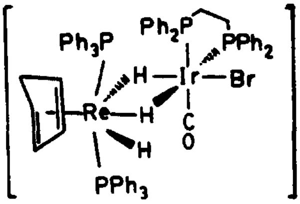
[208]



[209]

were present on silicon the rate of isomerization was decreased and over long periods of time [$IrH_2Br(CO)(DPPE)$] and [$IrHBr_2(CO)(DPPE)$] could be detected. In contrast to all the above results, oxidative addition of hydrogen bromide to [IrI(CO)(DPPE)] appears to go preferentially along the P-Ir-I axis. This was explained by noting that hydrogen bromide is electrophilic while the other substrates are nucleophilic and this difference is proposed to differently affect the stabilities of the two possible five-coordinate transition states (refs. 415-417). In related work, [$(\eta^4-C_5H_6)$-$ReH_3(PPh_3)_2$] reacts with [IrBr(CO)(DPPE)] to form [199] (X = Br) and

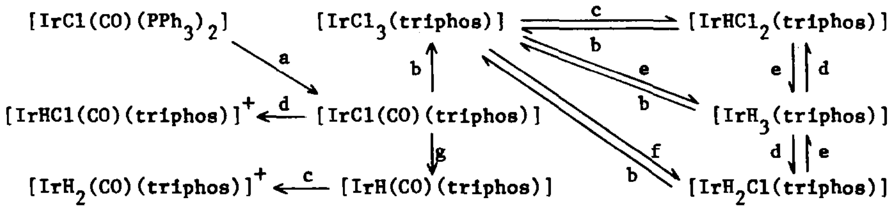
$[cpReH_2(PPh_2)_3]$. Since [199] is the thermodynamic isomer of $[IrH_2Br(CO)(DPPE)]$ this result argues for a direct intermolecular transfer of dihydrogen from rhenium to iridium possibly *via* [210] since intermediate formation



[210]

of free dihydrogen by reductive elimination from rhenium would be expected to give [198] (X = Br) (ref. 418).

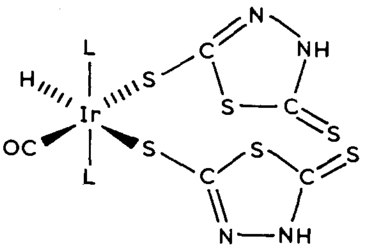
The chemistry of iridium with triphos is similar to that described above for rhodium (see ref. 395) and is outlined in Scheme XXXVII. The conversion



a) triphos, toluene. b) Cl_2, CH_2Cl_2. c) H_2, MeOH. d) HCl, CH_2Cl_2. e) $LiAlH_4$, THF. f) $NaBH_4$, THF. g) Me_4NBH_4, MeCN, H_2O.

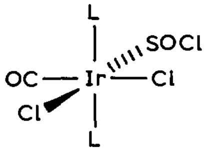
Scheme XXXVII

of $[IrCl_3(triphos)]$ to $[IrHCl_2(triphos)]$ is not complete under the specified conditions while [IrH(CO)(triphos)] is very air-sensitive and spontaneously decomposes (ref. 419). Several other papers report on chemistry of $[IrCl(CO)(PPh_3)_2]$. These include reaction with 1,3,4-thiadiazole-2,5-dithiol to form [211] (L = PPh_3) (ref. 420) and with an excess of thionyl chloride to give [212] (L = PPh_3). If the iridium complex is in large excess in this latter reaction, mer-$[IrCl_3(CO)L_2]$ is also formed. This product was obtained together with $[IrCl(CO)(SO_2)L_2]$ when equimolar quantities of [212] and $[IrCl(CO)L_2]$ were combined. It was proposed that the latter species attacks the SOCl ligand in [212] to form the trichloro complex and liberate sulfur monoxide which then decomposes to sulfur dioxide which in turn adds to $[IrCl(CO)L_2]$ (ref. 421). Other



[211]

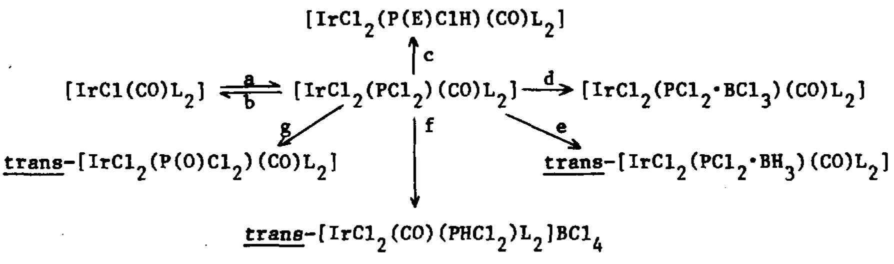
reactions are those with hexafluorophosphoric acid etherate to form trans-[IrH(FPF$_5$)Cl(CO)(PPh$_3$)$_2$] which can be hydrolyzed to trans-[IrH(OP(O)F$_2$)Cl-(CO)(PPh$_3$)$_2$] (ref. 422) and reacts with alkoxides to form [Ir(OR)(CO)-(PPh$_3$)$_2$] (R = Me, Pr^n, Bu^t, Ph). When R = Me, the product reacts with



[212]

water to yield [Ir(OH)(CO)(PPh$_3$)$_2$] which is unreactive towards carbon monoxide and with carbon monoxide in toluene to form [Ir(C(O)OMe)(CO)$_2$-(PPh$_3$)$_2$]. In this latter reaction, addition of carbon monoxide at low temperature initially generates [Ir(CO)$_3$(PPh$_3$)$_2$]OMe and it is therefore concluded that the final product arises from attack of methoxide on a coordinated carbonyl group (refs. 423, 424). In refluxing benzene [IrCl-(CO)(PPh$_3$)$_2$] reacts with sodium 8-oxoquinolinate (NaOq) to form [Ir(Oq)-(CO)(PPh$_3$)$_2$] as a five coordinate species with axial phosphine ligands. Related species were formed with a variety of β-diketonate ligands (ref. 425). Addition of pyrazole and related species to [IrCl(CS)(PPh$_3$)$_2$] in the presence of potassium hydroxide forms [Ir(L)(CS)(PPh$_3$)$_2$] (L = pz, 3-Mepz, 3,5-Me$_2$pz, idz, bzim). The dimethylpyrazolate complex loses one phosphine ligand on refluxing in benzene to give [Ir(3,5-Me$_2$pz)(CS)(PPh$_3$)]$_2$. Reaction of [RhCl(CS)(PPh$_3$)$_2$] with benzimidazole forms [Rh(CS)(PPh$_3$)(μ-bzim)]$_3$ and analogs result when [Rh(HL)(CS)(PPh$_3$)$_2$]ClO$_4$ (L = im, 2-Meim) is deprotonated with potassium hydroxide (ref. 426).

Reaction of phosphine with [IrX(CO)(PEt$_3$)$_2$] (X = Cl, Br) in toluene at room temperature forms [IrH(X)(CO)(PH$_2$)(PEt$_3$)$_2$] while at 180 K in dichloromethane the product is [Ir(CO)(PH$_3$)$_2$(PEt$_3$)$_2$]X. Above 230 K the latter complex converts to $[IrH(PH_2)(CO)(PH_3)(PEt_3)_2]X$ which is reversibly protonated by hydrogen chloride (X = Cl) to $[IrH(CO)(PH_3)_2(PEt_3)_2]Cl_2$ and deprotonated by trimethylamine to $[IrH(PH_2)_2(CO)(PEt_3)_2]$ (ref. 427). Chemistry of $[IrCl(CO)(PEt_3)_2]$ with phosphorus trichloride is outlined in Scheme XXXVIII (L = PEt_3) (ref. 428). Addition of difluorophosphine oxide to



a) PCl_3, CH_2Cl_2. b) HCl(anh.). c) H_2E (E = S, Se). d) BCl_3.
e) B_2H_6. f) HCl, BCl_3 (1:1), low temp. g) N_2O_4, CH_2Cl_2.

Scheme XXXVIII

$[IrH(CO)(PPh_3)_3]$ at low temperature forms mer-$[IrH_2(CO)(PPh_3)_3](P(O)F_2)$ and on warming the counterion replaces one triphenylphosphine. Initially cis- and trans-$[IrH_2(CO)(P(O)F_2)(PPh_3)_2]$ are seen but eventually the former converts to the latter. Analogous sulfide and selenide complexes were also prepared (ref. 429). Oxidative addition of hydrogen to $[Ir(L)(CO)(PPh_3)_2]ClO_4$ (L = RCN (R = Me, Et, Pr^n, Ph, $H_2C{=}CHCH_2$, cis- and trans-MeCH=CH)) occurs readily to give mer-$[IrH_2(CO)(L)(PPh_3)_2]ClO_4$ and for the unsaturated nitriles, hydrogenation of the double bond occurs (refs. 430, 431). The dioxygen complex $[Ir(O_2)(CO)Cl(PPh_3)_2]$ oxidizes a carbonyl ligand in $[PtCl_2(CO)(PPh_3)]$ and $[cpFe(CO)_3]PF_6$ to carbon dioxide and a binuclear μ-peroxycarbonate intermediate is proposed although it was not detected (ref. 432). Electrolytic oxidation of $[Ir(CO)_2(Tcbiim)]^-$ in acetonitrile forms the metal-metal bonded iridium(II) dimer $[Ir_2(CO)_4(MeCN)_2(Tcbiim)_2]$. One carbonyl ligand on each metal can be replaced by triethylphosphite. The structure of this derivative shows a substantial eclipsing of the planes of the Tcbiim ligands and it is suggested that it is the π-acceptor properties of this ligand which help to stabilize the dimer. Also, the mixed valence species $(Et_4N)_4[Ir(CO)_2(Tcbiim)]_6$ has been studied spectroscopically (refs. 433, 434).

The ^{31}P NMR spectra of $[IrCl(CO)(P(p\text{-}XC_6H_4)_3)_2]$ (X = H, Me, F, Cl, OMe)) have been measured and T_1 values for the phosphorus nuclei determined to be in the range 4.4-8.7 sec. (ref. 435). Flash photolysis of [IrCl(CO)-$(PPh_3)_2$] and $[IrH_2Cl(CO)(PPh_3)_2]$ produces a common transient proposed to be $[IrCl(PPh_3)_2]$. This result suggests that the photolytic elimination of hydrogen from the dihydride is not a concerted process as previously thought but probably occurs as in Scheme XXXIX (L = PPh_3) (ref. 436). An

$$\begin{tikzcd}
{[IrH_2Cl(CO)L_2]} \arrow[r, "h\nu"', "-CO"] & {[IrH_2ClL_2]} \arrow[d, shift left, "-H_2"] \\
{[IrCl(CO)L_2]} & {[IrClL_2]} \arrow[l, "+CO"'] \arrow[u, shift left, "+H_2"]
\end{tikzcd}$$

Scheme XXXIX

accurate measurement of the kinetics of oxidative addition of hydrogen and deuterium to $[IrCl(CO)(PPh_3)_2]$ has given kinetic isotope effects (k_H/k_D) varying from 1.18 at 0°C to 1.06 at 30°C. Calculations modelling the reaction coordinate give much better agreement with the experimental data when a side-on approach of H_2 or D_2 is used as opposed to an end-on approach. However, this model predicts the transition state to be much closer to the reactants than has been earlier proposed, a conclusion also reached by Eisenberg as discussed earlier. Significant hydrogen tunnelling in the transition state is also indicated. The small kinetic isotope effect is attributed to a combination of a large mass and moment of inertia term, a moderately large inverse excitation term and an inverse zero-point energy term (ref. 437). Another computational effort has proposed a quantitative determination of the σ- and π-components of metal-ligand bonding in transition metal complexes of phosphorus ligands to assess the origin of ligand effects in various reactions of organotransition metal complexes. One application is to oxidative addition reactions of [IrCl-$(CO)L_2$] (L = phosphine). When oxygen is the addend the data are consistent with Scheme XL with the last step being rate-limiting. This is similar to

$$[IrCl(CO)L_2] \rightleftharpoons [IrCl(CO)L] + L$$

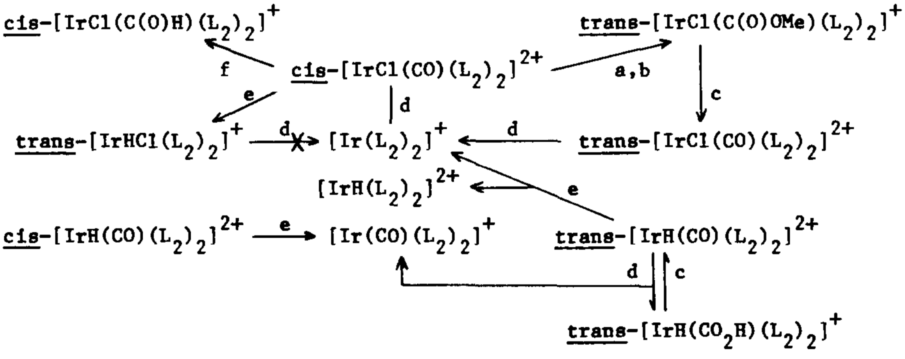
$$[IrCl(CO)L] + O_2 \rightleftharpoons [IrCl(CO)(O_2)L]$$

$$[IrCl(CO)(O_2)L] + L \longrightarrow [IrCl(CO)(O_2)L_2]$$

Scheme XL

that proposed earlier for the oxidative addition of aryl iodides although in that study the significance of the first step was thought to be the result of the forcing conditions used. The present analysis of this latter system suggests that the corresponding second step is rate limiting and the reaction is slow because aryl iodides are relatively unreactive not because the first step is difficult to achieve. It was thus concluded that the first step is not necessarily limited to systems employing forcing conditions and therefore a mechanism like Scheme XL may be more generally operational in oxidative addition reactions of these iridium complexes than previously thought. Analysis of the oxidative addition of methyl iodide, however, suggested that more than one path may be accessible. Overall the major factors affecting these reactions are steric and σ-donor effects of the phosphine ligands. Other systems analyzed in this paper include the reaction of trimethylphosphite with [cpRh(CO)$_2$] and [cp'Rh(CO)$_2$] and the oxidative addition of benzyl bromide to [Co(dmgH)$_2$(L)] (L = phosphine). In the former the extent of bond making in the transition state appears to be approximately the same in both and the rate differences are attributed to steric factors. In the latter both steric and electronic effects are important (ref. 438).

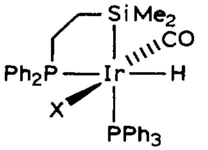
The chemistry of some cationic, DPPE complexes of iridium is outlined in Scheme XLI (L$_2$ = DPPE). No reaction was observed between trans-[IrCl(CO)(DPPE)$_2$]$^{2+}$ and water or between trans-[IrH(CO)(DPPE)$_2$]$^{2+}$ and carbon monoxide in refluxing aqueous acetone. Treatment of trans-[IrX(CO)(DPPE)$_2$]$^{2+}$ (X = H, Cl) with lithium tri-sec-butylborohydride at -45°C gave the formyl complex trans-[IrX(CHO)(DPPE)$_2$]$^+$ which could be protonated to form the hydroxycarbene complex trans-[IrX(=C(OH)H)(DPPE)$_2$] (ref. 439). Photolysis



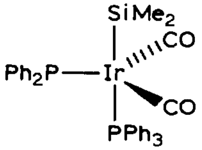
a) MeOH, Et$_3$N, CH$_2$Cl$_2$. b) NaOMe, CH$_2$Cl$_2$. c) H$^+$. d) OH$^-$, acetone, H$_2$O. e) acetone, H$_2$O. f) LiBHEt$_3$, CD$_2$Cl$_2$, -70°C.

Scheme XLI

of [213] (X = H) in the presence of carbon monoxide forms [214]. This can also be formed by reaction of [213] (X = Cl) with methylmagnesium chloride



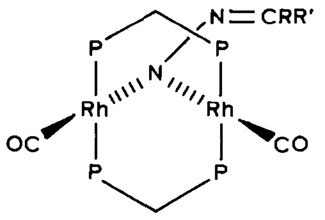
[213]



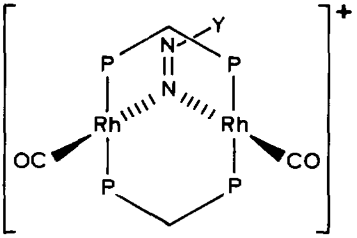
[214]

followed by carbon monoxide (ref. 440).

The study of "A-frame" and related complexes continues to be an area of considerable interest. Treatment of $[Rh_2H_2(CO)_2(DPM)_2]$ with diazoalkanes forms [215] (R = CO_2Et; R' = H, CO_2Et) which on protonation with tetrafluoroboric acid etherate (R' = H) forms [216] (Y = CH_2CO_2Et) or $[Rh_2(CO)_2(\mu\text{-}H)(DPM)_2]^+$ (R' = CO_2Et). Complex [216] (Y = CH_2CO_2Et) can be reconverted to [215] (R' = H; R = CO_2Et) by sodium ethoxide. A second example

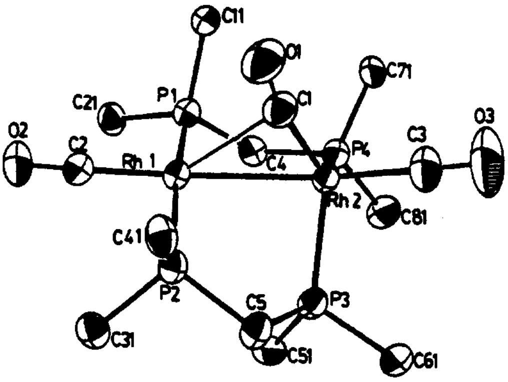


[215]



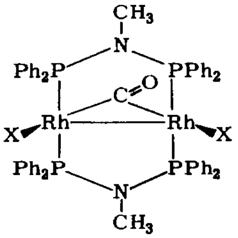
[216]

of [216] (Y = *p*-$NO_2C_6H_4$) can be formed from $[Rh_2H_2(CO)_2(DPM)_2]$ and *p*-nitrophenyldiazonium hexafluorophosphate (ref. 441). The complex originally formulated as $[Rh_2(CO)_2(\mu\text{-}CO)(DPM)_2]$ with an "A-frame" structure has now been found to have the structure [217]. The molecule is fluxional but the details of the rearrangement have not been fully elucidated (ref. 442). Whilst $[RhCl(CO)_2]_2$ reacts with $RN(PPh_2)_2$ (L_2: R = Me, Et) in methanol at room temperature to give $[Rh(L_2)_2][Rh(CO)_2Cl_2]$ or in benzene (R = Me) to form $[Rh(CO)(L_2)_2][Rh(CO)_2Cl_2]$, in refluxing methanol the "A-frame" [218] (X = Cl) is the product. Carbonylation of this complex in the presence of sodium tetraphenylborate or ammonium hexafluorophosphate forms $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(\mu\text{-}L_2)_2]A$ (A = BPh_4, PF_6) which can be decarbonylated to the "A-frame" $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}L_2)_2]PF_6$. Reaction of [218] (X = Cl) with



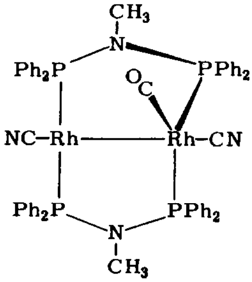
[217]

other monoanions in methanol produces analogs with X = Br, I, N_3, NCO, NCS, CN while with sulfur dioxide replacement of the bridging carbonyl by SO_2



[218]

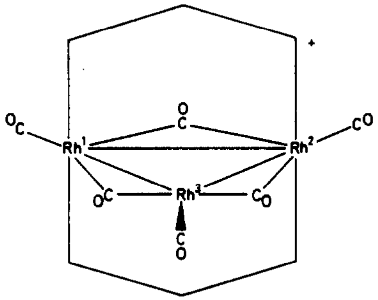
occurs. The cyano complex appears to rearrange in solution to form [219] (refs. 443, 444).



[219]

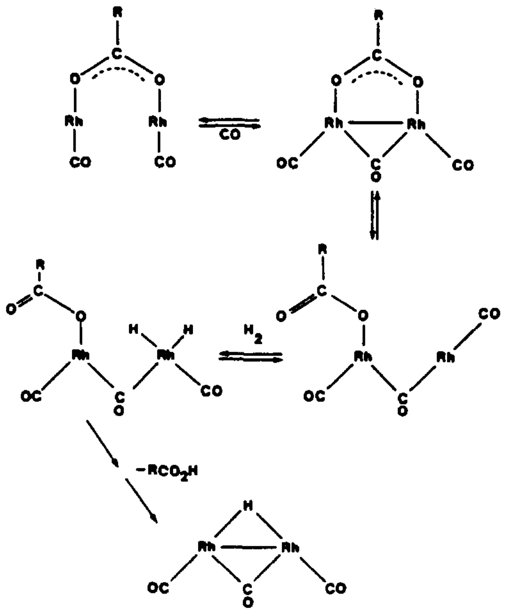
The face-to-face dimer $[RhCl(CO)(DPM)]_2$ on treatment with sodium alkoxide in the corresponding alcohol and then with perchlorate ion is converted to the "A-frame" $[Rh_2(CO)_2(\mu\text{-}OR)(DPM)_2]ClO_4$ (R = Me, Et) which reacts with perchloric acid in a mixture of dichloromethane and the alcohol to form $[Rh_2(CO)_2(\mu\text{-}OH)(DPM)_2]ClO_4$ and with carboxylic acids to give

$[Rh_2(CO)_2(\mu\text{-}O_2CR)(DPM)_2]ClO_4$ (R = H, Me, CF_3, CH_2Cl, $CHCl_2$). The trifluoroacetate complex with one equivalent of a monoanion forms $[Rh_2(CO)_2(\mu\text{-}X)(DPM)_2]ClO_4$ (X = N_3, NCO, NCS, SCN) while with an excess the product is $[Rh_2X_2(CO)_2(DPM)_2]$ (X = NCO, NCS). The same thiocyanate complex can be got together with a small amount of $[Rh_2(CO)_2(\mu\text{-}SCN)(DPM)_2]ClO_4$ from $[Rh_2(CO)_2(\mu\text{-}OEt)(DPM)_2]ClO_4$ and ammonium thiocyanate. If $[Rh_2Cl_2(CO)_2(DPM)_2]$ is treated with sodium carbonate in aqueous ethanol, the hydroxo-bridged "A-frame" is again formed but here the chloride counterion appears to be hydrogen bonded to the hydroxy group viz. $[Rh_2(CO)_2(\mu\text{-}OH...Cl)(DPM)_2]$ and on prolonged contact with deuterium oxide the methylene protons of the DPM ligand exchange with deuterium. This complex is unreactive towards carbon monoxide under ambient conditions but under pressure it is transformed to $[Rh_2Cl_2(CO)_2(DPM)_2]$. Similarly, $[Rh_2(CO)_2(\mu\text{-}OR)(DPM)_2]ClO_4$ (R = H, Me, Et) does not react with one atmosphere of carbon monoxide but on pressurization [220] forms. Only the unique terminal carbonyl ligand exchanges with



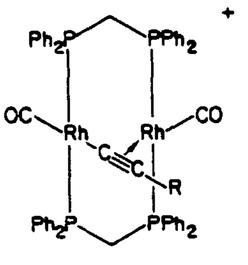
[220]

labelled carbon monoxide. It can also be replaced by phosphines ($PMePh_2$, PPh_3, PEt_3, DPM) and in the last derivative the monodentate DPM undergoes exchange of coordinated and uncoordinated ends of the ligand. The phosphine derivatives can be slowly converted back to [220] by carbon monoxide and in the process exchange of the two bridging carbonyls bound to Rh^3 now occurs. As attempts to form [220] from $[Rh_2(CO)_2(\mu\text{-}OR)(DPM)_2]ClO_4$ and stoichiometric quantities of $\{Rh(CO)_n\}$ moieties failed, it appears that formation of [220] involves more than simply the capture of such a monomeric fragment by the starting dimer. Several of the alkoxy-bridged "A-frames", although unreactive towards hydrogen alone, are converted to $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}H)(DPM)_2]ClO_4$ when carbon monoxide is also present. Scheme XLII depicts the proposed mechanism. A final reaction of $[Rh_2(CO)_2(\mu\text{-}OR)(DPM)_2]ClO_4$ (R = Me, CF_3) is with terminal acetylenes in which the fluxional product interconverts between [221a] and [221b] (R = H, Bu^t, Ph). These species form labile adducts with carbon monoxide and sulfur dioxide

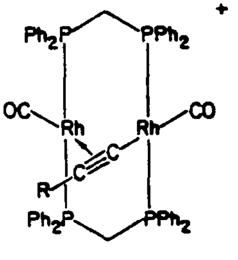


Scheme XLII

in which the added ligand bridges the two metals and although not overly reactive towards nucleophiles they do react with some phosphines and with

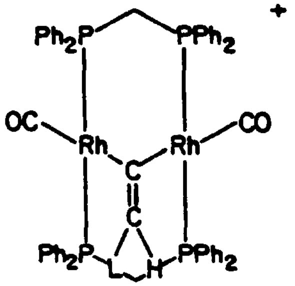


[221a]



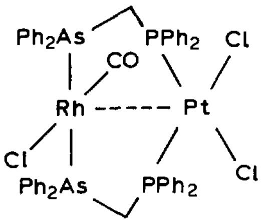
[221b]

hydride ion to form adducts proposed to be [222] (L = H, Bu^t, Ph, PMePh$_2$, PPh$_3$) (refs. 445-448).

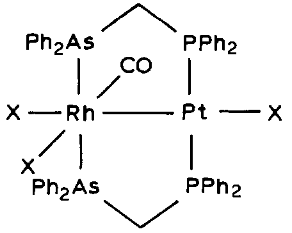


[222]

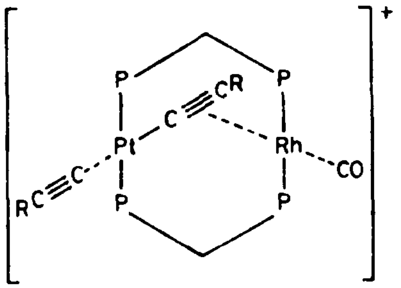
A number of heterobimetallic complexes bridged by DPM and analogs have been reported. Addition of an excess of DAPM to $[RhCl(CO)_2]_2$ forms trans-$[RhCl(CO)(DAPM)_2]$ in which the DAPM is coordinated only via phosphorus. Reaction of this with $[RhCl(CO)_2]_2$ or $[PtCl_2(COD)]$ forms $[Rh_2Cl_2(CO)_2$-$(\mu$-$DAPM)_2]$ in both instances as a mixture of head-to-head and head-to-tail isomers. In the latter reaction $[PtCl_2(DAPM)]$ is also formed while in the former the major isomer has the head-to-tail arrangement of the ligands. Reaction of $[PtCl_2(DAPM)_2]$ with $[RhCl(CO)_2]_2$ forms [223] which is converted to [224] (X = Cl) among other products in refluxing chloroform. Analogs (X = Br, I) can be prepared from [224] by metathesis. The carbonyl stretching frequency for [224] is rather low suggesting that there may be some semi-bridging character to this ligand (refs. 449, 450). Other heterobimetallic species result when $[RhCl(CO)_2]_2$ is added to $[PtR_2(DPM)_2]$ (R = C≡C-R' (R' = Me, Ph, p-tolyl, CH_2CH_2Ph, $C(Me)=CH_2$), CN, 1-naphthyl). The acetylide species have the structure [225] and are fluxional, presumably by a twisting of the $\{Pt(C{\equiv}CR)_2\}$ moiety about the P-Pt-P axis. In refluxing toluene replacement of the carbonyl group by the chloride counterion occurs (R = Ph, p-tolyl) and the same two complexes can also be obtained, together with homobimetallic and mononuclear species, from the reaction of $[Pt(C{\equiv}CR)_2$-$(DPM)_2]$ with $[RhCl(cyoct)_2]_2$. Other routes to [225] (R = Ph) include reaction of $[RhCl(CO)_2]_2$ with $[Pt(C_2Ph)_2(\mu$-$DPM)_2HgCl_2]$ and with $[Pt(C_2Ph)_2$-$(\mu$-$DPM)_2MX]$ (MX = CuI, AgCl, AuCl). The cyano complex is a face-to-face



[223]

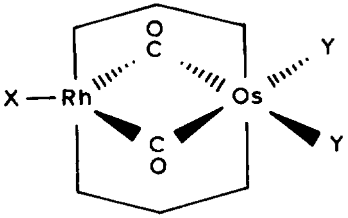


[224]



[225]

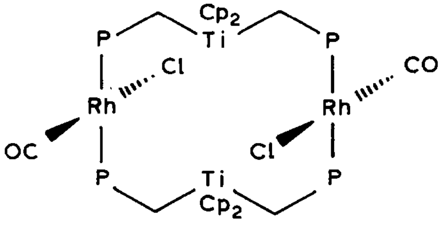
dimer and iridium and palladium analogs were also synthesized. The 1-naphthyl complex has cis coordination at platinum and shows evidence for the presence of both syn and anti arrangements of the naphthyl groups (refs. 451-453). The chelating DPM ligands in trans-$[OsCl_2(DPM)_2]$ are opened on reaction with $[RhCl(CO)_2]$ and [226] (X = Y = Cl) is formed.



[226]

Analogs with Y = Cl and X = Br, I, N_3, SCN can be prepared by metathesis and if this reaction is carried out for long periods of time species with X = Y = Br, I can be obtained (ref. 454).

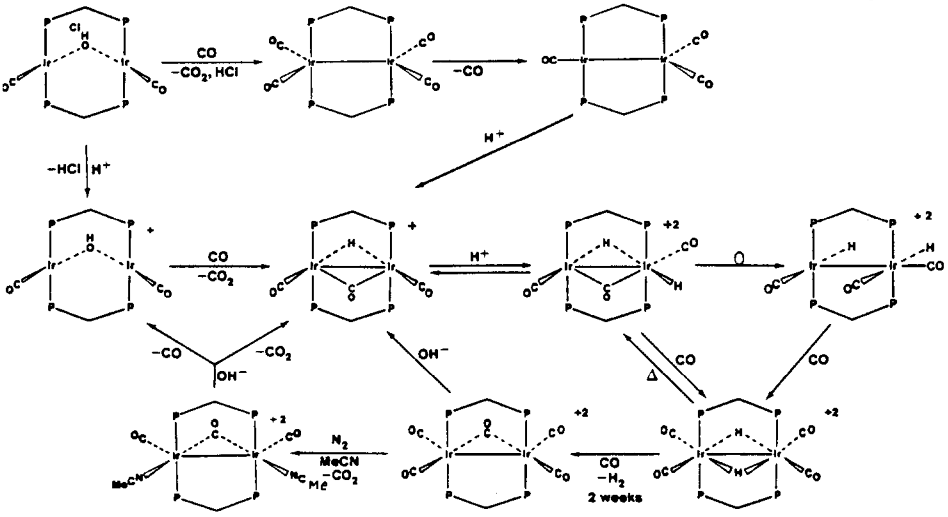
Benzene solutions of $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}DPM)]$ react with silver salts to form $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}Ag)(\mu\text{-}DPM)]X$ (X = BF_4, ClO_4, PF_6) and with $[Au(PPh_3)]X$ to yield $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}Au(PPh_3))(\mu\text{-}DPM)]X$ (X = BF_4, PF_6). When the first reaction was carried out with a sample of silver hexafluorophosphate which had been exposed to moisture, the product was $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}Ag(OP(O)F_2)\text{-}(\mu\text{-}DPM)]$. The difluorophosphate ion was shown to be present in the original sample of the silver hexafluorophosphate. Also, reaction of $[cp_2Rh_2(\mu\text{-}CO)\text{-}(\mu\text{-}DPM)]$ with tetrafluoroboric or hexafluorophosphoric acid yields $[cp_2Rh_2\text{-}(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}DPM)]X$ (X = BF_4, PF_6) (refs. 455, 456). Addition of mercury (II) chloride to $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]Cl$ in dichloromethane forms $[RhCl(CO)(\mu\text{-}CO)(\mu\text{-}HgCl)(\mu\text{-}DPM)_2RhCl_2(CO)]$ which is formulated as a mixed rhodium(I)-rhodium(III) species with an asymmetrically bridging {HgCl} moiety. A carbonyl-bridged species is obtained on reaction with carbon monoxide but it has not yet been characterized (ref. 457). The air-sensitive metallophosphine $[cp'_2Ti(CH_2PPh_2)_2]$ can be synthesized from $[cp_2TiCl_2]$ and diphenylphosphinomethyllithium and reacts with $[RhCl(CO)_2]_2$



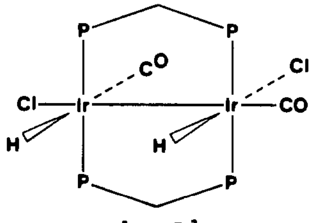
[227]

to form [227] (ref. 458). An analogous dimer $[Rh_2Cl_2(CO)_2(\mu\text{-}L_2)_2]$ (L_2 = $Ph_2P(CH_2)_nPPh_2$ (n = 10, 16)) can be prepared from $[RhCl(CO)(PPh_3)_2]$ while with $[RhCl(PPh_3)_3]$ the product is $[Rh_2Cl_2(PPh_3)_2(\mu\text{-}L_2)_2]$. Iridium analogs of the carbonyl complexes were also synthesized (ref. 459).

The catalysis of the WGSR by dimeric rhodium complexes has been explored using a non-catalytic iridium system as a model which starts with $[Ir_2(CO)_2(\mu\text{-}OH...Cl)(DPM)_2]$ whose rhodium analog has been discussed earlier (see ref. 445). This is prepared from $[Ir_2Cl_2(CO)_2(DPM)_2]$ and sodium hydroxide in aqueous THF. The chemistry of this system is outlined in Scheme XLIII. Despite the results which indicate the involvement of the hydroxo-bridged iridium species in WGSR chemistry it still appears that in the rhodium system the analogous hydride-bridged complex is a more important intermediate (ref. 460). Hydrogen reacts with $[Ir_2Cl_2(CO)_2(DPM)_2]$ and $[Ir(CO)_2(\mu\text{-}Cl)(DPM)_2]BF_4$ to form [228] and $[Ir_2H_4Cl(CO)_2(DPM)_2]BF_4$ respectively. Both are fluxional in solution, the former by Scheme XLIV, but as a static

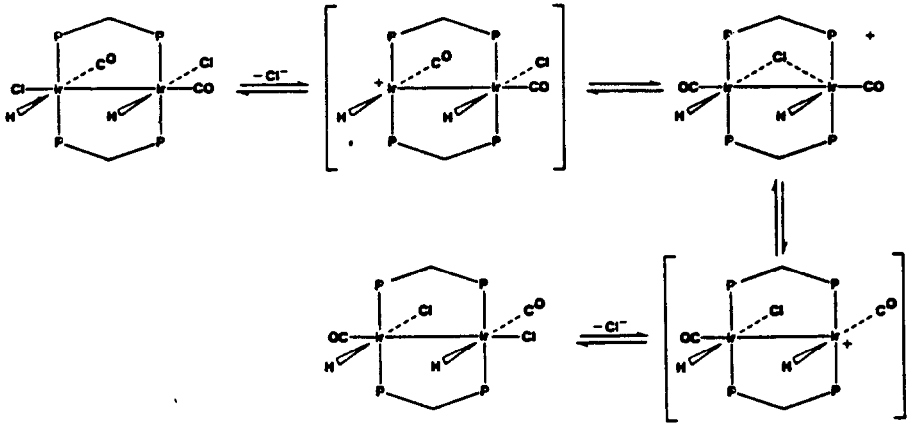


Scheme XLIII



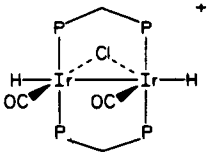
[228]

NMR spectrum could not be obtained for the latter, its structure has not been determined. Heating the tetrahydride under nitrogen in THF or

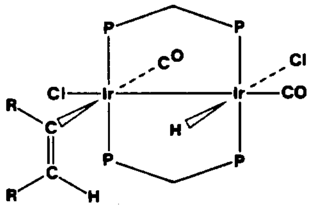


Scheme XLIV

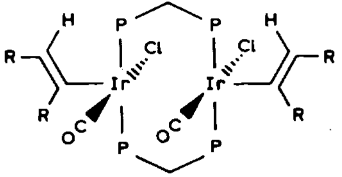
reacting [228] with silver tetrafluoroborate forms a species proposed to be [229]. DMAD reacts with [228] and [229] to form [230] and [231] (R = CO_2Me) respectively (ref. 461).



[229]

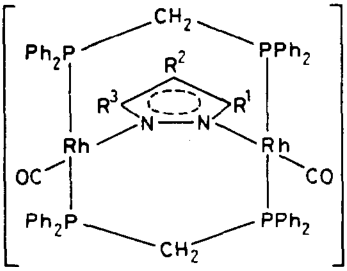


[230]

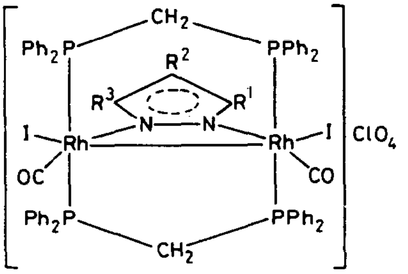


[231]

Reaction of [RhCl(CO)$_2$]$_2$ with one equivalent of sodium pyrazolate forms [Rh$_2$(CO)$_4$(μ-Cl)(μ-pz)] in low yield whose structure shows the dimers to be stacked in columns with some interdimer metal-metal interaction (ref. 462). Various pyrazoles with [RhCl(CO)(DPM)]$_2$ in acetone/methanol containing potassium hydroxide form [232] (X = Cl, $R^2 = R^3 = H$; R^1 = H, Me. $R^1 = R^3$ = Me; R^2 = H. $R^1 = R^3$ = H; R^2 = Br). Perchlorate and tetraphenylborate salts were also prepared. Oxidative addition of iodine to the perchlorate salts yields [233] (same combinations of R^1, R^2 and R^3). Complexes [234]

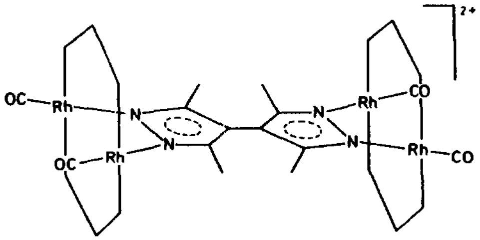


[232]

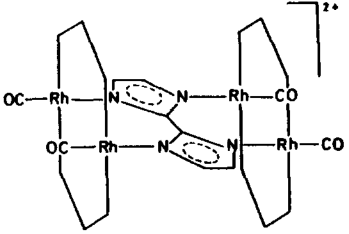


[233]

and [235] were prepared in a manner analogous to that used for [232] using 3,3',5,5'-tetramethyl-4,4'-bipyrazole and 2,2'-biimidazole respectively



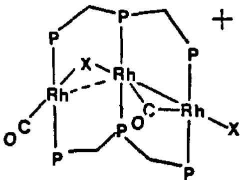
[234]



[235]

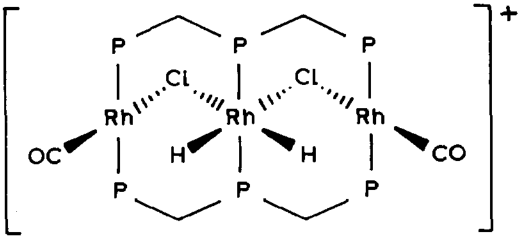
(ref. 463). Oxidative addition of iodine to $[Rh_2(CO)_4(\mu\text{-}pz)_2]$ to form $[Rh_2(CO)_4I_2(\mu\text{-}pz)_2]$ is accompanied by the formation of a metal-metal bond which is then cleaved by a second equivalent of iodine to form $[Rh_2(CO)_4I_4\text{-}(\mu\text{-}pz)_2]$. The diiodo complex reacts with DPM to form $[Rh_2I_2(CO)_2(\mu\text{-}DPM)\text{-}(\mu\text{-}pz)_2]$ (ref. 464).

The potentially tridentate ligand dpmp chelates to palladium, platinum and molybdenum through the terminal phosphorus atoms to form $[MX_2(dpmp)]$ (M = Pd, Pt; X = Cl. M = Pt; X = Me) and cis-$[Mo(CO)_4(dpmp)]$ which function as metallophosphine ligands (L) and with $[RhCl(CO)_2]_2$ give trans-$[RhCl(CO)L_2]$ (ref. 465). Loss of one carbonyl group from $[Rh_3X_2(CO)_3(dpmp)_2]BPh_4$ occurs in refluxing acetonitrile (X = Cl) or acetone (X = Cl, Br) to form [236]



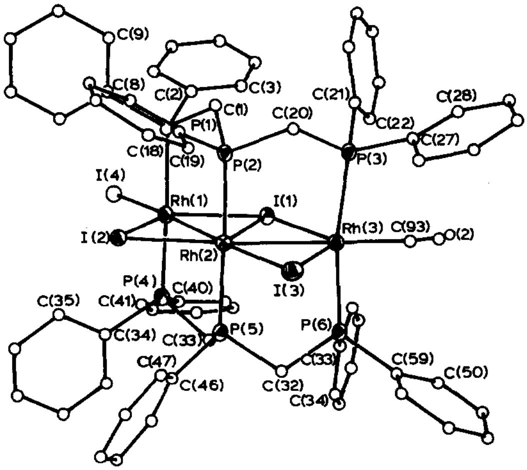
[236]

which is considered to be in effect a combination of $[Rh_2X_2(\mu\text{-}CO)(DPM)_2]$ and $[Rh_2(CO)_2(\mu\text{-}X)(DPM)_2]^+$. The chloro complex reacts with hydrogen selectively at the center metal to form [237] which catalyzes olefin



[237]

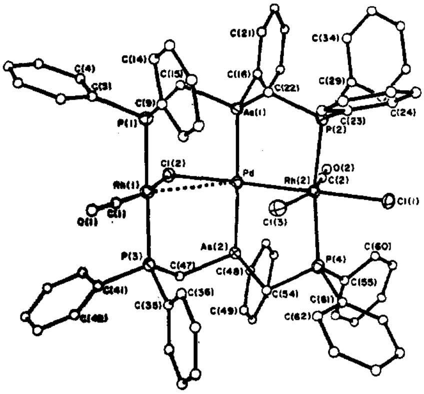
hydrogenation and in which there may be a semi-bridging interaction of the hydride ligands with the terminal rhodium atoms (refs. 466, 467). Oxidative addition of iodine to $[Rh_3I_2(CO)_3(dpmp)_2]BPh_4$ in dichloromethane followed by prolonged reflux forms $[Rh_3I_4(CO)(dpmp)_2]BPh_4$ whose cation has the structure [238]. The doubly-bridging iodide ligands are asymmetrically



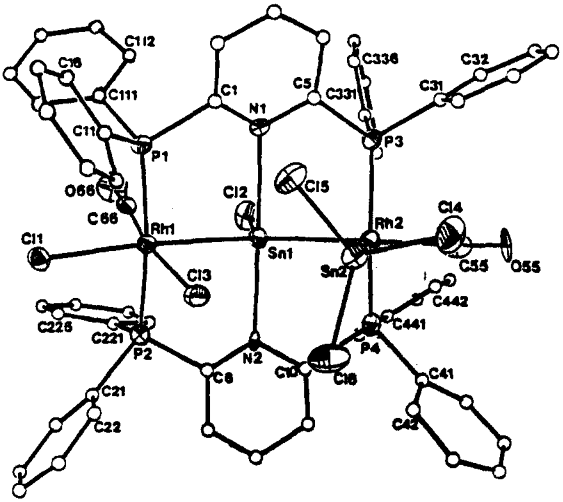
[238]

coordinated and are closer to the central metal. The apparently triply-bridging iodide appears to be nearly symmetrically disposed but due to a disorder in the structure its coordination may be more asymmetric than it appears. Although the average oxidation state for each metal is 5/3 as in $[Rh_3(CNbz)_{12}I_2]^{3+}$, if one considers the metal-metal bonds to be of unit bond order and all the iodides to be four-electron donors, then all metal atoms achieve an 18-electron configuration and formally the central iodide does not interact with the central metal. Complex [238] reversibly adds one carbonyl ligand but the structure of the product has yet to be determined (ref. 468). Reaction of $[RhCl(CO)_2]_2$ with dpma or PNP forms

$[Rh_2Cl_2(CO)_2(\mu\text{-}L)_2]$ (L = dpma, PNP) in which the ligands coordinate only through phosphorus. In both instances cis-isomers are formed although with the latter ligand both the trans isomer and $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}PNP)_2]Cl$ are also observed in the initial product. Each of the neutral complexes contains a cavity into which other metals can be placed. Reaction of $[Rh_2Cl_2(CO)_2(\mu\text{-}dpma)_2]$ with $[PdCl_2(NCPh)_2]$ forms [239] in which an effective oxidative addition of a palladium-chloride bond to one rhodium has occurred. An iridium analog was also synthesized. Reaction of the mixture of PNP complexes with four equivalents of tin(II) chloride in refluxing benzene forms [240] in which again an oxidative addition of a tin-chlorine bond to one metal (Rh(1)) has occurred. The nature of the Sn-Rh(2) interaction is less clear but as both tin-rhodium distances appear nearly equal



[239]

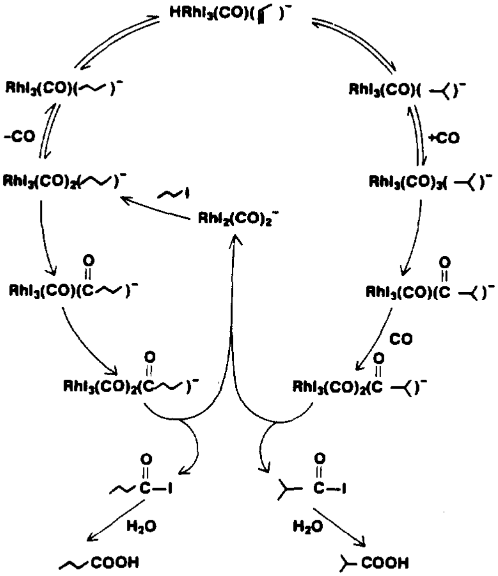


[240]

it is proposed that a complicated network of donor-acceptor interactions exists in the central core of the complex (refs. 469, 470).

The diffuse reflectance electronic spectra of several racemic or quasi-racemic mixtures of the complexes [M(CO)$_2$L] (M = Rh, Ir; L = (R)- or (S)-trifluoroacetylcamphorate) have been measured and the differences observed attributed to varying amounts of metal-metal interaction in the solid (ref. 471). Proton and ^{13}C NMR spectra for cis-[RhCl(CO)$_2$L] (L = tetramethylpyrazine, phenazine, phenazine-N-oxide, quinoxaline) (ref. 472) and the infrared and ^{1}H, ^{19}F and ^{31} P NMR spectra for [Rh(dike)(CO)$_{2-x}$L$_x$] (dike = acac, tfac, tta, benzoyl- or naphthoyltrifluoroacetone; L = PPh$_3$, P(OPh)$_3$; x = 0-2) (ref. 473) have been measured. In the latter system a fast exchange of phosphorus ligands is seen when free ligand is present. Three transient species are detected when trans-[RhCl(CO)(TPP)] is subjected to laser photolysis. These are proposed to be an isomer of the starting complex, the triplet state of the starting complex and [RhCl(TPP)] (ref. 474). Molecular orbital calculations on [Rh$_3$(CO)$_6$(μ_3-E)$_2$] (E = S, Se) suggest that little or no direct metal-metal bonding is present (ref. 475).

The regioselectivity of hydroformylation of 3,3,3-trifluoroprop-1-ene and pentafluorostyrene appears very sensitive to the choice of catalyst used. Thus with [Co$_2$(CO)$_8$] a high selectivity to the straight-chain aldehyde is observed while with [RhH(CO)(PPh$_3$)$_3$] the product is almost exclusively the branched-chain isomer. A mixture of both complexes permits the amidocarbonylation of allylic alcohols to N-acyl-α-amino acids to proceed with good yields (ref. 476). Two other applications of [RhH(CO)-(PPh$_3$)$_3$] are for the hydroformylation of cyclooctatetraene (ref. 477) and N-substituted tetrahydropyridines and related molecules (ref. 478). In the former system, the formation of di- and polyaldehydes is accompanied by electrocyclic ring-opening and ring-contraction reactions so that complex mixtures of products result. Co-oligomerization of ethylene with carbon monoxide occurs in the presence of [RhH(CO)(PPh$_3$)$_3$] or [RhCl(CO)(PPh$_3$)$_2$] in methanol or ethanol and acetic acid at 110°C. The products are H(CH$_2$CH$_2$-C(O))$_n$OR and H(CH$_2$CH$_2$C(O))$_n$CH$_2$CH$_3$ (n = 1-4; R = Me, Et) and a single chain mechanism involving alternate insertions of ethylene and carbon monoxide is proposed (ref. 479). A mixture of [RhCl(CO)$_2$]$_2$ with aqueous acetic and hydriodic acids catalyzes the carbonylation of low molecular weight alcohols. As in related systems, the rhodium is converted to [Rh(CO)$_2$I$_2$]$^-$ and here it is thought that for linear alcohols, the alcohol is converted to the corresponding alkyl iodide before undergoing a rate-determining displacement of iodide by [Rh(CO)$_2$I$_2$]$^-$ as illustrated in Scheme XLV for n-propanol. Presumably the corresponding acid is the primary product but under reaction conditions esters also form. By contrast, when isopropanol is used a change in the product composition with carbon monoxide pressure is seen and measureable kinetic isotope effects were detected suggesting that the simple S_N2 rate-limiting step of Scheme XLV is not significant here. Although mechanistic details are uncertain, a hydrocarboxylation pathway was proposed and the participation of radicals could not be excluded (refs. 480, 481). Mixtures of palladium(II) acetate and tri-n-butylphosphine with $[Rh(acac)(CO)_2]$, $[RhCl(PPh_3)_3]$ or $[Rh_6(CO)_{16}]$ form catalyst systems for the hydrocarbonylation of methyl acetate to ethylidene diacetate in reasonable yields (ref. 482). While little or no activity for the transfer hydrogenation of cyclohexanone by ethanol was noted for $[RhCl(P(OPh)_3)_3]$, $[Rh(CO)_2I_2]^-$, $[RhCl(AsPh_3)_3]$, $[RhH(CO)(PPh_3)_3]$ or $[IrCl(CO)(PPh_3)_2]$, $[cp'_2M_2Cl_4]$ (M = Rh, Ir) and particularly $[cp'_2Rh_2(\mu\text{-}OH)_3]^+$ formed active catalysts. Poor yields were noted with methanol as the hydrogen donor however (ref. 483). Addition of small amounts of $[Rh(acac)(CO)_2]$ to iodide-promoted, ruthenium carbonyl catalyst systems for carbon monoxide hydrogenation enhances the selectivity to ethylene glycol at the expense of methanol but the total yield of these two products is unaffected. It is proposed that a key intermediate in the process is $[HRu(CO)_4]^-$ which can generate a ruthenium formyl complex by hydride transfer to a ruthenium carbonyl species. This formyl can then be converted to methanol. The



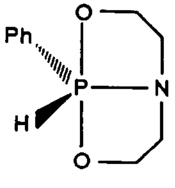
Scheme XLV

rhodium is presumed to exist as $[Rh(CO)_2I_2]^-$ initially and following conversion to $[Rh(CO)_2I_4]^-$ intercepts the $[HRu(CO)_4]^-$ which converts the rhodium(III) carbonyl species to a formyl which is the precursor to ethylene glycol (ref. 484).

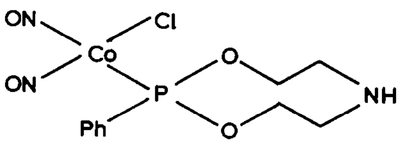
Other catalyst systems briefly described include $[Rh(CO)_2Cl_2]^-$ for the reduction of DMF by various silanes (ref. 485), $[RhCl(CO)_2]_2$ in the presence of iodide for the oxidative demercuration of aryl mercury compounds to give biaryls or, if carbon monoxide is present, diarylketones (refs. 486, 487) and for the polymerization of allene (ref. 488). Further reports cover the catalytic cyclotrimerization of phenylacetylene to predominantly 1,2,4-triphenylbenzene by [Rh(Oq)(CO)L] (Oq = 8-quinolinato; L = CO, $AsPh_3$, cyoct) (ref. 489), the determination that $[IrH(CO)(PPh_3)_3]$ is a poor catalyst for the dehydrocarboxylation of lactic acid because of a competing disproportionation reaction (ref. 490) and the support of $\{Rh(CO)_2\}$ moieties on a partially alkylated silica surface using $(MeO)_3Si(CH_2)_3SH$ to form pendant thiolate functionalities (ref. 491). Finally, a theoretical model for transport and reactivity in supported liquid phase catalysts has been satisfactorily tested with $[RhCl(CO)(PPh_3)_2]$ as a catalyst for ethylene hydrogenation in dioctyl phthalate (ref. 492) while adsorption isotherms for $[RhH(CO)(PPh_3)_3]$ in molten triphenylphosphine in contact with silica, alumina and porous Amberlite resin show that physisorption occurs in some cases but in others a strong chemisorption is evident (ref. 493).

Metal Nitrosyl and Aryldiazo Complexes

The phosphorane [241] tautomerizes on reaction with $[CoCl(NO)_2]_2$ giving [242] which reversibly absorbs carbon dioxide at -30°C to form the

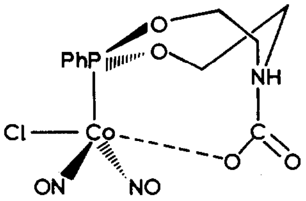


[241]



[242]

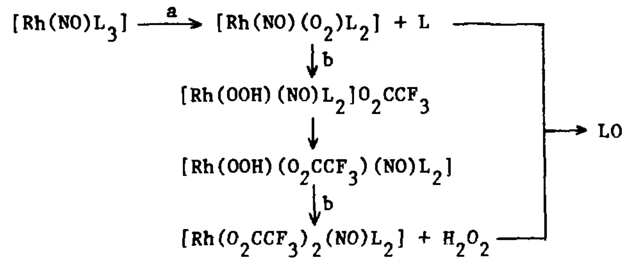
carbamato-like species [243] (ref. 494). $[CoX(NO)_2]_2$ (X = Cl, Br, I) has been rather extensively explored as a nitrosylating agent but only limited success was achieved. The bromide on reaction with $[Mn(CO)_5(L)]BF_4$ (L = $PEtPh_2$, $P(OPr^i)_3$) under photolysis gave only manganese(II) bromide and metallic manganese although $[Co(NO)(CO)_3]$, $[CoBr(NO)_2L]$ and $[Co(CO)_2(NO)L]$ were isolated. The whole range of halide complexes was allowed to react



[243]

with $[Mn_2(CO)_{10-n}L_n]$ (L = $PEtPh_2$; n = 1,2. L = PBu^i_3, $P(OPr^i)_3$; n = 2) under the same conditions and here $[Mn(NO)_3L]$ was formed together with *cis*-$[MnX(CO)_4L]$, $[Co(NO)(CO)_3]$ and $[Co(NO)(CO)_2L]$. The same series with $[VH(CO)_{6-n}L_n]$ (n = 2; L_n = DPPE) in acetonitrile or THF proceeds *via* $[V(CO)_3(DPPE)]$ and $[VXS_4(NO)]X$ to $[VS_4(NO)_2]X$ (X = Cl, Br, I; S = MeCN, THF) plus [Co(CO)(DPPE)(NO)]. The solvated vanadium nitrosyl is a useful precursor to a variety of dinitrosyl vanadium complexes (refs. 495-497). In an attempt to prepare $[cp_3Fe_2Co(CO)(NO)_2]$, $[cpCo(CO)_2]$ and $[cp_2Fe_2$-$(\mu\text{-}NO)_2]$ were reacted under photolysis but the only characterized products were $[cp_2Fe_2(CO)_4]$ and $[cp_3Co_3(\mu_3\text{-}NO)_2]$, both of which are well-known. The latter showed reversible one-electron reduction and oxidation steps in a cyclic voltammetric experiment (ref. 498). Alkylation of $[Co(NO)(CO)_2$-$(PPh_3)]$ with alkyllithium reagents forms $[RC(O)Co(CO)(NO)(PPh_3)]^-$ (R = Me, Bu^n, vy, bz, allyl), the first two examples of which function as acyl transfer reagents to α,β-unsaturated ketones such as benzalacetone, mesityl oxide, phorone and pulegone but, rather surprisingly, not cyclohexenone. The reaction also occurs with benzoquinones but is complicated by electron transfer reactions (ref. 499). Isolated $\{Co(NO)(CO)_2\}$ moieties can be supported on phosphinated styrene-divinyl benzene *via* coordination to phosphorus by reaction of $[Co(NO)(CO)_3]$ with the polymer (ref. 500) while an electron diffraction study of $[Co(NO)(CO)_3]$ suggests that the Co-N-O moiety is essentially linear. This is not the first such study but it is claimed to give more precise metrical parameters than previously determined (ref. 501).

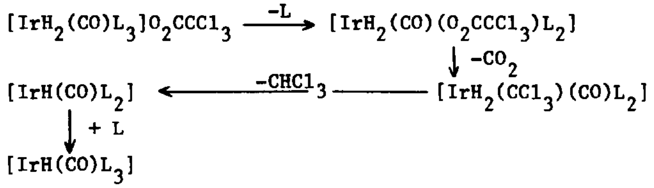
An acetone solution of $[Rh(NO)(PPh_3)_3]$ reacts with oxygen to form triphenylphosphine oxide and an unidentified rhodium complex containing nitrite ion and with TFA to form $[Rh(O_2CCF_3)(PPh_3)_3]$ *via* a species proposed to be $[Rh(NHO)(PPh_3)_3]O_2CCF_3$ since nitrous oxide is also a final product. Reaction of $[Rh(NO)(PPh_3)_3]$ with both TFA and oxygen forms $[Rh(O_2CCF_3)_2$-$(NO)(PPh_3)_2]$ and triphenylphosphine oxide by a route proposed to be that of Scheme XLVI (L = PPh_3). Analogs, $[Rh(NO)(O_2CR)_2(PPh_3)_2]$ (R = C_2F_5, C_6F_5,



a) TFA, O_2. b) TFA.

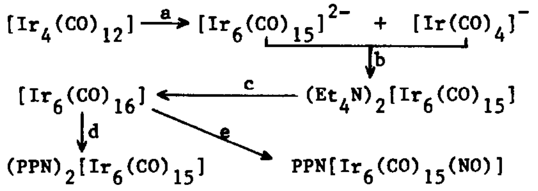
Scheme XLVI

CF_2Cl, $CHCl_2$, CH_2Cl, o-ClC_6H_4, o-$NO_2C_6H_4$, 3,5-$(NO_2)_2C_6H_3$) were also formed and all are considered to be square pyramidal with a bent, axial nitrosyl ligand. By contrast, $[Ir(NO)(PPh_3)_3]$ reacts with TFA, with or without oxygen present, to form a species having the same composition but with a trigonal bipyramidal structure and a linear nitrosyl group. As this reaction evolves hydrogen it is felt that it proceeds via intermediate formation of $[IrH(NO)(PPh_3)_3]O_2CCF_3$. Different behavior is noted with trichloroacetic acid which gives $[Rh(NO)(O_2CCCl_3)_2(PPh_3)_2]$ at low temperature but at room temperature decarboxylates to form $[Rh(NO)Cl_2(PPh_3)_2]$. The same product is formed when $[Rh(NO)(PPh_3)_3]$ reacts with $[Hg(CCl_3)_2]$ in hot toluene but if the reaction is run at 0°C the product is $[Rh(NO)(CCl_3)(HgCCl_3)(PPh_3)_2]$ suggesting that the decomposition of the trichloroacetate complex involves extrusion of carbon dioxide to form an intermediate trichloromethyl complex which then loses dichlorocarbene. The reaction of $[Ir(NO)(PPh_3)_3]$ with trichloroacetic acid appears to proceed analogously but no intermediates were detected. Similar behavior is noted with $[RhH(CO)(PPh_3)_3]$ and trichloroacetic acid which forms $[Rh(O_2CCCl_3)(CO)(PPh_3)_2]$ at low temperature followed by decarboxylation to $[RhCl(CO)(PPh_3)_2]$ on warming. Addition of further acid converts this to $[RhCl_3(CO)(PPh_3)_2]$. The iridium analog forms $[IrH_2(CO)(PPh_3)_3][H(O_2CCCl_3)_2]$ on reaction with excess trichloroacetic acid and $[IrH_2(CO)(PPh_3)_3]O_2CCCl_3$ when a limited amount of acid is present. The latter complex decomposes with formation of carbon dioxide and chloroform to regenerate $[IrH(CO)(PPh_3)_3]$. This is postulated to proceed as depicted in Scheme XLVII (L = PPh_3) and on paper represents a catalytic cycle for the decarboxylation of the acid. In practice, however, it doesn't work since as noted above, use of excess acid yields $[IrH_2(CO)(PPh_3)_3][H(O_2CCCl_3)_2]$ which does not react further unless heated and then it forms $[IrCl_3(CO)(PPh_3)_2]$ instead (refs. 502-504).



Scheme XLVII

In a study of photocatalysis by $[Rh(NO)(PPh_3)_3]$ it is proposed that the catalytic activity is related to distortions in the coordination sphere of the excited state (ref. 505) while oxidation of $[Rh(NO)_2(PPh_3)_2]ClO_4$ in the presence of pyridine or of $[Rh(NO)(NO_3)_2(PPh_3)_2]$ forms $[Rh(py)_4(NO_2)_2]ClO_4$ and $[Rh(NO_3)_3(PPh_3)_2]_n$ respectively (ref. 506). Further applications of $PPN(NO_2)$ as a possible route to nitrosyl complexes have been reported. From $[Co_4(CO)_{12}]$ are obtained $[Co(NO)(CO)_3]$, $PPN[Co(CO)_4]$ and a small yield of $PPN[Co_6N(CO)_{15}]$. The rhodium analog of the last is obtained in slightly better yield from $[Rh_4(CO)_{12}]$ under carbon monoxide and in good yield from $[Rh_6(CO)_{16}]$. Reaction of $[Ir_4(CO)_{12}]$ with $PPN(NO_2)$ forms a moderate yield of $PPN[Ir_4(NCO)(CO)_{11}]$ and this can be significantly increased if $PPN(N_3)$ is used instead. Also formed were $[Ir_6(CO)_{16}]^{2-}$ and $[Ir_8(CO)_{22}]^{2-}$ but these were not isolated. Other chemistry of this iridium system is outlined in Scheme XLVIII. The $[Ir_6(CO)_{15}(NO)]^-$ finally formed is contaminated by $[Ir_6(CO)_{16}]$ and $[Ir_6(CO)_{15}]^{2-}$. Thus it appears that the success



a) Na, CO, THF. b) $[Ir_4(CO)_{12}]$ then Et_4N^+. c) CO, CH_2Cl_2 then CF_3SO_3H.
d) xs $PPN(NO_2)$, THF. f) $PPN(NO_2)$, THF.

Scheme XLVIII

of PPN(NO_2) as a nitrosylating agent for mononuclear species does not hold with clusters (ref. 507). Nitrosyl tetrafluoroborate reacts with [Ir_2($COD)_2(\mu$-$pz)_2$] to form [Ir(NO)(COD)(μ-$pz)_2$Ir(COD)]BF_4 in which the nitrosyl group is strongly bent. While this appears to be a one-center oxidative addition to give a mixed-valence Ir(III)-Ir(I) species, the structural study shows no significant differences between the corresponding metal ligand distances in the two halves of the cation so the mixed-valence formulation does not seem likely. Further chemistry of this cation is given in Scheme XLIX. The same reaction with the 3,5-Me_2pz analog gave

$$\begin{tikzcd}
{[\mathrm{Ir(COD)(NO)(\mu\text{-}pz)_2Ir(COD)(CO)}]^+} & & {[\mathrm{Ir_2Me_2(COD)_2(\mu\text{-}pz)_2}]} \\
& {[\mathrm{Ir(COD)(NO)(\mu\text{-}pz)_2Ir(COD)}]^+} \arrow[ul, "a"] \arrow[ur, "b"'] \arrow[dl, "d"'] \arrow[dr, "c"] & \\
{[\mathrm{Ir_2I_2(COD)_2(\mu\text{-}pz)_2(\mu\text{-}NO)}]^+} \arrow[d, "e"] & & {[\mathrm{Ir_2Cl_2(COD)_2(\mu\text{-}pz)_2(\mu\text{-}NO)}]^+} \\
{[\mathrm{Ir_2I_2(COD)_2(\mu\text{-}pz)_2}]} & &
\end{tikzcd}$$

a) CO. b) MeMgI. c) HCl. d) I_2. e) $NOBF_4$.

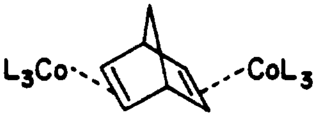
Scheme XLIX

[$Ir_2(COD)_2(\mu$-3,5-$Me_2pz)_2$]BF_4 which is paramagnetic. A rhodium analog was also prepared and the EPR spectra indicate delocalization of the odd electron over both metals (refs. 508, 509).

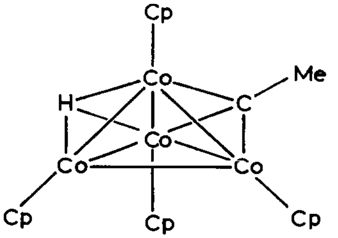
Addition of [p-$RC_6H_4N_2$]BF_4 to cis, mer-[$RhHCl_2(PEtPh_2)_3$] in methanol or acetonitrile containing chloride ion forms trans, mer-[Rh($NHNC_6H_4R)Cl_3$-$(PEtPh_2)_2$] (R = Cl, Me, OMe) but this does not really occur by an "insertion" of the diazonium cation into rhodium hydrogen bond. A detailed study of the reaction showed that initially one phosphine is replaced by solvent and this in turn is replaced by the diazonium cation. This is followed by proton loss from the metal, attachment of chloride and finally protonation of nitrogen (ref. 510).

Metal Alkene Complexes

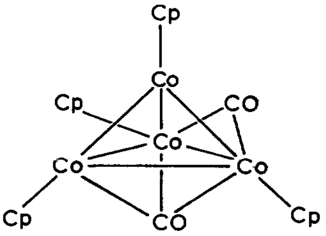
Complex [244] (L = PMe_3) can be formed either by reduction of a mixture of anhydrous cobalt(II) chloride, trimethylphosphine and NBD with magnesium in THF or from [Co(cyclo-$C_5H_8)(PMe_3)_3$] and NBD in pentane. It catalyzes the dimerization of NBD but careful addition of a second equivalent of NBD to [244] in cold pentane affords [Co(NBD)($PMe_3)_3$]. A strong antiferromagnetic coupling between the metals is seen in [244] which is proposed to involve a through-space interaction with the π-systems of the bridging NBD ligand. Formation of [Co(norbornene)$(PMe_3)_3$] occurs on reaction of norbornene with $[Co(C_2H_4)(PMe_3)_3]$ or on reduction of cobalt(II) chloride in the presence of the two ligands. In related work both anthracene and phenanthrene displace olefin from [Co(olefin)$(PMe_3)_3$] (olefin = cyclopentene, propylene) to form $[Co(C_{14}H_{10})(PMe_3)_3]$ in which the hydrocarbon is η^2-bonded via one of the outer rings. Reaction of these complexes with ethylene forms $[Co(C_2H_4)(PMe_3)_3]$. The hydride complexes $[CoH(C_{14}H_{10})(PMe_3)_3]$ result from reaction of the hydrocarbon with $[CoH(L)(PMe_3)_3]$ (L = N_2, C_4H_8) and on carbonylation form $[CoH(CO)(PMe_3)_3]$. By contrast, anthracene and phenanthrene replace a phosphine ligand in $[Ph_3SnCo(PMe_3)_3]$ to form $[Ph_3SnCo(\eta^4\text{-}C_{14}H_{10})(PMe_3)_2]$ where again binding is via one of the outer rings (refs. 511, 512). Thermolysis of $[cpCo(C_2H_4)_2]$ in hexane rather unexpectedly gives [245] while reaction with paraformaldehyde at approximately the same temperature in toluene forms [246]. Sampling the gas phase above the first reaction detected ethylene plus traces of hydrogen and it was suggested that the transformation of ethylene into the ethylidyne moiety occurred on the metals, possibly via reaction of a {cpCo} fragment with coordinated ethylene. Formation of [246] was suggested to arise from reaction of $[cpCo(CO)_2]$, formed by decarbonylation of the paraformaldehyde by $[cpCo(C_2H_4)_2]$, with more of the ethylene complex



[244]



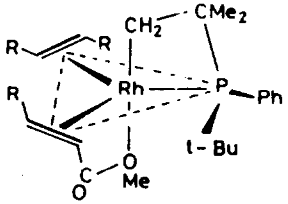
[245]



[246]

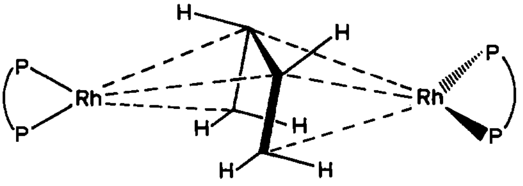
(ref. 513). The diene complexes $[(\eta^4\text{-diene})Co(PMe_3)_3]BPh_4$ (diene = buta-1,3-diene, 2,3-dimethylbuta-1,3-diene, isoprene) are formed from $[CoBr(PMe_3)_3]$ and the diene in acetonitrile at -10°C followed by treatment with methanolic sodium tetraphenylborate and are fluxional in solution (ref. 514). A kinetic study of the reversible reaction of $[Co_2(CO)_8]$ with NBD which forms $[Co_2(CO)_6(NBD)]$ suggested that the forward reaction involves initial formation of $[Co_2(CO)_7]$, a slow attachment of NBD in a monodentate fashion and then rapid loss of a second carbonyl with subsequent chelation of the diene. The reverse process envisages opening of the chelate ring followed by a slow addition of one carbonyl to regenerate $[Co_2(CO)_7(NBD)]$ (ref. 515). A cobalt-olefin species is proposed to be formed as an intermediate in the photolytic cleavage of allyl phenyl ether to propylene and phenol in the presence of $[CoH(PPh(OEt)_2)_4]$ (ref. 516).

While dimethylfumarate (L) simply forms trans-$[RhH(L)(PPr^i_3)_2]$ on reaction with $[RhH(PPr^i_3)_3]$, with $[RhH(N_2)(PPhBu^t_2)_2]$ the product is [247]



[247]

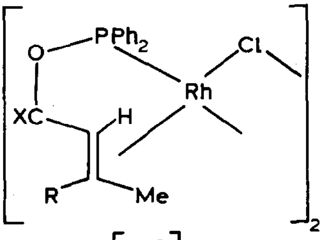
(R = CO_2Me). The metallation of the ligand is attributed to a combination of ligand bulk and the presence of the electron-withdrawing olefin ligands. The coordination of the methoxy group rather than the carboxyl oxygen is suggested to be the result of a lower amount of strain in this arrangement (ref. 517). An excess of buta-1,3-diene reacts with $[Rh_2(dippp)_2(\mu\text{-}H)_2]$ to form [248] as the major product together with some $[(\eta^3\text{-}1\text{-}MeC_3H_4)Rh(dippp)]$. Although the structural data suggest an η^3-interaction of the



[248]

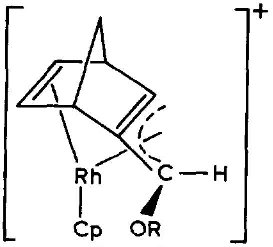
diene with each rhodium as depicted in the figure (there is a twist about the central carbon-carbon bond), the NMR data are more consistent with an

η^4-interaction with each metal (ref. 518). A series of chelate-stabilized olefin complexes, [249] (X = O; R = H, Me. X = H_2; R = Me) can be prepared from $[RhCl(C_2H_4)_2]_2$ and the appropriate ligand (ref. 519). The reaction of

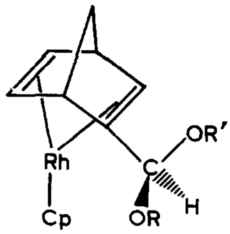


[249]

[250] with sodium alkoxides in ether is highly stereospecific and gives [251] (R = Et; R' = Me. R = Me; R' = Et) while [252] on acidification

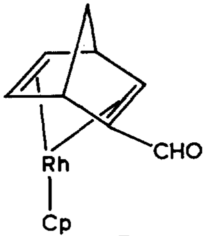


[250]

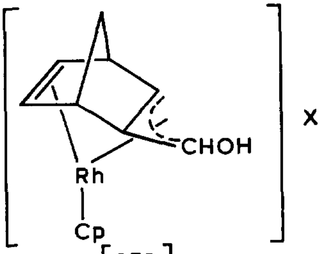


[251]

forms [253] (X = Cl, F_2PO_2) (refs. 520, 521). In methanol, $[RhCl(C_2H_4)_2]_2$ reacts with dicp to form $[RhCl(dicp)]_2$ which on subsequent treatment with

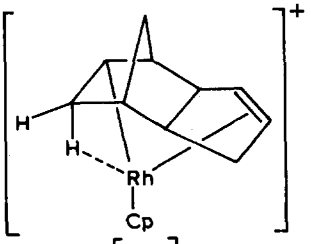


[252]



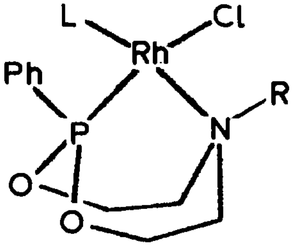
[253]

sodium cyclopentadienide gives [cpRh(dicp)]. Protonation of this last complex with hexafluorophosphoric acid forms [254] which contains an

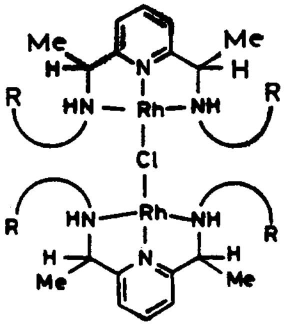


[254]

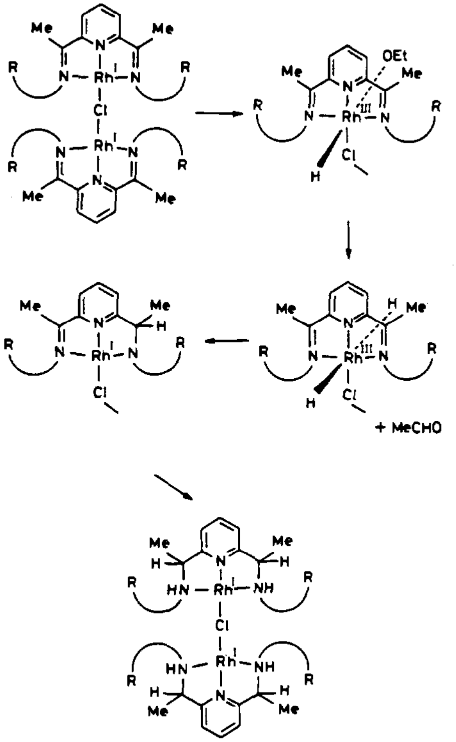
agostic hydrogen atom. Refluxing a mixture of $[cp'MCl_2]_2$ (M = Rh, Ir) and dicp in ethanolic sodium carbonate yields [cp'M(dicp)] from which analogs of [254] can be obtained in similar fashion (ref. 522). Complexes [255] (L = CO, C_2H_4; R = H, Me) have been investigated as catalysts for hex-1-ene hydrogenation. The carbonyl complexes are inactive while that with R = H, L = C_2H_4 is even more active than $[RhCl(PPh_3)_3]$. Both ethylene complexes are quite active for olefin isomerization under hydrogen however so their utility as hydrogenation catalysts is limited. The high isomerization activity is attributed to the possibility that following oxidative addition of hydrogen, transfer of one proton to the nitrogen atom in the ligand can occur (ref. 523). A series of diimine ligands derived from 2,6-diacetylpyridine react with $[RhCl(C_2H_4)_2]_2$ in acetonitrile/ethanol to form [256] (R = $(CH_2)_nCH=CH_2$ (n = 1,2), Pr^n). Reduction of the ligands must occur at some point during the reaction and since it does not occur in acetonitrile alone, a hydrogen transfer from the solvent is proposed as outlined in Scheme L (ref. 524). An apparently three-coordinate rhodium complex, $[RhL_2(C_2H_4)]PF_6$ (L_2 = bis(o-diphenylphosphinophenyl)ether), has been studied by fast-atom bombardment mass spectrometry (ref. 525).



[255]

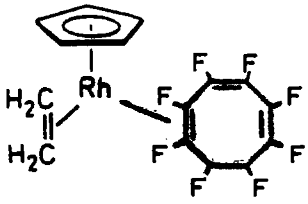


[256]

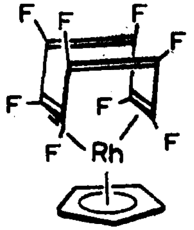


Scheme L

Reaction of $[RhCl(CO)(cyoct)_2]$ with cinnamylideneaniline(L) forms trans-$[RhCl(CO)L_2]$ in which the ligand coordinates only through its nitrogen atom (ref. 526). Photolysis of $[cp'RhH_2(SiEt_3)_2]$ in cyclohexane under an ethylene atmosphere partially converts it to $[cp'RhH(SiEt_3)(C_2H_4)]$ and $[cp'Rh(C_2H_4)_2]$ with the latter being the major product. The former was also detected in reactions between $[cp'Rh(C_2H_4)_2]$ and either triethylsilane or $[cp'RhH_2(SiEt_3)_2]$ under both thermal and photolylic conditions (ref. 527). At room temperature OFCOT and $[cpRh(C_2H_4)_2]$ form [257] which converts to [258] on heating. With $[(\eta^5-C_9H_7)Rh(C_2H_4)_2]$ only the indenyl



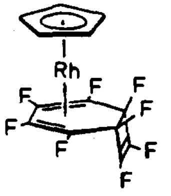
[257]



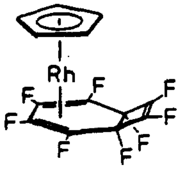
[258]

analog of [258] is seen. Addition of $[RhCl(cyoct)_2]_2$ to OFCOT in benzene at room temperature forms a polymeric species formulated as $[RhCl(OFCOT)]_n$

which can be converted to [259] plus a small amount of [260] by cyclopentadienyl thallium. If the first stage of this reaction is carried out at



[259]



[260]

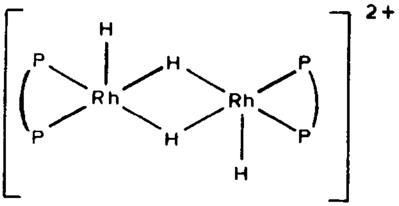
reflux then only [260] is obtained (ref. 528). Photolysis of [cpRh$(C_2H_4)_2$] at wavelengths greater than 290 nm is proposed to form [cpRh(C_2H_4)] which reacts further as indicated in Scheme LI. Evidence for the formation of

$$\begin{tikzcd}
 & {[\mathrm{cpRh}(\eta^4\text{-}C_4H_6)]} & \\
{[\mathrm{cpRh}(S(O)Me_2)(C_2H_4)]} & {[\mathrm{cpRh}(C_2H_4)]} \arrow[l, "b"'] \arrow[u, "a"'] \arrow[d, "c"] \arrow[r, "d"] & {[\mathrm{cpRh}(C_2H_4)(PPh_3)]} \arrow[d, "e"] \\
 & {[\mathrm{cpRhH}(SiR_3)(C_2H_4)]} & {[\mathrm{cpRh}(PPh_3)_2]}
\end{tikzcd}$$

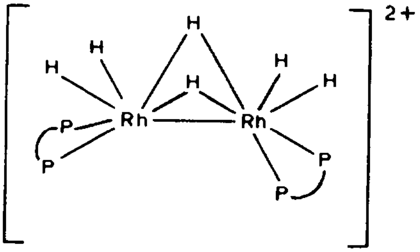
a) Buta-1,3-diene. b) DMSO. c) $HSiR_3$ (R = Me, Et).
d) PPh_3. e) PPh_3, hν.

Scheme LI

[cpRh(C_2H_4)] was also obtained when the bis(ethylene) complex was photolyzed in a nitrogen matrix while in a carbon monoxide matrix, [cpRh(C_2H_4)-(CO)] and then [cpRh$(CO)_2$] were detected. Unexpectedly however, photolysis in a methane matrix did not lead to any oxidative addition of a carbon-hydrogen bond to the metal (ref. 529). The ferrocenylphosphine complexes [Rh(NBD)((η^5-$C_5H_4PR^1R^2$)Fe(η^5-$C_5H_4PR^3R^4$))]ClO_4 (R^1-R^4 = Ph, Pr^i, Bu^t. R^1 = R^2 = Ph; R^3 = R^4 = Pr^i, Bu^t. R^1 = R^3 = Ph; R^2 = R^4 = Bu^t. R^1 = Ph; R^2 = R^3 = R^4 = Bu^t) have been prepared by standard methods and studied as olefin hydrogenation catalysts. The rates of hydrogenation increase as the number of tert-butyl substituents increases unless very bulky olefins are used and the one with R^1 = R^3 = Ph; R^2 = R^4 = Bu^t seems to provide the optimum balance between steric and electronic factors. The examples with R^1-R^4 = Ph, Pr^i and with R^1 = R^2 = Ph; R^3 = R^4 = Pr^i, Bu^t when hydrogenated in the absence of olefins form first [261], and then [262] and possibly [RhH_4-(L_2)]$^+$ as the final product. With [Rh(NBD)(dippe)]$^+$ the dippe analog of [262] is first seen which on further reaction with hydrogen forms a second

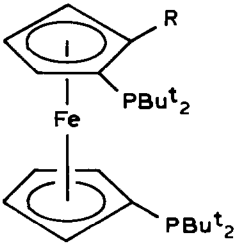


[261]

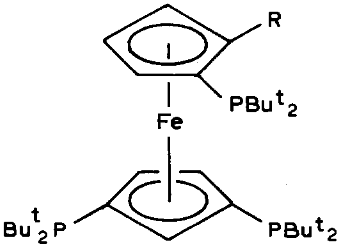


[262]

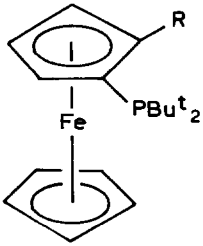
dimeric hydride of unknown structure. It was concluded that the course of the reactions of these complexes with hydrogen depends mainly on the nature of the substituents on phosphorus and not on the size of the chelate ring (refs. 530-532). In related work the complexes [Rh(NBD)(PN)]ClO_4 (PN = (S,R)- or (R,S)- [263], (R,R)- or (S,S)- [264], [265] (R = $CH(Me)NMe_2$))



[263]



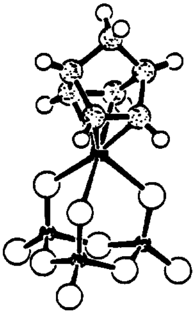
[264]



[265]

were synthesized. The complexes of [263] and [265] were fluxional owing to the interconversion of the two conformers while that of [264] as a catalyst for the asymmetric hydrogenation of prochiral olefins provided good optical yields (ref. 533).

The first example of an organometallic complex of the trimetaphosphate ion, $(Bu^n_4N)_2[Rh(NBD)(P_3O_9)]$, the anion of which is shown as [266], is



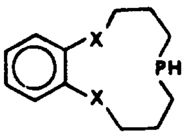
[266]

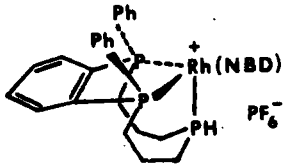
formed by treating $[RhCl(NBD)]_2$ with silver hexafluorophosphate in acetonitrile to first form $[Rh(NBD)(MeCN)_2]PF_6$ and then reacting this with $(Bu^n_4N)_3[P_3O_9]\cdot 2H_2O$ in dichloromethane. The pentamethylcyclopentadienyl analog, $(Bu^n_4N)[cp'Rh(P_3O_9)]$ can be synthesized in a similar fashion from $[cp'RhCl_2]_2$ (ref. 534). Some chemistry of $[Rh(NBD)_2]ClO_4$ is outlined in Scheme LII (ref. 535) while reaction of the corresponding hexafluorophosphate salt with [267] (X = PPh) forms [268] (ref. 536). The sulfur monoxide complexes trans-$[MCl(SO)L_2]$ (M = Rh, Ir; L = PPr^i_3, Pcy_3) can be obtained from $[MCl(cyoct)_2]_2$, a stoichiometric quantity of the ligand and thiirane-1-oxide at -40°C in toluene. Even at -70°C, carbon monoxide replaces the sulfur monoxide in the rhodium complex but in the iridium analog addition of a carbonyl group occurs to form square pyramidal $[IrCl(CO)(SO)L_2]$ with an apical sulfur monoxide ligand. This does lose sulfur monoxide at 0°C (ref. 537). The phosphonate $R_2P(O)H$ (R_2 = $OCH_2CMe_2CH_2O$) when allowed to react with $[RhCl(cyoct)_2]_2$ in a 4:1 ratio in refluxing benzene forms a mixture of [269] and [270] (X = H). The same reaction using greater than six equivalents of the ligand initially formed [269] and [270] (X = H, Cl) but after longer reaction times only the last two were present and could not be separated. Using five equivalents of ligand in the presence of triethylamine afforded only [270] (X = H) while with eight equivalents of the ligand in the presence of cyclohexanone only [270] (X =

$$\begin{tikzcd}
 & {[Rh(NBD)_2]ClO_4} \arrow[d, "a"] & \\
{[Rh(CO)LL'_2]ClO_4} \arrow[d, "d"'] & {[Rh(NBD)L_2]ClO_4} \arrow[l, "c"'] \arrow[r, "d"] \arrow[d, "b"] & {[Rh(NBD)(\eta^6\text{-}C_6H_5BPh_3)]} \\
{[Rh(CO)LL'_2]BPh_4} & {[Rh(NBD)LL']ClO_4} \arrow[ul, "c"] &
\end{tikzcd}$$

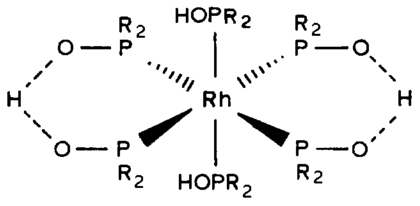
a) L (= $2\text{-}XC_5H_4N$ (X = F, Cl, Br)). b) L' (= PPh_3, $P(p\text{-tolyl})_3$).
c) CO, L' (= PPh_3, $P(p\text{-tolyl})_3$). d) BPh_4^-.

Scheme LII

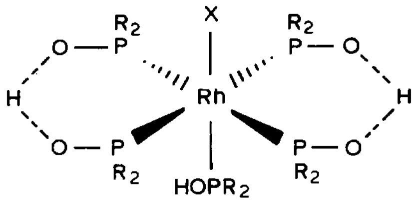

[267]



[268]

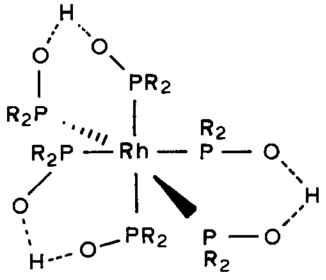


[269]

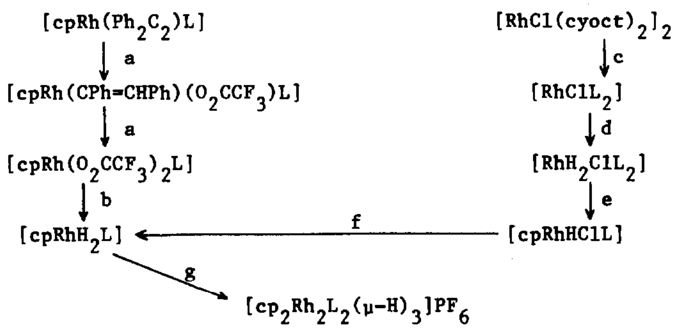


[270]

Cl) formed. Reaction of the same ligand with [Rh(acac)(cyoct)$_2$] in refluxing toluene produced [270] (X = H) and [271]. Iridium analogs of [269] and [270] were prepared similarly (ref. 538). Some chemistry of triisopropylphosphine (L) complexes of rhodium and iridium is outlined in Schemes LIII and LIV (ref. 539).

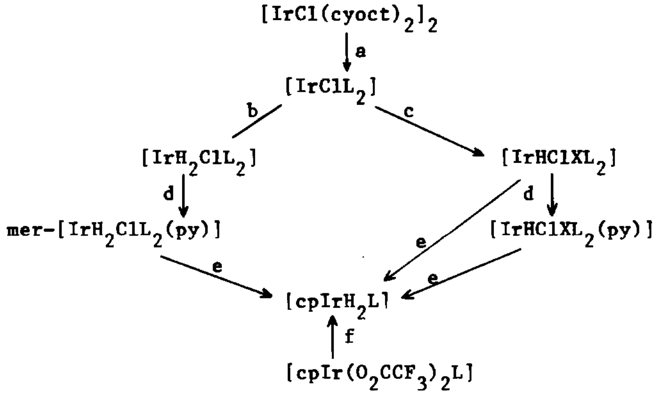


[271]



a) TFA. b) Na[AlH$_2$(O(CH$_2$)$_2$OMe)$_2$]. c) xs L, pentane. d) H$_2$, benzene. e) cpH. f) LiAlH$_4$. g) TFA, PF$_6^-$

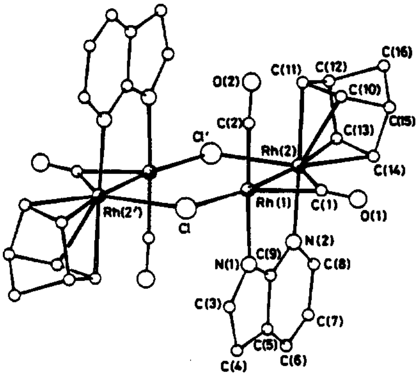
Scheme LIII



a) L, pentane. b) H_2. c) HX (X = Cl, I). d) py. e) Nacp.
f) $Na[AlH_2(O(CH_2)_2OMe)_2]$.

Scheme LIV

Chloride abstraction from $[RhCl(COD)]_2$ with silver triflate in acetone forms [Rh(COD)(OTf)] while successive treatment of [Rh(acac)(COD)] with perchloric acid in THF and diphosphines forms species of empirical formula $[Rh(COD)(L_2)]ClO_4$ (L_2 = $Ph_2P(CH_2)_nPPh_2$ (n = 2,5,8,11), $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 1-3)). These latter complexes are readily oxidized and tend to lose COD on standing. The complexes of the short-chain ligands appear to be monomers with chelating phosphine ligands but those of the longer ones are probably mixtures of monomers, dimers and possibly higher oligomers and/or metallated species (ref. 540). Another example of the $[RhCl_2(COD)]^-$ ion is found in $[Rh(COD)(ophen)][RhCl_2(COD)]$ which forms on addition of one equivalent of ophen to $[RhCl(COD)]_2$ (ref. 541). The Oro group continues to be very active in the study of rhodium and iridium diene complexes containing nitrogen-donor ligands. The first of its papers describes complexes of 1H-pyrrolo[2,3-b]pyridine(HL). With $[MCl(diene)]_2$ (M = Rh; diene = NBD, COD, TFB, Me_3TFB. M = Ir; diene = COD) one obtains [MCl(diene)(HL)] which can be carbonylated to $[MCl(CO)_2(HL)]$ while with $[Rh(diene)_2]ClO_4$ (diene = COD, NBD, TFB), $[Rh(diene)(HL)_2]ClO_4$ is the product which similarly forms $[Rh(CO)_2(HL)_2]ClO_4$ with carbon monoxide. [MCl(diene)(HL)] can be deprotonated by potassium hydroxide in methanol to give $[M_2(diene)_2(\mu\text{-}L)_2]$ and reaction of one example (M = Rh; diene = NBD) with $[RhCl(CO)_2]_2$ forms [272]. This can also be synthesized from



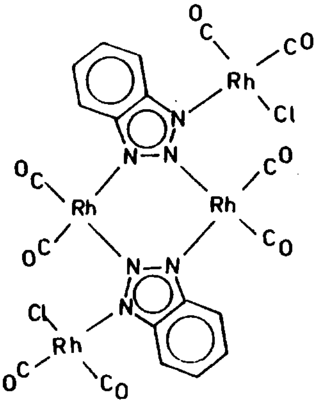
[272]

$[Rh_2(CO)_4(\mu\text{-}L)_2]$ and $[RhCl(NBD)]_2$ (ref. 542). Related chemistry with benzotriazole (bztH) and derivatives is outlined in Scheme LV. If $[RhCl(CO)_2]_2$ is added to $[Rh(COD)(\mu\text{-}bzt)]_2$, the product is [273] (ref. 543). On

$$\begin{tikzcd}
{[RhCl(COD)]_2} \arrow[r, "a"] \arrow[dr, "d"'] & {[RhCl(COD)(bztH)]} \arrow[r, "b"] \arrow[d, "c"] & {[RhCl(CO)_2(bztH)]} \\
 & {[Rh(COD)(\mu\text{-}bzt)]_2} \arrow[r, "b"] \arrow[d, "e"] & {[Rh(CO)_2(\mu\text{-}bzt)]_2} \arrow[d, "f"] \\
 & {[Rh_2(\mu\text{-}bzt)(\mu\text{-}Cl)(L_2)_2]} & {[Rh(CO)(PPh_3)(\mu\text{-}bzt)]_2}
\end{tikzcd}$$

a) bztH, acetone. b) CO. c) Et_3N. d) bztH, KOH, MeOH.
e) $[RhClL_2]_2$ (L_2 = COD, TFB). f) PPh_3.

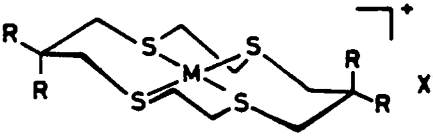
Scheme LV



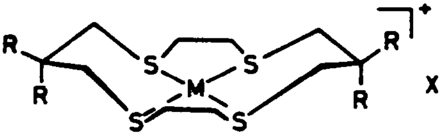
[273]

reaction with $[RhClL_2]_2$ (L_2 = COD, NBD, TFB, $(C_2H_4)_2$, $(cyoct)_2$) in the presence of triethylamine, 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (AH) behaves like acetylacetone and forms $[Rh(A)L_2]$ with the anion of the ligand coordinating like a β-diketonate. The same complexes can be synthesized from the thallium(I) salt of the ligand and $[RhClL_2]_2$. Coordination of $[Au(PPh_3)]^+$ to the free nitrogen did not occur but various ligands displaced COD from [Rh(A)(COD)] to form $[Rh(A)L_n]$ (L_n = $(PPh_3)_2$, DPPE, ophen, $(CNBu^t)_3$) and oxidative addition of iodine formed $[RhI_2(A)(COD)]$. Iridium analogs of some of these latter complexes were also prepared. Addition of the anion of the pyrazolone ligand to $[Rh_2Cl_2(COT)]_n$ or $[(\eta^3\text{-}C_3H_5)_2RhCl]_2$ formed $[Rh_2A_2(COT)]$ and $[(\eta^3\text{-}C_3H_5)_2Rh(A)]$ respectively (ref. 544). Addition of 2,3- or 1,8-diaminonaphthalene or the corresponding dihydroxynaphthalenes (LH_2) to $[Rh(OMe)(COD)]_2$ forms $[Rh_2(COD)_2(\mu\text{-}L)]$. Iridium analogs of the first two were also prepared. Conproportionation of $[Rh_2(COD)_2(\mu\text{-}L)]$ (L = $1,8\text{-}C_{10}H_6O_2^{2-}$) with its iridium analog formed $[(COD)Rh(\mu\text{-}L)Ir(COD)]$ which underwent ligand exchange with 1,8-diaminonaphthalene to form $[(COD)Rh(\mu\text{-}L)Ir(COD)]$ (L = $1,8\text{-}C_{10}H_6(NH)_2^{2-}$) (ref. 545).

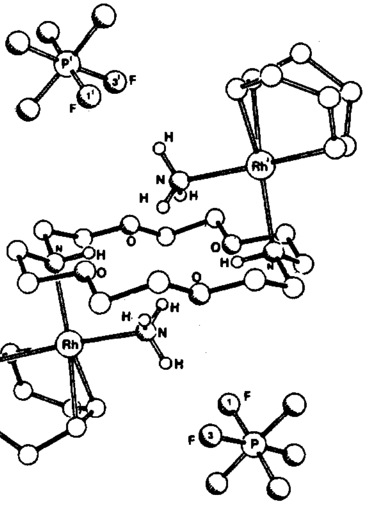
Bridge cleavage of $[RhCl(COD)]_2$ by cytosine occurs in methanol to yield [RhCl(COD)(cytosine)] (ref. 546). Complexes [274] (R = H, Me; X = Cl) are readily formed from the ligand and $[RhCl(cyoct)_2]_2$ in toluene. The latter on reaction with sodium tetraphenylborate in methanol underwent a conformational change to give [275] (R = Me; X = BPh_4). Interestingly both [274] (R = Me; X = Cl) and [275] (R = Me; X = BPh_4) are conformationally stable to 100°C in DMSO. All three complexes oxidatively add a carbon-chlorine bond of dichloromethane with [274] reacting significantly faster presumably because the metal is further out of the plane of the four sulfur atoms (ref. 547). As part of a study of second coordination sphere ligands $[Rh(COD)(NH_3)_2]PF_6$ was reacted with 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane and with α-cyclodextrin to form [276] and [277] respectively. A more stable analog of the latter used ethylenediamine in place of the two ammonia ligands. In [276] the crown is considered to act simultaneously as a first and a second sphere ligand (refs. 548, 549).



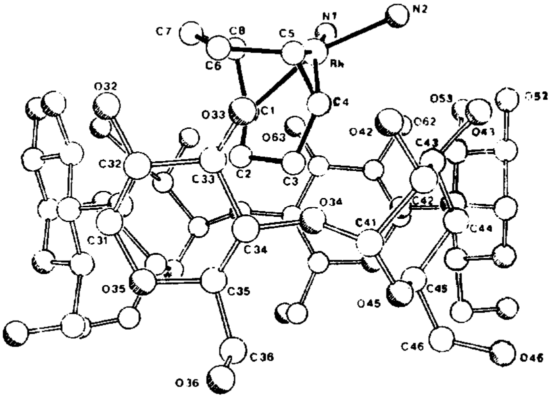
[274]



[275]

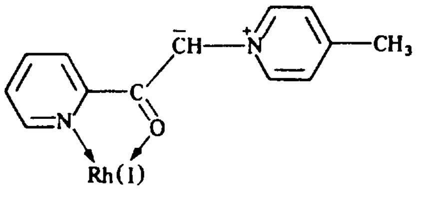


[276]

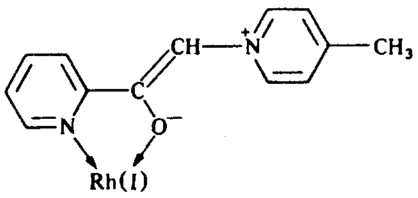


[277]

The complex $[Rh(COD)L_2]ClO_4$ (L = quinoline-N-oxide) is prepared from $[Rh(COD)(acetone)_x]ClO_4$ and undergoes replacement of one quinoline-N-oxide ligand by other donors to give $[Rh(COD)LL']ClO_4$ (L' = PPh_3, 4-aminopyridine). Analogs with some substituted pyridine-N-oxides were also prepared (ref. 550). The ylide 4-methyl pyridinium 2-pyridylcarbonylmethylide (Y) reacts with $[RhCl(COD)]_2$ and perchlorate ion in methanol to yield $[Rh(COD)(Y)]ClO_4$ whose structure suggests significant contributions from the two resonance forms [278a] and [278b]. Analogs with acetyl, acetoxy and phenyl substituents in place of the methyl group were also prepared and the electronic absorption and emission spectra were measured (ref. 551). In an



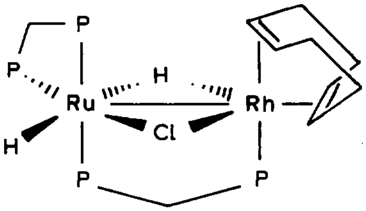
[278a]



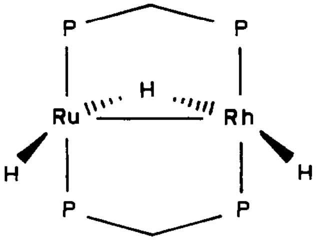
[278b]

attempt to prepare a bulky aryl oxide complex of rhodium, $[RhCl(L)(PPh_3)_2]$ (L = CO, PPh_3) was reacted with the lithium salt of 4-methyl-2,6-di-tert-butylphenol but instead the product was $[(\eta^5\text{-}2,6\text{-}Bu^t{}_2\text{-}4\text{-}MeC_6H_2O)Rh(L)(PPh_3)]$. The same result occurred with $[RhClL_2]_2$ (L_2 = $(C_2H_4)_2$, COD) and $[(\eta^5\text{-}2,6\text{-}Bu^t{}_2\text{-}4\text{-}MeC_6H_2O)RhL_2]$ formed (ref. 552).

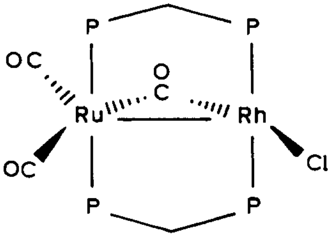
With $[MCl(L_2)]_2$ (L_2 = COD; M = Rh, Ir. L_2 = NBD, TFB; M = Rh), N,N'-diphenylbenzamidinate (DPBA) forms monomeric [M(COD)(DPBA)] but dimeric $[Rh_2(L_2)_2(DPBA)_2]$ (L_2 = NBD, TFB). The diene ligands in the latter can be replaced by carbon monoxide to form $[Rh_2(CO)_4(DPBA)_2]$ which oxidatively adds iodine to give $[Rh_2I_2(CO)_4(DPBA)_2]$. Reaction of $[Rh_2Cl_2(CO)_2(DPM)_2]$ with silver perchlorate and DPBA forms the "A-frame" complex $[Rh_2(CO)_2(\mu\text{-}DPBA)(\mu\text{-}DPM)_2]ClO_4$. With N,N'-diphenylbenzamidine $[MCl(L_2)]_2$ forms $[MCl(L_2)(PhN{=}C(Ph)NHPh)]$ (M = Rh, Ir; L_2 = COD. M = Rh; L_2 = TFB). When M = Rh; L_2 = COD, reaction with either carbon monoxide or $[Rh(acac)(CO)_2]$ causes deprotonation of the benzamidine ligand to form $[Rh_2(CO)_4(\mu\text{-}DPBA)_2]$. Protonation of [Rh(COD)(DPBA)] with perchloric acid followed by addition of triphenylphosphine forms $[Rh(COD)(PPh_3)(PhN{=}C(Ph)NHPh)]ClO_4$ but the analogous TFB complex could not be formed by this route. Instead it was necessary to react $[RhCl(TFB)(PhN{=}C(Ph)NHPh)]$ with silver perchlorate and the phosphine (ref. 553). Oxidation of the formamidinate complex $[Rh(COD)(RN\text{---}C(H)\text{---}NR)]_2$ (R = p-tolyl) with silver nitrate forms $[Rh_2(RN\text{---}C(H)\text{---}NR)_3(NO_3)_2]$ as the major product. The air-stable complex contains one unpaired electron and as the structure study suggests an equivalence of the metals, an average oxidation state of 2.5 is assigned (ref. 554). Mixing $[RuH_2(DPM)_2]$ and $[MCl(COD)]_2$ (M = Rh, Ir) forms [279] which is converted by borohydride (M = Rh) to [280]. The latter is considered to be electron-poor since it has only 28 electrons while the diplatinum analog has 30. Reaction of [279] (M = Rh) and trimethylphosphite forms $[RuHCl(P(OMe)_3)(DPM)_2]$ plus $[RhH(P(OMe)_3)_4]$ while with carbon monoxide and methyllithium the products are [281] and [282] respectively. The phenyl group on ruthenium in [282] evidently arises from cleavage of one DPM ligand (refs. 555, 556). Reaction of $[(\eta^5\text{-}C_5H_4(CH_2)_2SR)_2Mo(SR)_2]$ (R = Pr^n, Ph) with $[RhCl(COD)]_2$ or $[Rh(DPPE)(acetone)_x]BF_4$ forms $[(\eta^5\text{-}C_5H_4(CH_2)_2SR)_2Mo(\mu\text{-}SR)_2Rh(L_2)]X$



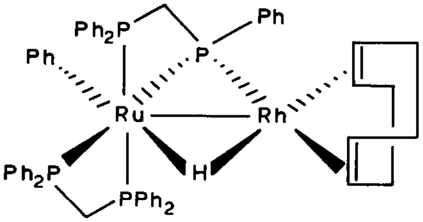
[279]



[280]

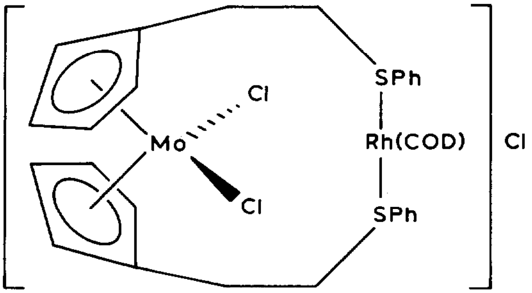


[281]



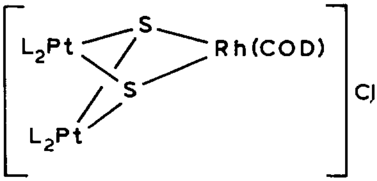
[282]

(L$_2$ = COD; X = Cl or L$_2$ = DPPE; X = BF$_4$ respectively). Conversion of the molybdenum complex (R = Ph) to [(η^5-C$_5$H$_4$(CH$_2$)$_2$SPh)$_2$MoCl$_2$] with hydrogen chloride followed by reaction with [RhCl(COD)]$_2$ however yields [283] (ref.



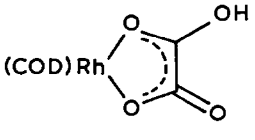
[283]

557). Addition of potassium tetrathiosquarate to [MClL$_2$]$_2$ (M = Rh, Ir; L$_2$ = COD. M = Rh; L = CO) forms [L$_2$M(μ-S$_2$C$_4$S$_2$)ML$_2$] (ref. 558) while [RhCl(COD)]$_2$ and [Pt$_2$S$_2$(PPh$_3$)$_4$] yield [284] (L = PPh$_3$). This does not react with carbon monoxide, sulfur dioxide or hydrogen but slowly converts to [Rh(DPPE)$_2$]$^+$ when DPPE is added (ref. 559).



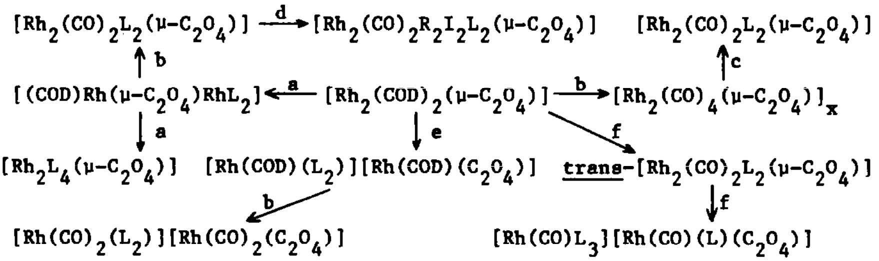
[284]

One equivalent of oxalic acid converts [Rh(acac)(COD)] to [285] which



[285]

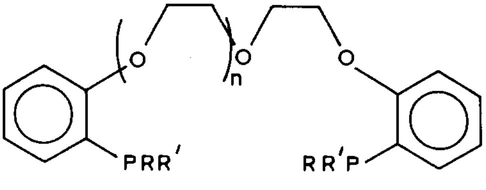
dimerizes in solution via hydrogen bonding and reacts further with [M(acac)-(diene)] (M = Rh, Ir; diene = COD. M = Rh; diene = TFB) to give [(COD)Rh-(μ-C_2O_4)M(diene)]. The original reaction using two equivalents of oxalic acid gives [$Rh_2(COD)_2(\mu\text{-}C_2O_4)$] directly. Malonic acid and [Rh(acac)-(diene)] (diene = COD, NBD, TFB) similarly yield [$Rh_2(diene)_2(\mu\text{-}O_2CCH_2\text{-}CO_2)$]. Some further chemistry of [$Rh_2(COD)_2(\mu\text{-}C_2O_4)$] is outlined in Scheme LVI. Some intermolecular metal-metal interaction is suggested in [$Rh_2(CO)_4\text{-}(\mu\text{-}C_2O_4)]_x$ because of its dark color but this is apparently rather weak



a) 2L (= $P(OPh)_3$). b) CO. c) PPh_3. d) RI (R = Me, I).
e) L_2 (= ophen, bipy). f) 2L (= $CNBu^t$).

Scheme LVI

(ref. 560). The phosphinoethers [286] (L_2: R = R' = Ph; n = 1, 2. R = Ph; R' = Me; n = 1) form [(COD)Rh(L_2)]ClO_4 when allowed to react with



[286]

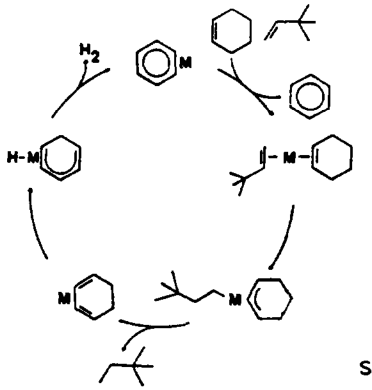
[Rh(acac)(COD)] in THF containing perchloric acid but these tend to lose COD. Reaction of these with carbon monoxide displaces COD but only monocarbonyl complexes form so it is proposed that an oxygen atom of the ligand backbone coordinates to the metal (ref. 561). The ^{103}Rh NMR spectra of complexes including [Rh(acac)(C_2H_4)$_2$], [RhCl(COD)]$_2$ and [(η^3-allyl)$_2$Rh-(acac)] have been obtained at a field strength of 9.4 T. At this field the T_1's of the rhodium nuclei are generally less than 5 sec. so that acquisition times are much reduced from what has previously been required. An enhanced sensitivity can also be achieved using a selective INEPT pulse sequence (ref. 562). Complexes of the type [(η^5-C_5H_4CHO)Rh(diene)] (diene = 2-chlorobuta-1,3-diene, trans-1-chlorobuta-1,3-diene, 2,3-dichlorobuta-1,3-diene, trans-trans-1,4-diphenyl-1,3-diene, 2-methylbuta-1,3-diene, COT) have been prepared by standard methods and the NMR spectra of these plus [(η^5-C_5H_4R)Rh(L_2)] (R = CO_2Me; L_2 = COT, (C_2H_4)$_2$. R = CPh_3; L_2 = COD. R = CHO; L_2 = (C_2H_4)$_2$, 2,4-dimethylpenta-1,3-diene) obtained. From EHMO calculations it appears that the extent of the "allyl-ene" contribution to the binding of the cyclopentadienyl group to rhodium is dependent on both the substituents on the diene and on the ring (ref. 563).

A good precursor to trimethylenemethane complexes appears to be 2-trimethylsilylmethylprop-1-en-3-yl methanesulfonate. Reaction with [IrX-(CO)L_2] (X = Cl; L = PPh_3, $AsPh_3$. X = Br; L = PPh_3), [IrH(CO)(PPh_3)$_3$] or [IrCl(cyoct)$_2$]$_2$ plus four equivalents of triphenylphosphine forms [(η^4-C_4H_6)IrX(CO)L], [(η^4-C_4H_6)Ir(CO)(PPh_3)$_2$]OSO_2Me and [(η^4-C_4H_6)IrCl(PPh_3)$_2$] respectively. The rhodium analog of the second product could not be prepared and instead [Rh(OSO_2Me)(CO)(PPh_3)$_2$] formed. The reaction forming the trimethylenemethane complexes is proposed to proceed via initial oxidative addition of the CH_2-OSO_2Me bond to the metal followed by conversion of the organic moiety to an η^3-allyl ligand followed by loss of trimethylsilyl methanesulfonate (ref. 564).

Dissolution of [IrH_3(CO)(PPh_3)$_2$] in neat acrylonitrile, methyl acrylate or styrene (olefin = ol) forms [IrH(ol)(CO)(PPh_3)$_2$] in which the resistance to loss of coordinated olefin increases in the order given. Solutions of these complexes in hydrocarbon solvents decompose with the styrene complex rapidly losing the olefin, the methyl acrylate complex slowly losing olefin but also showing a small amount of hydrogenation of the olefin and the acrylonitrile complex reacting at an intermediate rate to give propionitrile as the major product. No radicals appeared to be involved in the last reaction and the second equivalent of hydrogen required for the formation of the propionitrile apparently comes from the phosphine ligand via an o-metallated species. Addition of oxygen or acrylonitrile to this system enabled the intermediate alkyl complex to be trapped as [Ir(CH(Me)-CN)(CO)(L)$(PPh_3)_2$] (L = O_2, acrylonitrile) but attempts to trap it by carbon monoxide or phosphines only caused displacement of the olefin. The same result was obtained when oxygen was added to the styrene complex. The differing modes of decomposition of the olefin complexes were attributed to the carbon-carbon double bond axis being perpendicular to the iridium-hydrogen vector. Thus the relative ease of rotation of the olefin to place these two vectors in the same plane vs dissociation of the olefin determines whether significant insertion of the olefin into the iridium hydrogen bond occurs (ref. 565). While $[IrCl(O_2)(C_2H_4)(PPh_3)_2]$ is stable in an ethylene atmosphere, under nitrogen it decomposes to form triphenylphosphine oxide and acetaldehyde. Addition of oct-1-ene or styrene to this complex forms ketones and yields are increased if excess oxygen is present. On the other hand, oxygenation of $[IrCl(styrene)_2]_2$ forms only small amounts of acetophenone and benzaldehyde. Addition of 9-phenyldibenzophosphole(L) to $[IrCl(C_2H_4)_2]_2$ forms $[IrCl(C_2H_4)_2L_2]$ in which one ethylene ligand can be replaced by dioxygen but this species unlike its triphenylphosphine analog does not mediate the oxidation of oct-1-ene. It is suggested that the olefin to be oxidized adds to a preformed dioxygen complex of iridium. Also prepared in this work was $[Ir(C_2H_4)_3(PPh_3)_2]BF_4$ by treatment of $[IrCl(C_2H_4)(PPh_3)_2]$ with silver tetrafluoroborate in an ethylene atmosphere (ref. 566). The structure of $[Ir_2(PF_3)_4(\mu\text{-}Cl)_2]$ shows a significant folding along the chlorine-chlorine axis resulting in an intramolecular iridium-iridium distance of 2.942(1) Å. Association of the dimers in the solid state produces zig-zag chains with intermolecular metal-metal distances of 3.271(1) Å. An analysis of various inter- and intramolecular contacts in the solid state structure led to the suggestion that in planar iridium(I) complexes with trifluorophosphine or related ligands of similar size (e.g. $[IrCl(PF_3)_3]$, $[Ir(acac)(PF_3)_2]$ the intermolecular non-bonded interactions would be too great to permit formation of extended stacks of the monomers. This proposal was tested by the preparation of a variety of fluorophosphine complexes with PF_2NMe_2(L) and 2-fluoro-1,3,2-benzodioxaphosphole(L'). Both $[IrClL_3]$ and $[IrClL'_3]$ could be synthesized from $[IrCl(cyoct)_2]_2$ but only $[IrClL_2]_2$ could be obtained on reaction with more $[IrCl(cyoct)_2]_2$. As expected, no significant intermolecular association appeared to occur. The same conclusion was reached with $[RhClL'_2]_2$, prepared from $[RhCl(1,5\text{-}HD)]_2$, and $Me_4N[RhCl_2L'_2]$ and $Me_4N[IrCl_2L_2]$ prepared from tetramethylammonium chloride and the appropriate chloro-bridged dimer. On the other hand the color of $[Ir_2(L_2)_2(\mu\text{-}Cl)_2]$ (L_2 = $O{=}C(N(Me)PF_2)_2$), obtained from $[IrCl(cyoct)_2]_2$, suggested an extended metal-metal interaction but no satisfactory crystals could be obtained for a structure determination. Bridge cleavage by triphenylphosphine formed $[IrCl(PPh_3)(L_2)]$ which could not be purified but appeared not to be associated. Rhodium analogs of both were also prepared as were $[M(acac)(L_2)]$ (M = Rh, Ir) and $[IrCl_2(L_2)_2]^-$ (ref. 567). Using stoichiometric quantities, [MCl(CO)(bipy)] (M = Rh, Ir) can be prepared from $[RhCl(CO)_2]_2$ and from $[IrCl(cyoct)_2]_2$ plus carbon monoxide respectively. However, addition of an excess of bipy to $[RhCl(1,5\text{-}HD)]_2$ or $[IrCl(cyoct)_2]_2$ gave inseparable mixtures. Addition of sodium tetrafluoroborate to a chloroform solution of the rhodium mixture afforded $[Rh(bipy)_2]BF_4$ while carrying out the iridium reaction in the presence of sodium tetrafluoroborate gave $[IrH(bipy)_2]$ instead. The hydride ligand is thought to originate on the cyclooctene. Some of the oxalate complexes reported in ref. 560 were also prepared here (ref. 568).

Analogs of $[Ir_2(COD)_2(\mu\text{-}pz)_2]$ containing variously substituted pyrazolates and indazolate have been prepared primarily from $[IrCl(COD)]_2$ and the neutral ligand in the presence of triethylamine. When the pyrazole is quite bulky however, direct reaction with the pyrazolate anion is successful. The former route could be used to form $[Ir_2(COD)_2(\mu\text{-}pz)(\mu\text{-}(CF_3)_2pz)]$ from a mixture of the two pyrazoles but the two symmetrically bridged complexes also formed. Low yields of $[IrRh(COD)_2(\mu\text{-}pz)_2]$ could be obtained by the former route if a mixture of $[IrCl(COD)]_2$ and $[RhCl(COD)]_2$ is used but the best preparation involves reaction of $[Rh(COD)(pzH)_2]$ with $[IrCl(COD)]_2$ in the presence of triethylamine. All the complexes undergo a reversible, one-electron oxidation in cyclic voltammetric experiments (ref. 569). Similar dimeric complexes have been prepared from $[IrCl(COD)]_2$ and the sodium salt of 2-hydroxypyridine(L) and its 6-methyl analog. The former can be oxidatively cleaved to monomeric $[IrCl_2(L)(COD)]$ by chlorine or by photolysis in the presence of carbon tetrachloride. The net four-electron oxidation chemistry seen here contrasts with the two-electron, two-center oxidative additions undergone by the pyrazolate-bridged dimers and is unexpected since the electronic absorption and emission spectra of the two classes of compounds are quite similar (ref. 570).

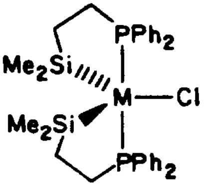
The complexes $[IrH_2S_2L_2]A$ (S = solvent, L = phosphine, A = non-coordinating anion) are modest catalysts for the disproportionation of cyclohexene to cyclohexane and benzene. The best one is $[IrH_2(acetone)_2(P(p\text{-}FC_6H_4)_3)_2]^+$ operating at 80°C in 1,2-dichloroethane and it is ultimately converted to $[Ir_2H_2L_4(\mu\text{-}Cl)_2(\mu\text{-}X)]^+$ (X = Cl, H) after all the substrate is consumed. Whichever isomer of methylcyclohexene is used in a related experiment, some 1-methylcyclohexene is always seen in the early stages suggesting isomerization of substrate proceeds more rapidly than dehydrogenation. The analog with S = MeCN shows comparable activity and as it does not react with the solvent it can be recovered unchanged at the end of the reaction. When 3,3-dimethylbut-1-ene is added to act as a hydrogen acceptor, a virtually quantitative dehydrogenation of cyclohexene to benzene is observed and the cycle of Scheme LVII is proposed. At 4°C $[IrH_2S_2(PPh_3)_2]^+$ (S = acetone, MeCN, MeOH) reacts over twenty-four hours with cyclohexa-1,3-diene to form $[(\eta^5\text{-}C_6H_7)IrH(PPh_3)_2]^+$ which on heating in the appropriate solvent reforms the starting complex with the liberation of benzene. The same complexes react with alkylbenzenes in the presence of 3,3-dimethylbut-2-ene on heating to give $[(\eta^6\text{-}C_6H_5R)Ir(PPh_3)]^+$. These also generate benzene and $[IrH_2S_2(PPh_3)_2]^+$ on heating with the extra hydrogen apparently being derived from the solvent. Both hydrogen-containing complexes on heating in cyclopentane form $[cpIrH(PPh_3)_2]^+$ (ref. 571). The complex $[IrH_2(O_2CCF_3)(L)_2]^+$ (L = $P(p\text{-}FC_6H_4)_3$, Pcy_3) can be prepared from $[IrH_2(acetone)_2(P(p\text{-}FC_6H_4)_3)_2]^+$ and sodium trifluoroacetate or from $[Ir(O_2CCF_3)(COD)]_2$, tricyclohexylphosphine and hydrogen respectively. Both will mediate hydrogen transfer from alkanes to 3,3-dimethylbut-2-ene but the tricyclohexylphosphine complex will catalyze the dehydrogenation of cyclooctane to cyclooctene under photolysis in the absence of 3,3-dimethylbut-2-ene (ref. 572).



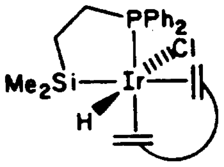
Scheme LVII

Hydrogenation of [Ir(COD)L_2]A in the presence of nitrogen-donor ligands at 0°C forms [$IrH_2L'L_2$]A (L = PPh_3; L' = 8-methylquinoline, caffeine; A = BF_4, SbF_6) in which the methyl group on L' contains an agostic hydrogen. This is presumed to be a precursor to carbon-hydrogen bond activation so calculations have been performed to attempt to define the trajectory for this oxidative addition process. These indicate that the agostic interaction develops to the point at which the C-H---Ir angle is about 130° after which the C-H vector rotates to diminish this angle and at the same time the C-H bond lengthens. The results suggest that conformational and steric factors will be important in determining whether metallation of a ligand or attack of the metal on an external carbon-hydrogen bond will occur. The latter should be favored if the metal is sterically uncongested (ref. 573).

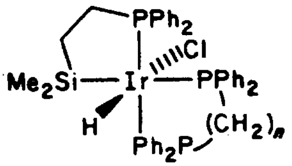
A full report has now appeared on the synthesis of some silylphosphine rhodium and iridium complexes. Reaction of $[MCl(COD)]_2$ with four equivalents of 2-dimethylsilylethyldiphenylphosphine forms [287] (M = Rh, Ir) while use of only two equivalents (M = Ir) gives [288] which is converted to [289] (n = 1,2) by DPM and DPPE. Addition of Lewis base ligands to [287] forms [290] (M = Ir; L = CO, PF_3, $P(OMe)_3$, $P(OEt)_3$, CNR (R = Pr^i, Bu^t, $CMe_2CH_2Bu^t$)) while chloride abstraction with silver tetrafluoroborate in the presence of carbon monoxide yields [291]. Reaction of [287] (M = Rh, Ir) with borohydride causes replacement of the chloride by hydride. This species was not isolated and for M = Ir reacted with neutral ligands to form [292] (L = CO, Bu^tNC) (ref. 574). In an extension of the work reported in ref. 379, $[IrCl(COD)]_2$ reacts with sodium dimethylbis(pyrazolyl)gallate at low temperature to form [(Me_2Gapz_2)Ir(COD)] and moderate amounts of [$Ir_2(COD)_2(\mu\text{-}pz)_2$] from decomposition of the pyrazolylgallate



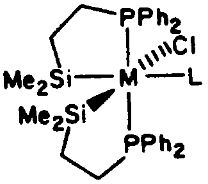
[287]



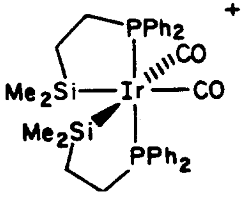
[288]



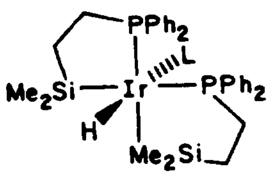
[289]



[290]

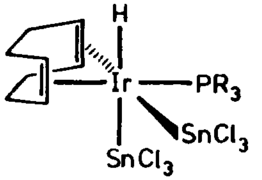


[291]

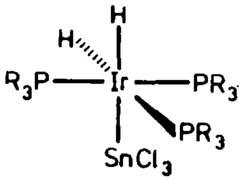


[292]

ligand. The former product on carbonylation at the same temperature formed [(Me$_2$Gapz$_2$)Ir(CO)$_2$] which reacted with triphenylphosphine to give [(Me$_2$Gapz$_2$)Ir(CO)(PPh$_3$)]. This complex proved difficult to purify and could also be obtained from [IrCl(CO)(PPh$_3$)$_2$] and the pyrazolylgallate ligand in refluxing THF or from [IrCl(CO)$_2$(*p*-toluidine)], triphenylphosphine and the same ligand in THF at room temperature. With the analogous dimethylbis(3,5-dimethylpyrazolyl)gallate a small amount of [(Me$_2$Ga(3,5-Me$_2$pz)$_2$)Ir(COD)] could be obtained but the major product here was [Ir$_2$(COD)$_2$(μ-3,5-Me$_2$pz)$_2$] and other routes attempted also failed to give significant amounts of the desired product (ref. 575). Hydrogenation of [Ir(COD)L$_2$]ClO$_4$ (L = THT, tms, SMe$_2$,SEt$_2$) forms [IrH$_2$(COD)L$_2$]ClO$_4$ but only the first two products are stable. Similarly [Ir$_2$H$_4$(COD)$_2$(μ-L$_2$)$_2$](ClO$_4$)$_2$ (L$_2$ = Bu^{t}S(CH$_2$)$_2$SBu^t, 1,4-dithiacyclohexane) could be formed from [Ir$_2$(COD)$_2$(μ-L$_2$)$_2$](ClO$_4$)$_2$ (ref. 576). Addition of two equivalents of the appropriate phosphine to [IrCl(COD)]$_2$ followed by two equivalents of tin(II) chloride forms [IrH$_2$(COD)(SnCl$_3$)(PR$_3$)] (PR$_3$ = PPh$_3$, (*p*-anisyl)$_3$P, (*p*-FC$_6$H$_4$)$_3$P, (*p*-ClC$_6$H$_4$)$_3$P). The triphenylphosphine complex frequently was obtained as a mixture of isomers. Reactions of [IrCl(COD)]$_2$ with two equivalents of the same phosphines and four of tin(II) chloride followed by hydrogen chloride formed [293] while using four equivalents of ligand and two of tin(II) chloride gave [Ir(SnCl$_3$)(COD)(PR$_3$)$_2$] (PR$_3$ = PPh$_3$, P(*p*-anisyl)$_3$). The last reacted with hydrogen and more ligand to form [294]. None of these complexes were active as hydrogenation catalysts (ref. 577).

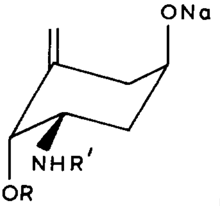


[293]

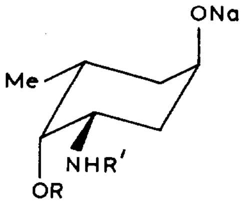


[294]

Addition of [MCl(COD)]$_2$ to [IrH$_5$(PPh$_3$)$_2$] yields [(COD)M(μ-H)(μ-Cl)IrH$_2$(PPh$_3$)$_2$] (M = Rh, Ir) which is unreactive towards hydrogen but is cleaved to a variety of mononuclear species by triphenylphosphine in refluxing THF. No tractable products could be obtained from $[IrH_5(PPh_3)_2]$ and $[RhCl(CO)_2]_2$ or $[(\eta^3-C_3H_5)PdCl]_2$ (ref. 578). The methylenecyclohexane [295] (R = bz, R' = PhC(O)) can be catalytically hydrogenated to [296] by

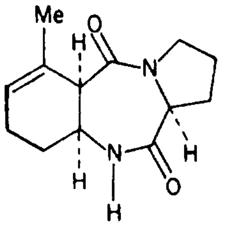


[295]

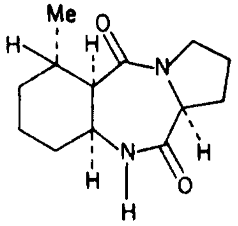


[296]

$[Ir(COD)(Pcy_3)(py)]PF_6$ or $[RhCl(PPh_3)_3]$ and quantitatively and selectively by $[Rh(NBD)(DPPE)]BF_4$ (ref. 579). Another highly selective hydrogenation is that of [297] to [298] catalyzed by $[Ir(COD)(Pcy_3)(py)]PF_6$. By contrast, catalysis by palladium-on-carbon gives no stereoselectivity.



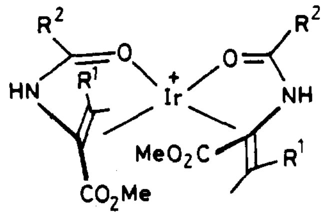
[297]



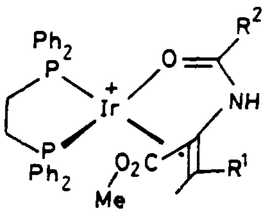
[298]

Related cyclohexenes containing carboxamine and carbalkoxy substituents trans to the double bond can also be hydrogenated with high stereoselectivity by this catalyst. Presumably these substituents coordinate to the metal thus preferentially orienting the double bond as has been suggested previously for cyclohexenols as substrates (ref. 580). The same iridium complex as well as $[Rh(DPPB)(NBD)]^+$ behave analogously in catalyzing the hydrogenation of methylenecyclohexane and methylcyclohexene carboxylic acid esters (ref. 581).

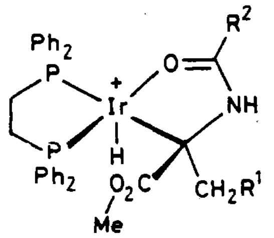
As was noted in the 1984 Annual Survey most of the papers dealing with the asymmetric hydrogenation of prochiral olefins do not dwell on mechanism. This year one paper has appeared which describes studies on iridium analogs of some of the rhodium systems from which many of the mechanistic details of this process have been obtained. The goal was to enhance the stability of the proposed alkyl hydride intermediates which have only infrequently been detected in the rhodium systems so that they could be more thoroughly characterized. The established procedures did not however lead to analogous enamide phosphine complexes of iridium and an alternate route was devised. Treatment of $[IrCl(C_2H_4)_4]$ with the appropriate enamide and then silver tetrafluoroborate yielded [299] (R^1 = Ph; R^2 = Ph, Me. R^1 = C_6D_5; R^2 = Me). These reacted cleanly with DPPE in dichloromethane or methanol to form [300] which readily reacted with hydrogen in methanol at -78°C to give [301] with no intermediates being detected. Complex [299] (R^1 = Ph; R^2 = Me) also reacted with DIPAMP(P͡P) to give a mixture of the diastereoisomeric complexes shown on the left of Scheme LVIII in approximately equal amounts. These equilibrated over two hours to give primarily the one in the upper left and reacted with hydrogen to give alkyl hydride complexes as indicated in the Scheme. This is in contrast to analogous



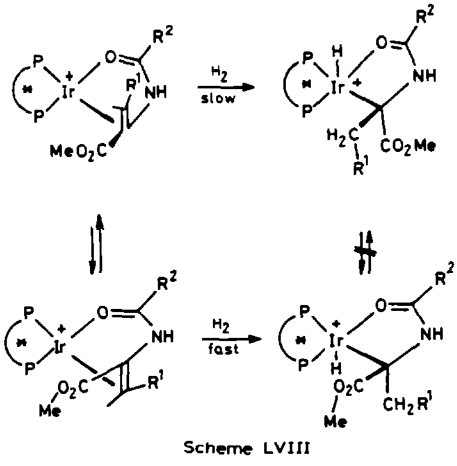
[299]



[300]



[301]

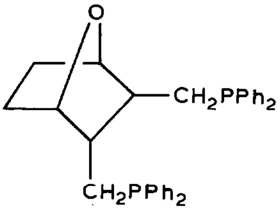


Scheme LVIII

rhodium systems where the thermodynamically preferred diastereoisomer isomerizes more rapidly than it reacts with hydrogen so only one alkyl hydride complex can be detected (ref. 582).

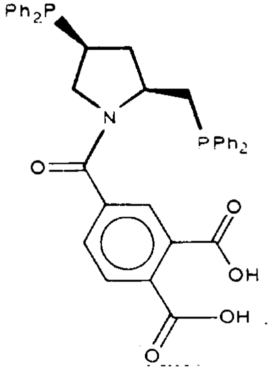
The asymmetric hydrogenation of α-(hydroxyalkyl)acrylate esters is catalyzed by $[Rh(L_2)(S_2)]^+$ (L_2 = DPPB, DIPAMP; S = MeOH, CH_2Cl_2, THF) with excellent optical yields. For example, ethyl 3-hydroxy-2-methylenebutanoate is converted exclusively into anti-ethyl-3-hydroxy-2-methylbutanoate (ref. 583). A quantitative expression of the relationships involved in the kinetic resolution of a racemic mixture containing a prochiral center has been tested with the [RhCl(DIOP)]-catalyzed hydrogenation of a dipeptide (ref. 584). Other systems include standard rhodium complexes of (R)-PROPHOS or (+)-DIOP for an asymmetric hydrogenation to form L-[3-^{11}C]-phenylalanine (ref. 585) and $[Rh(NBD)(L_2)]^+$ (L_2 = BDPP, BDPOP) for asymmetric hydrogenation of (Z)-α-acylaminoacrylic and -cinnamic acid derivatives (these are the most commonly used substrates and will be assumed in the subsequent discussion unless otherwise noted). The BDPP ligand gave a more selective catalyst and even was effective with α-ethylstyrene which, unlike the standard substrates, has no additional substituents which can bind it to the metal in a preferred orientation (refs. 586, 587). $[Rh(BINAP)(diene)]^+$ (diene = COD, NBD) is a catalyst precursor for the asymmetric isomerization of allyl amines to (E)-enamines. Addition of a second equivalent of BINAP sharply retards the rate at 40°C but at 80°C the presence of the extra ligand accelerates the rate significantly. $[Rh(BINAP)_2]^+$ has been isolated and the structural study shows considerable steric interaction between the ligands. This complex shows the same activity as the system containing a second equivalent of the ligand and gives the same chirality in the product as that containing only one ligand per metal and it is suggested that in the latter instance one phosphine ligand dissociates in solution (ref. 588).

Other asymmetric hydrogenation catalyst systems described include a rhodium BINAP complex for standard substrates (ref. 589), $[Rh(COD)(L_2)]Cl$ (L_2 = (-)-[302]) for itaconic acid (ref. 590), $[Rh(COD)(L_2)]Cl$ (L_2 =

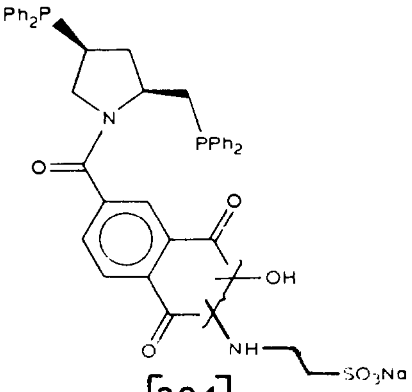


[302]

$[cpFe(\eta^5\text{-}1,2\text{-}(Ph_2P)_2C_5H_3)]$ for conversion of ω-(ethylamino)-3-hydroxyacetophenone hydrochloride to 2-ethylamino-1-(3-hydroxyphenyl)ethanol (ref. 591), $[Rh(L_2)(S)_n]^+$ (L_2 = (2R,3S)-1,2-bis(diphenylphosphino)-3-(tert-butoxycarbonyl)aminobutane; S = solvent) for standard substrates (ref. 592) and $[Rh(COD)(L_2)]Cl$ (L_2 = (2S,4S)-N-tert-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine) for conversion of ketopantolactone to D-(–)-pantolactone (ref. 593). In the last two, optical yields exceeding 90% were achieved. The ligands [303] and [304] (L_2) were used to form $[Rh(COD)(L_2)]^+$ to be employed as a water soluble catalyst for standard substrates in water solution. With [304] optical yields up to 60% were obtained (ref. 594). A final system for asymmetric hydrogenation of the same substrates used as ligands (5α-cholestan-3α(or β)-yl)diphenylphosphine and its 5H-dibenzophosphole analog on rhodium but optical yields were disappointingly low and in addition the latter gave very slow rates (ref. 595).

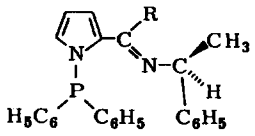


[303]

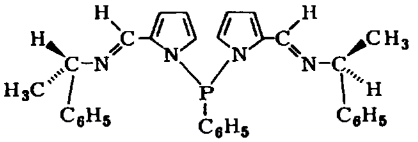


[304]

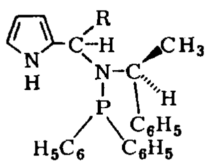
The asymmetric hydroformylation of olefins can be catalyzed by $[Rh((S,S)\text{-}CHIRAPHOS)(NBD)]Cl$ or $[RhH(CO)(PPh_3)_3]$ plus DIOP. The former provides higher optical yields but has a lower activity. It is felt that the asymmetric induction occurs prior to or during the formation of the diastereoisomeric metal alkyl complex (ref. 596). A large number of ligands (L_2) containing chiral substituents have been used to form $[Rh(COD)(L_2)]^+$ which were evaluated as catalysts for the asymmetric hydrosilylation of ketones, particularly acetophenone, by diphenylsilane. The amino phosphines [305] – [310] (R = H, Me) formed catalysts giving only rather low optical yields.



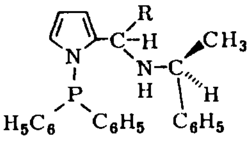
[305]



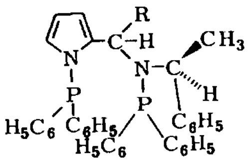
[306]



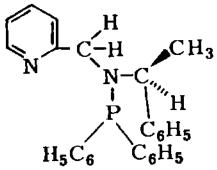
[307]



[308]

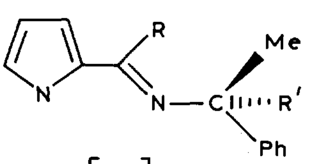


[309]

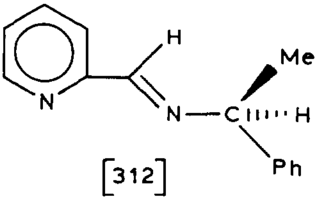


[310]

Better results were obtained with analogous complexes of [311] (R = H, Me; R' = H, Et) and [312] and these were studied in solution by NMR to determine the ligand conformations. The results suggested that the phenyl group

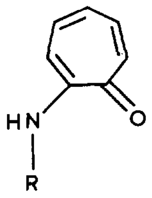


[311]

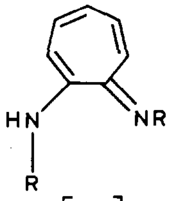


[312]

prefers to avoid eclipsing the coordination plane of the metal. Also, evidence was seen for a slow dissociation of the rhodium-imine nitrogen bond in [311] (R = R' = H) and [312]. Also examined were the neutral complexes $[Rh(COD)(L_2)]$ (L_2H = [313], [314] (R = CHMePh)) prepared from



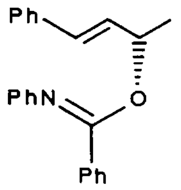
[313]



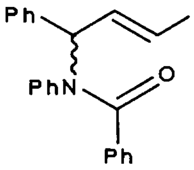
[314]

$[RhCl(COD)]_2$ and the ligand in the presence of tetrabutylammonium hydrogen sulfate and potassium hydroxide but essentially no asymmetric induction was seen (refs. 597-599). A final chiral catalyst system used $[Rh(diene)(L_2)]^+$ (diene = NBD, COD; L_2 = PROPHOS, (S,S)-CHIRAPHOS) in the presence of potassium hydroxide for the asymmetric hydrogenation of acetophenone by hydrogen transfer from isopropanol. Low to modest optical yields were obtained which varied depending on the time allowed for activation of the catalyst prior to addition of the substrate. These differences were suggested to possibly be due to differing degrees of oligomerization of the rhodium species in solution (ref. 600).

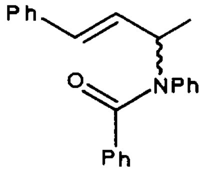
Non-chiral catalyst systems include one derived from $[RhCl(COD)]_2$ and two equivalents of an isocyanide ($2,6\text{-}R_2C_6H_3NC$ (R = Me, Pr^i)) for the hydrosilylation of oct-1-ene (ref. 601) and $[IrCl(cyoct)_2]_2$ itself which catalyzes the hydrosilylation of 2,3-dimethylbuta-1,3-diene to predominantly $Me_2C{=}C(Me)CH_2SiR_3$ (R = Et, OEt). Yields were decreased when triphenylphosphine was added but in the latter instance pent-1-yne could be converted to $Pr^nCH{=}CHSiEt_3$ by triethylsilane in excellent yield with good selectivity to the cis isomer. The phosphine/$[IrCl(cyoct)_2]_2$ system also was effective for hydrosilylation of cyclohexanone except when two equivalents of phosphine were used as inactive $[IrHCl(SiEt_3)(PPh_3)_2]$ then formed. Attempts to catalyze the asymmetric hydrosilylation of ethyl pyruvate were unsuccessful (ref. 602). The Claisen rearrangement of allyl imidates to allyl amides, e.g. [315] to [316] plus [317] is catalyzed by $[Rh(NBD)(DPPE)]ClO_4$, $[Ir(COD)_2]BF_4$, $[IrCl(COD)]_2$ and $[Ir(COD)L_2]BF_4$ (L_2 = DPPE; L = MeCN) and the carbonium ion mechanism of Scheme LIX is proposed (ref. 603).



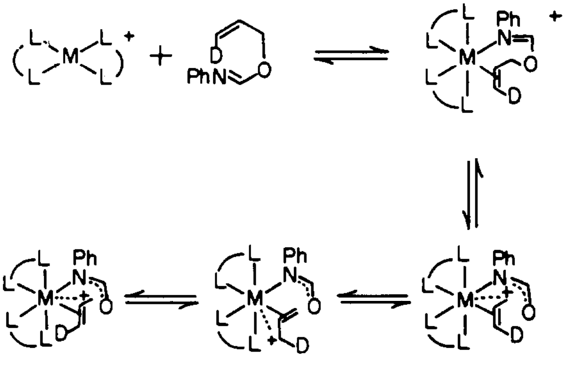
[315]



[316]

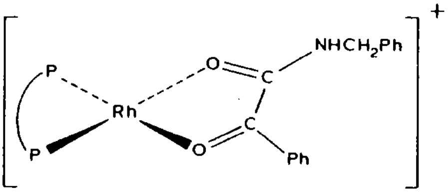


[317]

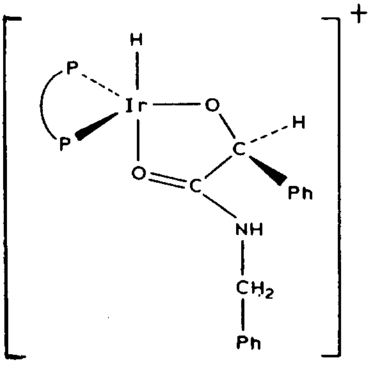


Scheme LIX

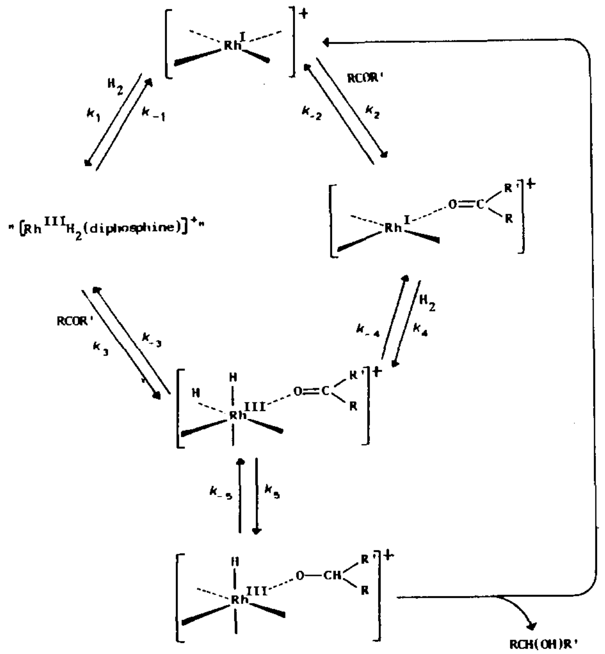
The rate of dimerization of allyl acrylates catalyzed by $[RhCl(C_2H_4)_2]_2$ is significantly enhanced by the addition of a combination of a Bronsted and a Lewis acid such as methanol and iron(III) or tin(IV) chloride. The nature of the Lewis acid has a large effect on the isomeric composition of the product (ref. 604). $[Rh(NBD)(Pr^i_2P(CH_2)_4PPr^i_2)]ClO_4$ is a catalyst precursor for the hydrogenation of ketones and the apparent steric effect on the rate occasioned by changes in the ketone substituents is attributed to variations in the ease of intramolecular transfer of hydrogen from the metal to the keto carbon of the O-bonded substrate. The facile reduction of benzophenone suggests that the enol form of the substrate is not important on the reaction coordinate. When the substrate is N-benzylphenylglyoxal, the initial formation of [318] can be detected and the observation of comparable rates of hydrogenation of this substrate here and where the diphosphine ligand is 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(dicyclohexylphosphino)butane suggests that chelation of the phosphine is maintained in both. NMR studies indicate that $[Rh(NBD)(L_2)]^+$ (L_2 = $Pr^i_2P(CH_2)_nPPr^i_2$ (n = 3,4)) is rapidly hydrogenated to $[Rh(L_2)S_2]^+$ (S = solvent) and more slowly to $[RhH_2S_2(L_2)]^+$. In an attempt to detect intermediates, $[Ir(COD)(Pr^i_2P(CH_2)_4PPr^i_2)]PF_6$ was treated with N-benzylphenylglyoxal under hydrogen and [319] formed. Scheme LX was proposed for the catalytic cycle (ref. 605).



[318]

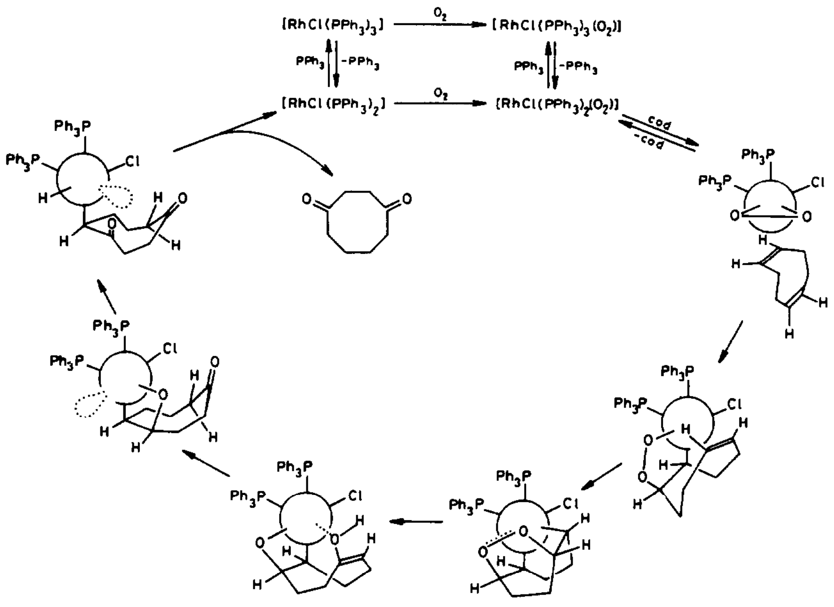


[319]



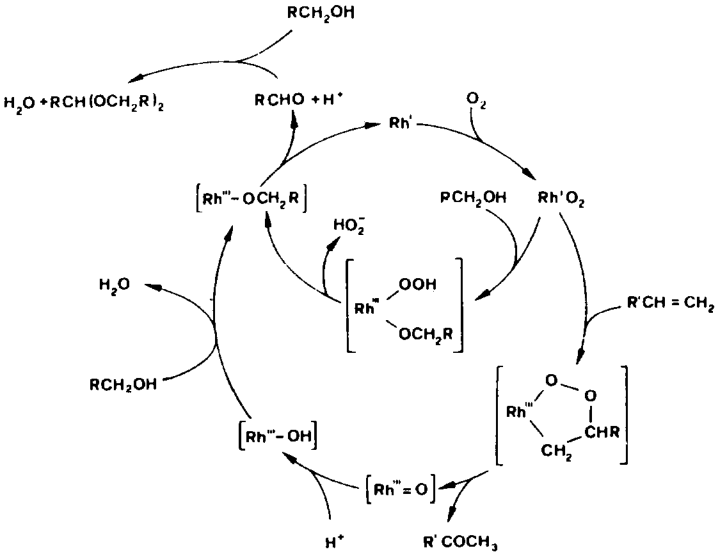
Scheme LX

Benzyl bromide can be converted to butyl phenylacetate by [RhCl(1,5-HD)]$_2$ promoted by potassium iodide in di-n-butyl ether under carbon monoxide. Other benzylic bromides and symmetric ethers react analogously (ref. 606). Alkyl, vinyl and aroyl bromides can be converted to carboxylate esters by carbon monoxide and organoborates in the presence of catalytic amounts of [RhCl(1,5-HD)]$_2$ plus [Pd(PPh$_3$)$_4$] while the same conversion of benzylic bromides can be effected using alkoxides of Ti(IV) and Zr(IV) in the presence of [RhCl(1,5-HD)]$_2$ or [RhCl(CO)$_2$]$_2$. Mechanisms similar to that shown in Scheme XLIX of the 1984 Annual Survey (J. Organomet. Chem., 305(1986)1) are presumed to operate here (refs. 607, 608). The hydroboration of olefins by 1,3,2-benzodioxaborazole is catalyzed by [RhCl(L)(PPh$_3$)$_2$] (L = PPh$_3$, CO) or [RhCl(COD)]$_2$ and an oxidative addition of the boron-hydrogen bond to the metal is proposed (ref. 609). Oxygenation of COD is catalyzed by [RhCl(O$_2$)L$_3$] (L = PPh$_3$, AsPh$_3$) and [IrCl(O$_2$)-(PPh$_3$)$_3$]. The first is best, gives cyclooctan-1,4-dione and, from labelling studies showing that both oxygen atoms on one complex transfer to the same substrate molecule, Scheme LXI is proposed (ref. 610). By contrast in the oxidation of terminal olefins to methyl ketones in alcohols catalyzed by [Rh(L$_2$)$_2$]BF$_4$ or [Rh(diene)(L$_2$)]BF$_4$ (L$_2$ = DPM, DPPE, DPPP, DPPB, vdiphos, Ph$_2$P(CH$_2$)$_n$SR (R = Ph; n = 1-3. R = Et; n = 2. R = Me; n = 3), PhS(CH$_2$)$_2$-SPh; diene = NBD, COD) only one oxygen atom of each oxygen molecule is transferred to the olefin and the other ends up in the solvent as shown in



Scheme LXI

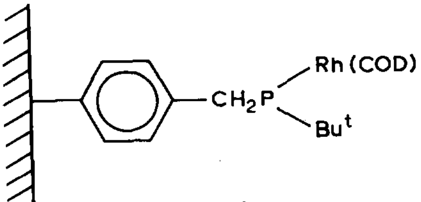
Scheme LXII (ref. 611). Sulfonated orthophenanthrolines react with [IrCl-(COD)]$_2$ to give catalysts for the WGSR. Both iridium hydride and iridium



Scheme LXII

carbonyl species were detected in the active system but otherwise it was not further characterized (ref. 612).

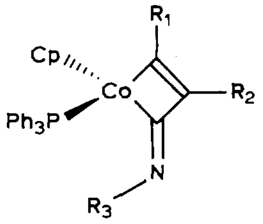
The species resulting from reaction of [RhCl(C$_2$H$_4$)(PPh$_3$)$_2$] with alkyl-diphenylphosphines were trapped in high-density polyethylene and combined with polyvinylpyridine chlorochromate to give a system for the concurrent catalytic reduction/stoichiometric oxidation of 4-hydroxymethylcyclohexene to formylcyclohexane. Catalyst recovery was excellent (ref. 613). Reaction of lithium tert-butylphosphide with cross-linked polystyrene-divinylbenzene copolymer gave pendent {p-$Bu^tHPCH_2C_6H_4$-} moieties which could be deprotonated and reacted with $[RhCl(COD)]_2$ to give [320] which catalyzed arene hydrogenation under ambient conditions. The activity was not as high as homogeneous analogs however. The same functionalized polymer was also used to support $\{Rh(CO)_2\}$, {Ir(COD)} and $\{Co(CO)_4\}$ moieties (ref. 614). Copolymerization of (4S,5S)-2-p-styryl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane with methyl acrylates formed a polymer with pendant DIOP-type ligands which could be used to support {Rh(COD)} moieties for the asymmetric hydrogenation of N-acylamino acrylic acids. Reasonable optical yields were obtained but they were not as high as with the homogeneous analogs (ref. 615). The same rhodium moieties supported on phosphinated cellulose catalyze the asymmetric hydrogenation of 2-phenylbut-1-ene in moderate optical yields (ref. 616). Rhodium-doped NaX and NaY zeolites are active for propylene hydroformylation but if the chloride ion concentration is on the order of 0.2 M when the rhodium is exchanged into the zeolite, the catalyst formed shows significant activity for the formation of C_7 ketones. This is thought to occur by reaction of propylene with the butyraldehyde formed in the hydroformylation reaction and is apparently catalyzed by the zeolite. Thus this latter system shows bifunctional catalysis (ref. 617).



[320]

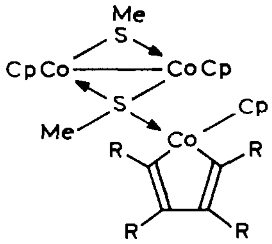
Metal Alkyne Complexes

The iminoborane $Bu^tB{\equiv}NBu^t$ reacts with $[Co_2(CO)_8]$ to form $[Co_2(CO)_6(Bu^tBNBu^t)]$ which has a structure analogous to the well-known $[Co_2(CO)_2$(acetylene)] complexes (ref. 618). At room temperature in benzene $[cpCo(PPh_3)(R_1C{\equiv}CR_2)]$ reacts with isocyanides to form [321] (R_1 = R_2 = Ph; R_3 = Ph, p-tolyl, 2,6-$Me_2C_6H_3$. R_1 = Ph; R_2 = CO_2Me; R_3 = p-tolyl, 2,6-$Me_2C_6H_3$. R_1 = Ph; R_2 = CN; R_3 = p-tolyl. R_1 = H; R_2 = Ph; R_3 = p-tolyl. R_1 = Me; R_2 = CO_2Me; R_3 = p-tolyl). The high regioselectivity observed is attributed to



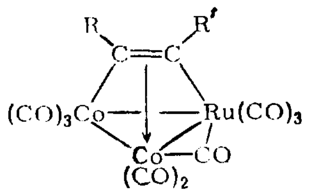
[321]

electronic factors with the acetylenic carbon bearing the more electron-donating substituent becoming the α-carbon. The observed products appear to form under kinetic control since when [321] (R_1 = Ph; R_2 = CO_2Me, CN) is heated, the recovered product has R_1 = CO_2Me, CN and R_2 = Ph (ref. 619). In refluxing THF electronegatively substituted acetylenes react with $[cp_2Co_2(\mu\text{-}SMe)_2]$ to form [322] (R = CF_3, CO_2Me, CN) (ref. 620). The room

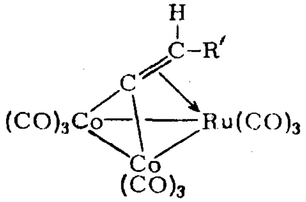


[322]

temperature reaction of acetylenes with $[RuCo_2(CO)_{11}]$ forms [323] (R = R' = H, Me, Et, Ph. R = H; R' = Me, Bu^t, Ph) which on heating (R = H only) forms [324] (ref. 621). Addition of trimethylsilylacetylene to $[Co_2(CO)_8]$

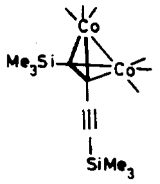


[323]

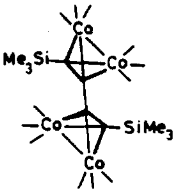


[324]

forms $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}HC{\equiv}CSiMe_3)]$ which on reaction with lithium diisopropyl- or bis(trimethylsilyl)amide yields $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}LiC{\equiv}CSiMe_3)]$. Hydrolysis of this with water or deuterium oxide forms a mixture of [325] and [326] (– = CO). The same species are also formed when the lithium complex is treated with electrophiles although in some instances the

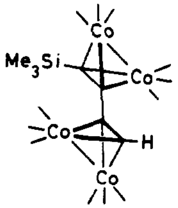


[325]

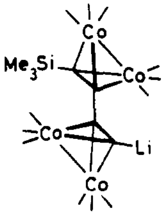


[326]

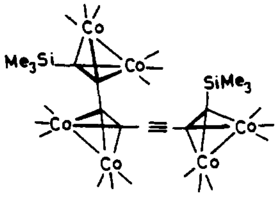
desired $[Co_2(CO)_6(\mu_2-\eta^2-Me_3SiC_2R)]$ (R = $SiMe_3$, bz) formed as well. Reaction of $[Co_2(CO)_8]$ with 4-trimethylsilylbuta-1,3-diyne forms [327] which is converted to [328] (– = CO) by lithium bis(trimethylsilyl)amide. The latter with *p*-nitrobenzylchloride forms [329] (– = CO) which can also be formed from 1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne. Treatment of [326] with methanol forms polymeric [330] (ref. 622). A mixture of $[cp_2Ni]$, $[Co_2(CO)_8]$ and phenyl isopropoxycarbonyl acetylene in refluxing heptane forms $[cp_2Ni_2(CO)_2]$, $[Co_2(CO)_6(PhC_2CO_2Pr^i)]$ and [331] (R = CO_2Pr^i).



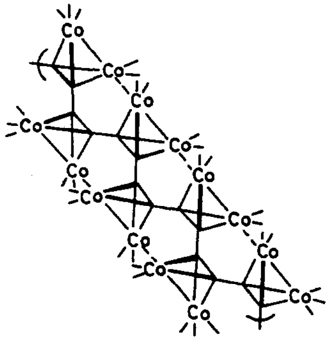
[327]



[328]

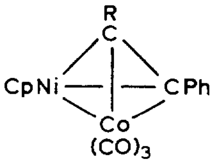


[329]

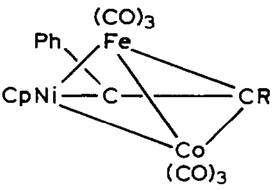


[330]

Reaction of [331] with [$Fe_2(CO)_9$] gives [332] which is fluxional by an



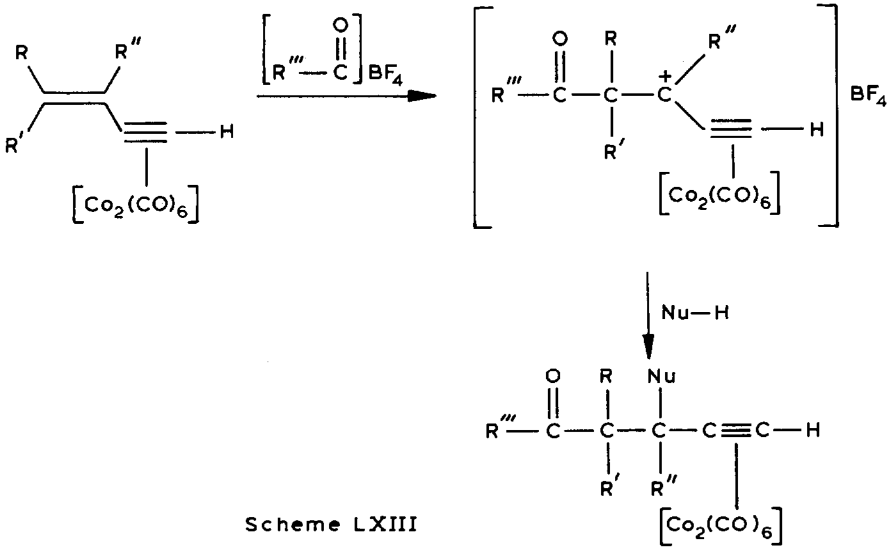
[331]



[332]

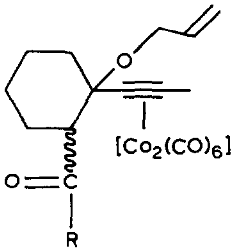
intramolecular process that is formally a rotation of the alkyne relative to the metal triangle and interconverts the diastereoisomeric forms (ref. 623).

Several more reports have appeared on various Ad_E reactions of cobalt-complexed enynes which generally proceed as outlined in Scheme LXIII (R =

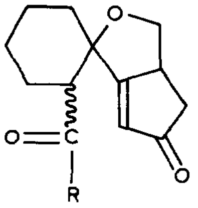


Scheme LXIII

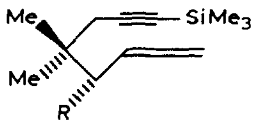
R' = R" = H, Me; R"' = Me, Pr^i, $Me_2C{=}CH$, Ph, adamantyl, cyclopropyl, cyclopentyl. R' = H; R, R" = $(CH_2)_n$ (n = 3,4). Nu = OH, OMe). Other combinations of substituents were also used and in the instance where the cobalt-stabilized propargyl cation contained R = H, R', R" = $(CH_2)_4$, R"' = Et, Bu^i, addition of 3-hydroxypropene formed [333] which converted to [334] on heating (refs. 624-628). This last is an example of the [$Co_2(CO)_8$]-mediated alkene-alkyne coupling (Pauson-Khand reaction). Another example is in the formation of bicyclo[3.3.0]octenones such as the conversion of [335] to [336] (R = $MeOCH_2O$). The stereoselectivity observed is attributed to steric factors (ref. 629). Further examples include the reaction of the



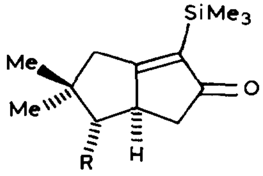
[333]



[334]

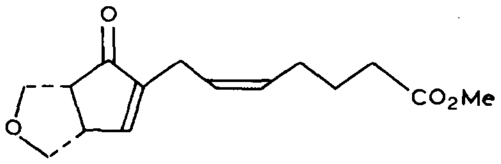


[335]

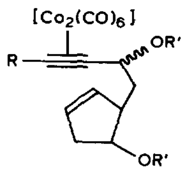


[336]

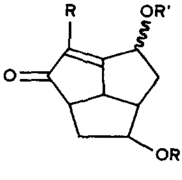
$\{Co_2(CO)_6\}$ adduct of methyl (Z)-non-5-en-8-ynoate with 2,5-dihydrofuran to form [337], a synthon for prostaglandin E_2 (ref. 630), and thermolysis of [338] in the presence of carbon monoxide to give [339] (R = $SiMe_3$; R' = $SiBu^tMe_2$) which is a synthon for the perhydrotriquinane skeleton (ref. 631). In another application of this reaction, *exo* ring fusion is observed



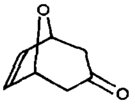
[337]



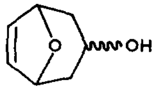
[338]



[339]

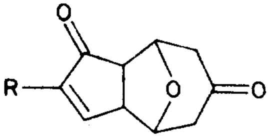


[340]

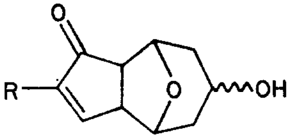


[341]

when [340] or [341] is allowed to react with $[Co_2(CO)_8]$ and alk-1-ynes in refluxing DMF under carbon monoxide. The products, [342] and [343] (R = H, Bu^n, Ph) respectively, are synthons for 11-oxatricyclo[5.3.1.0^{2,6}]undecanes which are precursors to some important natural products (ref. 632). Similarly, $\{Co_2(CO)_6\}$-complexed phenyl ethynyl sulfide couples with various olefins to give the corresponding 4,5-disubstituted 2-phenylthiocyclopent-2-en-1-ones (ref. 633). In a slightly different use of the $\{Co_2(CO)_6\}$-complexed acetylene, $[Co_2(CO)_6(R_2C(OH)C{\equiv}CC(OH)R'_2)]$ (R = R' = Me, Et. R = 17-deoxymestranol; R' = Me, Et) could be reduced to $[Co_2(CO)_6(R_2CHC{\equiv}CCHR'_2)]$ with borohydride in TFA and the acetylene then liberated by treatment with iron(III) chloride. The success of the reduction is attributed to the stabilization of the propargyl cation intermediates by the cobalt carbonyl moiety (ref. 634).



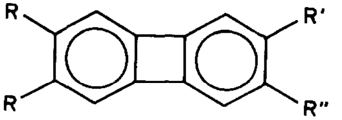
[342]



[343]

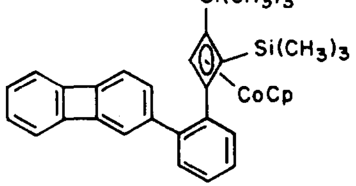
Hydrogenation of $[Co_2(CO)_6(R'C_2R)]$ (R = R' = H, Me, Ph. R = H; R' = Me, Et, Pr^n. R = Me; R' = Et) at 60°C in n-octane forms the corresponding olefins. At low conversions the internal acetylenes form cis-olefins but after longer times isomerization as well as hydrogenation to alkanes occurs presumably owing to the formation of some $[HCo(CO)_4]$. When R = R' = H, formation of $[Co_4(CO)_{10}(\mu_4\text{-}C_2H_2)]$ also occurs at first which is then converted to $[MeCCo_3(CO)_9]$ and finally $[Co_4(CO)_{12}]$. These tetracobalt complexes are more inert towards hydrogen so their formation results in decreased olefin production. Under catalytic conditions $[Co_2(CO)_6(C_2H_2)]$ mediates three reactions of acetylene: hydrogenation to ethylene, cyclotrimerization to benzene and dimerization and subsequent hydrogenation to butenes. Thus careful control of conditions in this last system are necessary in order to obtain a particular product (ref. 635). The ^{13}C NMR spectra of oct-1-ynes d_2-labelled at C_3, C_4, C_5 or C_6 have been measured and compared with those of the $\{Co_2(CO)_6\}$ derivatives. The chemical shifts of the alkyne carbons and the α-carbon are at lower field in the complexed alkyne than in the free molecule while the more remote carbons appear at approximately the same position. The T_1's of the carbon atoms in $\{Co_2(CO)_6\}$ derivatives of pent-1-yne through dodec-1-yne were also measured and were found to increase monotonically with the distance from the cobalt moiety (ref. 636).

Several more examples of [cpCo$(CO)_2$]-mediated alkyne coupling reactions have been published. The biphenylenes [344] (R = H, Cl; R' = R" = $SiMe_3$.



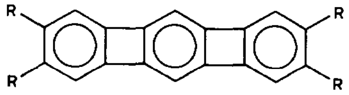
[344]

R = H; R' = R" = CO_2Me, Ph, Bu^n) are obtained from acetylenes ($R'C_2R"$) and the corresponding 1,2-bis(ethynyl)benzene in refluxing o-xylene under irradiation and in the presence of the cobalt complex. The system where R = H and R' = R" = $SiMe_3$ with BTMSA as the solvent and a larger concentration of the cobalt complex also forms [345]. Reaction of BTMSA and

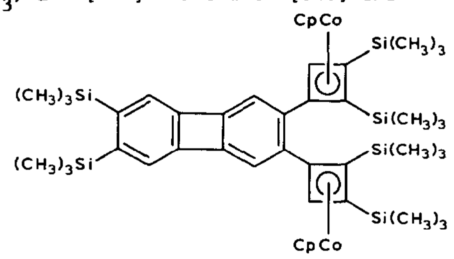


[345]

1,2,4,5-tetrakis(ethynyl)benzene under the conditions used to form [344] gives a mixture of [346] (R = $SiMe_3$) and [347] while with [348] the

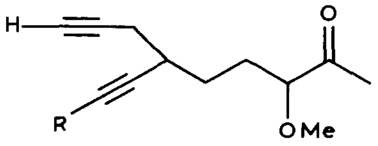


[346]

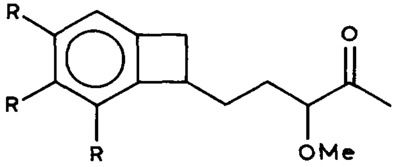


[347]

product is [349] (R = $SiMe_3$) (refs. 637, 638). Catalytic cyclization of undec-10-en-1,6-diyne with [cpCo$(CO)_2$] formed [350] rather than the

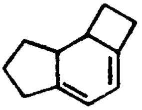


[348]

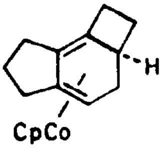


[349]

expected [351] with the rearrangement of the double bonds being possibly the result of cobalt-mediated hydrogen shifts. An even greater amount of

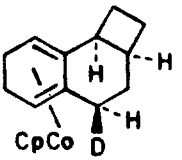


[350]

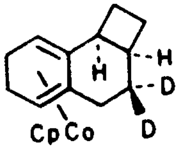


[351]

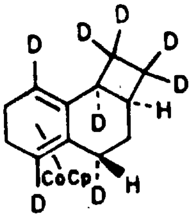
rearrangement occurred when dodec-11-en-1,7-diyne was the substrate although here the reaction was non-catalytic and the cobalt complex of the hydrocarbon was isolated. To probe the mechanism of this process the 1-d_1, 12,12-d_2 and 3,3,6,6,9,9,10,10-d_8 analogs were used as substrates and [352] - [354] respectively were formed. On the basis of these results, the



[352]

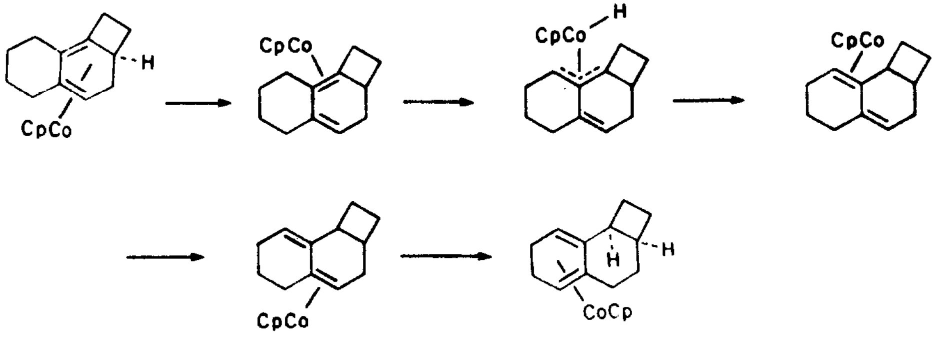


[353]



[354]

process of Scheme LXIV is proposed (ref. 639). Another report of the

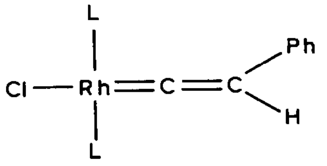


Scheme LXIV

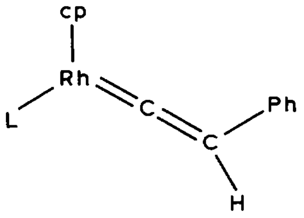
one-step construction of a steroid nucleus from the A-ring precursor first noted in the 1984 Annual Survey (J. Organomet. Chem. 305(1986)1, fig. [343]) has appeared (ref. 640).

In the gas phase, ion-molecule reactions of [$Co_2(CO)_6(RC_2R')$] (R = R' = Me, Ph, CH_2OH. R = H, R' = Ph, CH_2OH, CMe_2OH, CH_2NMe_2) with propylene, pent-1-ene, trans-pent-2-ene and pent-1-yne, the major processes appear to be protonation of the complexes by the gaseous ions derived from the olefins and substitution of two or more carbonyl groups by the neutral molecules. The latter predominates when R and R' are non polar (ref. 641). The complex $[Co_4(CO)_8(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C_2H_2)]$ and its deuterated and $^{13}C_2$ analogs have been synthesized. A detailed analysis of the infrared spectra in the C-C stretching region suggests that the coordinated acetylene has significant olefinic character. Also there appears to be a good correspondence between the vibrational modes of the acetylenic moiety in this complex and in instances where it is adsorbed on some metal surfaces (ref. 642). Cobalt(II) chloride is reported to catalyze the [4+2] cycloaddition of DMAD and 3-phenyl-2H-azirine but no information on the course of the reaction was given (ref. 643).

The phenylacetylene complex trans-$[RhCl(PhC_2H)(PPr^i_3)_2]$ is proposed to be in equilibrium with the oxidative adduct $[RhH(C_2Ph)Cl(PPr^i_3)_2]$ in solution since addition of pyridine forms trans-$[RhHCl(C_2Ph)(py)(PPr^i_3)_2]$. The last loses pyridine to form [355] and reacts with sodium cyclopentadienide to yield [356] (L = PPr^i_3). Analogs with acetylene and propyne

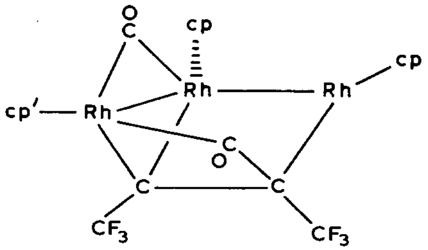


[355]



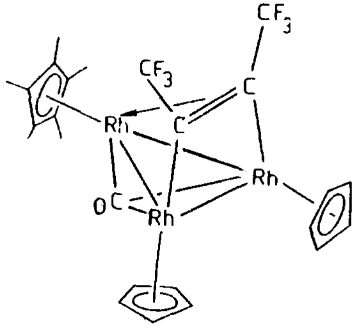
[356]

were also prepared. In the case of the corresponding iridium complexes, the acetylide hydride complex could be isolated at low temperature as a square pyramidal species with an axial hydride ligand. On warming this converted to the iridium analogs of [355] (ref. 644). After several days in hexane at room temperature, $[(\eta^5\text{-}C_5R_5)M(CO)_2]$ (R = H, Me; M = Co, Rh) and $[cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}HFB)]$ form the adducts $[(\eta^5\text{-}C_5R_5)Mcp_2Rh_2(CO)_3(HFB)]$ which are not particularly stable when R = H. The trimetallic product with R = Me and M = Rh is [357] but when R = H the analog of [357] is a minor



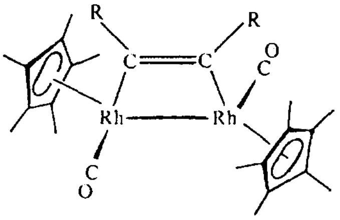
[357]

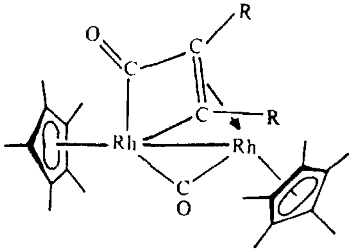
product and the major species is an isomer of unknown structure. Reaction of [cp'Rh(CO)L] (L = PPh_3, PMe_2Ph, $P(OMe)_3$) with [$cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}HFB)$] forms [$cp_2Rh_2(CO)_2(HFB)$], [$cp_2Rh_2(CO)(L)(HFB)$] and [358] (ref. 645).



[358]

Reaction of [$cp'_2Rh_2(\mu\text{-}CO)_2$] with acetylenes at room temperature proceeds slowly to form [359] (R = C_6F_5) or [360] (R = R' = Et, CO_2Me, CF_3, Ph. R =

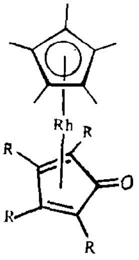


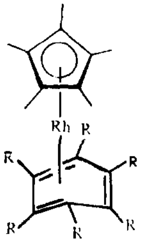


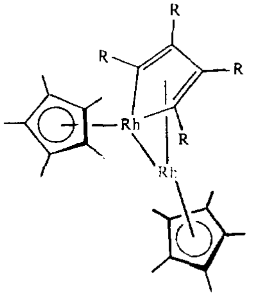
[359]

[360]

Ph; R' = Me, CO_2Me), although in solution both isomers are often seen and they appear to interconvert. With $PhC{\equiv}CC_6F_5$ both isomers can be isolated. Other products obtained are [361] (R = CF_3), [362] (R = CF_3, CO_2Me) and [363] (R = CO_2Me). Complex [363] is obtained as a mixture of regioisomers when the acetylene used is $PhC{\equiv}CC_6F_5$. With diphenylacetylene, products proposed to be [364] and [365] form in addition to [359] while with HFB



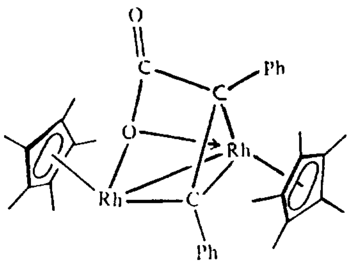




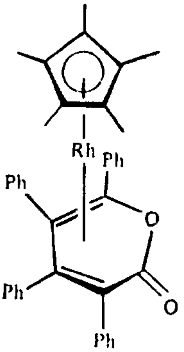
[361]

[362]

[363]

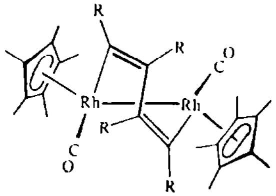


[364]



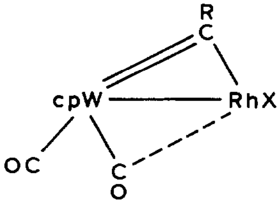
[365]

another minor product proposed to be [366] (R = CF_3) is obtained (ref. 646). Addition of acetylenes to [367] (X = η^5-C_9H_7, R = p-tolyl) forms



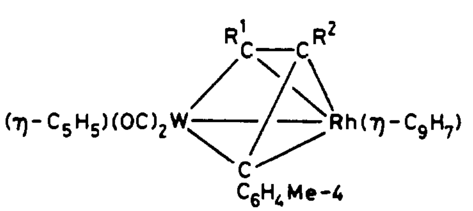
[366]

[368] and [369] (R^1 = R^2 = Ph, Me) or only [368] (R^1 = Ph; R^2 = H, Me). With diphenylacetylene at elevated temperature [367] (X = cp') forms the

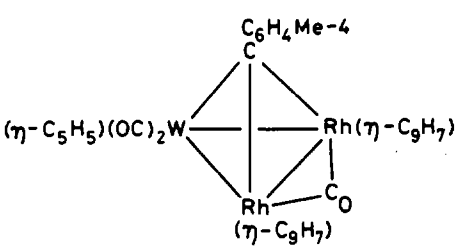


[367]

cp' analog of [368] (R^1 = R^2 = Ph) plus [cp'Rh(η^4-C_4Ph_4CO)]. The observation of [369] in the reactions of diphenylacetylene or but-2-yne with [367] (X = η^5-C_9H_7) suggests that [368] may not form directly from [367] in these cases (ref. 647).

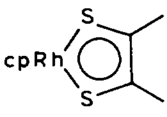


[368]

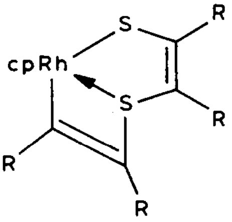


[369]

The formation of 2,3,4,5-tetracarboxymethylthiophene from elemental sulfur and DMAD in refluxing xylene is catalyzed by [cpM(CO)$_2$] (M = Co, Rh). At lower temperatures [370] and then [371] (R = CO$_2$Me) are formed



[370]



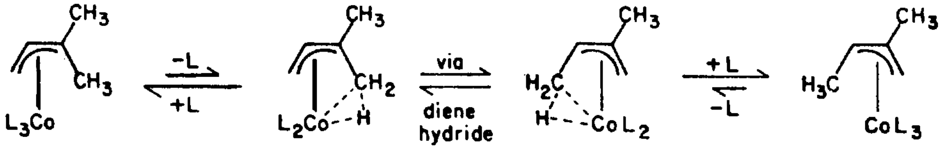
[371]

which are considered to be intermediates. Addition of tri-n-butylphosphine to [371] forms a phosphine adduct of [370] and liberates one molecule of DMAD (ref. 648). The complexes [(η^5-C$_5$R$_5$)Rh(COD)] (R = Me, Cl), [cpRh-(CO)$_2$], [cp'RhL$_2$] (L = CO, C$_2$H$_4$, PF$_3$) and [(η^5-C$_5$H$_4$PPh$_3$)Rh(CO)$_2$]PF$_6$ are catalysts for the cyclotrimerization of DMAD and hex-3-yne. With the COD complexes, the rate decreases as the π-acceptor strength of the cyclopentadienyl ligand increases when DMAD is the substrate and increases when it is hex-3-yne. For [cp'RhL$_2$] (L = CO, C$_2$H$_4$, PF$_3$; L$_2$ = COD) the rate varies with the nature of L suggesting at least one coordination site is occupied by L in the rate-limiting step. Since [(η^5-C$_9$H$_7$)Rh(COD)] gives much faster rates with DMAD as the substrate then do the cyclopentadienyl analogs it is proposed that a "ring-slip" occurs at some intermediate stage as well (ref. 649).

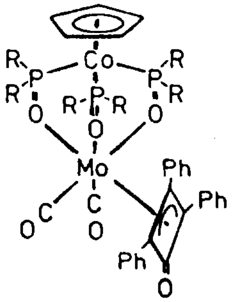
The dimetallated olefin complexes [Ir$_2$(COD)$_2$(μ-pz)$_2$(μ-RC=CR')] (R = R' = CF$_3$, CO$_2$Me. R = H; R' = CO$_2$Me) result when the acetylenes are reacted with [Ir$_2$(COD)$_2$(μ-pz)$_2$]. The structure of the methyl propiolate derivative shows that both iridium-carbon distances are equivalent (ref. 650).

Metal π-allyl Complexes

Heating [(η^3-1,1-dimethylallyl)Co(CO)$_3$] causes a partial isomerization to the 1,2-dimethylallyl analog and Scheme LXV is proposed (ref. 651). Treatment of [(cpCo(P(O)R$_2$)$_3$)Mo(CO)$_3$]$^-$ (R = OEt) with triphenylcyclopropenium tetrafluoroborate forms [372] (ref. 652). The metallacyclopentanes

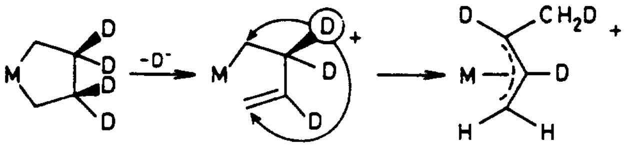


Scheme LXV



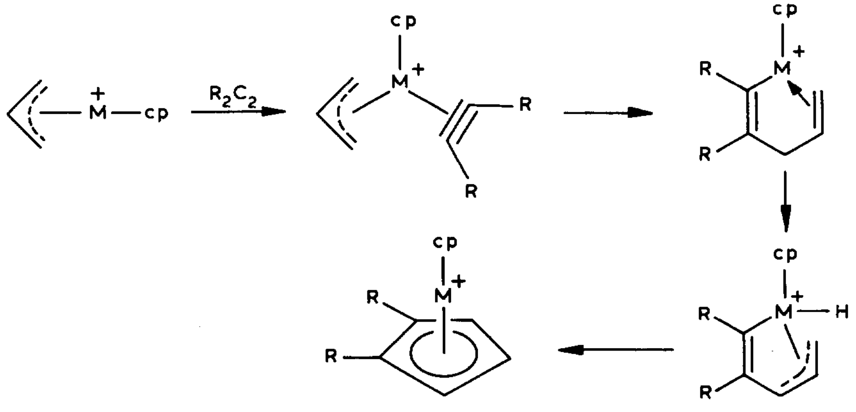
[372]

$[cp'(PPh_3)\overline{MCH_2(CH_2)_2CH_2}]$ (M = Rh, Ir) are converted to $[cp'(PPh_3)M(\eta^3\text{-}1\text{-}MeC_3H_4)]^+$ by hydride abstraction with trityl cation. Labelling studies indicate that a β-hydrogen is abstracted followed by the steps of Scheme LXVI. Also, $[cp'RhI_2(PPh_3)_3]$ reacts with but-3-en-1-yl magnesium bromide



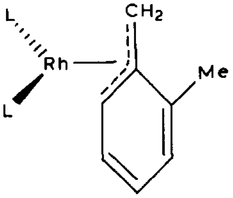
Scheme LXVI

to yield $[cp'Rh(\eta^3\text{-}1\text{-}MeC_3H_4)I]$ which can be converted to $[cp'(PPh_3)Rh(\eta^3\text{-}1\text{-}MeC_3H_4)]BF_4$ by silver tetrafluoroborate and the phosphine (ref. 653). Coupling of acetylenes with the allyl ligand in cationic rhodium and iridium cyclopentadienyl allyl complexes has been observed. Thus for example $[cpRh(\eta^3\text{-}C_3H_5)Cl]$ on treatment with silver tetrafluoroborate and then diphenylacetylene forms first $[cpRh(\eta^3\text{-}C_3H_5)]BF_4$ and then $[cpRh(\eta^5\text{-}C_5H_3Ph_2)]BF_4$. Scheme LXVII is proposed (ref. 654). Addition of o-tolyl-



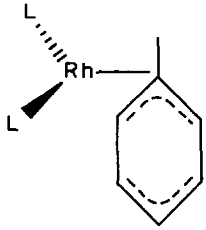
Scheme LXVII

methylmagnesium bromide to [RhCl(PPh$_3$)$_3$] yields [373] (L = PPh$_3$) from which the allylic ligand is removed by tetrafluoroboric acid in acetone (ref. 655).



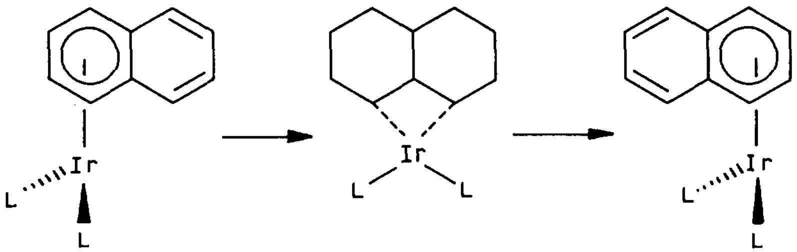
[373]

A theoretical study has been made of the haptotropic rearrangement of complexes like [373]. The least-motion path *via* [374] with maintenance of significant overlap between a π orbital on the metal with a p_π orbital of the exocyclic carbon appears to be the most favorable process.



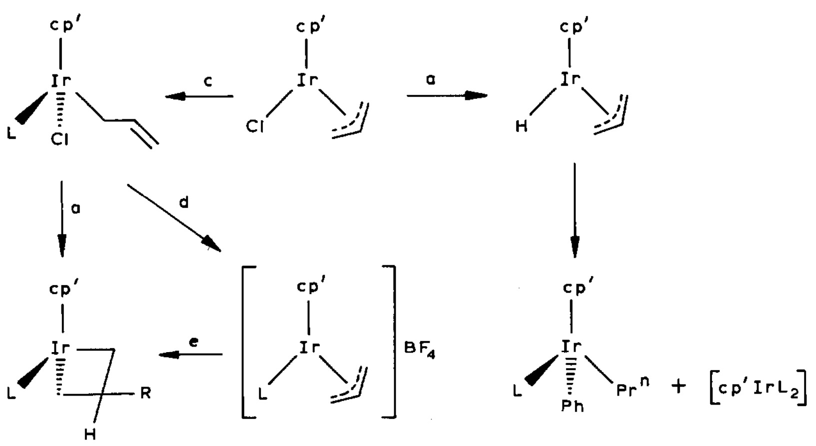
[374]

Also modelled was the rearrangement of [(η^6-C$_{10}$H$_8$)Ir(PPh$_3$)$_2$] and Scheme LXVIII was proposed (the π-electron distribution in the intermediate not specified) (ref. 656).



Scheme LXVIII

Some chemistry of [cp'Ir(η^3-C$_3$H$_5$)Cl], prepared from [cp'IrCl$_2$]$_2$ and allyl magnesium chloride, is outlined in Scheme LXIX. In step b) it is proposed that propylene is lost initially and benzene oxidatively adds a carbon hydrogen bond to the {cp'Ir} fragment. Subsequent insertion of propylene into the iridium hydrogen bond gives the observed product. Also [cp'IrH$_2$(PMe$_3$)] is converted to Li[cp'IrH(PMe$_3$)] by *tert*-butyllithium and subsequent reaction with allyl tosylate forms [cp'IrH(η^1-C$_3$H$_5$)(PMe$_3$)] (ref. 657). Loading of [(η^3-C$_3$H$_5$)$_3$Rh] into an NaX zeolite forms a catalyst



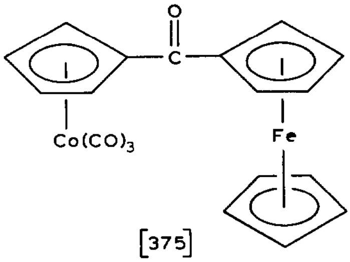
a) LiBHEt$_3$. b) L(= PMe$_3$), Δ, benzene. c) L(= PMe$_3$). d) AgBF$_4$.
e) LiBHEt$_3$ (R = H) or MeLi (R = Me).

Scheme LXIX

used for the competitive hydrogenation of cyclopentene and 4-methylcyclohexene. In the best case a nearly fifty-fold preference for the smaller olefin was noted suggesting this could be a system for shape selective catalysis although a selective poisoning of the rhodium sites on the surface by bulky phosphines (to leave the sites within the zeolite cages open) would be required to obtain a highly selective catalyst (ref. 658).

Metal Carbocyclic Complexes

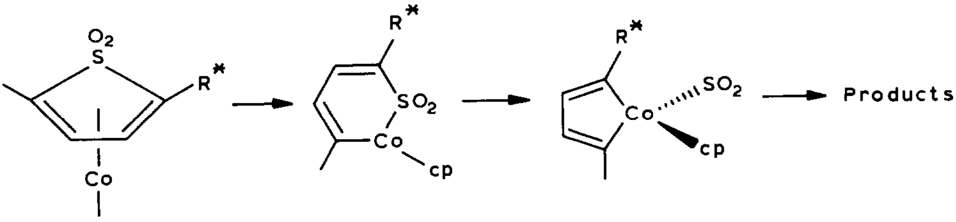
Reaction of $[Co_2(CO)_8]$ with iodine and then substituted thallium(I) cyclopentadienides gives $[(\eta^5\text{-}C_5H_4X)Co(CO)_2]$ (X = Cl, Br, I). The rhodium analog of the chlorocyclopentadienyl complex was also prepared from $[RhCl(CO)_2]_2$. Treatment of the cobalt complex (X = Br) with *n*-butyllithium at -78°C formed the very unstable $[(\eta^5\text{-}C_5H_4Li)Co(CO)_2]$ which reacted with carbon dioxide or acetone in the presence of moisture to give $[(\eta^5\text{-}C_5H_4R)\text{-}Co(CO)_2]$ (R = CO_2H, CMe_2OH respectively) (ref. 659). The reaction of sodium cyclopentadienide with dialkyl carbonates gave $Na[C_5H_4CO_2R]$ (R = Me, Et) which on addition to a $[Co_2(CO)_8]/I_2$ mixture formed $[(\eta^5\text{-}C_5H_4CO_5R)\text{-}Co(CO)_2]$. These could be hydrolyzed to the free acid also mentioned in the previous paper on treatment with potassium hydroxide in aqueous ethanol followed by hydrochloric acid and this in turn converted to $[(\eta^5\text{-}C_5H_4\text{-}C(O)Cl)Co(CO)_2]$ with oxalyl chloride. Amination gave $[(\eta^5C_5H_4C(O)NHR)\text{-}Co(CO)_2]$ (R = H, Ph) while reaction with ferrocene under Friedel-Crafts conditions formed [375] (ref. 660). Pentamethylcyclopentadienyllithium and cobalt(II) acetylacetonate react at low temperature followed by warming to form [cp'Co(acac)] which reacts further with methylmagnesium iodide and



[375]

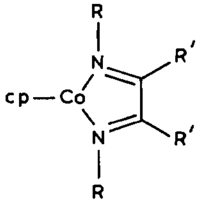
carbon monoxide or with sodium cyclopentadienide to form [cp'Co(CO)Me]$_2$ and [cp'Cocp] respectively (ref. 661).

A full report has now appeared on sulfur dioxide-extrusion reactions of thiophene-1,1-dioxide complexes of cobalt. Thus photolysis of [cpCo(CO)$_2$] with 2,5-dimethylthiophene-1,1-dioxide in hot benzene forms [cpCo(η^4-C_4H_2-Me_2SO_2)] which affords a 50% yield of [cpCo(η^4-$C_4H_2Me_2$)] on flash-vacuum-pyrolysis. The crossover experiment using [(Mecp)Co(η^4-$C_4H_2Me_2SO_2$)] together with [cpCo(η^4-2-Me-5-Et-$C_4H_2SO_2$)] gave, upon flash-vacuum-pyrolysis, only [(Mecp)Co(η^4-1,2-$Me_2C_4H_2$)] and [cpCo(η^4-1-Me-2-EtC_4H_2)] indicating no crossover had occurred and therefore that the process is apparently intramolecular. A further probe of the mechanism examined the flash-vacuum pyrolysis of the separated diastereoisomers of the analogous 2-methyl-5-sec-butylthiophene-1,1-dioxide complexes. In each instance complete diastereoisomerization of the product cyclobutadiene complexes occurred but in the recovered starting complexes only partial diastereoisomerization resulted. The mechanism of Scheme LXX was concluded to be



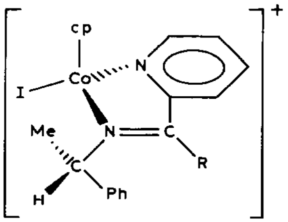
Scheme LXX

the most probable (ref. 662). Solubilization of potassium cyanide with crown ethers enables the very air-sensitive [cpCo(CO)(CN)]$^-$ ion to be formed from [cpCo(CO)$_2$]. Heating this with phosphorus ligands in acetonitrile gives low to modest yields of [cpCo(CO)L] (L = PPh_3, $P(OCH_2)_3CMe$) while with diphenylacetylene a moderate yield of [cpCo(η^4-C_4Ph_4CO)] results together with traces of [cpCo(η^4-C_4Ph_4)]. With iodine, [cpCo(CO)(CN)]$^-$ gave what was thought to be [cpCo(CN)I_2] but the product decomposed on attempts at isolation while with mercury(II) cyanide, [cpCo(CN)$_3$]$^-$ was obtained. With alkyl halides or acyl chlorides, the anion only gave mixtures of paramagnetic products which could not be separated or characterized except in two instances where [cpCo(CNC(O)R)$_2$] (R = Bu^t, 1-adamantyl) was isolated (ref. 663). The diazadiene complexes [376] (R' = H; R = Pr^i, Bu^t, CHPr$^i_2$, 2,6-R"C$_6$H$_3$ (R" = Me, Pr^i). R' = Me; R' = Pr^i, CH$_2$CH$_2$OMe, Ph, p-anisyl, 2,6-Me$_2$C$_6$H$_3$) can be prepared from the appropriate diazadiene and [cpCo(CO)$_2$] (either thermally or photochemically in xylene),



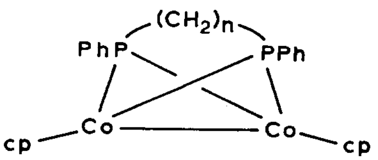
[376]

[cpCo(C$_2$H$_4$)$_2$] (thermally), [cp$_2$Co] plus lithium or a mixture of [Co(acac)$_3$], magnesium and cyclopentadiene. The complexes generally have good thermal stability but are readily oxidized. A variety of spectroscopic data was collected on them (ref. 664). The structure of the chiral complex [377] (R = Me) has been determined and it and its analog with R = H were studied in solution. Racemization at cobalt appears facile apparently via dissociation of the iodide ligand (ref. 665).



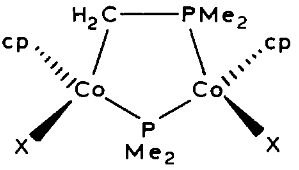
[377]

A variety of attempts to synthesize [cpCo(PMe$_2$H)$_2$] failed. Reaction of the phosphine with [cp$_2$Co] in benzene formed [cp$_2$Co$_2$(μ-PMe$_2$)$_2$] which also resulted from reduction of [cpCo(PMe$_2$H)$_3$]I$_2$ with sodium hydride and from addition of the phosphine to [cpCo(PMe$_3$)(μ-CO)$_2$Mn(CO)(Mecp)]. Analogs containing diethyl-, diphenyl- and methylphenylphosphido bridges were also prepared by the first route as was [378] (n = 2,3) from the corresponding di(secondary phosphines). All the dimers reacted with sulfur dioxide or

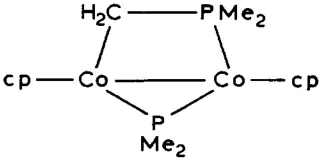


[378]

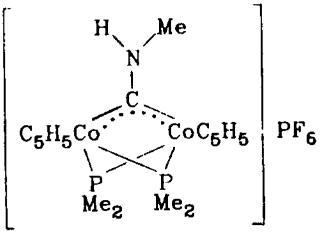
protons to form $[cp_2Co_2(\mu\text{-}PRR')_2(\mu\text{-}SO_2)]$ and $[cp_2Co_2(\mu\text{-}PRR')_2(\mu\text{-}H)]^+$ (R = R' = Me, Et, Ph. R = Me; R' = Ph) respectively. Addition of dihalomethanes to $[cp_2Co_2(\mu\text{-}PMe_2)_2]$ in benzene forms a mixture of *trans*-$[cp_2Co_2X_2(\mu\text{-}PMe_2)_2]$ and [379] (X = Br, I) plus the *trans*-isomer of the latter. Reduction of [379] (X = Br) with sodium amalgam forms [380]. Addition of carbon monoxide or methylisocyanide to $[cp_2Co_2(\mu\text{-}PMe_2)_2(\mu\text{-}H)]X$ (X = BF_4, PF_6) gives *cis*- plus *trans*-$[cpCo(CO)(\mu\text{-}PMe_2)_2Co(H)cp]BF_4$ and *trans*-$[cpCo(CNMe)(\mu\text{-}PMe_2)_2Co(H)cp]PF_6$ plus *cis*-and *trans*-$[cp_2Co_2(CNMe)_2(\mu\text{-}PMe_2)_2](PF_6)_2$, $[cp_2Co_2(\mu\text{-}PMe_2)_2]$ and [381] respectively. The latter reaction at low temperature forms mainly [381] which reacts with methylamine to give [382]. Attempts to induce hydride transfer in $[cpCo(CO)(\mu\text{-}PMe_2)_2Co(H)cp]BF_4$ to give a formyl led only to decomposition (refs. 666-669). Addition of phosphorus ligands to $[cpCoL_2]$ forms $[cpCoLL']$ (L = PMe_3; L' = $P(OR)_3$ (R = Me, Et, Pr^i). L = C_2H_4; L' = PMe_3, $P(OMe)_3$, CO). With $[cpCo(PMe_3)(P(OMe)_3)]$, dibromomethane yields $[cpCoBr(PMe_3)(P(OMe)_3)]Br$ while $[cpCo(CO)(PMe_3)]$ and dihalomethanes give $[cpCoX_2(PMe_3)]$ (X = Br, I). The latter reaction with chloroiodomethane at low temperature forms $[cpCo(PMe_3)(I)(CH_2Cl)]$ plus $[cpCo(PMe_3)I(Cl)]$ but at room temperature in the presence of other ligands the product is $[cpCo(PMe_3)(L)(CH_2Cl)]^+$ (L = PMe_3, $P(OMe)_3$, CNMe). Dihalomethanes react with $[cpCo(CO)(PMe_3)]$ in the presence of triethylamine to give $[cpCo(CH_2PMe_3)(PMe_3)X]X$ (X = Br, I) (ref. 670). Thiobenzophenone replaces one ligand in $[cpCpL_2]$ or $[cpRh(PMe_3)(C_2H_4)]$ to form $[cpM(S{=}CPh_2)L]$ (M = Co, Rh; L = PMe_3. M = Co; L = PMe_2Ph). With thiocyclohexanone however the product is [383] (M = Co, Rh), which can be alkylated



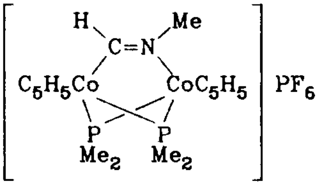
[379]



[380]

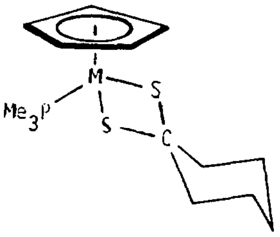


[381]

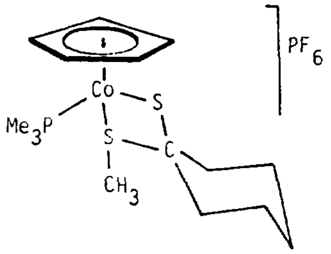


[382]

(M = Co) with methyl triflate to give [384]. The reaction of [cpCoL$_2$] (L = PMe$_3$) with S=C(XPh)$_2$ (X = O, S) forms [cpCo(L)(S=C(XPh)$_2$)] which is methylated by methyl triflate or protonated by triflic acid (X = O) to form [385]

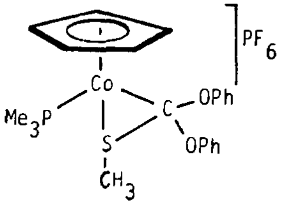


[383]

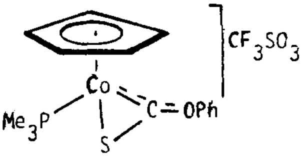


[384]

and [386] respectively. The latter reacts with methyl isocyanide to form

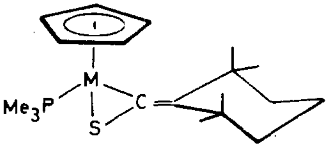


[385]

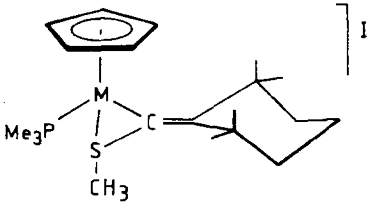


[386]

[cpCo(C(S)OPh)(PMe$_3$)(CNMe)]OSO$_2$CF$_3$ (ref. 671). Both [cpCoL$_2$] and [cpRh(C_2H_4)L] (L = PMe$_3$) react with the thioketene, 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane to form [387] (M = Co, Rh). The cobalt complex adds methyl iodide to give [388] (M = Co) (ref. 672).

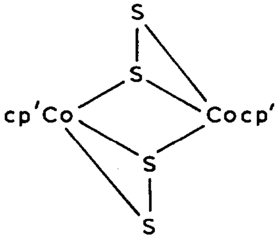


[387]



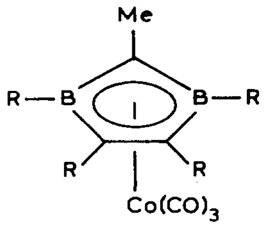
[388]

Halogens and pseudohalogens oxidatively add to [(Mecp)Co(CO)$_2$] giving [(Mecp)Co(CO)X$_2$] (X = Cl, Br, NCS) when used in stoichiometric quantities. With an excess however the product is [(Mecp)$_2$Co$_2$X$_2$(μ-X)$_2$] (X = Cl, Br, I) which can also be got by heating [(Mecp)Co(CO)X$_2$] (X = Cl, Br) to 100°C. The dimers can be converted to [(Mecp)$_2$Co$_2$X$_2$(μ-H)(μ-X)] by potassium hydroxide in ethanol. [(Mecp)Co(CO)$_2$] also reacts with sulfur(II) cyanide to form [(Mecp)Co(CO)(CN)(NCS)] (ref. 673). In chloroform solution, [cpCo(CO)X(SnX$_3$)] (X = Cl) reversibly converts to a carbonyl-free complex apparently with the intermediate formation of some [cpCo(CO)$_2$]. Addition of phosphorus ligands forms [cpCo(L)X(SnX$_3$)] (L = PPh$_3$; X = Cl, Br, I. L = P(OPh)$_3$; X = Br), the last example of which converts to [cpCo(CO)$_2$] on carbonylation (ref. 674). Diphosphine ligands chelate to the metal in [cpCo(L$_2$)I] (L$_2$ = DPM, DPPE, DPPP, DPPB) which is readily formed from [cpCo(CO)I$_2$] in dichloromethane under nitrogen. On prolonged treatment with air in solution about 20% of the DPM complex and all of the DPPB complex are converted to equal amounts of [cpCoI$_2$(L$_2$O)] (L$_2$O = monooxide of L$_2$) and [cpCoI$_2$(μ-L$_2$)CocpI$_2$]. Little or no reaction occurs with the other two. [cpCoI$_2$(L$_2$O)] could also be prepared directly from [cpCoI$_2$(CO)] and the half-oxidized ligands. The fact that [cpCo(DPPB)I]X (X = BF$_4$,PF$_6$) is unreactive towards oxygen suggests that when X = I, slow displacement of one end of the DPPB ligand by iodide occurs in solution and the free end of the ligand can then be oxidized. Reaction of [cpCoI$_2$(CO)] with one half equivalent of the diphosphine ligands in air gives a mixture of [cpCo(L$_2$)I]I, [cpCoI$_2$(L$_2$O)] and [cpCoI$_2$(μ-L$_2$)CocpI$_2$] when L$_2$ = DPM, mostly the first and small amounts of the last when L$_2$ = DPPE, DPPP and mostly the last together with significant amounts of the other two when L$_2$ = DPPB. These results suggest that the ligands coordinate to [cpCoI$_2$(CO)] in a stepwise fashion in the formation of the chelate complexes and in fact reaction of the [cpCoI$_2$(CO)] with DPM in benzene initially forms [cpCoI$_2$(DPM)] in which the DPM is monodentate (ref. 675). Cleavage of [cp'$_2$Co$_2$(μ-X)$_2$] (X = Cl, Br) occurs on addition of pyridine to form paramagnetic [cp'CoX(py)] (ref. 676) while elemental sulfur adds to [cp'$_2$Co$_2$(μ-CO)$_2$] giving [389] (ref. 677).

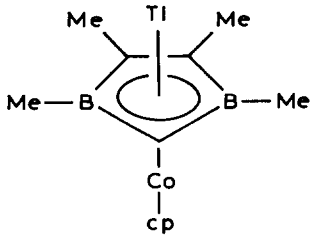


[389]

Diborolene and related complexes continue to attract significant interest. Low yields of [390] (R = Et) can be obtained from 1,3,4,5-tetraethyl-2,3-dihydro-2-methyl-1H-1,3-diborole and [Co$_2$(CO)$_8$] or [HCo(CO)$_4$] but with [(η^3-C$_3$H$_5$)Co(CO)$_3$] these are much higher (ref. 678). Reaction of thallium(I) cyclopentadienide with cyclopentadienyl(η^5-1,3,4,5-tetramethyl-2,3-dihydro-1H-1,3-diborolyl)cobalt forms [391] which appears to be a molecular species rather than ionic like thallium cyclopentadienide (ref.

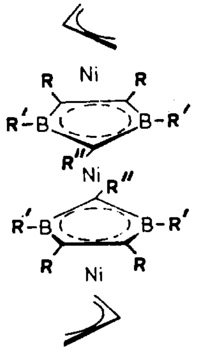


[390]

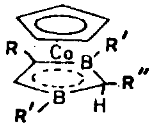


[391]

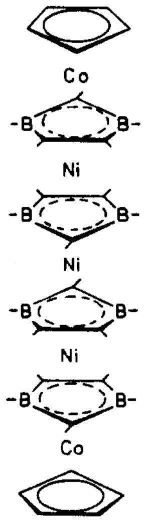
679). In refluxing mesitylene, [392] and [393] (R = Et; R' = Me; R" = H) form low yields of [394], [395] and [396] (M = Ni; substituents on the diborolene rings as for the starting materials and omitted for clarity here and subsequently). The same reaction when R = R' = Et and R" = Me forms



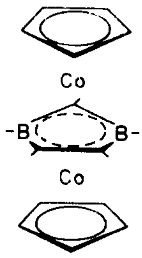
[392]



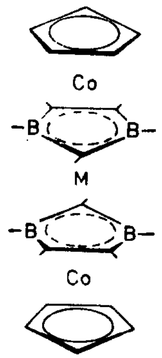
[393]



[394]

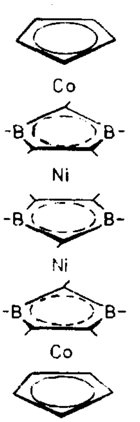


[395]



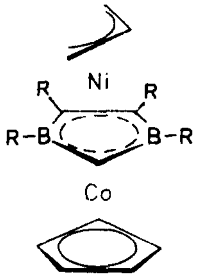
[396]

the analog of [394] plus [397]. An alternate route to [394] containing diborolene rings with two different sets of substituents is the reaction of

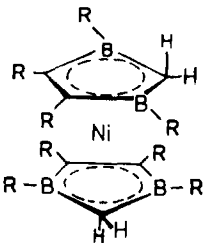


[397]

[398] (R = Et) with [399] (R = Me). Here the two rings sandwiching the central nickel atom bear methyl substituents while the other two contain

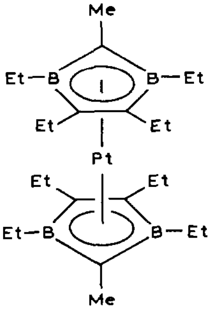


[398]

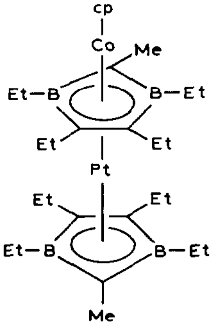


[399]

ethyl groups. A higher yield of [396] (M = Ni; ring substituents = Et) was also obtained (ref. 680). Reaction between [cpCo(C_2H_4)$_2$] and [400] forms [401] (ref. 681). In refluxing toluene, [402] forms from [cpCo(CO)$_2$] and

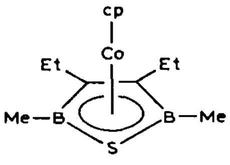


[400]



[401]

the corresponding thiadiborole (ref. 682). Nickel tetracarbonyl reacts with $[(\eta^6\text{-}C_5H_5BMe)_2Co]$ in refluxing diglyme forming $[(\eta^6\text{-}C_5H_5BMe)Co(CO)_2]$

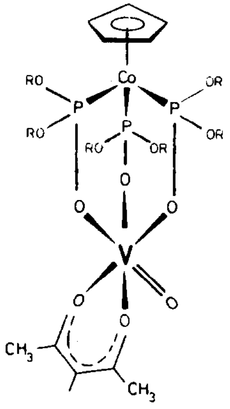


[402]

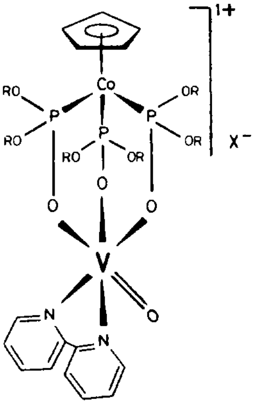
and $[(\eta^6\text{-}C_5H_5BMe)_2Ni_2(\mu\text{-}CO)_2]$ rather than a mixed-metal sandwich compound. Also reported is the reaction of $[(\eta^4\text{-}C_4H_4)Co(CO)_2I]$ and $Tl[C_5H_5BR]$ (R = Me, Ph) which forms $[(\eta^6\text{-}C_5H_5BR)Co(\eta^4\text{-}C_4H_4)]$ and $[(\eta^6\text{-}C_5H_5BR)Co(CO)_2]$ (ref. 683).

Dissolution of $[cp_2Co]$ in neat diethyl cadmium appears to lead to a catalytic decomposition of the latter since ca 70% of the $[cp_2Co]$ is recovered unchanged and large amounts of ethylene and ethane are formed. Apparently some unstable cobalt-ethyl species are generated and the desired $[cpCo(\eta^4\text{-}C_5H_5Et)]$ formed only in low yield. A much better yield of this species was obtained using three equivalents of diethyl cadmium in benzene (ref. 684). Cobaltacene has also been used as a one-electron reductant for a variety of quadruply bonded dirhenium complexes such as $[Re_2Cl_6L_2]$ (L = PEt_3, $PPr^n{}_3$, PMe_2Ph, $PEtPh_2$) (refs. 685, 686). Conversion of $[(\eta^5\text{-}C_5H_4\text{-}CO_2H)_2Co]PF_6$ to $[(\eta^5\text{-}C_5H_4C(O)Cl)_2Co]PF_6$ can be accomplished with hot thionyl chloride and the latter reacts with 3-aminopropyltriethoxysilane in the presence of triethylamine to give $[(\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3Si(OEt)_3)_2Co]PF_6$ which was formed in situ and allowed to polymerize in contact with tin(IV) oxide coated glass or platinum electrodes. These derivatized electrodes show a reversible electrochemical response and are more optically transparent and durable at negative potentials than those based on viologen derivatives. Coating p-type silicon electrodes with the cobalt complex followed by further coating with rhodium generates a surface able to photochemically generate hydrogen (ref. 687).

Displacement of bromide from $[MBr(CO)_5]$ (M = Mn, Re) by $[cpCo(P(O)R_2)_3]^-$ (R = OMe, OEt) forms $[cpCo(\mu\text{-}P(O)R_2)_3M(CO)_3]$ (ref. 688) while with $[V(O)\text{-}(acac)_2]$ the product is [403] (R = OEt). Treatment of [403] with hexafluorophosphoric acid and then bipy forms [404] ($X = PF_6$). An ophen analog was also prepared. Cyclic voltammetric measurements established the presence of reversible Co(III)-Co(II) and pseudo reversible V(IV)-V(V) couples and all three complexes were catalysts for the transfer of an



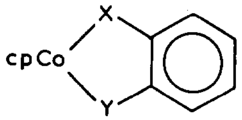
[403]



[404]

oxygen atom from oxygen or hydrogen peroxide to 3,5-di-*tert*-butylcatechol (ref. 689). Brief reflux of a triptycene/[$Co_4(CO)_{12}$] mixture in dodecane/dioxane forms a miniscule yield of [(η^6-triptycene)$Co_4(CO)_9$]. The structure study shows that the bridgehead carbon atoms are not coplanar with the η^6-ring and this bending is attributed to an attempt to reduce non-bonded interactions of the {$Co_4(CO)_9$} moiety with the ring adjacent to it. The proton NMR spectrum of the complex indicates a significant perturbation of this ring (ref. 690). Rearrangement of the methyl substituents in 2,2,6,6-tetramethylcyclohexane carboxylic acid occurs on reduction at a cobalt electrode. A π-complex of the tetramethylcyclohexyl radical with cobalt is proposed as an intermediate (ref. 691). The complexes [(η^5-C_5H_3RR')Co(COD)] (R = H; R' = H, Me, Ph. R,R' = $(CH_2)_3$) catalyze the co-cyclotrimerization of propyne with propionitrile to form isomeric dimethylethylpyridines. The related complexes [(η^6-C_5H_5BR)Co(COD)] (R = Et, Ph) were more active and slightly more selective catalysts and also were used to form 2-vinylpyridine from acetylene and acrylonitrile (ref. 692). Computational errors have been discovered in the determination of the rate constants and activation parameters for the Arbusov-type reaction of [cpCo(DPPE)X] (X = halide) with phosphites which forms [cpCo(DPPE)(P(O)(OR)$_2$)] (see Inorg. Chem., 23(1984) 4177). Correction of these errors does not appear to require any change in the proposed mechanism but now the nucleophilicity of the halide ion appears to be more important in determining the rate than originally thought (ref. 693).

The ^{59}Co NQR spectra of [$cpCoI_2L$] (L = CO, $P(OPh)_3$, CNPh, $AsPh_3$, NH_2CH_2Ph), [cpCoI(L_2)] (L_2 = en, ophen), [$cpCoL_3$]$^+$ (L = $P(OEt)_3$, $P(OMe)_3$, MeCN), [405] (X = Y = O, NH, S, Se. X = O; Y = NH. X = S; Y = NH, Se) and pentamethylcyclopentadienyl analogs of the last three groups have been measured. The pentamethylcyclopentadienyl ligand generally appears to be a

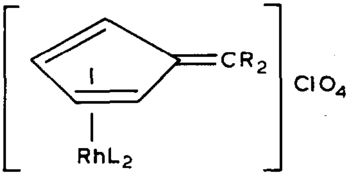


[405]

better electron donor than the cyclopentadienyl ligand but the actual increase in electron density at the metal is quite small, a conclusion in agreement with molecular orbital calculations and the photoelectron spectra. In [405] the NQR parameters derived appear to depend primarily on the electronegativities of X and Y while in the cationic complexes the electric field gradient at cobalt is the most sensitive to substitution on the cyclopentadienyl ring of all the series examined (ref. 694). In another extensive study, the ^{59}Co NMR spectra of $[\mathrm{cpCo(R)}(\eta^3\text{-}\mathrm{C_3H_5})]$ (R = Br, Me, bz), $[(\eta^3\text{-2-R-}\mathrm{C_3H_4})_3\mathrm{Co}]$ (R = H, Me), $[\mathrm{cpCoL_2}]$ (L = $\mathrm{C_2H_4}$, acrylonitrile, methylenecyclopropane; $\mathrm{L_2}$ = COD, 1,5-HD, hepta-1,6-diene), $[(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{CoL_2}]$ (L = $\mathrm{C_2H_4}$; $\mathrm{L_2}$ = COD, 1,5-HD) $[(\eta^3\text{-}\mathrm{C_8H_{13}})\mathrm{Co(COD)}]$, and pentamethylcyclopentadienyl analogs of the third set have been measured and molecular orbital calculations were made on most of the complexes. The ^{59}Co chemical shifts appear to be dominated by the paramagnetic shielding term and to correlate with the HOMO-LUMO gap (ref. 695). From a study of the dynamics of electron transfer from the conduction band of laser-excited colloidal titanium dioxide to $[(\eta^5\text{-}\mathrm{C_5H_4CO_2})_2\mathrm{Co}]^-$ it was concluded that the cobalt complex is superior to methyl viologens as an electron-relay for the photogeneration of hydrogen in aqueous chloroplast suspension (ref. 696). The mass spectra of $[(\eta^5\text{-}\mathrm{C_5H_4R})_2\mathrm{Co}]$ (R = Me, Et, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$) and $[\mathrm{cp_2Co}]\mathrm{X}$ (X = $\mathrm{PF_6}$, $\mathrm{BPh_4}$) have been determined and the tetraphenylborate salt found to form phenyl-substituted cyclopentadienyl rings in the mass spectrometer (ref. 697). Photoelectron spectra and INDO molecular orbital calculations have been correlated for $[(\eta^6\text{-}\mathrm{MeBC_5H_5})\mathrm{CoL_2}]$ (L = CO; $\mathrm{L_2}$ = $\eta^4\text{-}\mathrm{C_4H_4}$). The predicted ground state orientation of the $\{\mathrm{Co(CO)_2}\}$ moiety agrees with that found in the structure study and it appears that significant orbital reorganization occurs in both complexes on ionization (ref. 698). A fragment molecular orbital approach to studying the binding of phosphinidines to transition metal-containing moieties with a d^8 configuration modeled the ligand by $\mathrm{P\text{-}PH_2}$. Of those considered, the {cpCo} moiety was predicted to give the least stable complex (ref. 699).

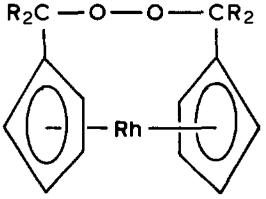
Reaction of $[\mathrm{RhCl(cyoct)_2}]_2$ with bis(bis(trimethylsilyl)amido)tin(II) in toluene forms $[(\eta^6\text{-}\mathrm{C_6H_5Me})\mathrm{Rh(cyoct)(SnCl(NR_2)_2)}]$ (R = $\mathrm{SiMe_3}$), the first neutral η^6-arene complex of rhodium(I). The same reaction in hexane forms

$[RhCl(Sn(NR_2)_2)_2]_2$ from which the same arene complex can be obtained by adding more of the tin reagent and cyclooctene in toluene indicating that the stannane diyl complex is probably an intermediate in the first reaction. The analogous hexamethylbenzene complex can be got by arene displacement from the toluene complex or directly from $[RhCl(cyoct)_2]_2$, hexamethylbenzene and the tin reagent in ether (ref. 700). Chloride abstraction from $[RhCl(DQ)]_2$ with silver hexafluorophosphate in acetone followed by addition of an arene forms $[(\eta^6\text{-arene})Rh(DQ)]PF_6$ (arene = C_6H_6, C_6H_5Me, p-xylene, mesitylene, 1,2,4,5-$Me_4C_6H_2$, C_6Me_6) while with Lewis base ligands, $[Rh(DQ)L_2]PF_6$ (L = MeCN, py; L_2 = ophen) is obtained (ref. 701). Dissociation of the arene ligand from $[(\eta^6\text{-arene})Rh(P(OPh)_3)_2]ClO_4$ (arene = mesitylene, C_6H_5Me, C_6H_6) in deuterochloroform containing 5% acetone-d_6 has been studied by NMR. The process is first order and the rate increases with the arene in the order given. In the $[Rh(P(OPh)_3)_2(acetone)_x]ClO_4$ product the phosphites are equivalent unless moisture is present in which case a new species, thought to be a monoaquo complex, is detected (ref. 702). Reaction of $[RhClL_2]_2$ with silver perchlorate followed by addition of a fulvalene forms [406] (R = Ph, p-ClC_6H_4; L_2 = $(P(OPh)_3)_2$, COD. R = p-XC_6H_4



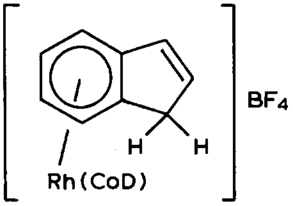
[406]

(X = H, Cl, Me, OMe); L = CO). The carbonyl complexes react with oxygen to form [407] (ref. 703). At low temperature, bis(indenyl)magnesium converts



[407]

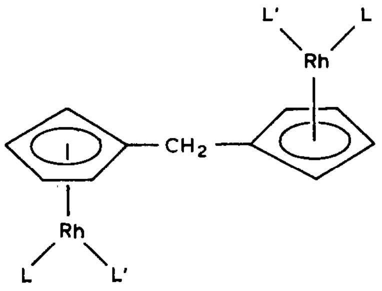
$[RhClL_2]_2$ to $[(\eta^5\text{-}C_9H_7)RhL_2]$ (L = C_2H_4; L_2 = NBD, COD) which reacts with carbon monoxide to form $[(\eta^5\text{-}C_9H_7)Rh(CO)_2]$ and can be protonated with tetrafluoroboric acid (L_2 = COD) to yield [408]. Reduction of $[(\eta^5\text{-}C_9H_7)_2Co]$ with lithium in the presence of COD forms $[(\eta^5\text{-}C_9H_7)Co(COD)]$ in which the COD can be replaced with two carbonyl ligands (ref. 704). Acetylenes can be catalytically cyclotrimerized by $[(\eta^5\text{-}C_9H_7)RhL_2]$ (L = C_2H_4, cyoct;



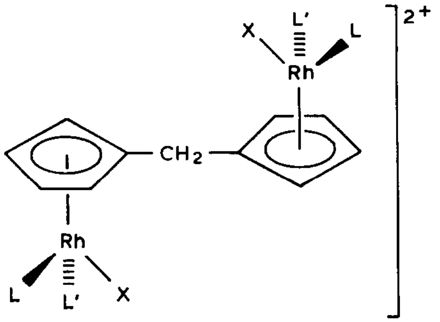
[408]

L_2 = COD) with high chemoselectivity in most cases. However with stoichiometric quantities of diphenylacetylene, the ethylene and COD complexes give $[(\eta^5\text{-}C_9H_7)Rh(Ph_2C_2)_2]$ and $[(\eta^5\text{-}C_9H_7)Rh(\eta^4\text{-}C_4Ph_4)]$ which are poor and inactive catalysts respectively (ref. 705).

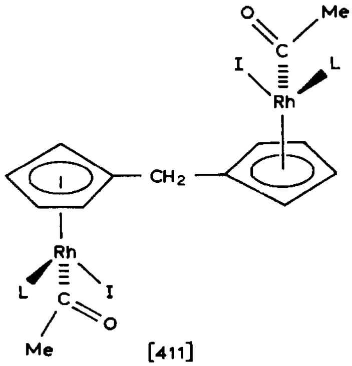
Complexes [409] (L = L' = C_2H_4, PMe_3. L = C_2H_4; L' = PMe_3) can be prepared from $[RhClLL']_2$ and $Li_2[C_5H_4CH_2C_5H_4]$ and when L = L' = PMe_3 can be carbonylated to give the analog with L = PMe_3 and L' = CO. Protonation with ammonium hexafluorophosphate (L = L' = PMe_3) or triflic acid (L = PMe_3; L' = C_2H_4, CO) forms [410] (X = H) while with methyl triflate (L = PMe_3; L' = PMe_3, C_2H_4, CO) gives the analog with X = Me. By contrast methyl iodide converts [409] (L = PMe_3; L' = CO) to [411] while $[RhCl(CO)_2]_2$ and $Li_2[C_5H_4CH_2C_5H_4]$ form [412] (ref. 706). Treatment of $[RhClL_2]_2$



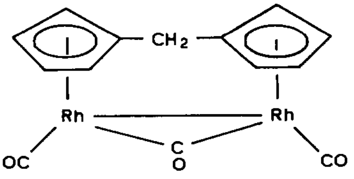
[409]



[410]

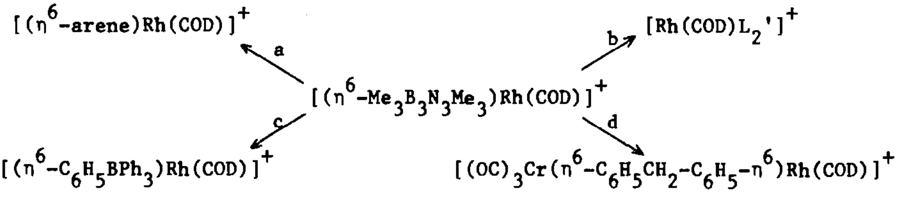


[411]



[412]

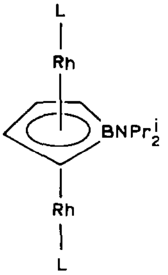
with silver hexafluorophosphate and hexamethylborazine in dichloromethane yields $[(\eta^6\text{-}Me_3B_3N_3Me_3)RhL_2]PF_6$ ($L = CO, C_2H_4$; L_2 = COD, NBD, TFB, Me_3TFB). The analogous $[(\eta^6\text{-naphthalene})Rh(COD)]PF_6$ was prepared similarly. The borazine ligand could be readily replaced as outlined in Scheme LXXI (ref. 707). The dianion of 1-diisopropylaminoborole reacts with $[cp'RhCl_2]_2$ to



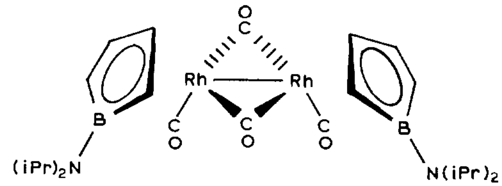
a) arene. b) L'(= PPh_3, MeCN). c) $NaBPh_4$. d) $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Ph)]$.

Scheme LXXI

form $[cp'Rh(\eta^5\text{-}C_4H_4BNPr^i_2)]$ in low yield. The same reagent with $[RhClL_2]_2$ forms [413] ($L = C_2H_4$; L_2 = COD, $\eta^5\text{-}C_4H_4BNPr^i_2$) or [414] (L = CO) and with

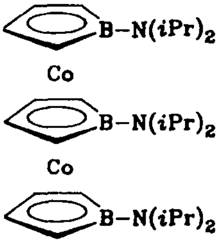


[413]



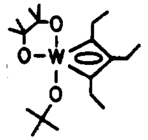
[414]

anhydrous cobalt(II) bromide or $[cpCo(CO)_2]$ gives [415] and $[cpCo(\eta^5\text{-}C_4H_4BNPr^i_2)]$ respectively. The reaction with cobalt(II) bromide gives the cobalt analog of [414] if performed in the presence of carbon monoxide (ref. 708).

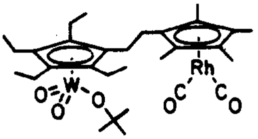


[415]

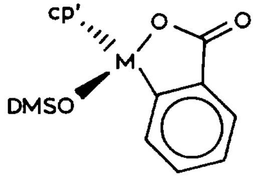
Cocyclization of the acetylenic substituent in $[(\eta^5-C_5Me_4R)Rh(CO)_2]$ (R = $CH_2CH_2C{\equiv}CEt$), prepared by standard methods, with [416] forms [417], the first example of a peralkylated cyclopentadienyl system linked by a two-carbon chain (ref. 709). Reaction of either $[cp'RhMe_2(DMSO)]$ with benzoic acid or of silver benzoate with $[cp'IrCl_2(DMSO)]$ forms [418] (M = Rh, Ir) which with methyl iodide gives [419] (M = Rh, Ir). With more benzoic acid, [418] (M = Rh) forms $[cp'Rh(O_2CPh)_2]$ while heating at 80°C under 50 atm of carbon monoxide forms some maleic anhydride and $[cp'Rh(CO)_2]$ (ref. 710). Addition of silver salts to $[cp'_2Rh_2(\mu-CO)_2]$ forms either [420] (X = Cl, NO_3, O_2CCMe, O_2CCF_3; L = cp') or [421] (X = BF_4, PF_6; L = cp') but the same reaction with $[cp'_2Co_2(\mu-CO)_2]$ only decomposed the complex. With $[cp'_2RhIr(\mu-CO)_2]$, $[cp'_2RhIr(\mu-CO)_2(\mu-AgCl)]$ can be obtained while reaction of [420] (X = Cl, NO_3, O_2CCMe) with diazomethane formed $[cp'_2Rh_2(CO)_2(\mu-AgCH_2X)]$ and $[cp'_2Rh_2(CO)_2(\mu-CH_2)]$ (ref. 711). The structure of $[cp'_3Rh_3(\mu_3-CO)_2]$ has been determined and the carbonyl groups found to be unsymmetrically attached to the metal triangle as predicted from molecular orbital calculations. Analogs, $[cp'_3MM'_2(\mu_3-CO)_2]$, (M = Co, Rh; M' = Co. M = Ir; M' = Rh)



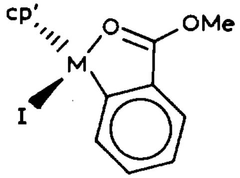
[416]



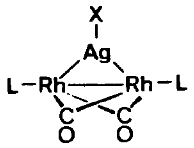
[417]



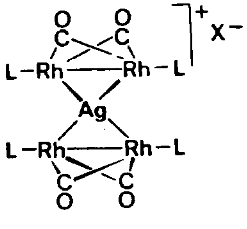
[418]



[419]

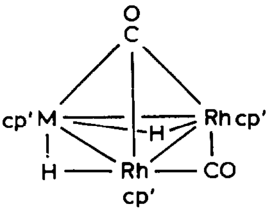


[420]



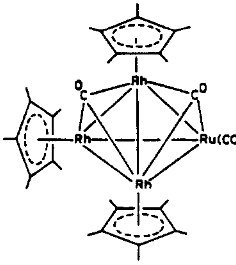
[421]

can be prepared from $[cp'Co(C_2H_4)_2]$ and $[cp'_2CoM(\mu\text{-}CO)_2]$ (M = Co, Rh) or from $[cp'Rh(C_2H_4)_2]$ and $[cp'_2IrRh(\mu\text{-}CO)_2]$ respectively and on reaction with hydrogen [422] (M = Co, Rh, Ir) forms (ref. 712). In refluxing toluene,

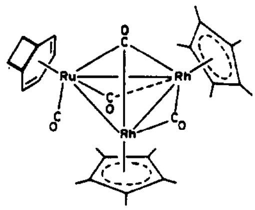


[422]

$[cp'Rh(CO)_2]$ adds to the cycloocta-1,3,5-triene complex $[(\eta^6\text{-}C_8H_{10})Ru(COD)]$ to form a mixture of [423] and [424] (ref. 713) while in refluxing heptane

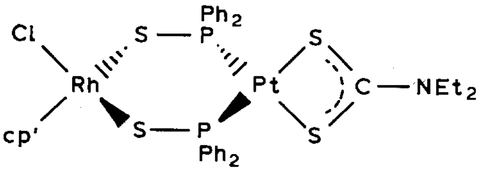


[423]



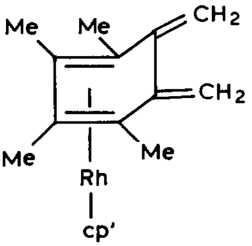
[424]

[423] and $[cp'_2Rh_2(\mu\text{-}CO)_2]$ are obtained with $[(\eta^6\text{-}C_6Me_6)Ru(C_2H_4)_2]$ (ref. 714). Reaction of $[cp'_2Rh_2(\mu\text{-}OH)_3]ClO_4$ with pyrazole-type ligands in methanolic potassium hydroxide forms $[cp'_2Rh_2(L)_2(\mu\text{-}L)_2]$ (L = pz, 4-Brpz, idz) which can be converted to $[cp'_2Rh_2(LH)_2(\mu\text{-}L)_2](ClO_4)_2$ (L = idz, 4-Brpz) by perchloric acid. The same complexes can also be obtained from $[cp'_2Rh_2(\mu\text{-}OH)_3]ClO_4$ and the appropriate ligands in aqueous perchloric acid (ref. 715). Coordination of rhodium to the free sulfur atoms in $[Pt(Ph_2P(S))_2(S_2CNEt_2)]$ forms [425] on reaction with $[cp'RhCl_2]_2$ (ref. 716). The



[425]

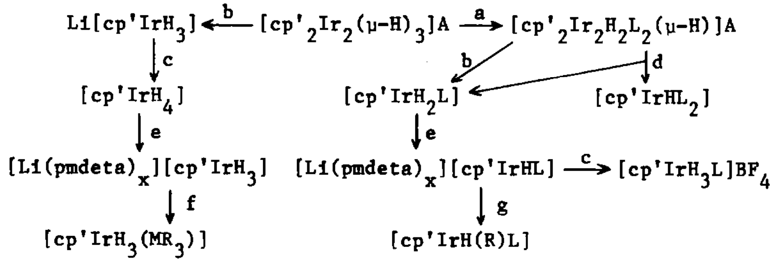
substitution of methoxide for fluoride in fluorobenzene and o-, m- or p-fluorotoluene is catalyzed by $[(\eta^5\text{-}C_5Me_4Et)Rh(\eta^6\text{-}C_6H_6)](PF_6)_2$ in nitromethane/acetone containing methanol (ref. 717). Two one-electron reduction processes are observed for [cp'Rh(η^6-C_6Me_6)]$^{2+}$ the first of which is reversible and the second only quasi-reversible while for the iridium analog a chemically reversible two electron reduction step is seen. The latter is presumed to involve two one-electron steps as well but the failure to observe them separately was attributed to the second having a more positive potential than the first. The final product is [cp'M(η^4-C_6Me_6)] (M = Rh, Ir) and the change in hapticity of the hexamethylbenzene ligand is thought to accompany the second reduction step. Reaction of oxygen with [cp'Rh(η^4-C_6Me_6)] forms [426] (ref. 718). An examination of



[426]

the metal-phosphorus and phosphorus-carbon distances in [409] (L = PPh_3; L' = CO), its dication, [$Rh_2(CO)_2(PPh_3)_2(\mu$-$RN_3R)_2$], [cpCo($PEt_3)_2$] and the mono-cations of the last two shows that on oxidation, which is predominantly metal-centered, the former distances increase while the latter decrease. The results are interpreted to suggest that the metal-phosphorus bond contains a significant π-component and that the σ* component of the phosphorus-carbon bond is mixed into the π-acceptor orbital on phosphorus. While [409] (L = PPh_3; L' = CO) has the trans-structure shown, its dication is cis and contains a metal-metal bond. EHMO calculations on models for these two species indicate that in both, the fulvalene ligand can best be described as a dianion leading to the conclusion that the formal oxidation states of the metals are +1 in the neutral species and +2 in the dication. Interestingly, the oxidation of the neutral complex and the reduction of the dication give identical plots in cyclic voltammetric experiments suggesting that in the former, the cis and trans rotamers are rapidly interconverting. Thus it appears that it is the cis form which is oxidized in this experiment and in fact the calculations indicate that it should be slightly more readily oxidized than the trans form (refs. 719, 720). The He(I) and He(II) photoelectron spectra of [cpM(PMe_3)X] (M = Co, Rh; X = CO, CS) and [cp'Rh(PMe_3)CO] have been measured and indicate that rhodium binds more strongly to the cyclopentadienyl ligand than does cobalt. This in turn indicates that rhodium is less involved in π-backbonding to the other ligands (ref. 721). Some chemistry of [$cp'_2Ir_2(\mu$-$H)_3$]$^+$ is outlined in

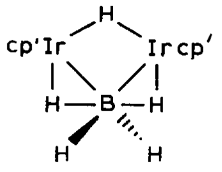
Scheme LXXII. Both $[cp'_2Ir_2H_2(PMe_3)_2(\mu\text{-}H)]A$ (A = PF_6, BF_4) and $[cp'IrH_3(PMe_3)]BF_4$ are fluxional, the former by a bridge-terminal exchange of



a) L(= PMe_3; A = BF_4, PF_6). b) $LiBHEt_3$. c) $HBF_4{\cdot}Et_2O$. d) Δ, PMe_3, acetone. e) $Bu^nLi{\cdot}$pmdeta. f) R_3MX (= $Me_3SiOSO_2CF_3$, Me_3SnCl, Ph_3SnBr). g) RX (R = Pr^n, Bu^n, Np, n-pentyl, $CH_2{=}CHCH_2$; X = Br, I).

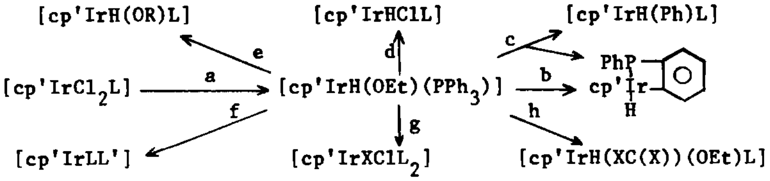
Scheme LXXII

hydride ligands. For the second, the low temperature limiting proton NMR spectrum showed one hydrogen to reside in a unique environment, the other two to be equivalent and a coupling between the two sets to be 56.3 Hz. Possible some sort of "non-classical" hydride complex has been formed here. If $[cp'_2Ir_2(\mu\text{-}H)_3]^+$ is reduced with sodium borohydride instead of lithium triethylborohydride, the product is [427]. This can be converted further



[427]

to $[cp'IrH_3]^-$ with lithium triethylborohydride and on contact with methanol or alumina forms $[cp'_2Ir_2H_6]$ which can be cleaved by trimethylphosphine to give $[cp'IrH_2(PMe_3)]$. Both $[Li(pmdeta)_x][cp'IrH_3]$ and $[Li(pmdeta)_x][cp'IrH_2(SiMe_3)]$, which is prepared in like fashion from $[cp'IrH_3(SiMe_3)]$, show measurable $^1H\text{-}^7Li$ coupling which is temperature dependent, a feature which is attributed to a combination of effects: a fast ^7Li quadrupolar relaxation dominant at low temperature and fast intermolecular exchange at higher temperatures (refs. 722-724). Scheme LXXIII (L = PPh_3) depicts the synthesis and chemistry of an iridium alkoxide hydride complex. The kinetics of reactions f) (L = PPh_3) and h) suggest an intermediate forms



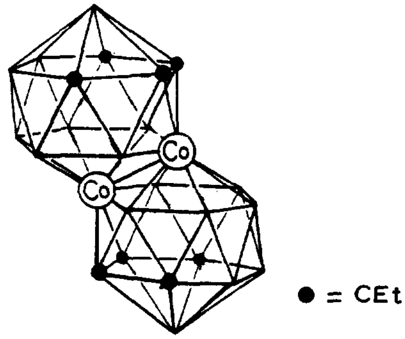
a) NaOEt, EtOH. b) hν, octane. c) hν, benzene. d) HCl or LiCl. e) Pr^nOH, C_2D_5OD (R = Pr^n, C_2D_5). f) L' (= CO, C_2H_4, PPh_3). g) CCl_4 (X = Cl) or $CHCl_3$ (X = H, Cl mixture), benzene. h) CX_2 (X = O, S).

Scheme LXXIII

which is thought to be [cp'IrH(L)]OEt or [cp'IrH(L)(OEt)] in which the cp' ring has "slipped" or [(η^4-C_5Me_5(OEt))IrH(L)] (ref. 725). Addition of [$LMCl_2$(pzH)] (M = Ru; L = η^6-p-cymene. M = Rh, Ir; L = cp') to [M'(acac)-(TFB)] (M' = Rh, Ir) forms species formulated as [$LMCl_2$(pz)M'(TFB)]. In the rhodium-ruthenium complex the pyrazolate and both chloride ligands bridge the metals but it is uncertain in the rest whether both chlorides are bridging. The rhodium-iridium complex is considered unusual because formally it is a Rh(III)-Ir(I) species. Also prepared was [cp'IrCl$(pz)_2$-Rh(TFB)] from [cp'IrCl(acac)] and [Rh(TFB)$(pzH)_2$] (ref. 726). The proton NMR spectrum of [(η^5-C_9H_7)IrH$(PPh_3)_2$]BF_4 shows an unusual upfield shift of the protons on the six-membered ring portion of the indenyl ligand which attributed to an eclipsing of this ring by a phenyl ring of the phosphine ligand. This is apparently a preferred orientation of the indenyl ligand which places the six-membered ring trans to the ligand (here hydride) having the largest trans influence. Accompanying this is a "ring-slip" which is evident from the structure and which allows significant recovery of aromatic character in the six-membered ring, a factor which is thought to provide the driving force for the process (ref. 727).

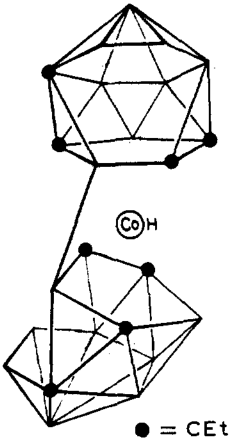
Metallaborane and -carbaborane Complexes

A mixture of anhydrous cobalt(II) chloride, DPPE and Na[nido-2,3-Et_2C_2-B_4H_5] in THF forms [(η^5-$B_4H_4C_2Et_2$)CoCl(DPPE)] from which the cyano and iodo analogs can be got by metathesis with sodium cyanide in methanol and by reaction with methyl magnesium iodide respectively (ref. 728). Addition of excess cobalt(II) chloride to $Na_2[Et_4C_4B_8H_8]$ in THF at low temperature forms [428] plus $[(Et_4C_4B_8H_7)_2Co_2]$ and several minor products. The same



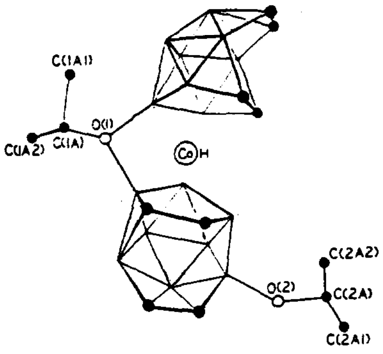
[428]

reaction in the presence of $[B_5H_8]$ also forms [428], an isomer of the $[(Et_4C_4B_8H_7)_2Co_2]$ formed in the first reaction plus $[(Et_4C_4B_8H_8)Co(Et_4C_4B_8H_7OC_4H_8)]$, $[(Et_4C_4B_4H_6)CoH(Et_4C_4B_8H_8)]$ and [429]. Treatment of [428]

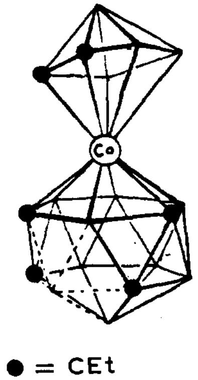


[429]

with iodine in acetone gives the second isomer of $[(Et_4C_4B_8H_7)_2Co_2]$ mentioned above plus [430], two isomers of $[(Et_4C_4B_8H_7)_2Co(OH)]$ and $[(Et_4C_4B_8H_6OH)_2CoH]$. If the reaction used to form [428] is carried out with Na[*nido*-$Et_2C_2B_4H_5$] present, the products are [431], $[(Et_2C_2B_4H_3)Co(Et_4C_4B_8H_6OC_4H_8)]$, the second isomer of $[(Et_4C_4B_8H_7)_2Co_2]$ mentioned above, [429] and [432] (refs. 729, 730). Ruthenium(III) chloride reacts with Na[2-cpCoB_4H_7] in THF to form three isomers of $[cp_2Co_2B_8H_{12}]$ thought to be [433a-c] while with Na[1-cpCoB_4H_7] the product is a single isomer, not any of those from the first reaction, and proposed to be [434] (ref. 731). The ^{11}B NMR

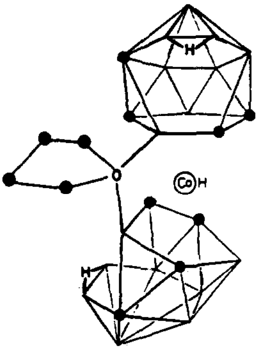


[430]



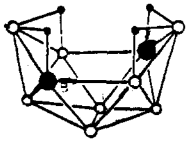
[431]

spectra of [*closo*-1,2-$(cpCo)_2B_4H_6$] and [*nido*-2-$cpCoB_4H_8$], among others,



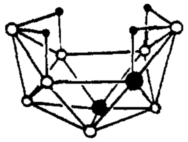
[432]

show significantly solvent-dependent chemical shifts. The largest effects are on the apical boron and the basal boron *trans* to cobalt in the latter complex. These data correlate with existing bonding models for these complexes but it was not possible to distinguish between a solvent-induced

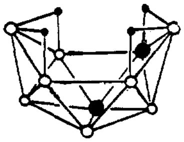


o = BH ● = Cocp • = H

[433 a]

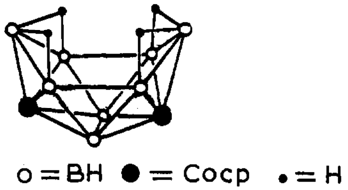


[433 b]



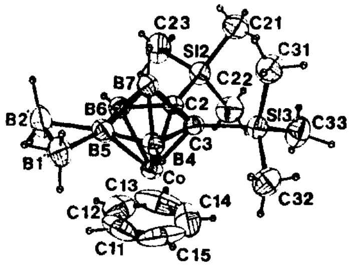
[433 c]

shielding at the metal which is selectively transmitted to the boron atoms in question and an increased susceptibility of these boron atoms to direct

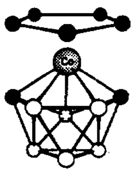


[434]

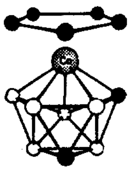
solvent influences due to the presence of the metal (ref. 732). The cocondensation of cobalt atoms with cyclopentadiene, $[B_6H_{10}]$ and BTMSA forms [435] - [437] as major products and [438] and [439] as minor products (filled circles in the cage = $CSiMe_3$). Thermolysis of [435] forms [438] and [439] in good yield. Similarly, cocondensation of cobalt atoms, cyclopentadiene, $[B_5H_9]$ and carbonyl sulfide formed [440] plus smaller amounts



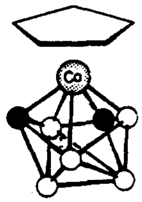
[435]



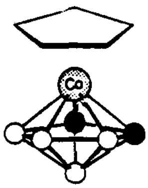
[436]



[437]

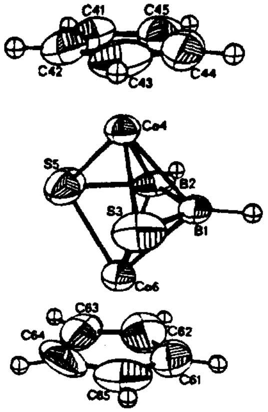


[438]



[439]

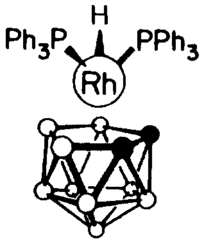
of [4,6-$(cpCo)_2$-3,5-$S_2B_2H_2$] and the known compounds [2,3-$(cpCo)_2$-6-SB_5H_7], [6,8-$(cpCo)_2$-7,9-$S_2B_5H_5$], [1,2-$(cpCo)_2B_4H_6$], [1,2,3-$(cpCo)_3B_3H_5$] and

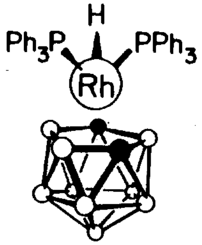


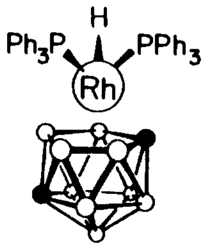
[440]

[$cp_3Co_3B_4H_4$] (refs. 733, 734). Exposure of a THF solution of [(η^6-C_6Me_6)$_2$-Co]PF_6 and Tl[$C_2B_9H_{11}$] to oxygen forms [3,1,2-(endo-H-η^5-C_6HMe_6)$CoC_2B_9H_{11}$] and Tl[(1,2-$C_2B_9H_{11}$)$_2$Co] (ref. 735).

Attempts to form [closo-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$]$^-$ from [RhCl$(PPh_3)_3$] and [nido-7,8-$C_2B_9H_{11}$]$^{2-}$ or by sodium amalgam reduction of [$(Ph_3P)RhC_2B_9$-H_{11}]$_2$ in the presence of triphenylphosphine apparently gave the desired compound but it could not be isolated. The most successful preparation involved deprotonation of [441] with potassium hydroxide solubilized with 18-crown-6, butyllithium or potassium tri-sec-butylborohydride. The corresponding 2,1,7- and 2,1,12-RhC_2 isomers could be obtained similarly from [442] and [443] respectively on deprotonation with tetramethylammonium hydroxide. Reprotonation of the anions can be effected by methanol or ethanol suggesting that the parent hydride complexes have acidities comparable to these alcohols. The structures of the 3,1,2 and 2,1,7 isomers of the anions as the [K(18-crown-6)]$^+$ and tetramethylammonium salts respectively, show the rhodium atom to be bound equally to the five atoms of the B_3C_2 face of the carbaboranyl moiety in the former but mainly to the



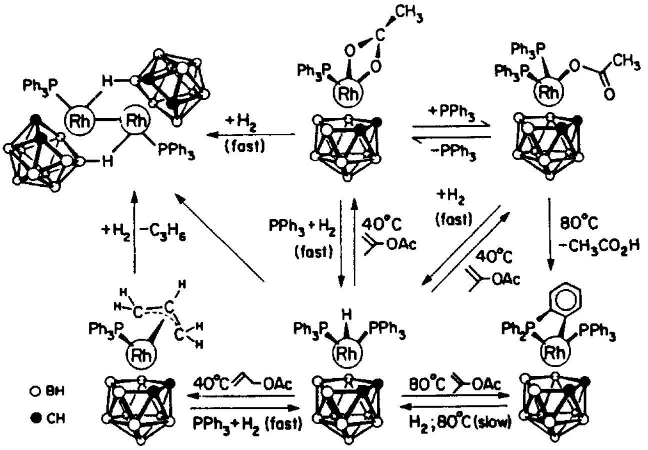




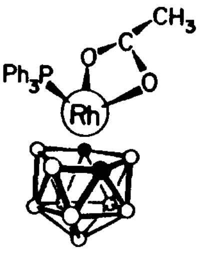
O = BH ● = CH

[441] [442] [443]

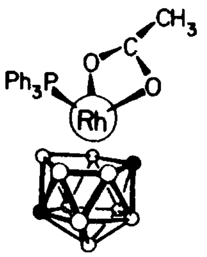
three boron atoms in the latter which is in accord with molecular orbital calculations. All three anions react with carbon monoxide to replace one triphenylphosphine while in the first two, a similar substitution by ethylene occurs. The iridium analog, [closo-3,3-$(PPh_3)_2$-3,1,2-$IrC_2B_9H_{11}]^-$ can be obtained from the corresponding hydride by deprotonation with potassium hydride but not with potassium hydroxide. Reaction of the hydride with potassium tri-sec-butylborohydride and 18-crown-6 forms [K(18-crown-6)][closo-3-(PPh_3)-3,3-H_2-3,1,2-$IrC_2B_9H_{11}$] if the product is precipitated soon after the reaction is initiated. A carbonyl derivative, PPN[closo-3-(PPh_3)-3-(CO)-3,1,2-$IrC_2B_9H_{11}$] can be obtained from [IrCl-(CO)$(PPh_3)_2$] and PPN[closo-3,1,2-$TlC_2B_9H_{11}$] (ref. 736). The reactions of [441] with olefinic acetates is outlined in Scheme LXXIV. With isopropenyl acetate, [442] and [443] form only [444] and [445] respectively at both 40°C and 80°C whereas with vinyl acetate, [442] forms [444] at the lower temperature but [446] (R_1 = H; R_2 = Me. R_1 = Me; R_2 = H) at the higher. Schemes LXXV and LXXVI outline proposed mechanisms for three of the processes shown in Scheme LXXIV (ref. 737). A high-yield synthesis of [447]



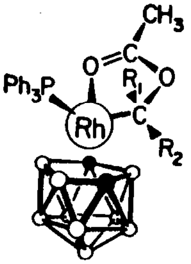
Scheme LXXIV



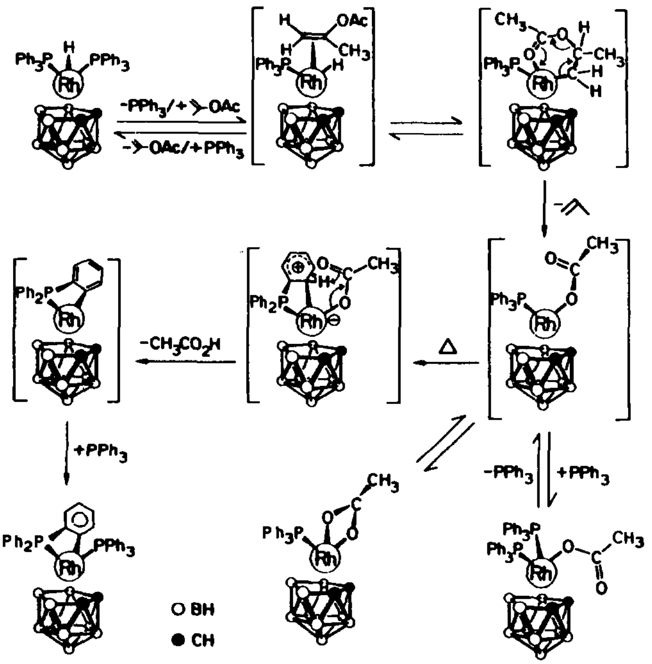
[444]



[445]



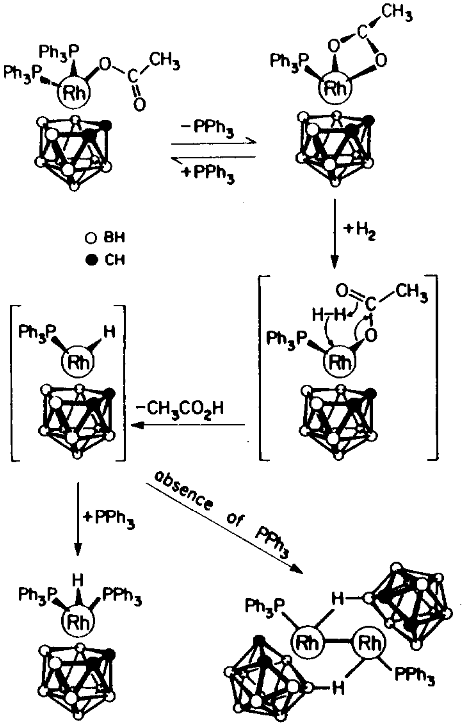
[446]



Scheme LXXV

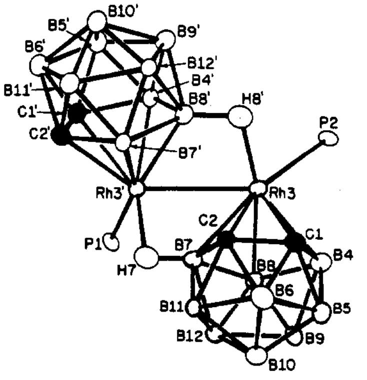
(phenyl rings of PPh$_3$ omitted) involves reactions of [RhCl(COD)(PPh$_3$)] with [*nido*-7,8-C$_2$B$_9$H$_{12}$]$^-$ in refluxing THF and an analog can be prepared similarly from [*nido*-7-Ph-7,8-C$_2$B$_9$H$_{11}$]$^-$. A similar reaction between [448] and [RhCl(COD)(PEt$_3$)] forms a mixture of [449] and [450]. The formation of

[447] is proposed to occur as depicted in Scheme LXXVII (ref. 738). Standard methods have been used to prepare [closo-2,2-(PPh$_3$)$_2$-2-H-1-Me-7-Ph-2,1,7-RhC$_2$B$_9$H$_9$] in which, because of the greater bulk of the carbonyl moiety, there was no formation of the exo-nido tautomer that had previously



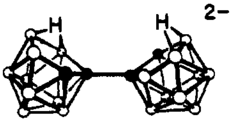
Scheme LXXVI

been detected for less substituted analogs. Also, no rotation of the {Rh(PPh$_3$)$_2$H} moiety about the face of the carboranyl moiety was observed

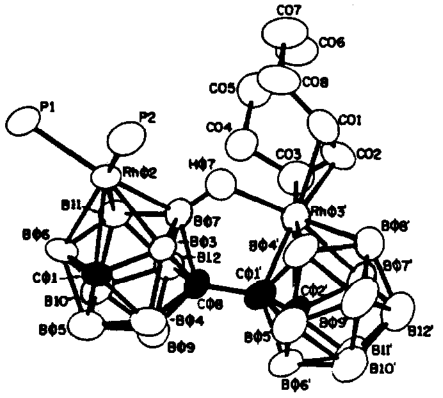


[447]

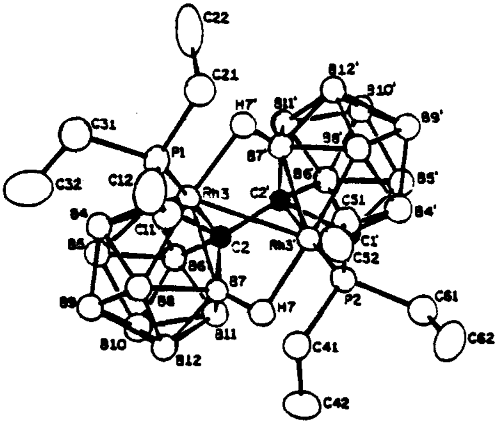
but the complex proved to be a fairly stable catalyst precursor for olefin hydrogenation (ref. 739). Reaction of $[RhCl(COD)]_2$ with [*nido*-7,8-Me$_2$-7,8-$C_2B_9H_{10}$]$^-$ and sodium isopropoxide forms [*closo*-3,3-(η^4-COD)-1,2-Me$_2$-3,1,2-Rh$C_2B_9H_9$]$^-$ which is shown at the top of Scheme LXXVIII. This scheme also shows the low-temperature protonation of this complex to give a



[448]

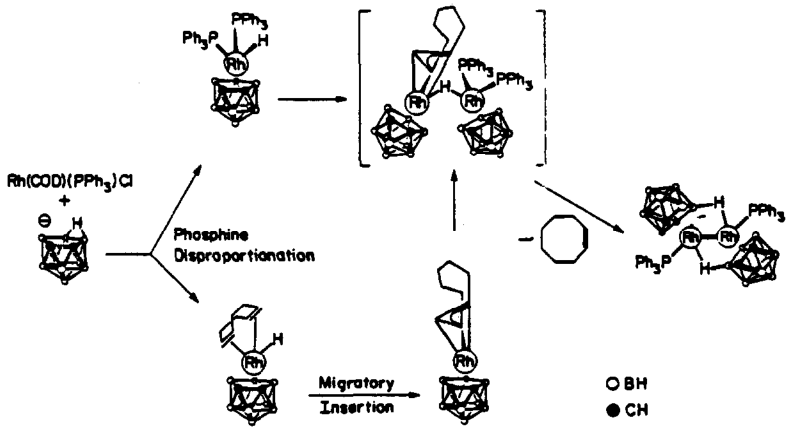


[449]

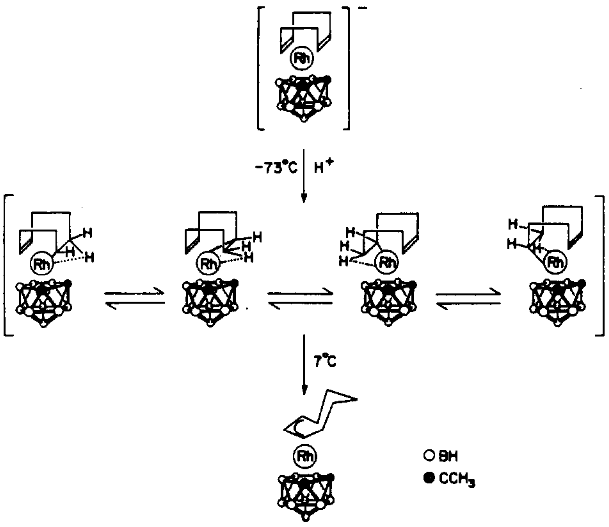


[450]

fluxional species containing an agostic hydrogen and its subsequent conversion to a cyclooctenyl derivative. The same initial result is seen for the

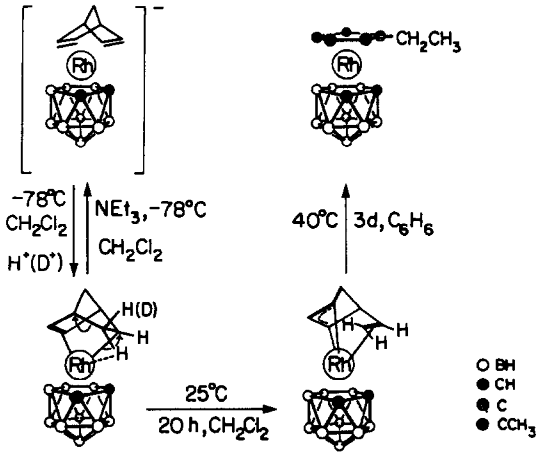


Scheme LXXVII



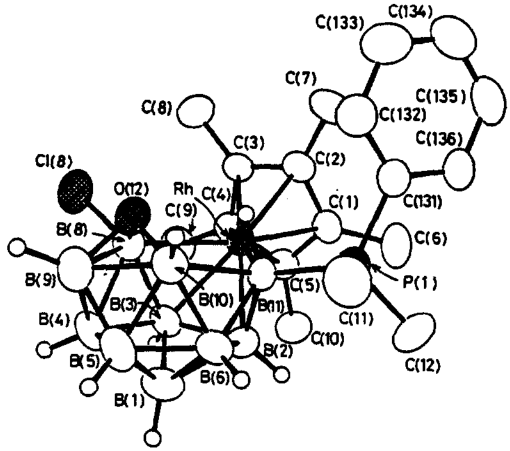
Scheme LXXVIII

NBD analog but this rearranges on warming and ultimately a novel aromatization of the NBD to an ethylcyclopentadienyl moiety occurs as shown in Scheme LXXIX (refs. 740, 741).

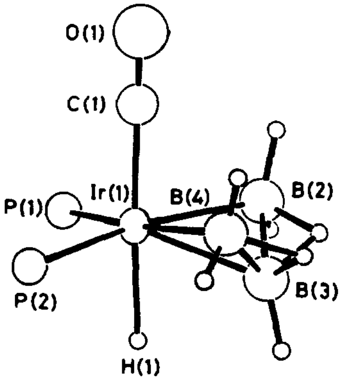


Scheme LXXIX

The eleven-vertex species [nido-cp'$RhB_{10}H_{11}Cl(PMe_2Ph)$] reacts with water in dichloromethane to form [nido-cp'$RhB_{10}H_9OCl(PMe_2Ph)$], [451], in which the oxygen atom bridges three boron atoms on the open face (ref. 742). A comparison of the structure of [452] (P = PPh_3) with that of $[(\eta^3\text{-}C_3H_5)Ir(CO)Cl(PMe_2Ph)_2]^+$ suggests that to describe the $\{B_3H_7\}$ moiety as a "bora-allyl" ligand is not appropriate. Instead, the complex should be considered to contain seven-coordinate iridium(V) with three two-center, two-electron iridium-boron bonds (ref. 743). Reaction of $[(OC)(PMe_3)Ir(H)B_8H_{12}]$

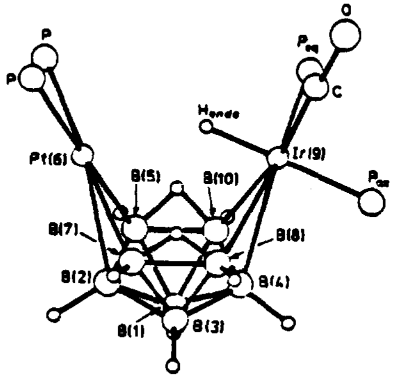


[451]

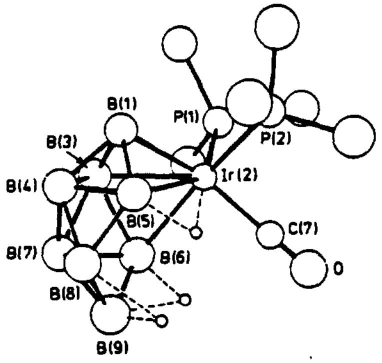


[452]

with potassium hydride and then $[PtCl_2(PMe_3)_2]$ gives a bimetallic complex proposed to be [453] while thermolysis of the initial iridium complex forms [454] (ref. 744).



[453]



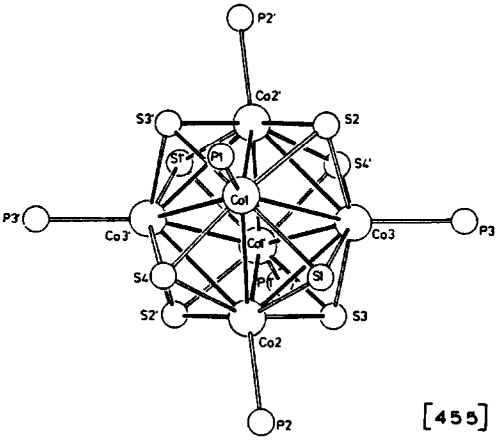
[454]

Miscellaneous Complexes

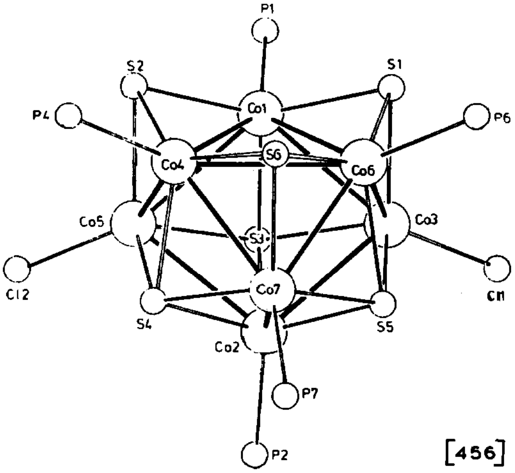
As in previous Annual Surveys, the compounds described in this section cannot be conveniently categorized in any of the preceeding sections but are of potential interest to organometallic chemists. A substantial number of papers have appeared which describe the gas-phase reactions of ions containing one or more bare or ligated transition metal atoms with a variety of organic molecules using ion-cyclotron resonance, laser-ionization FTMS, and related techniques. These include a study of the mechanism of alkane dehydrogenation by Co^+ (ref. 745) and the reactions of Co^+ and/or Rh^+ with methyl nitrite, nitroalkanes (refs. 746, 747), thiols, ketones, carboxylic acids (refs. 748) and primary alkyl halides and alcohols (ref. 749). In the case of methyl nitrite, Co^+ reacts primarily by insertion into the internal nitrogen-oxygen bond to form $\{Co(OMe)^+\}$ while Rh^+ forms mainly $\{RhH(CO)^+\}$ and $\{RhH(NO)^+\}$. With nitroalkanes attack at carbon-nitrogen, nitrogen-oxygen and carbon-carbon bonds occurs and significant isomerization of the nitro compounds to the nitrites is also seen. While thiols generally show attack at carbon-hydrogen bonds, with the alcohols insertion into carbon-carbon bonds predominates. The ketones seem to initially coordinate to Co^+ via oxygen followed by insertion into the α-carbon-carbon bond but the carboxylic acids show a preference for attack at the C-OH bond. The $CoFe^+$ ion is unreactive towards cyclic C_3-C_6 or C_1-C_6 acyclic alkanes but with alkenes containing a linear C_4 unit, dehydrogenation is the primary process (ref. 750). The reactivity of $\{M(CH_2)^+\}$ (M = Co, Rh) towards alkanes and alkenes generally suggests formulation as $\{M{=}CH_2{}^+\}$. The cobalt species, unlike Co^+, preferentially attacks carbon-hydrogen bonds in acyclic alkanes and in cyclopentane and cyclohexane but with cyclopropane and cyclobutane, carbon-carbon bond cleavage occurs initially. With ethylene, the exclusive product is propylene and from labelling studies very little metathesis occurs. By contrast in the reaction with propylene, metathesis is dominant. The rhodium analog shows a more varied chemistry than either the cobalt or iron species (refs. 751-754). Aliphatic alkanes and alkynes react with $\{CoCH_3{}^+\}$ primarily by coupling with the methyl group followed by dehydrogenation which contrasts with the behavior of Co^+ which prefers to attack carbon-carbon bonds (ref. 755). The propylene complexes $\{M(C_3H_6)^+\}$ (M = Co, Rh) undergo several H/D exchange steps with C_2D_4 and while in the cobalt system there is only one exchange per encounter, in the rhodium system multiple exchanges occur in each encounter (ref. 756). A combination of ion-cyclotron resonance and infrared multiphoton dissociation techniques has been used to probe the potential energy surface for the reaction of Co^+ and $\{Co(CO)^+\}$ with C_5

hydrocarbons (ref. 757) while other papers report on the reactions of {cpCo$^+$} with hydrocarbons (ref. 758), of [cp$_2$M] (M = Fe, Ni) with {Co(isobutene)$^+$} (ref. 759) and on the oxidative addition of alkyl radicals in the gas phase to cobalt(II) compounds such as [Co(acac)$_2$], [Co(acacen)] and [Co(salen)] (ref. 760).

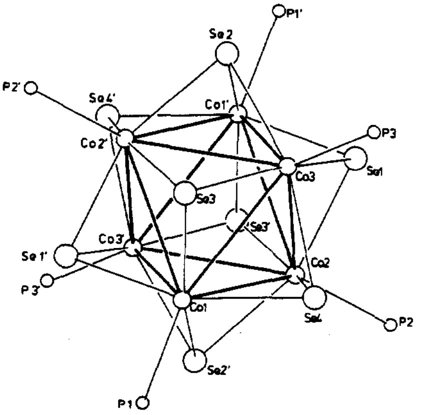
Complexes formulated as [cp$_2$Mo(μ-H)$_2$CoX$_2$](X = Cl, Br, I) and considered as Lewis acid-base adducts form when anhydrous cobalt(II) halides react with [cp$_2$MoH$_2$] (ref. 761). Reaction of [CoCl$_2$(PPh$_3$)$_2$]$_2$ with bis(trimethylsilyl)sulfide in THF forms [Co$_6$S$_8$L$_6$][CoCl$_3$(THF)] ([455]) and [Co$_7$S$_6$L$_5$Cl$_2$] ([456]) L = PPh$_3$) while with the corresponding selenide the isolated products are [Co$_4$(PPh$_3$)$_4$(μ_3-Se)$_4$] which contains a tetrahedron of metal atoms, neutral [Co$_6$Se$_8$(PPh$_3$)$_6$] ([457]) and [Co$_9$Se$_{11}$(PPh$_3$)$_6$] ([458]) (refs.



[455]

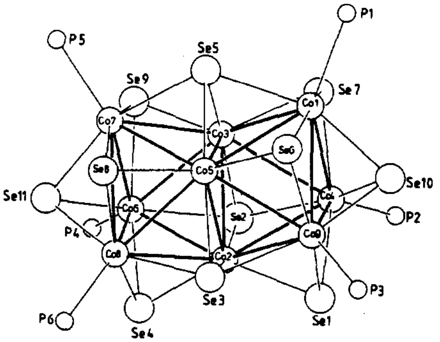


[456]

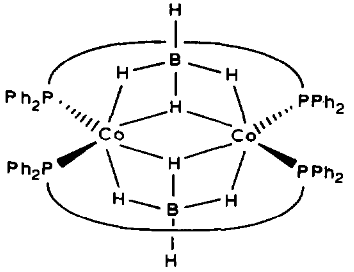


[457]

762, 763). Reduction of hexaquocobalt(II) chloride with borohydride in the presence of bidentate phosphines forms $[CoH(L_2)_2]$ (L_2 = $Ph_2P(CH_2)_nPPh_2$ (n = 2-6), vdiphos) but with the trans isomer of the last, reduction of the ligand also occurs and $[CoH(DPPE)_2]$ is obtained. In the case of the two largest ligands, the intermediate [459] could be isolated (ref. 764).

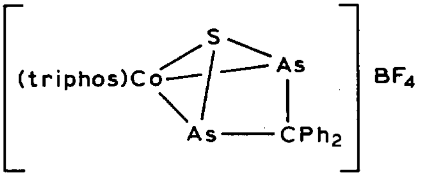


[458]



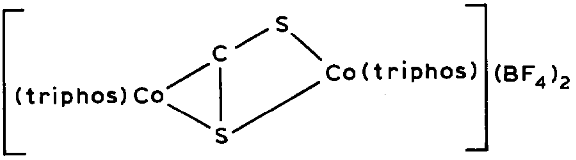
[459]

The paramagnetic, zerovalent cobalt dimer, $[(triphos)_2Co_2(\mu\text{-}N_2)]$, is formed by the sodium amalgam reduction of a mixture of cobalt(II) chloride and the ligand in THF under nitrogen followed by recrystallization from *n*-butanol (ref. 765). In a mixture of THF and ethanol, $[Co(H_2O)_6](BF_4)_2$, triphos and tris(trimethylsilyl)heptaphosphanortricyclene react to give $[(triphos)Co(\eta^3\text{-}P_3)]$ (ref. 766). The reaction of $[(triphos)Co(\eta^3\text{-}As_2S)]BF_4$ with an excess of diphenyldiazomethane in refluxing butan-2-one forms [460]



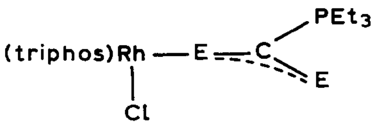
[460]

in which diphenylcarbene has effectively inserted into the arsenic-arsenic bond to generate a metal-stabilized 3,3-diphenyl-1,2,4-thiadiarsete moiety. The participation of a competing radical process could not be ruled out however (ref. 767). The same cobalt complex and its phosphorus analog react with $[Co(H_2O)_6](BF_4)_2$ or $[Rh(COD)(acetone)_x]BF_4$ in acetone containing excess triphos to form $[(triphos)Co(\mu\text{-}E_2S)M(triphos)](BF_4)_2$ (M = Co, Rh; E = P, As). When the latter reaction is carried out at reflux temperature however the product is $[(triphos)Rh(\mu\text{-}E_2S)Rh(triphos)]^{2+}$ (ref. 768). Attempted protonation of $[(triphos)Co(\eta^2\text{-}CS_2)]$ with tetrafluoroboric acid in THF formed [461] instead (ref. 769).



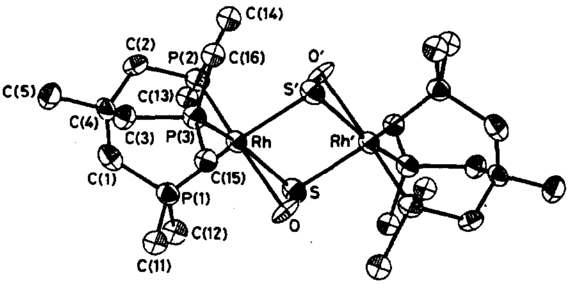
[461]

Addition of triethylphosphine to $[(triphos)RhCl(\eta^2\text{-}CE_2)]$ (E = S, Se) forms [462] which reacts further with oxygen to generate [(triphos)RhCl-

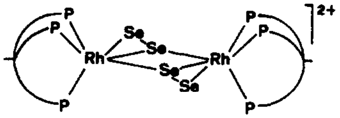


[462]

$(E_2C{=}O)]$ in which the chloride ligand is labile. In the presence of tetraphenylborate, cationic $[(triphos)Rh(E_2C{=}O)]BPh_4$ is obtained. This also reacts with oxygen to generate carbon dioxide and $[Rh_2(triphos)_2(\mu\text{-}SO_2)_2]^{2+}$ ([463]) or $[Rh_2(triphos)_2(\mu\text{-}Se_2)_2]^{2+}$ ([464]). $[(triphos)RhCl(Se_2C{=}O)]$ is

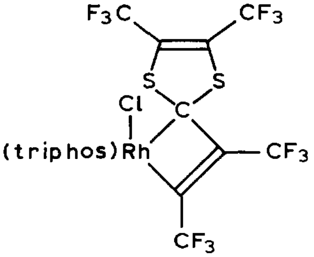


[463]

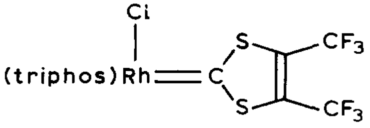


[464]

evidently the first example of a diselenocarbonate complex (refs. 770, 771). Another reaction of $[(triphos)RhCl(\eta^2\text{-}CS_2)]$ is with HFB where the product is [465] which may form <u>via</u> [466] as an intermediate (ref. 772).

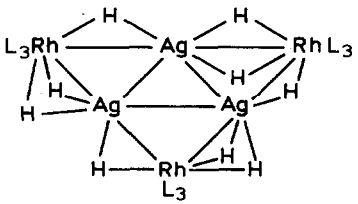


[465]



[466]

Reaction of hydrogen with a solution of $[RhCl_3(triphos)]$ previously treated with four equivalents of silver triflate forms $[Rh_3Ag_3H_9(triphos)_3](OSO_2\text{-}CF_3)_3$ ([467]); L_3 = triphos). The hydride ligands were not located in the x-ray structure determination and the postulated arrangement is derived



[467]

from NMR measurements (ref. 773). In THF solution, carbon disulfide reacts with $[RhH(np_3)]$ to form $[(np_3)Rh(SCH{=}S)]$ and on treatment of the filtrate with tetraphenylborate ion some $[(np_3)Rh(\eta^2\text{-}CS_2)]BPh_4$ is obtained. By contrast, the cobalt analog forms the $\eta^2\text{-}CS_2$ complex in the *absence* of tetraphenylborate while in its presence $[(np_3)Co(CS)]BPh_4$ is formed. The difference is attributed to variations in the ease of rearrangements of the coordination sphere of the $\{(np_3)M\}$ moiety and the strength of interaction of the bridgehead nitrogen with the metal. Successive reactions of $[RhCl(C_2H_4)_2]_2$ with np_3 in refluxing THF containing thallium(I) hexafluorophosphate, with refluxing carbon disulfide and then with tetraphenylborate ion in *n*-butanol forms the thiocarbonyl $[(np_3)Rh(CS)]BPh_4$ (ref. 774).

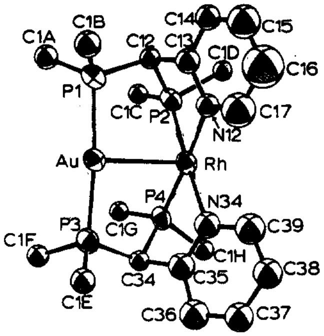
The kinetics of the addition of hydrogen to $[Rh(L_2)_2]^+$ (L_2 = DPPP, DPPB, DIOP) show the reaction to be second order while the reverse reaction is first order. In the case of the DIOP complex the kinetic data suggest the opening of one chelate ring prior to oxidative addition of hydrogen (ref. 775). A reexamination of the chemical reduction of $[Rh(DPPE)_2]BF_4$ indicates the behavior shown in Scheme LXXX. No reaction was observed

$$\begin{tikzcd}
\mathrm{[Rh(DPPE)_2]^+} \arrow[r, "a"] \arrow[dr, "b"] & \mathrm{[Rh(DPPE)_2]} \arrow[d, shift left, "a"] & +\ \mathrm{[RhH(DPPE)_2]} \\
\mathrm{[RhH(DPPE)_2]} & \mathrm{[Rh(DPPE)_2]^-} \arrow[l, "d"'] \arrow[u, shift left, "c"]
\end{tikzcd}$$

a) Sodium naphthalenide (1 equiv.), benzene. b) Sodium naphthalenide (2 equiv.), benzene. c) $[Rh(DPPE)_2]^+$, benzene. d) MeOH or MeCN.

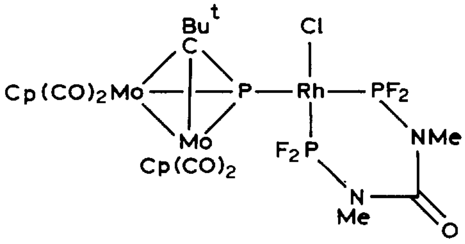
Scheme LXXX

between $[Rh(DPPE)_2]$ and methanol or acetonitrile or between $[RhH(DPPE)_2]$ and the triphenylmethyl radical. The results indicate that in benzene the reduction occurs in two one-electron steps. In THF, $[Rh(DPPE)_2]^-$ is also generated by two equivalents of sodium naphthalenide but with one equivalent an equilibrium mixture of $[Rh(DPPE)_2]^n$ ($n = \pm1,0$) results with the first two predominating. This suggests that in this solvent the rhodium(0) complex has a greater tendency to disproportionate (ref. 776). $[Rh(NPP)_2]BF_4$, (NPP = 2-[bis(diphenylphosphino)methyl]pyridine) in which the ligand coordinates only through phosphorus, is synthesized from $[Rh(NBD)(NPP)]BF_4$ and a second equivalent of the ligand in acetone. It reacts with two equivalents of $[Au(PPh_3)(NO_3)]$ to form [468] which is a dication (ref. 777). The initial reaction occurring on addition of tri-*n*-butylphosphine to $[RhH(SnCl_3)_5]^{3-}$ is deprotonation to form $[Rh(SnCl_3)_5]^{4-}$ but with excess phosphine(L) present, this as well as the tributylphosphonium cation react



[468]

further to form *cis*- and *trans*-$[RhH(L)(SnCl_3)_4]^{2-}$ and then *trans*-$[RhHClL_2(SnCl_3)_2]^-$, *mer*-$[RhHL_2(SnCl_3)_3]^-$ and *trans*-$[RhL_2(SnCl_3)_3]^{2-}$ (ref. 778). Bridge cleavage in $[Rh_2((F_2PNMe)_2CO)_2(\mu\text{-}Cl)_2]$ by the phosphorus atom of the phosphaalkyne complex $[cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}Bu^tCP)]$ occurs to form [469] (see

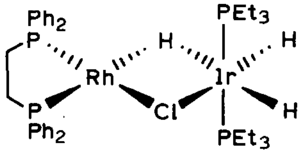


[469]

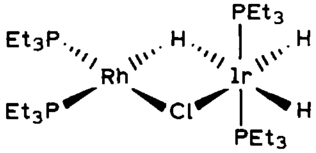
also ref. 335) (ref. 779). Reaction of $[RhCl(O_2)(PPh_3)_3]$ with 1.5 equivalents of acetylacetone and two of triphenylphosphine in benzene forms $[Rh(acac)Cl(O_2H)(PPh_3)_2]$ in which the hydrogen of the hydroperoxo moiety originates on acetylacetone. Refluxing this product in benzene with more acetylacetone forms $[RhCl(acac)_2(PPh_3)]$ while reaction with triphenylphosphine in chloroform forms $[RhCl_2(acac)(PPh_3)_2]$ and triphenylphosphine oxide *via* $[RhCl(OH)(acac)(PPh_3)_2]$ as an intermediate. Neither $[RhCl(O_2)(PPh_3)_2]_2$ nor $[IrCl(O_2)(CO)(PPh_3)_2]$ reacted with acetylacetone and the rhodium hydroperoxide complex did not oxidize olefins (ref. 780). Addition of $[RhCl(PPh_3)_3]$ to the polyether $Me(OCH_2CH_2)_{10}O(CH_2CH_2)_8H$ forms $[Rh_2H_2Cl_2(PPh_3)_4]$ plus some rhodium olefin complexes which were not well-characterized. It was proposed that the rhodium(I) complex dehydrogenates some of the $\{-CH_2CH_2-\}$ moieties in the polyether to olefinic groups (ref. 781). Replacement of one triphenylphosphine ligand in $[RhCl(PPh_3)_3]$ by *o*-phenylenediamine or diaminomaleonitrile (L) forms $[RhCl(PPh_3)_2L]$ which on reaction with oxygen forms the corresponding rhodium(II) complexes containing the ligands *semi-o*-benzoquinonediimine and diiminosuccinonitrile respectively (ref. 782). Triphenylphosphine reacts with $[Rh_2(MeCN)_6(\mu\text{-}O_2CMe)_2](BF_4)_2$ in methanol to form a mixture of $[Rh_2(MeCN)_4(PPh_3)_2(\mu\text{-}O_2CMe)_2](BF_4)_2$ and $[Rh(MeCN)(PPh_3)_3]BF_4$. The latter species can also be obtained from $[RhCl(PPh_3)_3]$ and trimethyloxonium tetrafluoroborate in acetonitrile (ref. 783).

The coordinated tetrafluoroborate as well as the dinitrogen ligand in $[IrHCl(FBF_3)(N_2)(PPh_3)_2]$ are replaced by 9-methylguanine (L) at -20°C in dichloromethane and binding of L through both nitrogen and oxygen appears to occur. On standing in methanol solution the cationic product is transformed into $[IrHCl_2(L)(PPh_3)_2]$ where the guanine ligand binds only *via* nitrogen. However with $[IrHCl(X)(N_2)(PPh_3)_2]$ (X = perfluorobutane sulfonate) the product is $[IrHCl(L)(N_2)(PPh_3)_2]^+$ which reacts with water to form $[IrHCl(H_2O)(L)(PPh_3)_2]^+$ (ref. 784). In refluxing benzene or 2-methoxyethanol, $[IrH_3(PPh_3)_3]$ reacts with pyridine-2-thiol or 2-hydroxypyridine respectively to form $[IrH_2(NE)(PPh_3)_2]$ (NE = $2\text{-}EC_5H_4N^-$ (E = S, O)) (ref. 785). Either *fac*- or *mer*-$[IrH_3L_3]$ (L = PMe_2Ph) can be protonated with tetrafluoroboric acid etherate to form $[IrH_4L_3]^+$ in which the added proton appears to be approximately in the same plane as the original three hydrogens. Deprotonation of this species at low temperature yields *mer*-$[IrH_3L_3]$ so that starting with the *fac* isomer, the protonation/ deprotonation sequence is effectively an acid-promoted, *fac*→*mer* isomerization. Flushing a solution of $[IrH_4L_3]^+$ with nitrogen forms *cis-mer*-$[IrH_2(N_2)L_3]^+$ and analogs with carbon monoxide or acetonitrile in place of the dinitrogen ligand can be similarly synthesized. If $[IrH_4L_3]^+$ is prepared using substoichiometric quantities of acid, the remaining trihydride material is an 88:12 mixture of *fac* and *mer* isomers irrespective of which isomer was used initially. This suggests that some $[IrH_2L_3]^+$ may be present which serves the function of the base to deprotonate $[IrH_4L_3]^+$ (ref. 786). Protonation of $[IrH_5L_2]$ (L = Pcy_3) at -80°C reversibly forms $[IrH_6L_2]^+$ which loses two molecules of hydrogen in acetonitrile with formation of $[IrH_2(MeCN)L_2]^+$. From NMR measurements, particularly the T_1 values obtained, this complex is formulated as $[IrH_2(H_2)_2L_2]^+$ and contains two coordinated dihydrogen *molecules*. It is thus a non-classical, iridium (III) complex and not an Ir(VII) species (ref. 787). Its precursor (L = PPr^i_3) can be obtained by lithium aluminum hydride treatment of $[IrHCl_2L_2]$ (L = PPr^i_3) followed by mild hydrolysis. A neutron diffraction study showed the structure to be very nearly pentagonal bipyramidal with axial phosphine ligands (ref. 788). The same complex catalyzes the dehydrogenation of methylcyclohexane and *n*-hexane to methylene cyclohexane and hex-1-

ene respectively in the presence of tert-butylethylene as a hydrogen acceptor. Competition experiments indicated that the reactivity of carbon-hydrogen bonds was greatest in a terminal methyl group and least in a methylene group with a methyl group attached to a secondary carbon showing an intermediate reactivity. The turnover numbers in these systems were very low however (ref. 789). Reaction of $[IrH_5(PEt_3)_2]$ with either $[Rh_2Cl_2(DPPE)_2]$ or $[RhCl(C_2H_4)(DPPE)]$ forms [470] while with $[RhCl(C_2H_4)_2]_2$ and triethylphosphine, the product is [471]. The triisopropylphosphine analog

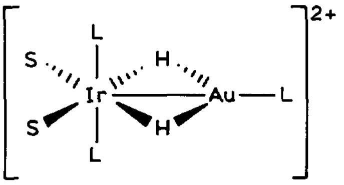


[470]

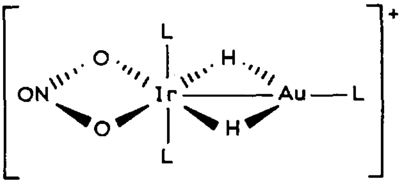


[471]

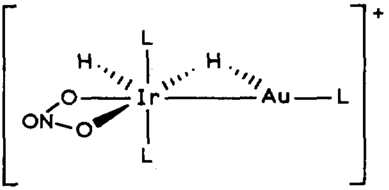
of [470] can be obtained similarly but the presence of hydrogen is necessary and $[(DPPE)Rh(\mu\text{-}Cl)_2IrH_2(PPr^i_3)_2]$ is also formed. Attempts to convert [471] to a trinuclear complex with $[Rh(DPPE)(acetone)_x]^+$ failed and the only stable product was [470]. The binuclear complexes are poor catalysts for olefin hydrogenation (ref. 790). Addition of $[(PPh_3)AuNO_3]$ to $[IrH_2S_2L_2]BF_4$ (S = acetone; L = PPh_3) at -78°C reversibly forms [472] and on warming [473] and [474] are seen with the final product being [475]. Successive reactions of this with $[Au(PPh_3)(NO_3)]$, methyl magnesium chloride



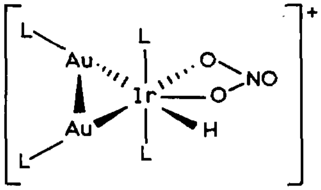
[472]



[473]

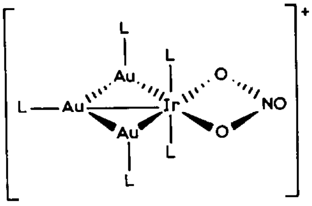


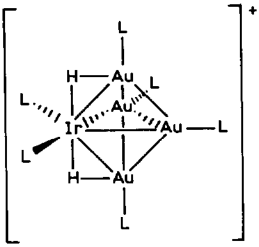
[474]



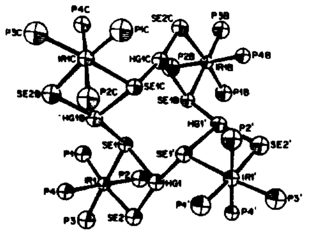
[475]

and more of the gold reagent in THF at 0°C formed [476] which reacted with hydrogen to form [477]. In the latter the hydrides could not be located crystallographically but the proton NMR spectrum is most consistent with the location shown. The ^{31}P NMR spectrum showed that the phosphines on the axial and equatorial gold atoms appeared to interconvert and this


[476]


[477]

was proposed to occur via a rearrangement of the whole $\{Au_4\}$ moiety rather than by a migration of only the phosphine ligands. In related work, $[Ir(DPPE)_2]BF_4$ does not react with $[Au(PPh_3)(NO_3)]$ by itself but in the presence of tetrafluoroboric acid, which generates $[IrH(DPPE)_2]^{2+}$, $[(PPh_3)$-$AuIr(DPPE)_2](BF_4)_2$ forms. This suggests that a necessary precursor to the formation of gold-iridium bonds in these systems is the $\{Ir(\mu\text{-}H)Au\}$ moiety such as is seen in [474] (refs. 791-793). Reaction of $[Cu(MeCN)_4]PF_6$ and fac-$[IrH_3L_3]$ (L = PMe_2Ph) in a 3:2 ratio at 78°C in THF followed by warming to room temperature forms $[Ir_2L_6Cu_3(MeCN)_3(\mu\text{-}H)_6]^{3+}$ whose structure consists of a trigonal bipyramidal cluster of metal atoms with $\{IrL_3\}$ moieties in axial sites and with all the iridium-copper bonds bridged by the hydrides (ref. 794). Addition of elemental mercury to acetonitrile solutions of $[M(Se_2)(L_2)_2]^+$ (M = Rh; L_2 = dmpe. M = Ir; L_2 = DPPE) simply removes the diselenium moiety to form mercury(II) selenide. With $[Ir(Se_2)$-$(dmpe)_2]^+$ however the product is $[(dmpe)_2Ir(\mu\text{-}Se)_2Hg]_4{}^{4+}$ whose heavy atom core is shown as [478]. The central $\{Hg_4Se_4\}$ moiety has a conformation


[478]

much like that of As_4S_4 and S_4N_4 and the net result of this last reaction is an oxidative addition of the mercury across the selenium-selenium bond of the coordinated $\{Se_2\}$ moiety (ref. 795).

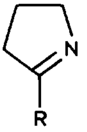
Self-consistent-field molecular orbital calculations have been performed on the model compounds $[RhCl(L)(PH_3)_2]$ (L = N_2, C_2H_4, CO, CNH). Relative to related nickel(0) complexes, the HOMO-LUMO gap is smaller indicating a better capability for bonding to ligands using either σ-donor or π-acceptor interactions or both (ref. 796). The $[Rh_2(O_2CR)_4]/P(OR')_3$ (R = Me, Et, Ph; R' = Me, Et, Pr^n, Ph) system has been studied by ^1H, ^{13}C, ^{31}P and ^{103}Rh NMR spectroscopies. Both mono- and bis(phosphite) adducts were seen and a strong trans influence across the metal-metal bond appeared to exist. A trans-influence series for the ligands L (= P-, As-, Sb-, Bi-, N-, O-, S-donors) in $[Rh_2(O_2CMe)_4(P(OMe)_3)(L)]$ was obtained from further NMR data (ref. 797). The single crystal, cross-polarized, magic-angle-spinning ^{31}P NMR spectrum of the red form of $[RhCl(PPh_3)_3]$ has been used to obtain all three ^{31}P shielding tensors and their orientations. The complex is not axially symmetric and the direction of the largest tensor in each instance is approximately parallel to the rhodium-phosphorus axis (ref. 798). The complexes $[M(X_2)(L_2)_2]Cl$ (M = Rh, Ir; X = S; L_2 = dmpe, DPPE. M = Rh; X = Se; L_2 = dmpe. M = Ir; L_2 = dmpe; X = O) are photochromic at liquid nitrogen temperature in the solid and in a diethyl ether-isopentane-ethanol glass. Bleaching occurred on warming or irradiation with 400-600 nm light. The dioxygen complex loses dioxygen rather easily but the others are more stable. Using SCF-Xα-Sw calculations on models it is proposed that irradiation induces an approximately 45° rotation of the $\{X_2\}$ moiety from the equatorial MP_2 plane (ref. 799). Luminescence studies on $[Ir(vdiphos)_2]ClO_4$ at 9.5 K in the presence of a magnetic field have detected the largest magnetically induced shift of the emission band yet reported (ref. 800). Measurements of the T_1's for the hydride ligands in fac-$[IrH_3(AsPh_3)_3]$ and $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)(\mu\text{-}Cl)_2]BF_4$ show that they have values less than 0.5 sec which is generally significantly less than those for the ligand protons. Also in the latter complex the T_1 for the terminal hydride is slightly smaller than that for the bridging hydride (ref. 801).

Reaction of $[Co(N_2)H(PPh_3)_3]$ with 1-trimethylsiloxybut-1- or 2-ene forms $[Co(OSiMe_3)(PPh_3)_3]$ and predominantly but-2-enes in both instances while with trimethylsiloxyethylene, the same cobalt complex plus ethylene form. It is proposed that the cobalt-hydrogen bond adds to the double bond followed by migration of the trimethylsiloxy group to the metal (ref. 802). Both $[Co(PPh_3)_4]$ and $[Co_2(N_2)(PPh_3)_6]$ catalyze the hydroacylation of 4-pentenal to cyclopentanone but the intermediate cobalt hydride species formed generate side products such as pent-4-en-1-ol and coupling products (ref. 803). Reduction of $[Co(SCN)_2(PPh_3)_2]$ with zinc in DME containing triphenylphosphine forms $[Co(SCN)(PPh_3)_3]$ which can be used in situ to catalyze the selective hydrogenation of conjugated dienes to mono-olefins (ref. 804).

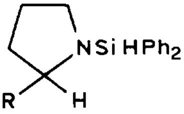
$[RhH_2(PhN\overset{\cdots}{-}N\overset{\cdots}{-}NPh)(PPh_3)_2]$ catalyzes the polymerization of methyl methacrylate (ref. 805) while applications of $[RhCl(PPh_3)_3]$ in catalysis include the hydrogenation of 4-*tert*-butyl-1-methylcyclohexene and its 1-methoxy and 1-carboxymethyl analogs to form predominantly *trans* cyclohexanes (ref. 806) and the disproportionation of 1,2-dihydronaphthalene to naphthalene and tetralin. In this work about a 20% yield of products was observed and $[RhH(PPh_3)_4]$ and $[IrCl(CO)(PPh_3)_2]$ were less active. A two-step process is proposed wherein there is little specificity for the first hydrogen removed but the second comes specifically from the vicinal *cis* position and the acceptor is *cis* hydrogenated (ref. 807). Other uses of $[RhCl(PPh_3)_3]$ include its conversion to $[RhCl_4(PPh_3)(Me_2N_2H_2)]$ by dimethylhydrazine dihydrochloride to form a catalyst for the asymmetric hydrogenation of the exocyclic methylene group in methacycline hydrochloride (ref. 808) and its catalysis of the isomerization of methyl formate to acetic acid in the presence of methyl iodide (ref. 809), the transfer hydrogenation of saturated ketones by sodium formate under phase-transfer conditions (ref. 810) and the conversion of α,β-unsaturated alcohols to the corresponding ketones (ref. 811). In the last study, $[RhH(PPh_3)_4]$ and $[RhCl(COD)]_2$ either alone or in the presence of triphenylphosphine were also used. Catalytic amounts of $[RhCl(PPh_3)_3]$ in HMPA effect the coupling of the carbonyl groups in 9,9'-bis(*o*-carboranyl)mercury (ref. 812). In a comparison of $[RhCl(PPh_3)_3]$ and polymer supported analogs for the selective reduction of polynuclear heteroaromatics used as models for coal liquids, it was found that the supported complex showed a high regioselectivity for the reduction of the nitrogen-containing ring (see also ref. 254) (ref. 813).

Another widely studied catalyst is $[RhH(PPh_3)_4]$ which in combination with two equivalents of tri-*n*-butylphosphine effects the allylation of carbonucleophiles such as the coupling of 2-methyl-3-oxabutanoate and allyl methyl carbonate to methyl 2-allyl-2-methyl-3-oxabutanoate (ref. 814). It also effects the isomerization of (Z)-dimethylbutendioate to the (E) isomer although deactivation occurs at high substrate concentrations (ref. 815), the isomerization of monoepoxides of 1,3-dienes to α,β-unsaturated ketones and aldehydes with a high degree of regio- and stereoselectivity (ref. 816) and the conversion of β-trimethylsilylalcohols to α-trimethylsilylketones using cyclohex-2-en-1-one as the hydrogen acceptor (ref. 817). Its reaction with allylic aryl sulfides forms $[Rh_2(PPh_3)_4(\mu\text{-}SAr)_2]$ (Ar = Ph, *p*-tolyl, *o*-tolyl, *p*-anisyl) and the corresponding olefin (ref. 818) while with atactic polyacrylic acid a supported catalyst is generated which has good stability and activity for pent-1-ene hydrogenation provided the dispersion of the rhodium moieties is not too great (ref. 819).

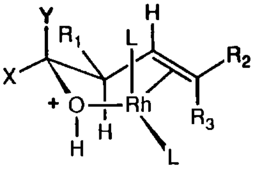
The hydrosilylation of [479] to [480] (R = H, o-anisyl, p-BrC$_6$H$_4$, 3,4-(MeO)$_2$C$_6$H$_3$, 3,4,5-(MeO)$_3$C$_6$H$_2$) by diphenylsilane is catalyzed by [Rh-(COD)(DIOP)]Cl and in some instances as much as 64% optical yields were achieved (ref. 820). Attempts to catalytically decarbonylate racemic aldehydes with [Rh((S,S)-CHIRAPHOS)$_2$]X (X = Cl, BF$_4$) were unsuccessful but if the aldehydes are unsaturated, a kinetic resolution of the mixture could be achieved in the course of generating cyclopentanones. For example a mixture of (R)- and (S)-2-methyl-2-phenylpent-4-enal and the rhodium complex preferentially formed (-)-(S)-2-methyl-2-phenylcyclopentanone while the unreacted aldehyde remaining was predominately the (-)-(R) enantiomer (ref. 821). Both [Rh(dppb)]$^+$ and [Ir(py)Pcy$_3$]$^+$, generated from appropriate precursors, are active catalysts for the asymmetric hydrogenation of homoallylic alcohols in high optical yields. As noted previously, the stereoselection is attributed to the coordination of the hydroxy group to the metal as in [481] (Y = H; X = Et; R$_1$ = Bu^{t}Me$_2$SiOCH$_2$; R$_2$ = bzOCH$_2$; R$_3$ = Me)



[479]



[480]



[481]

(ref. 822).

List of Abbrevations

acac = acetylacetonate
acacen = bis(acetylacetone)ethylenediiminato
(R,R)-BDPODP = (1R,3R)-bis(diphenylphosphinyloxy)-1,3-diphenylpropane
BDPOP = 2,4-bis(diphenylphosphinyloxy)pentane

BDPP = 2,4-bis(diphenylphosphino)pentane
(-)-BINAP = (S)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
bipy = 2,2'-bipyridine
br = 1,3-diisocyanopropane
BTMSA = bis(trimethylsilyl)acetylene
bz = benzyl
bzac = benzoylacetonato
bzim = benzimidazolate
(S,S)-CHIRAPHOS = (S,S)-2,3-bis(diphenylphosphino)butane
CIDNP = Chemically Induced Dynamic Nuclear Polarization
4-CNpy = 4-cyanopyridine
COD = cycloocta-1,5-diene
cp = cyclopentadienyl
cp' = pentamethylcyclopentadienyl
CTAB = cetyltrimethylammonium bromide
cy = cyclohexyl
cyoct = cyclooctene
DAPM = diphenylarsinodiphenylphosphinomethane
dbm = dibenzoylmethanato
dicp = dicyclopentadiene
DIOP = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DIPAMP = (R,R)-1,2-bis(*o*-anisylphenylphosphino)ethane
dippe = 1,2-bis(diisopropylphosphino)ethane
dippp = 1,3-bis(diisopropylphosphino)propane
DMAD = dimethylacetylenedicarboxylate
dmgH = dimethylglyoximate
DMF = N,N-dimethylformamide
dmpe = 1,2-bis(dimethylphosphino)ethane
DMSO = dimethylsulfoxide
(DO)(DOH)pn = diacetylmonoxime diacetylmonoximato propane-1,3-diyldiimino
DPM = bis(diphenylphosphino)methane
dpmp = bis(diphenylphosphinomethyl)phenylphosphine
DPPB = 1,4-bis(diphenylphosphino)butane
DPPE = 1,2-bis(diphenylphosphino)ethane
DPPP = 1,3-bis(diphenylphosphino)propane
dth = 2,5-dithiahexane
DQ = duroquinone
EHMO = Extended Hückel Molecular Orbital

en = ethylenediamine
EXAFS = Extended X-ray Absorption Fine Structure
FTIR = fourier transform infrared
Hbzim = benzimidazole
1,5-HD = hexa-1,5-diene
Hpz = pyrazole
idz = indazolate
im = imidazolate
ind = indenyl
Mecp = methylcyclopentadienyl
1-Meim = 1-Methylimidazolate
3-Mepz = 3-methylpyrazolate
3,5-Me$_2$pz = 3,5-dimethylpyrazolate
7-Mesalen = N-(2-aminoethyl)-7-methylsalicylaldiminato
Me$_3$TFB = trimethyltetrafluorobenzobarrelene
NBD = bicyclo[2.2.1]heptadiene
NOE = Nuclear Overhauser Enhancement
Np = neopentyl
NP$_2$ = 2-[bis(diphenylphosphino)methyl]pyridine
np$_3$ = tris(2-(diphenylphosphino)ethyl)amine
OEP = octaethylporphyrin
OFCOT = octafluorocyclooctatraene
ophen = 1,10-phenanthroline
OTf = trifluoromethanesulfonate
pmdeta = pentamethyldiethylenetriamine
PNNHP = 3,5-bis(diphenylphosphinomethyl)pyrazole
PNNP = 3,5-bis(diphenylphosphinomethyl)pyrazolate
PNP = 2,6-bis(diphenylphosphino)pyridine
PPN = bis(triphenylphosphine)iminium cation
(R)-PROPHOS = (R)-1,2-bis(diphenylphosphino)propane
py = pyridine
pz = pyrazolate
salen = N,N'-ethylenebis(salicylaldiminato)
saloph = N,N'-*o*-phenylenebis(salicylaldiminato)
Tcbiim = 4,4',5,5'-tetracyano-2,2'-biimidazolate
TCNE = tetracyanoethylene
TCNQ = tetracyanoquinodimethane
TFA = trifluoracetic acid
tfac = trifluoroacetylacetonate
TFB = tetrafluorobenzobarrelene

THF = tetrahydrofuran

THT = tetrahydrothiophene

TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene

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

TMEDA = tetramethylethylenediamine

tms = trimethylene sulfide

TPM = tris(diphenylphosphino)methane

TPP = tetraphenylporphyrin

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

tta = thenoyltrifluoroacetone

UPS = Ultraviolet Photoelectron Spectroscopy

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

vy = vinyl

WGSR = Water-Gas-Shift Reaction

XPS = X-ray Photoelectron Spectroscopy

References

1 R.S. Dickson, "Catalysis by Metal Complexes: Homogeneous Catalysis with Compounds of Rhodium and Iridium", D. Reidel, Dordrecht, 1985.
2 M.E. Vol'pin, I. Ya. Levitin, A.L. Sigan and A.T. Nikitaev, J. Organometal. Chem., 279(1985)263.
3 J. Halpern, Angew. Chem. Int. Ed. Engl., 24(1985)274.
4 D.B. Porreau and G.L. Geoffroy, Adv. Organometallic Chem., 24(1985) 249.
5 J. Halpern, Inorg. Chim. Acta, 100(1985)41.
6 R.H. Crabtree, Chem. Revs., 85(1985)245.
7 J. Schwartz, Accts. Chem. Res., 18(1985)302.
8 N. Bresciani-Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers and P.J. Toscano, Coord. Chem. Revs., 63(1985)1.
9 Y.-T. Fanchiang, Coord. Chem. Revs., 68(1985)131.
10 M.Y. Darensbourg, Progr. Inorg. Chem., 33(1985)221.
11 F. Basolo, Inorg. Chim. Acta, 100(1985)33.
12 A.E. Stiegman and D.R. Tyler, Coord. Chem. Revs., 63(1985)217.
13 R.D. Adams and I.T. Horváth, Progr. Inorg. Chem., 33(1985)127.
14 W.E. Geiger and N.G. Connelly, Adv. Organometallic Chem., 24(1985)87.
15 R.A.W. Johnstone, A.H. Wilby and I.D. Entwistle, Chem. Revs., 85 (1985)129.
16 J.M. Basset, B. Besson, A. Choplin and A. Theolier, Mekh. Katal., (Rab. Obsuzhdennyi Vses. Konf. Mekh. Katal. Reakts.), 3rd, Boreskov and Andrushkevich Eds., 2(1984)154 (Chem. Abstr., 103(1985)214260d).
17 E. Sappa, A. Tiripicchio and P. Braunstein, Coord. Chem. Revs., 65(1985)219.
18 K. Mackay and B. Nicholson, Chem. N. Z., 48(1984)159 (Chem. Abstr., 103(1985)87921t).
19 R.J. Cross, Chem. Soc. Revs., 14(1985)197.
20 A.A. Ioganson, Usp. Khim., 54(1985)479.

21 P.V. Broadhurst, Polyhedron, 4(1985)1801.

22 W.L. Gladfelter, Adv. Organometallic Chem., 24(1985)41.

23 R.D. Ernst, Accts. Chem. Res., 18(1985)56.

24 R.C. Mehrotra, S.K. Agarwal and Y.P. Singh, Coord. Chem. Revs., 68(1985)101.

25 S. Masamune, W. Choy, J.S. Petersen and L.R. Sita, Angew. Chem. Int. Ed. Engl., 24(1985)1.

26 J. Halpern, New Front. Organomet. Inorg. Chem., Proc. China-Jpn.-U.S.A. Trilateral Semin., 2nd. 1982 (Pub. 1984)269.

27 D.J. Pasto, D.A. Smith, D.R. Metra and N.Z. Huang, New Front. Organomet. Inorg. Chem., Proc. China-Jpn.-U.S.A. Trilateral Semin., 2nd. 1982 (Pub. 1984) 321.

28 K.P.C. Vollhardt, Kagaku Zokan (Kyoto), 105(1985)165 (Chem. Abstr., 103(1985)123762c).

29 H. Bönnemann, Angew. Chem. Int. Ed. Engl., 24(1985)248.

30 E.A. Karakhanov, A.G. Redov and A.S. Loktev, Usp. Khim., 54(1985)289.

31 W.E. Geiger, Progr. Inorg. Chem., 33(1985)275.

32 W. Siebert, Angew. Chem. Int. Ed. Engl., 24(1985)943.

33 S.F. Clark, R.J. Watts, D.L. Dubois, J.S. Connolly and J.C. Smart, Coord. Chem. Revs., 64(1985)273.

34 P.E. Garrou, Chem. Revs., 85(1985)171.

35 G.G. Hlatky and R.H. Crabtree, Coord. Chem. Revs., 65(1985)1.

36 M.A. Kulzick, Diss. Abstr. Int. B, 46(1985)1159.

37 M.F. Summers, Diss. Abstr. Int. B, 46(1985)158.

38 J.R. Blou, Diss. Abstr. Int. B, 46(1985)1553.

39 M.R. Rhodes, Diss. Abstr. Int. B, 45(1985)3816.

40 P.D. Enlow, Diss. Abstr. Int. B, 45(1985)3228.

41 R.E. Stevens, Diss. Abstr. Int. B, 45(1985)3816.

42 M.Y.-N. Chiang, Diss. Abstr. Int. B, 45(1985)2546.

43 N.K. Bhattacharyya, Diss. Abstr. Int. B, 46(1985)1911.

44 G.F. Meyers, Diss. Abstr. Int. B, 46(1985)1557.

45 J.R. Matachek, Diss. Abstr. Int. B, 46(1985)156.

46 W.L. Olsen, Diss. Abstr. Int. B, 46(1985)1913.

47 J.M. Boncella, Diss. Abstr. Int. B, 46(1985)1157.

48 A.D. Hailey, Diss. Abstr. Int. B, 45(1985)3232.

49 W.S. Uchiyama, Diss. Abstr. Int. B, 45(1985)3502.

50 A.L. Stuart, Diss. Abstr. Int. B, 46(1985)517.

51 T.C. Wright, Diss. Abstr. Int. B, 46(1985)1163.

52 B.M. Louie, Diss. Abstr. Int. B, 46(1985)3813.

53 J.E. Anderson, Diss. Abstr. Int. B, 46(1985)1156.

54 M.J. DiPiero, Diss. Abstr. Int. B, 45(1985)2911.

55 C.D. Valenilla, Diss. Abstr. Int. B, 46(1985)1162.

56 W.C. Mercer, Diss. Abstr. Int. B, 46(1985)1160.

57 T.G. Schenck, Diss. Abstr. Int. B, 46(1985)1557.

58 T.S. Targos, Diss. Abstr. Int. B, 46(1985)1916.

59 R.L. Ernest, Diss. Abstr. Int. B, 46(1985)1554.

60 C.-A. Chang, Diss. Abstr. Int. B, 46(1985)1167.

61 B.D. Murray, Diss. Abstr. Int. B, 45(1985)3501.

62 S.J. Landon, Diss. Abstr. Int. B, 45(1985)3508.

63 R.L. Bedard, Diss. Abstr. Int. B, 46(1985)1156.

64 J.S. Drage, Diss. Abstr. Int. B, 46(1985)1170.

65 E.J. Miller, Diss. Abstr. Int. B, 45(1985)3501.

66 M.E. Rerek, Diss. Abstr. Int. B, 45(1985)2151.

67 L.J. Wagner, Diss. Abstr. Int. B, 45(1985)3230.

68 M.W. Droege, Diss. Abstr. Int. B, 45(1985)3811.

69 J.D. Hewes, Diss. Abstr. Int. B, 46(1985)155.

70 D.M. Speckman, Diss. Abstr. Int. B, 46(1985)157.

71 P.E. Behnken, Diss. Abstr. Int. B, 45(1985)3227.

72 M. Lombarski, Diss. Abstr. Int. B, 46(1985)1538.

73 D.B. Jacobson, Diss. Abstr. Int. B, 46(1985)1555.

74 M.F. Mellea, Diss. Abstr. Int. B, 46(1985)836.

75 C.P. Parnell, Diss. Abstr. Int. B, 46(1985)837.

76 L.F. Rhodes, Diss. Abstr. Int. B, 45(1985)3489.

77 A.L. Casalnuovo, Diss. Abstr. Int. B, 45(1985)3499.

78 S.-T. Lin, R.N. Narske and K.J. Klabunde, Organometallics, 4(1985) 571.

79 C. Eaborn, P.B. Hitchcock, J.D. Smith and A.C. Sullivan, J. Chem. Soc., Chem. Commun., (1985)534.

80 A. Pietrzykowski, Bull. Pol. Acad. Sci., Chem., 33(1985)49 (Chem. Abstr., 103(1985)178407w).

81 L.I. Zakharkin and N.F. Shemyakin, Izv. Akad. Nauk SSSR, Ser. Khim., (1984)2807.

82 S. Fukuzumi, K. Ishikawa and T. Tanaka, Nippon Kagaku Kaishi, (1985) 62(Chem. Abstr., 103(1985)142144u).

83 S. Fukuzumi, K. Ishitawa and T. Tanaka, J. Chem. Soc., Dalton Trans., (1985)899.

84 Y. Wakatsuki and H. Yamazaki, Nippon Kagaku Kaishi, (1985)586 (Chem. Abstr., 104(1986)68992w).

85 L.S. Liebeskind and C.F. Jewell, Jr., J. Organometal. Chem., 285 (1985)305.

86 C.F. Jewell, Jr., L.S. Liebeskind and M. Williamson, J. Am. Chem. Soc., 107(1985)6715.

87 M. Tasi and G. Pályi, Organometallics, 4(1985)1523.

88 C.D. Hoff, F. Ungváry, R.B. King and L. Markó, J. Am. Chem. Soc., 107(1985) 666.

89 I. Kovács, C.D. Hoff, F. Ungváry and L. Markó, Organometallics, 4(1985)1347.

90 Y. Koyasu, A. Fukuoka, Y. Uchida and M. Hidai, Chem. Lett., (1985) 1083.

91 G.F. Schmidt and M. Brookhart, J. Am. Chem. Soc., 107(1985)1443.

92 R.D. Riecke, Gov. Rep. Announce. Index (U.S.), 85(1985)54 (Chem. Abstr., 103(1985)31489r).

93 N.N. Kostitsyna, I.A. Oreshkin, B.A. Dolgloplosk, E.I. Tinyakova and A.I. Mikaya, Dokl. Akad. Nauk SSSR, 277(1984)1405.

94 H. Kanai, K. Hirabayashi and T. Nakayama, Nippon Kagaku Kaishi, (1985)394 (Chem. Abstr., 104(1986)68349s).

95 Y. Zhou, Y. Wang, and Z. Zhang, Huaxue Xuebao, 43(1985)178 (Chem. Abstr., 102(1985)221006h).

96 J.H. Ammeter, C. Elschenbroich, T.J. Groshens, K.J. Klabunde, R.O. Kühne and R. Möckel, Inorg. Chem., 24(1985)3307.

97 G. Vlaic, J.C.J. Bart, M. Foá, F. Francalanci and R. Clement, J. Organometal. Chem., 287(1985)369.

98 C.M. Arewgoda, A.M. Bond, R.S. Dickson, T.F. Mann, J.E. Moir, P.H. Rieger, B.H. Robinson and J. Simpson, Organometallics, 4(1985)1077.

99 H. Brunner, B. Hammer, C. Krüger, K. Angermund and I. Bernal, Organometallics, 4(1985)1063.

100 K.F. Purcell, Organometallics, 4(1985)509.

101 W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 107(1985)620.

102 D.L. Thorn, Organometallics, 4(1985)192.

103 J.W. Suggs, M.J. Wovkulich and S.D. Cox, Organometallics, 4(1985) 1101.

104 J.W. Suggs and C.-H. Jun, J. Chem. Soc., Chem. Commun., (1985)92.

105 J.W. Suggs, M.J. Wovkulich and K.S. Lees, J. Am. Chem. Soc., 107 (1985)5546.

106 E. Lindner, R. Fawzi and H.A. Mayer, Z. Naturforsch., 40b(1985)1333.

107 J. Vincente, J. Martin, M.-T. Chicote, X. Solans and C. Miravitlles, J. Chem. Soc., Chem. Commun., (1985)1004.

108 A.R. Chakravarty, F.A. Cotton, D.A. Tocher, and J.H. Tocher, Organometallics, 4(1985)8.

109 A.R. Chakravarty, F.A. Cotton and D.A. Tocher, Organometallics, 4(1985)863.

110 F. Barceló, P. Lahuerta, M.A. Ubeda, C. Foces-Foces, F.H. Cano and M. Martinez-Ripoll, J. Chem. Soc., Chem. Commun., (1985)43.

111 W.J. Carter, S.J. Okrasinski and J.R. Norton, Organometallics, 4(1985)1376.

112 P.G. Gassman, D.W. Macomber and S.M. Willging, J. Am. Chem. Soc., 107(1985)2380.

113 V.S. Petrosyan, A.B. Perruin, V.I. Bogdashkina and D.P. Krut'ko, J. Organometal. Chem., 292(1985)303.

114 L. Dahlenburg and F. Mirzaei, Inorg. Chim. Acta, 97(1985)L1.

115 E. Arpac and L. Dahlenburg, Chem. Ber., 118(1985)3188.

116 L. Dahlenburg and A. Yardimcioglu, J. Organometal. Chem., 291(1985) 371.

117 L. Dahlenburg and N. Höck, Inorg. Chim. Acta, 104(1985)L29.

118 R.H. Crabtree and M. Lavin J. Chem. Soc., Chem. Commun., (1985)794.

119 K.A. King, P.J. Spellane and R.J. Watts, J. Am. Chem. Soc., 107(1985) 1431.

120 L. Dahlenburg, F. Mirzaei and B. Pietsch, Inorg. Chim. Acta, 97(1985) L5.

121 A.A. Vitale and J. San Filippo, Jr., J. Organometal. Chem., 286(1985)91.

122 W.M. Rees, M.R. Churchill, Y.-J. Li and J.D. Atwood, Organometallics, 4(1985)1162.

123 K. Bowman, A.J. Deeming and G.P. Proud, J. Chem. Soc., Dalton Trans., (1985)857.

124 J.W. Faller and H. Felkin, Organometallics, 4(1985)1488.

125 M.D. Fryzuk, P.A. MacNeil and S.J. Rettig, Organometallics, 4(1985)1145.

126 M.D. Fryzuk, P. A. MacNeil and S.J. Rettig, J. Am. Chem. Soc., 107(1985)6708.

127 M. Gómez, P.I.W. Yarrow, D.J. Robinson and P.M. Maitlis, J. Organometal. Chem., 279(1985)115.

128 M. Gómez, J.M. Kisenzi, G.J. Sunley and P.M. Maitlis, J. Organometal. Chem., 296(1985)197.

129 P.O. Stoutland and R.G. Bergman, J. Am. Chem. Soc., 107(1985)4581.

130 S. Zecchin, G. Zotti and G. Pelloni, J. Organometal. Chem., 294(1985)379.

131 H. Werner, B. Heiser, U. Schubert and K. Ackerman, Chem. Ber., 118(1985)1517.

132 B. Heiser, A. Kuhn and H. Werner, Chem. Ber., 118(1985)1531.

133 U. Schubert, B. Heiser, L. Hee and H. Werner, Chem. Ber., 118(1985)3151.

134 H. Werner and B. Heiser, Chem. Ber., 118(1985)2282.

135 H. Werner and B. Heiser and H. Otto, Chem. Ber., 118(1985)3932.

136 H. Werner, L. Hofmann, R. Feser and W. Paul, J. Organometal. Chem., 281(1985)317.

137 W. Paul and H. Werner, Chem. Ber., 118(1985)3032.

138 H. Werner, W. Paul, F. Feser, R. Zolk and P. Thometzek, Chem. Ber., 118(1985)261.

139 H. Werner, L. Hofmann, J. Wolf and G. Müller, J. Organometal. Chem., 280(1985)C55.

140 H. Werner, F.J. Garcia Alonso, H. Otto, K. Peters and H.G. von Schnering, J. Organometal. Chem., 289(1985)C5.

141 E.N. Jacobsen and R.G. Bergman, J. Am. Chem. Soc., 107(1985)2023.

142 W.A. Herrmann and C. Weber, J. Organometal. Chem., 282(1985)C31.

143 W.A. Herrmann, C. Weber, M.L. Ziegler and O. Serhaldi, J. Organometal. Chem., 297(1985)245.

144 D.H. Berry and R. Eisenberg, J. Am. Chem. Soc., 107(1985)7181.

145 M.J. Krause and R.G. Bergman, J. Am. Chem. Soc., 107(1985)2972.

146 B.E. Mann, N.J. Meanwell, C.M. Spencer, B.F. Taylor and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1985)1555.
147 M. Green, A.G. Orpen, C.J. Schaverien and I.D. Williams, J. Chem. Soc., Dalton Trans., (1985)2483.
148 R.S. Dickson, R.J. Nesbit, H. Pateras, W. Bainbridge, J.M. Patrick and A.H. White, Organometallics, 4(1985)2128.
149 R.S. Dickson, G.D. Fallon, R.J. Nesbit and G.N. Pain, Organometallics, 4(1985)355.
150 A. Schäfer and W.A. Herrmann, J. Organometal. Chem., 297(1985)229.
151 M. El Amane, A. Maisonnat, F. Dahan, R. Pince and R. Poilblanc, Organometallics, 4(1985)773.
152 Z. Szeverényi and L.I. Simándi, J. Organometal. Chem., 279(1985)259.
153 Y. Nagel and W. Beck, Z. Naturforsch., 40b(1985)1181.
154 M.R. Ashcroft, P. Bougeard, A. Bury, C.J. Cooksey and M.D. Johnson, J. Organometal. Chem., 289(1985)403.
155 C. Bongars, P. Bougeard, A. Bury, C.J. Cooksey, M.D. Johnson, S. Mitchell, P.A. Owens and F. Rajah, J. Organometal. Chem., 289(1985) 163.
156 P. Bougeard, C.J. Cooksey, M.D. Johnson, M.J. Lewin, S. Mitchell and P.A. Owens, J. Organometal. Chem., 288(1985)349.
157 M.D. Johnson and S. Derenne, J. Organometal. Chem., 286(1985)C47.
158 N.W. Alcock, B.T. Golding and S. Mrvesigye-Kibende, J. Chem. Soc., Dalton Trans., (1985)1997.
159 Y. Ohkatsu, M. Ohno and S. Inoue, Sekiyu Gakkaishi, 28(1985)219 (Chem. Abstr., 103(1985)178408x).
160 L.G. Marzilli, M.F. Summers, N. Bresciani-Pahor, E. Zangrando, J.-P. Charland and L. Randaccio, J. Am. Chem. Soc., 107(1985)6880.
161 N. Bresciani-Pahor, L. Randaccio, E. Zangrando, M.F. Summers, J.H. Ramsden, Jr., P.A. Marzilli and L.G. Marzilli, Organometallics, 4(1985)2086.
162 L. Randaccio, N. Bresciani-Pahor, J.D. Orbell, M. Calligaris, M.F. Summers, B. Snyder, P.J. Toscano and L.G. Marzilli, Organometallics, 4(1985)469.
163 K. Miyokawa, T. Kawarada and I. Matsuda, Thermochim. Acta, 83(1985)235 (Chem. Abstr., 103(1985)70780y).
164 W.O. Parker, Jr., N. Bresciani-Pahor, E. Zangrando, L. Randaccio and L.G. Marzilli, Inorg. Chem., 24(1985)3908.
165 S. Balt, M.W.G. DeBolster, C.J. van Garderen, A.M. van Herk, K.R. Lammers and E.G. van der Velde, Inorg. Chim. Acta, 106(1985)43.
166 N. Bresciani-Pahor, M. Calligaris, L. Randaccio, L.G. Marzilli, M.F. Summers, P.J. Toscano, J. Grossman and D. Liotta, Organometallics, 4(1985)630.
167 D.W. Christianson and W.N. Lipscomb, J. Am. Chem. Soc., 107(1985) 2682.
168 A.W. Herlinger and K. Ramakrishna, Polyhedron, 4(1985)551.
169 Y. Ohgo and S. Takeuchi, J. Chem. Soc., Chem. Commun., (1985)21.
170 K.L. Brown, S. Ramamurthy and D.S. Marynick, J. Organometal. Chem., 287(1985)377.
171 K.L. Brown, J.M. Hakimi and Y.-J. Huang, Inorg. Chim. Acta, 106(1985) 123.
172 W.L. Mock and C. Bieniarz, Organometallics, 4(1985)1917.
173 G. Costa, A. Puxeddu and C. Tavagnacco, J. Organometal. Chem., 296(1985)161.
174 A.D. Ryabov, I.Ya. Levitin, A.T. Nikitaev, A.N. Kitaigorodskii, V.I. Bakhmutov, I.Yu. Gromov, A.K. Yatsimirsky and M.E. Vol'pin, J. Organometal. Chem., 292(1985)C4.
175 I.Ya. Levitin, A.N. Kitiagorodskii, A.T. Nikitaev, V.I. Bakhmutov, A.L. Sigan and M.E. Vol'pin, Inorg. Chim. Acta, 100(1985)65.
176 J.-C. Folest, J.-M. Duprilot, J. Perichon, Y. Robin and J. Devynck, Tetrahedron Lett., 26(1985)2633.

177 J.-M. Duprilot, F. Bedioui, J. Devynck, J.-C. Folest and C. Bied-Charreton, J. Organometal. Chem., 286(1985)77.

178 H.J. Callot, F. Metz and R. Cromer, Nouv. J. Chim., 8(1984)759.

179 H.J. Callot, R. Cromer, A. Louati and M. Gross, Nouv. J. Chim., 8(1984)765.

180 G.A. Shagisultanova, K. Ortigosa and I.V. Voyakin, Zh. Fiz. Khim., 58(1984)2833 (Chem. Abstr., 102(1985)132248w).

181 M.J. Tang and W.S. Hwang, Proc. Natl. Sci. Counc., Repub. China, Part A: Phys. Sci. Eng., 9(1985)214 (Chem. Abstr., 104(1986)12169r).

182 S. Rapsomanskis, J.J. Ciejka and J.H. Weber, Inorg. Chim. Acta, 89(1984)179.

183 Y.-T. Fanchiang, Organometallics, 4(1985)1515.

184 R.J.Blau and J.H. Espenson, J. Am. Chem. Soc., 107(1985)3530.

185 J.J. Pignatello and Y.-T. Fanchiang, J. Chem. Soc., Dalton Trans., (1985)1381.

186 M. Rossi, J.P. Glusker, L. Randaccio, M.F. Summers, P.J. Toscano and L.G. Marzilli, J. Am. Chem. Soc., 107(1985)1729.

187 D.A. Baldwin, E.A. Betterton, S.M. Chemaly and J.M. Pratt, J. Chem. Soc., Dalton Trans., (1985)1613.

188 E.A. Betterton, S.M. Chemaly and J.M. Pratt, J. Chem. Soc., Dalton Trans., (1985)1619.

189 P. Dowd and B.K. Trivedi, J. Org. Chem., 50(1985)206.

190 B. Kräutler and C. Caderas, Helv. Chim. Acta, 67(1985)1891.

191 K.J. Del Rossi and B.B. Wayland, J. Am. Chem. Soc., 107(1985)7941.

192 R.S. Paonessa, N-C. Thomas and J. Halpern, J. Am. Chem. Soc., 107 (1985)4333.

193 S.L. Van Voorhees and B.B. Wayland, Organometallics, 4(1985)1887.

194 Y. Aoyama, T. Yoshida and H. Ogoshi, Tetrahedron Lett., 26(1985)6107.

195 M. Hoshino, K. Yasufuku, H. Seki and H. Yamazaki, J. Phys. Chem., 89(1985)3080.

196 M. Hoshino, Sci. Pap. Inst. Phys. Chem. Res. (Jpn.), 78(1984)113 (Chem. Abstr., 103(1985)169704p).

197 H.J. Callot and F. Metz, Nouv. J. Chim., 9(1985)167.

198 A.M. Van der Bergen, R.L. Elliott, C.J. Lyons, K.P. Mackinnon and B.O. West, J. Organometal. Chem., 297(1985)361.

199 D.W. Macomber and R.D. Rogers, Organometallics, 4(1985)1485.

200 U. Plaia, H. Stoltzenberg and W.P. Fellhammer, J. Am. Chem. Soc., 107(1985)2171.

201 M.J. Doyle, M.F. Lappert, P.L. Pye and P. Terreros, J. Chem. Soc., Dalton Trans., (1984)2355.

202 A.W. Coleman, P.B. Hitchcock, M.F. Lappert, R.K. Maskell and J.H. Muller, J. Organometal. Chem., 296(1985)173.

203 G.R. Clark, T.R. Green and W.R. Roper, J. Organometal. Chem., 293 (1985)C25.

204 C.A.L. Becker, R. Rezaaiyan and F. Moattar, Inorg. Chim. Acta, 100(1985)227.

205 W.P. Felhammer, K. Bartel, B. Weinberger and U. Plaia, Chem. Ber., 118(1985)2220.

206 H. Werner and B. Heiser, Synth. React. Inorg. Met.-Org. Chem., 15(1985)43 (Chem. Abstr., 103(1985)71473n).

207 A.W. Hanson, A.J. McAlees and A. Taylor, J. Chem. Soc., Perkin Trans. I, (1985)441.

208 G. Matsubayashi, I. Iinuma, T. Tanaka, K. Oka and K. Nakatsu, Inorg. Chim. Acta, 102(1985)145.

209 P.D. Enlow and C. Woods, Inorg. Chem., 24(1985)1273.

210 V.M. Miskowski, T.P. Smith, T.M. Loehr and H.B. Gray, J. Am. Chem. Soc., 107(1985)7925.

211 S.J. Milder and D.S. Kliger, J. Phys. Chem., 89(1985)4170.

212 S.J. Milder, Inorg. Chem., 24(1985)3376.

213 C.R. Langrick and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985)511.

214 A.M. Arif, A.H. Cowley and M. Pakulski, J. Chem. Soc., Chem. Commun., (1985)1707.
215 A.M. Arif, A.H. Cowley, M. Pakulski, M.B. Hursthouse and A. Karauloz, Organometallics, 4(1985)2227.
216 A.M. Arif, A.H. Cowley, N.C. Norman, A.G. Orpen and M. Pakulski, J. Chem. Soc., Chem. Commun., (1985)1267.
217 M. Lattman, S.A. Morse, A.H. Cowley, J.G. Lasch and N.C. Norman, Inorg. Chem., 24(1985)1364.
218 R. Appel, W. Schuhn and F. Knoch, Angew. Chem. Int. Ed. Engl., 24(1985)420.
219 G. Doyle and D. van Engen, J. Organometal. Chem., 280(1985)253.
220 H. Schumann, J. Organometal. Chem., 290(1985)C34.
221 F. Babonneau, M. Henry, R.B. King and N. El Murr, Inorg. Chem., 24(1985)1946.
222 R. Yan and H. Wang, Huaxue Xuebao, 43(1985)654 (Chem. Abstr., 103 (1985)150776s).
223 G. Fachinetti, F. del Cima, G. Sbrana and T. Funaioli, J. Organometal. Chem., 287(1985)C23.
224 T.M. Bockman, J.F. Garst, R.B. King, L. Markó and F. Ungváry, J. Organometal. Chem., 279(1985)165.
225 T.V. Harris and W.R. Pretzer, Inorg. Chem., 24(1985)4437.
226 C. Kim, Y. Matsui and J. Halpern, J. Organometal. Chem., 279(1985)159.
227 M.S. Borovikov and V.A. Rybakov, Kinet. Katal., 26(1985)837 (Chem. Abstr., 104(1986)19262z).
228 H. Lövevich and M. Röper, C_1 Mol. Chem., 1(1984)155 (Chem. Abstr., 103(1985)214462w).
229 K. Watanabe, K. Kudo and N. Sugita, Bull. Chem. Soc. Jpn., 58(1985) 2029.
230 J.F. Knifton, J. Mol. Catal., 39(1985)281 (Chem. Abstr., 104(1986) 5342p).
231 I. Ojima, K. Hirai, M. Fujita and T. Fuchikami, J. Organometal. Chem., 279(1985)203.
232 K.-T. Kang and W. P. Weber, Tetrahedron Lett., 26(1985)5753.
233 T. Murai, S. Kato, S. Murai, Y. Hatayama and N. Sonoda, Tetrahedron Lett., 26(1985)2683.
234 K.-T. Kang and W.P. Weber, Tetrahedron Lett., 26(1985)5415.
235 S. Murai, Y. Seki and N. Sonoda, New Front. Organomet. Inorg. Chem., Proc. China-Jpn.-U.S.A. Trilateral Semin., 2nd 1982 (Pub. 1984)135 (Chem. Abstr., 102(1985)185141n).
236 T. Murai, T. Sakane and S. Kato, Tetrahedron Lett., 26(1985)5145.
237 S.C. Shim, S. Antebi and H. Alper, Tetrahedron Lett., 26(1985)1935.
238 S. Antabi and H. Alper, Tetrahedron Lett., 26(1985)2609.
239 P. Eilbracht, E. Baiss and M. Acker, Chem. Ber., 118(1985)825.
240 M.G. Katsnel'son, V.B. Del'nik, S.Sh. Kagna and E.I. Leevson, Zh. Prikl. Khim. (Leningrad), 57(1984)2715 (Chem. Abstr., 102(1985) 166311b).
241 K. Murata, A. Matsuda and T. Masuda, Bull. Chem. Soc. Jpn., 58(1985) 2141.
242 V.B. Del'nik and M.G. Kalsnel'son, Neftekhimiya, (1985)93 (Chem. Abstr., 103(1985)214827u).
243 V.B. Del'nik, M.G. Katsnel'son, A.V. Naqin, T.A. Semenova and B.P. Tarasov, Neftekhimiya, (1985)99 (Chem. Abstr., 104(1986)61033a).
244 M.A. Brook, J.R. Lindsay Smith, R. Higgins and D. Lester, J. Chem. Soc., Perkin Trans. II, (1985)1049.
245 J. Prandi, J.L. Namy, G. Menoret and H.B. Kagan, J. Organometal. Chem., 285(1985)449.
246 J.C. Gressier, G. Levesque, H. Patin and F. Varret, Met.-Containing Polym. Syst., (1985)291 (Chem. Abstr., 104(1986)19891d).
247 V. Massonneau, P. LeMaux and G. Simonneaux, J. Organometal. Chem., 288(1985)C59.

248 P. LeMaux, V. Massonneau and G. Simonneaux, J. Organometal. Chem., 284(1985)101.

249 I. Pri-Bar and O. Buckman, J. Org. Chem., 49(1984)4009.

250 F. Francalanci, A. Gardarno and M. Foà, J. Organometal. Chem., 282(1985)277.

251 M. Foà, F. Francalanci, E. Bencini and A. Gardano, J. Organometal. Chem., 285(1985)293.

252 C. Ungurenasu and C. Cotzur, Polym. Bull. (Berlin), 14(1985)411 (Chem. Abstr., 104(1986)69268b).

253 H. Alper, H. Arzoumanian, J.-F. Petrignani and M. Saldana-Maldonado, J. Chem. Soc., Chem. Commun., (1985)340.

254 R.H. Fish, G.A. Cremer and A.D. Thormodsen, Proc.-Int. Conf. Coal Sci., (1983)67 (Chem. Abstr., 102(1985)187756r).

255 T. Ziegler, Organometallics, 4(1985)675.

256 C. Daniel, I. Hyla-Kryspin, J. Demuynck and A. Veillard, Nouv, J. Chim., 9(1985)581.

257 A.S. Lisitsyn, A.V. Golovin, V.L. Kuznetsov and Yu. I. Yermakov. J. Catal., 95(1985)527.

258 A.S. Lisitsyn, A.V. Golovin, V.L. Kuznetsov and Ya. L. Ermakov, C_1 Mol. Chem., 1(1984)115 (Chem. Abstr., 103(1985)104295m).

259 R. Alvès, D. Ballivet-Tkatchenko, G. Coudurier, N. Duc Chau and M. Santra, Bull. Soc. Chim. Fr., (1985)386.

260 B.J. Aylett and A.A. Tannahill, Vacuum, 35(1985)435 (Chem. Abstr., 104(1986)40567n).

261 D.J. Darensbourg and D.J. Zalewski, Organometallics, 4(1985)92.

262 N.J. Bailey, G. DeLeeuw, J.S. Field, R.J. Haines, I.C.D. Stuckenberg and R.B. English, S. Afr. J. Chem., 38(1985)139 (Chem. Abstr., 103(1985)188412h).

263 L. Markó, G. Gervasio, P.L. Stanghellini and G. Bor, Transition Met. Chem. (Weinheim, Ger.), 10(1985)344 (Chem. Abstr., 103(1985)188465c).

264 M.G. Richmond, J.D. Korp and J.K. Kochi, J. Chem. Soc., Chem. Commun., (1985)1102.

265 S. Liu and U. Honrath, Gaodeng Xuexiao, Huaxue Xuebao, 6(1985)377 (Chem. Abstr., 103(1985)170960a).

266 G. Balavoine, J. Collin, J.J. Bonnet and G. Lavigne, J. Organometal. Chem., 280(1985)429.

267 S. Martinengo, D. Strumolo, P. Chini, V.G. Albano and D. Braga, J. Chem. Soc., Dalton Trans., (1985)35.

268 V.G. Albano, D. Braga, F. Fumagalli and S. Martinengo, J. Chem. Soc., Dalton Trans., (1985)1137.

269 G.F. Holland, D.E. Ellis and W.C. Trogler, J. Chem. Phys., 83(1985) 3507.

270 D.F. Foster, J. Harrison, B.S. Nicholls and A.K. Smith, J. Organometal. Chem., 295(1985)99.

271 J. Rimmelin, P. Lemoine, M. Gross, A.A. Bahsoun and J.A. Osborn, Nouv. J. Chim., 9(1985)181.

272 A.S.C. Chan, H.-S. Shieh and J.R. Hill, J. Organometal. Chem., 279(1985)171.

273 S. Martinengo, A. Fumagalli, and P. Chini, J. Organometal. Chem., 284(1985)275.

274 V.G. Albano, D. Braga, D. Strumolo, C. Seregni and S. Martinengo, J. Chem. Soc., Dalton Trans., (1985)1309.

275 G. Ciani, A. Sironi and S. Martinengo, J. Chem. Soc., Chem. Commun., (1985)1757.

276 R.A. Jones and B.R. Whittlesey, J. Am. Chem. Soc., 107(1985)1078.

277 F. Oldani and G. Bor, J. Organometal. Chem., 279(1985)459.

278 J. Koutecký, G. Paccioni and P. Fantucci, Chem. Phys., 99(1985)87.

279 S.K. Kong, T.A. Albright, T.C. Wright and R.A. Jones, Organometallics, 4(1985)666.

280 R.G. Woolley, Inorg. Chem., 24(1985)3519.

281 R.G. Woolley, Inorg. Chem., 24(1985)3525.
282 B.K. Teo, Inorg. Chem., 24(1985)1627.
283 B.K. Teo and N.J.A. Sloane, Inorg. Chem., 24(1985)4545.
284 D.M.P. Mingos, J. Chem. Soc., Chem. Commun., (1985)1352.
285 R.L. Johnston and D.M.P. Mingos, J. Organometal. Chem., 280(1985)407.
286 R.L. Johnston and D.M.P. Mingos, J. Organometal. Chem., 280(1985)419.
287 T.-Y. Luh, H.N.C. Wong and B.F.G. Johnson, Angew. Chem. Int. Ed. Engl., 24(1985)45.
288 A. Ceulemans and P.W. Fowler, Inorg. Chim. Acta, 105(1985)75.
289 W. Xie, F. Jiao, S. Yang, Y. Yin and D. Li, Cuihua Xuebao, 6(1985)172 (Chem. Abstr., 103(1985)93537p).
290 Yu.B. Kagan, E.V. Slivinskii, V.L. Kurkin, G.A. Korneeva, R.A. Aranovich, I.G. Fal'kov, N.N. Rzhevskaya and S.M. Loktev, Neftekhimiya, 25(1985)791 (Chem. Abstr., 104(1986)56974d).
291 R. Lazzaroni, S. Bertozzi, P. Pocai, F. Troiani and P. Salvadori, J. Organometal. Chem., 295(1985)371.
292 J. Kaspar, R. Spogliarich and M. Graziani, J. Organometal. Chem., 281(1985)299.
293 K. Kanada, T. Mori, M. Kobayshi, T. Imanaka and S. Teranishi, Chem. Lett.,(1985)1339.
294 F. Joó and H. Alper, Can. J. Chem., 63(1985)1157.
295 P. Hong, T. Mise, and H. Yamazaki, New Front. Organomet. Inorg. Chem., Proc. China-Jpn.-U.S.A. Trilateral Semin., 2nd 1982 (Pub. 1984)225 (Chem. Abstr., 102(1985)113195k).
296 P. Hong and H. Yamazaki, J. Mol. Catal., 26(1984)297 (Chem. Abstr., 102(1985)131648q).
297 V.G. Albano, D. Braga, R. Ros and A. Scrivanti, J. Chem. Soc., Chem. Commun., (1985)866.
298 D. Braga, E. Ros and R. Roulet, J. Organometal. Chem., 286(1985)C8.
299 E. Alessio, G. Clauti and G. Mestroni, J. Mol. Catal., 29(1985)77 (Chem. Abstr., 102(1985)166136y).
300 S.I. Woo and C.G. Hill, Jr., J. Mol. Catal., 29(1985)209 (Chem. Abstr., 103(1985)29394n).
301 D. Wang, Y. Li and Y. Jiang, Gaofenzi Tongxun, (1984)318 (Chem. Abstr., 102(1985)155471c).
302 S.I. Woo and C.G. Hill, Jr., J. Mol. Catal., 29(1985)231 (Chem. Abstr., 103(1985)22054t).
303 Y. Luo, H. Fu, Y. Wang, N. Wu and A. Zhang, Cuihua Xuebao, 5(1984)347 (Chem. Abstr., 102(1985)138405s).
304 G.F. Meyers and M.B. Hall, Organometallics, 4(1985)1770.
305 P. Bosch, D. Acosta, J. Zenith, D.M. Nicolson and B.C. Gates, J. Mol. Catal., 31(1985)73 (Chem. Abstr., 103(1985)141220d).
306 J.M. Basset, A. Theolier, D. Commereuc and Y. Chauvin, J. Organometal. Chem., 279(1985)147.
307 A.A. Efremov, N.I. Bakhmutova, Yu. D. Pankratiev and B.N. Kuznetsov, React. Kinet. Catal. Lett., 28(1985)103 (Chem. Abstr., 103(1985) 166844y).
308 H.F.J. van't Blik, J.B.A.D. van Zon, T. Huizinga, J.C. Vis, D.C. Konigsberger and R. Prins, J. Am. Chem. Soc., 107(1985)3139.
309 E. Rode, M.E. Davis and B.E. Hanson, J. Chem. Soc., Chem. Commun., (1985)1477.
310 P. Gelin, C. Naccache, Y. Ben Taârit and Y. Diab, Nouv. J. Chim., 8(1984)675.
311 J.M. Basset, A. Choplin and A. Theolier, Nouv. J. Chim., 9(1985)655.
312 E.P. Giannelis and T.J. Pinnavaia, Inorg. Chem., 24(1985)3602.
313 C.P. Casey and F. Nief, Organometallics, 4(1985)1218.
314 J.F. Reynoud, J.C. LeBlanc and C. Moise, Transition Met. Chem. (Weinheim, Ger.), 10(1985)291 (Chem. Abstr., 104(1985)6007v).
315 J.C. Jeffrey, D.B. Lewis, G.E. Lewis and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985)2001.

316 H. Brunner, W. Meier, J. Wachter, H. Pfisterer and M. Ziegler, Z. Naturforsch., 40b(1985)923.

317 H. Brunner, H. Kauermann, U. Klement, J. Wachter, T. Zahn and M.L. Ziegler, Angew. Chem. Int. Ed. Engl., 24(1985)132.

318 T.R. Halbert, S.A. Cohen and E.I. Stiefel, Organometallics, 4(1985) 1689.

319 M.H. Chisholm, K. Folting, J.C. Huffman and J.J. Koh, Polyhedron, 4(1985)893.

320 A. Vizi-Orosz, G. Pályi, L. Markó, R. Boese and G. Schmid, J. Organometal. Chem., 288(1985)179.

321 C.P. Horwitz, E.M. Holt and D.F. Shriver, Organometallics, 4(1985) 1117.

322 V.E. Lopatin, M.Ts. Tsybenov, N.M. Mikova and S.P. Gubin, Koord. Khim., 11(1985)1099 (Chem. Abstr., 104(1986)27803s).

323 V.E. Lopatin, S.P. Gubin, N.M. Mikova, M.Ts. Tsybenov, Yu.L. Slovokhotov and Yu.T. Struchkov, J. Organometal. Chem., 292(1985) 275.

324 P. Brounstein, J. Rosé, A. Tiripicchio and M.T. Camellini, Angew. Chem. Int. Ed. Engl., 24(1985)767.

325 S. Liu and U. Honrath, Huaxue Xuebao, 43(1985)30 (Chem. Abstr., 102(1985)142216y).

326 H.R. Allcock, P.R. Suszko, L.J. Wagner, R.R. Whittle and B. Boso, Organometallics, 4(1985)446.

327 N.C. Schroeder, J.W. Richardson, Jr., S.-L. Wang, R.A. Jacobson and R.J. Angelici, Organometallics, 4(1985)1226.

328 M. Imaeda, H. Nishihara, K. Nakano, H. Ichida, A. Kobayashi, T. Saito and Y. Sasaki, Inorg. Chem., 24(1985)1246.

329 C. G. Benson, G.J. Long, J.W. Kolis and D.F. Shriver, J. Am. Chem. Soc., 107(1985)5297.

330 E. Roland and H. Vahrenkamp, Chem. Ber., 118(1985)1133.

331 J. Persiainen, M. Ahlgren and T.A. Pakkanen, J. Organometal. Chem., 297(1985)391.

332 P. Braunstein, H. Lehner, D. Matt, A. Tiripicchio and M.T. Camellini, Nouv. J. Chim., 9(1985)597.

333 W.A. Herrmann, C.E. Barnes, T. Zahn and M.L. Ziegler, Organometallics, 4(1985)172.

334 A. Arrigoni, A. Ceriotti, R.D. Pergola, M. Manassero and M. Sansoni, J. Organometal. Chem., 296(1985)243.

335 R. Bartsch, J.F. Nixon and N. Sarjudeen, J. Organometal. Chem., 294(1985)267.

336 P. Klüfers, Angew. Chem. Int. Ed. Engl., 24(1985)70.

337 G. Doyle, K.A. Ericksen and D. Van Engen, Organometallics, 4(1985) 877.

338 J. Bashkin, C.E. Briant, D.M.P. Mingos and R.W.M. Wardle, Transition Met. Chem. (Weinheim, Ger.), 10(1985)113 (Chem Abstr., 102(1985) 21434v).

339 J.M. Burlitch, S.E. Hayes and J.T. Lemley, Organometallics, 4(1985) 167.

340 J.M. Ragosta and J.M. Burlitch, J. Chem. Soc., Chem. Commun., (1985) 1187.

341 M. Van Rentergem and G.P. Van der Kelen, J. Mol. Struct., 127(1985) (Chem. Abstr., 102(1985)194224u).

342 W.J. Evans, I. Bloom, J.W. Grate, L.A. Hughes, W.E. Hunter and J.L. Atwood, Inorg. Chem., 24(1985)4620.

343 G.Z. Suleimamov, V.N. Khandozhko, R.R. Shifriena, L.T. Abdullaeva, N.E. Kolobova and I.P. Beletskaya, Dokl. Akad. Nauk SSSR, 277(1984) 1407.

344 J.M. Boncella, Energy Res. Abstr., 19(1985)Abstr. No. 989 (Chem. Abstr., 103(1985)88019s).

345 S.P. Foster, K.M. Mackay and B.K. Nicholson, Inorg. Chem., 24(1985) 909.

346 S. Onaka, Y. Kondo, M. Yamashita, Y. Tatematsu, Y. Koto, M. Goto and T. Ito, Inorg. Chem., 24(1985)1070.

347 F. Calderazzo, R. Poli and G. Pelizzi, J. Chem. Soc., Dalton Trans., (1984)2535.

348 A.M. Bonny, T.J. Crane and N.A.P. Kane-Maguire, J. Organometal. Chem., 289(1985)157.

349 U. Honrath, S.-T. Liu and H. Vahrenkamp, Chem. Ber., 118(1985)132.

350 R.L. De and H. Vahrenkamp, Z. Naturforsch., 40b(1985)1250.

351 W.-R. Dietrich and H. Vahrenkamp, J. Chem. Res. Synop., (1985)200.

352 D. Mani and H. Vahrenkamp, Angew. Chem. Int. Ed. Engl., 24(1985)424.

353 K. Fischer, W. Deck, M. Schwarz and H. Vahrenkamp, Chem. Ber., 118(1985)4946.

354 J.C. Jeffery and J.G. Lawrence-Smith, J. Organometal. Chem., 280(1985) C34.

355 M. Mlekuz, P. Bougeard, B.G. Sayer, R. Faggiani, C.J.L. Lock, M. J. McGlinchey and G. Jaouen, Organometallics, 4(1985)2046.

356 P. Gusbeth and H. Vahrenkamp, Chem. Ber., 118(1985)1143.

357 P. Gusbeth and H. Vahrenkamp, Chem. Ber., 118(1985)1746.

358 P. Gusbeth and H. Vahrenkamp, Chem. Ber., 118(1985)1770.

359 P. Gusbeth and H. Vehrenkamp, Chem. Ber., 119(1985)1758.

360 M.R. Awang, R.D. Barr, M. Green, J.A.K. Howard, T.B. Marder and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985)2009.

361 J.C. Jeffery, C. Marsden and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985)1315.

362 L.J. Farrugia, A.D. Miles and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984)2415.

363 S. Attali and R. Mathieu J. Organometal. Chem., 291(1985)205.

364 J.A. Hriljac, P.N. Swepston and D.F. Shriver, Organometallics, 4(1985)158.

365 W.E. Lindsell, C.B. Knobler and H.D. Kaesz, J. Organometal. Chem., 296(1985)209.

366 J. Pursiainen, T.A. Pakkanen and J. Jääskeläinen, J. Organometal. Chem., 290(1985)85.

367 M.R. Churchill, L.V. Biondi, J.R. Shapley and C.H. McAteer, J. Organometal. Chem., 280(1985)C63.

368 F.W.B. Einstein, R.K. Pomeroy, P. Rushman and A.C. Willis, Organometallics, 4(1985)250.

369 A. Fumagalli, F. Demartin and A. Sironi, J. Organometal. Chem., 279(1985)C33.

370 J.M. Stencel, L.E. Makovsky, R.E. Tischer and G.A. Melson, Proc.-Int. Conf. Coal Sci., (1983)82 (Chem. Abstr., 102(1985)187759u).

371 E. Guglielmenotti, D. Osella and P.L. Stanghellini, J. Organometal. Chem., 281(1985)291.

372 T. Yokoyama, N. Kosugi, H. Kuroda, M. Ichikawa and T. Fukushima, Springer Proc. Phys., 2(1984)192 (Chem. Abstr., 102(1985)194529x).

373 J. Lieto, M. Wolf, B.A. Matrana, M. Prochazka, B. Tesche, H. Knözinger and B.C. Gates, J. Phys. Chem., 89(1985)991.

374 J.R. Budge, B.F. Lücke, B.C. Gates and J. Toran, J. Catal., 91(1985) 272.

375 R. Hemmerich, Energy Res. Abstr., 9(1984) No. 49579 (Chem. Abstr., 102(1985)116166v).

376 C. Bianchini and A. Meli, Organometallics, 4(1985)1537.

377 G.L. Geoffroy, W.C. Mercer, R.R. Whittle, L. Markó and S. Vastag, Inorg. Chem., 24(1985)3771.

378 F.R. Askham, G.G. Stanley and E.C. Marques, J. Am. Chem. Soc., 107(1985)7423.

379 B.M. Louie, S.J. Rettig, A. Storr and J. Trotter, Can. J. Chem., 63(1985)503.

380 B.M. Louie, S.J. Rettig, A. Storr and J. Trotter, Can. J. Chem., 63(1985)3019.
381 J.G. Leipoldt, G.J. Lamprecht and D.E. Graham, Inorg. Chim. Acta, 101(1985)123.
382 J. Ellermann and Gy. Szucsányi, Z. Anorg. Allg. Chem., 520(1985)113.
383 F.A. Hart and D.W. Owen, Inorg. Chim. Acta, 103(1985)L1.
384 H. Schumann, S. Jurgis, E. Hahn, J. Pickardt, J. Blum and M. Eisen, Chem. Ber., 118(1985)2738.
385 M. Eisen, J. Blum, H. Schumann and S. Jurgis, J. Mol. Catal., 31 (1985)317 (Chem. Abstr., 104(1986)5539h).
386 W. Kläui, M. Scotti, M. Valderrama, S. Rojas, G.M. Sheldrick, P.G. Jones and T. Schroeder, Angew. Chem. Int. Ed. Engl., 24(1985)683.
387 E.E. Nifant'ev, A.T. Teleshev, G.M. Grishina and A.A. Borisenko, Koord. Khim., 10(1984)1573 (Chem. Abstr., 102(1985)113700w).
388 E.E. Nifant'ev, A.T. Teleshev, G.M. Grishina and A.A. Borisenko, Phosphorus and Sulfur, 24(1985)333.
389 A.G. Kent, B.E. Mann and C.P. Manuel, J. Chem. Soc., Chem. Commun., (1985)728.
390 M.A. Murphy, B.L. Smith, G.P. Torrence and A. Aguilo, Inorg. Chim. Acta, 101(1985)L47.
391 Yu.S. Varshavskii, T.G. Cherkasova, N.V. Kiseleva, L.S. Bresler, N.A. Buzina and A.S. Khachaturov, Zh. Neorg. Khim., 30(1985)152.
392 E.E. Nifant'ev, T.S. Kukhareva, M.Yu. Antipin and Yu.T. Struchkov, Zh. Obshch. Khim., 55(1985)298.
393 R. Van Eldik, S. Aygen, H. Kelm, A.M. Trzeciak and J.J. Ziólkowski, Transition Met. Chem. (Weinheim, Ger.), 10(1985)167 (Chem. Abstr., 103(1985)28016d).
394 A. Tiripicchio, F.J. Lahoz, L.A. Oro, M.T. Pinillos and C. Tejel, Inorg. Chim. Acta, 100(1985)L5.
395 J. Ott, L.M. Venanzi, C.A. Ghilardi, S. Midollini and A. Orlandini, J. Organometal. Chem., 291(1985)89.
396 A.R. Sanger, Can. J. Chem., 63(1985)571.
397 E.A.V. Ebsworth, N.T. Manus and D.W.H. Rankin, J. Chem. Soc., Dalton Trans., (1984)2573.
398 M.K. Lee, I.B. Kim and C.S. Chin, J. Organometal. Chem., 290(1985) 115.
399 M.B. Hursthouse, N.P.C. Walker, C.P. Warrens and J.D. Wollins, J. Chem. Soc., Dalton Trans., (1985)1043.
400 J.N. Gangali and T. Bora, Indian J. Chem., Sect. A, 24A(1985)246 (Chem. Abstr., 103(1985)47225n).
401 C. Woods and C. Daffron, Inorg. Chim. Acta, 101(1985)13.
402 E. Kwaskowska-Chec, A.M. Trzciak and J.J. Ziólkowski, React. Kinet. Catal. Lett., 26(1984)35 (Chem. Abstr., 102(1985)155571k).
403 D. Wink and P.C. Ford, J. Am. Chem. Soc., 107(1985)1794.
404 L.I. Danilina, A.V. Iretskii and Yu.N. Kukushkin, Koord. Khim., 11(1985)1271 (Chem. Abstr., 104(1986)27813v).
405 W. Willis and K.M. Nicholas, Gov. Rep. Announce, Index (U.S.), 85(1985)81 (Chem. Abstr., 102(1985)196869g).
406 D. Mahajan, C. Creutz and N. Sutin, Inorg. Chem., 24(1985)2063.
407 P.R. Brown, F.G.N. Cloke and M.L.H. Green, Polyhedron, 4(1985)869.
408 M. Hoshino and K. Yasufuku, Inorg. Chem., 24(1985)4408.
409 J.G. Gaudiello, T.C. Wright, R.A. Jones and A.J. Bard, J. Am. Chem. Soc., 107(1985)888.
410 D. Parker, J.-M. Lehn and J. Rimmer, J. Chem. Soc., Dalton Trans., (1985)1517.
411 A.A. Bahsoun and R. Ziessel, Nouv, J. Chim., 9(1985)225.
412 T.G. Schenck, J.M. Downes, C.R.C. Milne, P.B. MacKenzie, H. Boucher, J. Whelan and B. Bosnich, Inorg. Chem., 24(1985)2334.
413 T.G. Schenck, C.R.C. Milne, J.F. Sawyer and B. Bosnich, Inorg. Chem., 24(1985)2338.

414 C.W.G. Ansell, M.K. Cooper, K.P. Dancey, P.A. Duckworth, K. Henrick, M. McPartlin, G. Organ and P.A. Tasker, J. Chem. Soc., Chem. Commun., (1985)437.

415 C.E. Johnson and R. Eisenberg, J. Am. Chem. Soc., 107(1985)3148.

416 A.J. Kunin, R. Farid, C.E. Johnson and R. Eisenberg, J. Am. Chem. Soc., 107(1985)5315.

417 C.E. Johnson and R. Eisenberg, J. Am. Chem. Soc., 107(1985)6531.

418 W.D. Jones and J.A. Maguire, J. Am. Chem. Soc., 107(1985)4544.

419 P. Janser, L.M. Venanzi and F. Bachechi, J. Organometal. Chem., 296(1985)229.

420 P. Mura, B.G. Olby and S.D. Robinson, Inorg. Chim. Acta, 97(1985)45.

421 R.A. Vanderpool and H.B. Abrahamson, Inorg. Chem.,24(1985)2985.

422 H. Bauer, U. Nagel and W. Beck, J. Organometal. Chem., 290(1985)219.

423 W.M. Rees and J.D. Atwood, Organometallics, 4(1985)402.

424 W.M. Rees, M.R. Churchill, J.C. Fettinger and J.D. Atwood, Organometallics, 4(1985)2179.

425 S. Gopinathan, K. Joseph and C. Gopinathan, Polyhedron, 4(1985)955.

426 J. Reyes, L.A. Oro, M.A. Ciriano and D. Carmona, Transition Met. Chem. (Weinheim, Ger.), 10(1985)28 (Chem. Abstr., 102(1985)105099s).

427 E.A.V. Ebsworth and R. Mayo, Angew. Chem. Int. Ed. Engl., 24(1985)68.

428 E.A.V. Ebsworth, R.O. Gould, N.T. McManus, J.J. Pilkington and D.W.H. Rankin, J. Chem. Soc., Dalton Trans., (1984)2561.

429 E.A.V. Ebsworth, P.G. Page and D.W.H. Rankin, J. Chem. Soc., Dalton Trans., (1984)2569.

430 C.S. Chin, H.-K. Park and W.-C. Joo, Polyhedron, 4(1985)1673.

431 S.H. Park, H.-K. Park and C.S. Chin, Inorg. Chem., 24(1985)1120.

432 M. Kubota, F.S. Rosenberg and M.J. Sailor, J. Am. Chem. Soc., 107 (1985)4558.

433 P.G. Rasmussen, J.E. Anderson, O.H. Bailey, M. Tamres and J.C. Bayón, J. Am. Chem. Soc., 107(1985)279.

434 P.G. Rasmussen, M. Tamres, J.E. Anderson and O.H. Bailey, Mol. Cryst. Liq. Cryst., 126(1985)77 (Chem. Abstr., 103(1985)114087j).

435 S. Jans-Buerli and P.S. Pregosin, Magn. Reson. Chem., 23(1985)198 (Chem. Abstr., 102(1985)177834h).

436 D.A. Wink and P.C. Ford, J. Am. Chem. Soc., 107(1985)5566.

437 P. Zhou, A.A. Vitale, J. San Filippo, Jr. and W.H. Saunders, Jr., J. Am. Chem. Soc., 107(1985)8049.

438 M.N. Golovin, Md. M. Rahman, J.E. Belmonte ans W.P. Giering, Organometallics, 4(1985)1981.

439 M.A. Lilga and J.A. Ibers, Organometallics, 4(1985)590.

440 M.J. Auburn, S.L. Grundy, S.R. Stobart and M.J. Zaworotko, J. Am. Chem. Soc., 107(1985)266.

441 C. Woodcock and R. Eisenberg, Organometallics, 4(1985)4.

442 C. Woodcock and R. Eisenberg, Inorg. Chem., 24(1985)1285.

443 J. Ellermann, G. Szucányi and E. Wilhelm, Chem. Ber., 118(1985)1588.

444 J. Ellermann and G. Szucsányi, Chem. Ber., 118(1985)1868.

445 S.P. Deraniyagala and K.R. Grundy, Inorg. Chem., 24(1985)50.

446 S.P. Deraniyagala and K.R. Grundy, J. Chem. Soc., Dalton Trans., (1985)1577.

447 S.P. Deraniyagala and K.R. Grundy, Inorg. Chim. Acta, 101(1985)103.

448 S.P. Deraniyagala and K.R. Grundy, Organometallics, 4(1985)424.

449 A.L. Balch, R.R. Guimerans, J. Linehan and F.E. Wood, Inorg. Chem., 24(1985)2021.

450 A.L. Balch, R.R. Guimerans, J. Linehan, M.M. Olmstead and D.E. Oram, Organometallics, 4(1985)1445.

451 A.T. Hutton, C.R. Langrick, D.M. McEwan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985)2121.

452 F.S.M. Hassan, D.P. Markham, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985)279.

453 A.T. Hutton, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985)1677.

454 J.A. Iggo, D.P. Markham, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1985)432.

455 G. Bruno, S. Lo Schavio, P. Piraino and F. Faraone, Organometallics, 4(1985)1098.

456 S.Lo Schavio, G. Bruno, F. Nicolò, P. Piraino and F. Faraone, Organometallics, 4(1985)2091.

457 A.R. Sanger, Inorg. Chim. Acta, 99(1985)95.

458 M. Etienne, R. Choukroun, M. Basso-Bert, F. Dahan and D. Gervais, Nouv. J. Chim., 8(1984)531.

459 R.V. Parish and S.M. Razzoki, Inorg. Chim. Acta, 96(1985)49.

460 B.R. Sutherland and M. Cowie, Organometallics, 4(1985)1637.

461 B.R. Sutherland and M. Cowie, Organometallics, 4(1985)1801.

462 B.M. Louie, S.J. Rettig, A. Storr and J. Trotter, Can. J. Chem., 63(1985)688.

463 L.A. Oro, D. Carmona, P.L. Pérez, M. Esteban, A. Tiripicchio and M. Tiripicchio-Camellini, J. Chem. Soc., Dalton Trans., (1985)973.

464 L.A. Oro, M.T. Pinillos, A. Tiripicchio and M. Tiripicchio-Camellini, Inorg. Chim. Acta, 99(1985)L13.

465 A.L. Balch, R.R. Guimerans and J. Linehan, Inorg. Chem., 24(1985)290.

466 A.L. Balch, L.A. Fossett, R.R. Guimerans and M.M. Olmstead, Organometallics, 4(1985)781.

467 A.L. Balch, J.C. Linehan and M.M. Olmstead, Inorg. Chem., 24(1985) 3975.

468 A.L. Balch and M.M. Olmstead, Isr. J. Chem., 25(1985)189.

469 A.L. Balch, L.A. Fossett, M.M. Olmstead, D.E. Oram and P.E. Reedy, Jr., J. Am. Chem. Soc., 107(1985)5272.

470 A.L. Balch, H. Hope and F.E. Wood, J. Am. Chem. Soc., 107(1985)6936.

471 V. Schurig, W. Pille, K. Peters and H.G. von Schnering, Mol. Cryst. Liq. Cryst., 120(1985)385 (Chem. Abstr., 102(1985)229655x).

472 R.A. Newmark and A.R. Siedle, Magn. Reson. Chem., 23(1985)67 (Chem. Abstr., 102(1985)210036s).

473 A.M. Trzeciak and J.J. Ziólkowski, Inorg. Chim. Acta, 96(1985)15.

474 M. Hoshino and K. Yasufuku, Chem. Phys. Letters, 117(1985)259.

475 C. Mealli, J. Am. Chem. Soc., 107(1985)2245.

476 I. Ojima, T. Fuchikami and K. Hirai, New Front. Organomet. Inorg. Chem., Proc. China-Jpn,-U.S.A. Trilateral Semin., 2nd 1982 (Pub. 1984)169 (Chem. Abstr., 102(1985)203330e).

477 B. Falk, B. Fell and W. Meltzow, J. Mol. Catal., 31(1985)93 (Chem. Abstr., 104(1986)68483f).

478 D. Banach, G.O. Evans, II, D.G. McIntyre, T. Predmore, M.G. Richmond, J.H. Supple and R.P. Steward, Jr., J. Mol. Catal., 31(1985)15 (Chem. Abstr., 104(1985)33977t).

479 A. Sen and J.S. Brumbaugh, J. Organometal. Chem., 279(1985)C5.

480 T.W. Dekleva and D. Forster, J. Am. Chem. Soc., 107(1985)3565.

481 T.W. Dekleva and D. Forster, J. Am. Chem. Soc., 107(1985)3568.

482 K. Kudo, S. Mori and N. Sugita, Chem. Lett., (1985)265 (Chem. Abstr., 103(1985)70922w).

483 T.A. Smith and P.M. Maitlis, J. Organometal. Chem., 289(1985)385.

484 B.D. Dombek, Organometallics, 4(1985)1707.

485 L.I. Kopylova, N.D. Ivanova and M.G. Voronkov, Zh. Obshch. Khim., 55(1985)1649.

486 N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1984)2580.

487 N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1984)2586.

488 J.P. Scholten and H.J. van der Ploeg, Macromol. Synth., 9(1985)1 (Chem. Abstr., 103(1985)105353r).

489 V.S. Shestakova, G.K. Shestakov, L.P. Yur'eva, A.A. Belyi and O.N. Temkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1985)534.

490 B. Odell, G. Earlam and D.J. Cole-Hamilton, J. Organometal. Chem., 290(1985)241.

491 R.S. Drago and D.C. Pribich, Inorg. Chem., 24(1985)1983.

492 R. Datta, J. Rydant and R.G. Rinker, J. Catal., 95(1982)202.

493 H.L. Pelt, G. van der Lee and J.J.F. Scholten, J. Mol. Catal., 29(1985)319 (Chem. Abstr., 103(1985)27934q).

494 M. Aresta, D. Ballivet-Tkatchenko, M.C. Bonnet, R. Faure and H. Loiseleur, J. Am. Chem. Soc., 107(1985)2994.

495 P. Oltmanns and D. Rehder, J. Organometal. Chem., 281(1985)263.

496 F. Näumann and D. Rehder, Z. Naturforsch., 39b(1984)1647.

497 F. Näumann and D. Rehder, Z. Naturforsch., 39b (1984)1654.

498 K.A. Kubat-Martin, A.D. Rae and L.F. Dahl, Organometallics, 4(1985) 2221.

499 L.S. Hegedus and R.J. Perry, J. Org. Chem., 50(1985)4955.

500 K.J. Shea and E.A. Thompson, Macromolecules, 18(1985)814 (Chem. Abstr., 102(1985)16788m).

501 K. Hedberg, L. Hedberg, K. Hagen, R.R. Ryan and L.H. Jones, Inorg. Chem., 24(1985)2771.

502 A. Dobson, D.S. Moore, S.D. Robinson, A.M.R. Galas and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1985)611.

503 E.B. Boyar, D.S. Moore, S.D. Robinson, B.R. James, M. Preece and I. Thorburn, J. Chem. Soc., Dalton Trans., (1985)617.

504 E.B. Boyar and S.D. Robinson, J. Chem. Soc., Dalton Trans., (1985) 2113.

505 J. Zink, Photochem. Photobiol., Proc. Int. Conf., 2(1983)1277 (Chem. Abstr., 102(1985)122946h).

506 L.I. Danilina, A.V. Iretskii and Yu.N. Kukushkin, Zh. Neorg. Khim., 30(1985)1889.

507 R.E. Stevens, P.C.C. Liu and W.L. Gladfelter, J. Organometal. Chem., 287(1985)133.

508 D.O. Kimberly Fjeldsted, S.R. Stobart and M.J. Zaworotko, J. Am. Chem. Soc., 107(1985)8258.

509 D.O. Kim Fjelsted and S.R. Stobart, J. Am. Chem. Soc., 107(1985)908.

510 R.A. Henderson, J. Chem. Soc., Dalton Trans., (1985)2067.

511 H.-F. Klein, L. Fabry, H. Witty, U. Schubert, H. Leuken and U. Stamm, Inorg. Chem., 24(1985)683.

512 H.-F. Klein, K. Ellrich, S. Lamac, G. Lull, L. Zsolnai and G. Huttner, Z. Naturforsch., 40b(1985)1377.

513 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Organometal. Chem., 296(1985)C6.

514 L.C. Ananias de Carahlo, Y. Pérès, M. Dartiguenave, Y. Dartiguenave and A.L. Beauchamp, Organometallics, 4(1985)2021.

515 F. Ungváry, J. Shanshool and L. Markó, J. Organometal. Chem., 296 (1985)155.

516 S. Oishi, N. Kihara and A. Hosaka, Chem. Lett., (1985)621 (Chem. Abstr., 103(1985)122803e).

517 T. Yoshida, T. Okano, S. Otsuka, I. Miura, T. Kubota, K. Kafuku and K. Nakatsu, Inorg. Chim. Acta, 100(1985)7.

518 M.D. Fryzuk, W.E. Piers and S.J. Rettig, J. Am. Chem. Soc., 107(1985) 8259.

519 D.C. Cupertino, M.M. Harding and D.J. Cole-Hamilton, J. Organometal. Chem., 294(1985)C29.

520 I.T. Chizhevskii, N.V. Rastova, N.E. Kolobova, P.V. Petrovskii and D.V. Zagorevskii, Zh. Obshch. Khim., 55(1985)465.

521 I.T. Chezhevsky, N.V. Rastova, N.E. Kolobova, P.V. Petrovskii, L.E. Vinogradova and L.A. Leites, Tetrahedron Lett., 26(1985)3605.

522 M.A. Bennett, I.J. McMahon, S. Pelling, G.B. Robertson and W.A. Wickramasinghe, Organometallics, 4(1985)754.

523 M.C. Bonnet, B. Stitou and I. Tkatchenko, J. Organometal. Chem., 279(1985)C1.

534 A. Lavery and S.M. Nelson, J. Chem. Soc., Dalton Trans., (1985)1053.

525 G. Dube, D. Selent and R. Taube, Z. Chem., 25(1985)154 (Chem. Abstr., 103(1985)78842r).

526 H. tom Dieck, L. Stamp, R. Diercks and C. Müller, Nouv. J. Chim., 9(1985)289.

527 P.O. Bentz, J. Ruiz, B.E. Mann, C.M. Spencer and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1985)1374.

528 N.M. Doberty, B.E. Ewels, R.P. Hughes, D.E. Samkoff, W.D. Saunders, R.E. Davis and B.B. Laird, Organometallics, 4(1985)1606.

529 D.M. Haddleton and R.N. Perutz, J. Chem. Soc., Chem. Commun., (1985) 1372.

530 I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig and J. Trotter, Organometallics, 4(1985)972.

531 I.R. Butler, W.R. Cullen, B.E. Mann and C.R. Nurse, J. Organometal. Chem., 280(1985)C47.

532 W.R Cullen, T.-J. Kim, F.W.B. Einstein and T. Jones, Organometallics, 4(1985)346.

533 T.D. Appleton, W.R. Cullen, S.V. Evans, T.-J. Kim and J. Trotter, J. Organometal. Chem., 279(1985)5.

534 C.J. Besecker, V.W. Day and W.G. Klemperer, Organometallics, 4(1985) 564.

535 E. Pinella, J.V. Heras and M. Martinez, An. Quim., Ser. B, 79(1983) 533 (Chem. Abstr., 102(1985)185242w).

536 E.P. Kyba and S.-T. Liu, Inorg. Chem., 24(1985)1613.

537 W.A. Schenk, J. Leissner and C. Burschka, Z. Naturforsch., 40b(1985) 1264.

538 M.A. Bennett and T.R.B. Mitchell, J. Organometal. Chem., 295(1985) 223.

539 H. Werner, J. Wolf and A. Höhn, J. Organometal. Chem., 287(1985)395.

540 D.H.M.W. Thewissen, K. Timmer, J.G. Noltes and J.W. Marsman, Inorg. Chim. Acta, 97(1985)143.

541 V. Garcia, M. Angeles Garralda and L. Ibarlucea, Transition Met. Chem. (Weinheim, Ger.), 10(1985)288 (Chem. Abstr., 104(1986)6006u).

542 L.A. Oro, M.A. Ciriano, B.E. Villarroya, A. Tiripicchio and F.H. Lahoz, J. Chem. Soc., Dalton Trans., (1985)1891.

543 L.A. Oro, M.T. Pinillos and C. Tejel, J. Organometal. Chem., 280 (1985)261.

544 F. Bonati, L.A. Oro and M.T. Pinillos, Polyhedron, 4(1985)357.

545 L.A. Oro, M.J. Fernandez, J. Modrago and J.M. Lopez, J. Organometal. Chem., 287(1985)409.

546 Y. Rosopulos, U. Nagel and W. Beck, Chem. Ber., 118(1985)931.

547 T. Yoshida, T. Ueda, T. Adachi, K. Yamamoto and T. Higuchi, J. Chem. Soc., Chem. Commun., (1985)1137.

548 H.M. Colquhoun, S.M. Doughty, A.M.Z. Slawin, J.F. Stoddart and D.J. Williams, Angew. Chem. Int. Ed. Engl., 24(1985)135.

549 D.R. Alston, A.M.Z. Slawin, J.F. Stoddart and D.J. Williams, Angew. Chem. Int. Ed. Engl., 24(1985)786.

550 A. Christofides and I. Labrinou, Inorg. Chim. Acta, 99(1985)195.

551 G. Matsubayashi and S. Akazawa, Polyhedron, 4(1985)419.

552 L. Dahlenburg and N. Hock, J. Organometal. Chem., 284(1985)129.

553 F.J. Lahoz, A. Tiripicchio, M.T. Camellini, L.A. Oro and M.T. Pinillos, J. Chem. Soc., Dalton Trans., (1985)1487.

554 P. Piraino, G. Bruno, F. Nicolo, F. Faraone and S. Lo Schavio, Inorg. Chem., 24(1985)4760.

555 B. Delavaux, B. Chaudret, N.J. Tayler, S. Arabi and R. Poilblanc, J. Chem. Soc., Chem. Commun., (1985)805.

556 B. Delavaux, B. Chaudret, F. Dahan and R. Poilblanc, Organometallics, 4(1985)935.

557 D. O'Hare, M.L.H. Green and F.G.N. Cloke, J. Organometal. Chem., 282(1985)225.
558 F. Götzfried, R. Grenz, G. Urban and W. Beck, Chem. Ber., 118(1985) 4179.
559 C.E. Briant, D.I. Gilmour, M.A. Luke and D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1985)851.
560 L.A. Oro, M.T. Pinillos and M.P. Jarauta, Polyhedron, 4(1985)325.
561 K. Timmer and D.H.M.W. Thewissen, Inorg. Chim. Acta, 100(1985)235.
562 R. Benn, H. Brenneke and R.-D. Reinhardt, Z. Naturforsch., 40b(1985) 1763.
563 M. Arthurs, H. Karodia, M. Sedgwick, D.A. Morton-Blake, C.J. Cardin and H. Parge, J. Organometal. Chem., 291(1985)231.
564 M.D. Jones and R.D.W. Kemmitt, J. Chem. Soc., Chem. Commun., (1985) 811.
565 M. Drouin and J.F. Harrod, Can. J. Chem., 63(1985)353.
566 J.M. Brown, R.A. John and A.R. Lucy, J. Organometal. Chem., 279 (1985)245.
567 P.B. Hitchcock, S. Morton and J.F. Nixon, J. Chem. Soc., Dalton Trans., (1985)1295.
568 S. Morton and J.F. Nixon, J. Organometal. Chem., 282(1985)123.
569 G.W. Bushnell, D.O. Kimberley Fjeldsted, S.R. Stobart, M.J. Zaworotko, S.A.R. Knox and K.A. Macpherson, Organometallics, 4(1985) 1107.
570 G.S. Rodman and K.R. Mann, Inorg. Chem., 24(1985)3507.
571 R.H. Crabtree and C.P. Parnell, Organometallics, 4(1985)519.
572 M.J. Burk, R.H. Crabtree and D.V. McGrath, J. Chem. Soc., Chem. Commun., (1985)1829.
573 R.H. Crabtree, E.M. Holt, M. Lavin and S.M. Morehouse, Inorg. Chem., 24(1985)1986.
574 M.J. Auburn and S.R. Stobart, Inorg. Chem., 24(1985)318.
575 S. Nussbaum, S.J. Rettig, A. Storr and J. Trotter, Can. J. Chem., 63(1985)692.
576 J.C. Rodriguez, C. Claver and A. Ruiz, J. Organometal. Chem., 293 (1985)115.
577 M. Kretschmer, P.S. Pregosin, A. Albinati and A. Togni, J. Organometal. Chem., 281(1985)365.
578 G.G. Hlatky, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1985)1277.
579 A.S. Machado, A. Olesker, S. Castillon and G. Lukocs, J. Chem. Soc., Chem. Commun., (1985)330.
580 A.G. Schultz and P.J. McCloskey, J. Org. Chem., 50(1985)5907.
581 J.M. Brown and S.A. Hall, J. Organometal. Chem., 285(1985)333.
582 N.W. Alcock, J.M. Brown, A.E. Derome and A.R. Lucy, J. Chem. Soc., Chem. Commun., (1985)575.
583 J.M. Brown and I. Cutting, J. Chem. Soc., Chem. Commun., (1985)578.
584 S. El-Baba, J.-C. Poulin and H.B. Kagan, Tetrahedron, 40(1984)4275.
585 C. Halldin and B. Laangstrom, Int. J. Appl. Radiat. Isot., 35(1984) 945 (Chem. Abstr., 102(1985)149736b).
586 J. Bakos, I. Tóth and B. Heil, Tetrahedron Lett., 25(1984)4965.
587 J. Bakos, I. Tóth, B. Heil and L. Markó, J. Organometal. Chem., 279(1985)23.
588 K. Tani, T. Yamagata, Y. Tatsuno, Y. Yamagata, K. Tomita, S. Akatagawa, H. Kumobayashi and S. Otsuka, Angew. Chem. Int. Ed. Engl., 24(1985)217.
589 R. Noyori, New. Front. Organomet. Inorg. Chem., Proc. China-Jpn.-U.S.A. Trilateral Semin., 2nd 1982 (Pub. 1984) 159 (Chem. Abstr., 102(1985)203440r).
590 H.J. Kreuzfeld and C. Doebler, Z. Chem., 24(1984)405 (Chem. Abstr., 103(1985)105049w).

591 H. Knorr, R. Reichl, W. Traunecker, F. Knappen and K. Brandt, Arzneim.-Forsch., 34(1984)1709 (Chem. Abstr., 103(1985)47952x).

592 K. Saito, S. Saijo, K. Kotera and T. Date, Chem. Pharm. Bull., 33(1985)1342 (Chem. Abstr., 103(1985)215395p).

593 I. Ojima, T. Kogure and Y. Yoda, Org. Synth., 63(1985)18 (Chem. Abstr., 104(1985)68661n).

594 R. Benhamza, Y. Amrani and D. Sinou, J. Organometal. Chem., 288 (1985)C37.

595 W.R. Jackson, R.J. Thomson and M.K. Mackay, Aust. J. Chem., 38(1985) 111.

596 G. Consiglio, F. Morandini, M. Scalone and P. Pino, J. Organometal. Chem., 279(1985)193.

597 H. Brunner and H. Weber, Chem. Ber., 118(1985)3380.

598 H. Brunner, P. Beier, G. Riepl, I. Bernal, G.M. Reisner, R. Benn and A. Rufińska, Organometallics, 4(1985)1732.

599 H. Brunner, A. Knolt, R. Benn and A. Rufińska, J. Organometal. Chem., 295(1985)211.

600 R. Spogliarich, J. Kaspar and M. Graziani, J. Catal., 94(1985)292.

601 K.P. Adams, J.A. Joyce, T.A. Nile, A.I. Patel, C.D. Reid and J.M. Walters, J. Mol. Catal., 29(1985)201 (Chem. Abstr., 103(1985)123637r).

602 D.C. Apple, K.A. Brady, J.M. Chance, N.E. Heard and T.A. Nile, J. Mol. Catal., 29(1985)55 (Chem. Abstr., 103(1985)178404t).

603 T.G. Schenck and B. Bosnich, J. Am. Chem. Soc., 107(1985)2058.

604 W.A. Nugent and R.J. McKinney, J. Mol. Catal., 29(1985)65 (Chem. Abstr., 103(1985)5686r).

605 K. Tani, E. Tanigawa, Y. Tatsuno and S. Otsuka, J. Organometal. Chem., 279(1985)87.

606 C. Buchon, N. Hamel, J.B. Woell and H. Alper, Tetrahedron Lett., 26(1985)5743.

607 K.E. Hashem, J.B. Woell and H. Alper, Tetrahedron Lett., 25(1984) 4879.

608 J.B. Woell, S.B. Fergusson and H. Alper, J. Org. Chem., 50(1985)2134.

609 D. Männig and H. Nöth, Angew. Chem. Int. Ed. Engl., 24(1985)878.

610 G. Read and M. Urgelles, J. Chem. Soc., Dalton Trans., (1985)1591.

611 M. Bressan, F. Morandini, A. Morvillo and P. Rigo, J. Organometal. Chem., 280(1985)139.

612 J.P. Collin, R. Ruppert and J.P. Sauvage, Nouv. J. Chim., 9(1985)395.

613 D.E. Bergbreiter and R. Chandian, J. Am. Chem. Soc., 107(1985)4792.

614 R.A. Jones and M.H. Seeberger, J. Chem. Soc., Chem. Commun., (1985) 373.

615 R. Deschenaux and J.K. Stille, J. Org. Chem., 50(1985)2299.

616 K. Kaneda, H. Yamamoto, T. Imanaka and S. Teranishi, J. Mol. Catal., 29(1985)99 (Chem. Abstr., 103(1985)5761d).

617 E. Rode, M.E. Davis and B.E. Hanson, J. Chem. Soc., Chem. Commun., (1985)716.

618 P. Paetzold and K. Delpy, Chem. Ber., 118(1985)2552.

619 Y. Wakatsuki, S. Miya, S. Ikuta and H. Tamazaki, J. Chem. Soc., Chem. Commun., (1985)35.

620 F.Y. Pétillon, J.J. LeQuéré, F. Le Floch-Pérennou, J.E. Guerchais and P. L'Haridon J. Organomet. Chem., 281(1985)305.

621 E. Roland, W. Bernhardt and H. Vahrenkamp, Chem. Ber., 118(1985)2858.

622 P. Magnus and D.P. Becker, J. Chem. Soc., Chem. Commun., (1985)640.

623 M. Mlekuz, P. Bougeard, B.G. Sayer, S. Peng, M.J. Glinchey, A. Marinetti, J.-Y. Saillard, J. Ben Naceur, B. Mentzen and G. Jaouen, Organometallics, 4(1985)1123.

624 W.A. Smit, A.A. Schegolev, A.S. Gybin, G.S. Mikaelyan and R. Caple, Synthesis, (1984)887.

625 A.A. Shchegolev, W.A. Smit, G.S. Mikaelyan, A.S. Gybin, Yu.V. Kal'yan, M.Z. Krimer and R. Caple, Izv. Akad. Nauk SSSR, Ser. Khim., (1984)2571.

626 G.S. Mikaelyan, A.S. Gybin, W.A. Smit and R. Caple, Tetrahedron Lett., 26(1985)1269.
627 G.S. Mikaelyan, V.A. Smit, A.S. Batsanov and Yu.T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1984)2105.
628 G.S. Mikaelyan and V.A. Smit, Izv. Akad. Nauk SSSR, Ser. Khim., (1984)2652.
629 P. Magnus and L.M. Principe, Tetrahedron Lett., 26(1985)4851.
630 L. Daalman, R.F. Newton, P.L. Pauson, R.G. Taylor and A. Wadsworth, J. Chem. Research (S) (1984)344.
631 E. Carceller, V. Centallas, A. Moyano, M.A. Pericas and F. Serratosa, Tetrahedron Lett., 26(1985)2475.
632 B.E. LaBelle, M.J. Knudsen, M.M. Olmstead, H. Hope, M.D. Yanuck and N.E. Schore, J. Org. Chem., 50(1985)5215.
633 L. Daalman, R.F. Newton, P.L. Pauson and A. Wadsworth, J. Chem. Research (S) (1984)346.
634 K.M. Nicholas and J. Siegel, J. Am. Chem. Soc., 107(1985)4999.
635 D. Osella, S. Aime, D. Boccado, M. Castiglioni and L. Milone, Inorg. Chim. Acta, 100(1985)97.
636 J.M. Bernassau, M. Bertranne, C. Collongues and M. Fetizon, Tetrahedron, 41(1985)3063.
637 B.C. Berris, G.H. Hovakeemian, Y.-H. Lai, H. Mestdagh and K.P.C. Vollhardt, J. Am. Chem. Soc., 107(1985)5670.
638 R.L. Halterman, N.H. Nguyen and K.P.C. Vollhardt, J. Am. Chem. Soc., 107(1985)1379.
639 E. Duñach, R.L. Halterman and K.P.C. Vollhardt, J. Am. Chem. Soc., 107(1985)1664.
640 E.D. Sternberg and K.P.C. Vollhardt, New Front. Organomet. Inorg. Chem., Proc. China-Jpn.-U.S.A. Trilateral Semin., 2nd 1982 (Pub. 1984)353 (Chem. Abstr., 102(1985)221074d).
641 G. Cetini, P.M. Lausarot, L. Operti, G.A. Vaglio and P. Volpe, Int. J. Mass Spectrom. Ion Processes, 64(1985)25 (Chem. Abstr., 102(1985) 194589s).
642 G. Gervasio, R. Rosetti and P.L. Stanghellini, Organometallics, 4(1985)1612.
643 T. Siese and U. Schuchardt, Actas Simp. Iberoam. Catal., 9th, 2(1984) 1493 (Chem. Abstr., 102(1985)131995a).
644 F.J. Garcia Alonso, A. Höhn, J. Wolf, H. Otto and H. Werner, Angew. Chem. Int. Ed. Engl., 24(1985)406.
645 R.A. Dickson, G.S. Evans, G.D. Fallon and G.N. Pain, J. Organometal. Chem., 295(1985)109.
646 R.S. Dickson, G.S. Evans and G.D. Fallon, Aust. J. Chem., 38(1985)273.
647 M. Green and J.A.K. Howard, S.J. Porter, F.G.A. Stone and D.C. Tyler, J. Chem. Soc., Dalton Trans., (1984)2553.
648 M. Kajitani, T. Suetsugu, R. Wakabayashi, A. Igarashi, T. Akiyama and A. Sugimori, J. Organometal. Chem., 293(1985)C15.
649 K. Abdulla, B.L. Booth and C. Stacey, J. Organometal. Chem., 293 (1985)103.
650 G.W. Bushnell, M.I. Decker, D.T. Eadie, S.R. Stobart, R. Vefghi, J.L. Atwood and M.J. Zaworotko, Organometallics, 4(1985)2106.
651 F. Timmers and M. Brookhardt, Organometallics, 4(1985)1365.
652 R.P. Hughes, W. Kläui, J.W. Reisch and A. Müller, Organometallics, 4(1985)1761.
653 P. Barabotti, P. Diversi, G. Ingrosso, A. Lucherini and F. Nuti, J. Chem. Soc., Dalton Trans., (1984)2517.
654 Z.L. Lutsenko, G.G. Aleksandrov, P.V. Petrovskii, E.S. Shubina, V.G. Andrianov, Yu.T. Struchkov and A.Z. Rubezhov, J. Organometal. Chem., 281(1985)349.
655 S.D. Chappell, D.J. Cole-Hamilton, A.M.R. Galas, M.B. Hursthouse and N.P.C. Walker, Polyhedron, 4(1985)121.

656 J. Silverstre and T.A. Albright, J. Am. Chem. Soc., 107(1985)6829.

657 W.D. McGhee and R.G. Bergman, J. Am. Chem. Soc., 107(1985)3388.

658 D.R. Corbin, W.C. Seidel, L. Abrams, N. Herron, G.D. Stucky and C.A. Tolman, Inorg. Chem., 24(1985)1800.

659 B.G. Conway and M.D. Rausch, Organometallics, 4(1985)688.

660 W.P. Hart, D. Shihua and M.D. Rausch, J. Organometal. Chem., 282 (1985)111.

661 E.E. Bunel, L. Valle and J.M. Manriquez, Organometallics, 4(1985) 1680.

662 J.S. Drage and K.P.C. Vollhardt, Organometallics, 4(1985)389.

663 S.J. Carter and L.S. Stuhl, Organometallics, 4(1985)197.

664 H. Tom Dieck and M. Haarich, J. Organometal. Chem., 291(1985)71.

665 J. Bernal, G.M. Reisner, H. Brunner and G. Riepl, Inorg. Chim. Acta, 103(1985)179.

666 L. Chen, D.J. Kountz and D.W. Meek, Organometallics, 4(1985)598.

667 H. Werner, W. Hofmann, R. Zolk, L.F. Dahl, J. Kocal and A. Kühn, J. Organometal. Chem., 289(1985)173.

668 H. Werner and R. Zolk, Organometallics, 4(1985)601.

669 R. Zolk and H. Werner, Angew. Chem. Int. Ed. Engl., 24(1985)577.

670 L. Hofmann and H. Werner, J. Organometal. Chem., 289(1985)141.

671 H. Werner and O. Kolb, Chem. Ber., 118(1985)880.

672 H. Werner, O. Kolb, U. Schubert and K. Achermann, Chem. Ber., 118 (1985)873.

673 S. Delgado, J. Macazaga, C. Moreno and J.R. Masaguer, J. Organometal. Chem., 289(1985)397.

674 P.T. Murray and A.R. Manning, J. Organometal. Chem., 288(1985)219.

675 Q.B. Bao, S.J. Landon, A.L. Reingold, T.M. Haller and T.B. Brill, Inorg. Chem., 24(1985)900.

676 E. Raabe and U. Koelle, J. Organometal. Chem., 279(1985)C29.

677 H. Brunner, N. Janietz, W. Meier, G. Sergeson, J. Wachter, T. Zahn and M.L. Ziegler, Angew. Chem. Int. Ed. Engl., 24(1985)1060.

678 M. Bochman, K. Geilich and W. Siebert, Chem. Ber., 118(1985)401.

679 L. Stumpf, H. Pritzkow and W. Siebert, Angew. Chem. Int. Ed. Engl., 24(1985)71.

680 T. Kuhlmann and W. Siebert, Z. Naturforsch., 40b(1985)167.

681 H. Wadepohl, H. Pritzkow and W. Siebert, Chem. Ber., 118(1985)729.

682 W. Siebert, M. El-Din, M. El-Essawi, R. Full and J. Heck, Z. Naturforsch., 40b(1985)458.

683 G.E. Herberich, H.J. Becker, B. Hessner and L. Zelenka, J. Organometal. Chem., 280(1985)147.

684 G.A. Razuvaev, S.G. Yudenich and V.A. Dodonov, Zh. Obshch. Khim., 55(1985)613.

685 A.R. Cutler and R.A. Walton, Inorg. Chim. Acta, 105(1985)219.

686 K.R. Dunbar and R. A. Walton, Inorg. Chem., 24(1985)5.

687 R.A. Simon, T.E. Mallouk, K.A. Daube and M.S. Wrighton, Inorg. Chem., 24(1985)3119.

688 W. Kläui, J. Okuda, M. Scotti and M. Valderrama, J. Organometal. Chem., 280(1985)C26.

689 E. Roman, F. Tapia, M. Barrera, M.-T. Garland, J.-Y. Le Marouille and C. Gianotti, J. Organometal. Chem., 297(1985)C8.

690 R.A. Gancarz, J.F. Blount and K. Mislow, Organometallics, 4(1985)2028.

691 V. Amir-Ebrahimi, J. Grimshaw, E.A. McIlgorm, T.R.B. Mitchell and J.J. Rooney, J. Mol. Catal., 27(1985)337 (Chem. Abstr., 102(1985) 131342k.

692 H. Bönnemann, W. Brijoux, R. Brinkmann and W. Meurers, Helv. Chim. Acta, 67(1984)1616.

693 S.J. Landon and T.B. Brill, Inorg. Chem., 24(1985)2863.

694 E.J. Miller, S.J. Landon and T.B. Brill, Organometallics, 4(1985)533.

695 R. Benn, K. Cibura, P. Hofmann, K. Jonas and A. Rufińska, Organometallics, 4(1985)2214.

696 U. Kölle, J. Moser and M. Grätzel, Inorg. Chem., 24(1985)2253.

697 D.V. Zagorevskii, Yu.S. Nekasov, A.V. Malkov and E.V. Leonova, J. Organometal. Chem., 284(1985)109.

698 M. Böhm, R. Gleiter, G.E. Herberich and B. Hessner, J. Phys. Chem., 89(1985)2129.

699 G. Trinquier and G. Bertrand, Inorg. Chem., 24(1985)3842.

700 S.M. Hawkins, P.B. Hitchcock and M.F. Lappert, J. Chem. Soc., Chem. Commun., (1985)1592.

701 M. Valderrama, M. Scotti, R. Ganz, L.A. Oro, F.J. Lahoz, C. Foces-Foces and F.H. Cano, J. Organometal. Chem., 288(1985)97.

702 B. Bittersmann, K. Hildenbrand, A. Cervilla and P. Lahuerta, J. Organometal. Chem., 287(1985)255.

703 J. Jeffery, E.J. Probitts and R.J. Mawby, J. Chem. Soc., Dalton Trans., (1984)2423.

704 A. Salzer and C. Täschler, J. Organometal. Chem., 294(1985)261.

705 A. Borrini, P. Diversi, G. Ingrosso, A. Lucherini and G. Serra, J. Mol. Catal., 30(1985)181 (Chem. Abstr., 103(1985)122676r).

706 H. Werner, H.J. Scholz and R. Zolk, Chem. Ber., 118(1985)4531.

707 M. Scotti, M. Valederrama, R. Ganz and H. Werner, J. Organometal. Chem., 286(1985)399.

708 G. Herberich and H. Ohst, Chem. Ber., 118(1985)4303.

709 S.A. MacLaughlin, R.C. Murray, J.C. Dewan and R.R. Schrock, Organometallics, 4(1985)796.

710 J.M. Kisenyi, J.A. Cabeza, A.J. Smith, H. Adams, G.J. Sunley, N.J.S. Salt and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1985)770.

711 W.A. Herrmann and W. Kalcher, Chem. Ber., 118(1985)3861.

712 A.C. Broy, M. Green, D.R. Hankey, J.A.K. Howard, O. Johnson and F.G.A. Stone, J. Organometal. Chem., 281(1985)C12.

713 L.J. Farrugia, J.C. Jeffrey, C. Marsden and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985)645.

714 R.P. Hughes, A.L. Rheingold, W.A. Herrmann and J.L. Hubbard, J. Organometal. Chem., 286(1985)361.

715 L.A. Oro, D. Carmona, M.P. Lamata, C. Foces-Foces and F.H. Cano, Inorg. Chim. Acta, 97(1985)19.

716 J.D. Fotheringham and T.A. Stephenson, J. Organometal. Chem., 284 (1985)C12.

717 V.V. Litvak, L.I. Goryunov and V.D. Shteingarts, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1985)132 (Chem. Abstr., 103(1985)22227b).

718 W.J. Bowyer and W.E. Geiger, J. Am. Chem. Soc., 107(1985)5657.

719 A.G. Orpen and N.G. Connelly, J. Am. Chem. Soc., 107(1985)1310.

720 M.J. Freeman, A.G. Orpen, N.G. Connelly, I. Manners and S.J. Raven, J. Chem. Soc., Dalton Trans., (1985)2283.

721 C. Cauletti, C. Furlani, C. Puliti and H. Werner, J. Organometal. Chem., 289(1985)417.

722 T.M. Gilbert and R.G. Bergman, J. Am. Chem. Soc., 107(1985)3502.

723 T.M. Gilbert, F.J. Hollander and R.G. Bergman, J. Am. Chem. Soc., 107(1985)3508.

724 T.M. Gilbert and R.G. Bergman, J. Am. Chem. Soc., 107(1985)6391.

725 L.J. Newman and R.G. Bergman, J. Am. Chem. Soc., 107(1985)5314.

726 L.A. Oro, D. Carmona, M.P. Garcia, F.J. Lahoz, J. Reyes, C. Foces-Foces and F.H. Cano, J. Organometal. Chem., 296(1985)C43.

727 J.W. Faller, R.H. Crabtree and A. Habib, Organometallics, 4(1985)929.

728 H.A. Boyter, Jr., R.G. Swisher, E. Sinn and R.N. Grimes, Inorg. Chem., 24(1985)3810.

729 Z.-T. Wang, E. Sinn and R.N. Grimes, Inorg. Chem., 24(1985)826.

730 Z.-T. Wang, E. Sinn and R.H. Grimes, Inorg. Chem., 24(1985)834.

731 C.T. Brewer and R.N. Grimes, J. Am. Chem. Soc., 107(1985)3552.

732 T.L. Venable, C.T. Brewer and R.N. Grimes, Inorg. Chem., 24(1985)4751.

733 J.J. Briguglio and L.G. Sneddon, Organometallics, 4(1985)721.

734 R.P. Micciche, P.J. Carroll and L.G. Sneddon, Organometallics, 4(1985)1619.

735 T.P. Hanusa, J.C. Huffman, T.L. Curtis and L.J. Todd, Inorg. Chem., 24(1985)787.

736 J.A. Walker, C.B. Knobler and M.F. Hawthorne, Inorg. Chem., 24(1985) 2688.

737 R.E. King, III, D.C. Busby and M.F. Hawthorne, J. Organometal. Chem., 279(1985)103.

738 P.E. Behnken, T.B. Marder, R.T. Baker, C.B. Knobler, M.R. Thompson and M.F. Hawthorne, J. Am. Chem. Soc., 107(1985)932.

739 J.D. Hewes, M. Thompson and M.F. Hawthorne, Organometallics, 4(1985) 13.

740 D.M. Speckman, C.B. Knobler and M.F. Hawthorne, Organometallics, 4(1985)426.

741 D.M. Speckman, C.B. Knobler and M.F. Hawthorne, Organometallics, 4(1985)1692.

742 X.L.R. Fontaine, H. Fowkes, N.N. Greenwood, J.D. Kennedy and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1985)1722.

743 J. Bould, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, J. Chem. Soc., Dalton Trans., (1985)1843.

744 J. Bould, N.N. Greenwood and J.D. Kennedy, J. Chem. Soc., Dalton Trans., (1984)2477.

745 M.A. Hanratty, J.L. Beauchamp, A.J. Illes and M.T. Bowers, J. Am. Chem. Soc., 107(1985)1788.

746 C.J. Cassady and B.S. Freiser, J. Am. Chem. Soc., 107(1985)1566.

747 C.J. Cassady and B.S. Freiser, J. Am. Chem. Soc., 107(1985)1573.

748 M. Lombarski and J. Allison, Int. J. Mass Spectrom. Ion Processes, 65(1985)31 (Chem. Abstr., 104(1986)68367w).

749 A. Tsarbopoulos and J. Allison, J. Am. Chem. Soc., 107(1985)5085.

750 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107(1985)1581.

751 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107(1985)4373.

752 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107(1985)67.

753 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107(1985)5870.

754 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107(1985)2605.

755 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107(1985)5876.

756 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107(1985)72.

757 M.A. Hanratty, C.M. Paulsen and J.L. Beauchamp, J. Am. Chem. Soc., 107(1985)5074.

758 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107(1985)7399.

759 D.B. Jacobson and B.S. Freiser, Organometallics, 4(1985)1048.

760 G.W. Dillow, I.K. Gregor and M. Guilhaus, J. Organometal. Chem., 294(1985)131.

761 V.K. Bel'skii, B.M. Bulychev and A.V. Aripovskii, Koord. Khim., 11(1985)540 (Chem. Abstr., 103(1985)142150t).

762 D. Fenske, J. Hachgenei and J. Ohmer, Angew. Chem. Int. Ed. Engl., 24(1985)706.

763 D. Fenske, J. Ohmer and J. Hachgenei, Angew. Chem. Int. Ed. Engl., 24(1985)993.

764 D.G. Holah, A.N. Hughes, S. Maciaczek, V.R. Magnuson and K.O. Parker, Inorg. Chem., 24(1985)3956.

765 F. Cecconi, C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, and M. Bacci, J. Chem. Soc., Chem. Commun., (1985)731.

766 M. Peruzzini and P. Stoppioni, J. Organometal. Chem., 288(1985)C44.

767 M. DiVaira, L. Niccolai, M. Peruzzini and P. Stoppioni, Organometallics, 4(1985)1888.

768 M. DiVaira, F. Mani, S. Moneti, M. Peruzzini, L. Sacconi and P. Stoppioni, Inorg. Chem., 24(1985)2231.

769 C. Bianchini, C.A. Ghilardi, A. Meli and A. Orlandini, J. Organometal. Chem., 286(1985)259.

770 C. Bianchini, C. Mealli, A. Meli and M. Sabat, J. Chem. Soc., Chem. Commun., (1985)1024.

771 C. Bianchini, C. Mealli, A. Meli and M. Sabat, J. Am. Chem. Soc., 107(1985)5317.

772 C. Bianchini, C. Mealli, A. Meli and M. Sabat, Organometallics, 4(1985)421.

773 F. Bachechi, J. Ott and L.M. Venanzi, J. Am. Chem. Soc., 107(1985) 1760.

774 C. Bianchini, D. Masi, C. Mealli, A. Meli and M. Sabat, Organometallics, 4(1985)1014.

775 B.R. James and D. Mahajan, J. Organometal. Chem., 279(1985)31.

776 A.J. Kunin, E.J. Nanni and R. Eisenberg, Inorg. Chem., 24(1985)1852.

777 R.J. McNair, P.V. Nilsson and L.H. Pignolet, Inorg. Chem., 24(1985) 1935.

778 D.P. Krut'ko, A.B. Permin, V.S. Petrosyan and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1985)909.

779 M.F. Meidine, C.J. Meir, S. Morton and J.F. Nixon, J. Organometal. Chem., 297(1985)255.

780 H. Suzuki, S. Matsuura, Y. Moro-oka and T. Ikawa, J. Organometal. Chem., 286(1985)247.

781 M.L. Deem, Inorg. Chim. Acta, 103(1985)L19.

782 S.-M. Peng, K. Peters, E.-M. Peters and A. Simon, Inorg. Chim. Acta, 101(1985)L35.

783 G. Pimblett, C.D. Garner and W. Clegg, J. Chem. Soc., Dalton Trans., (1985)1977.

784 H. Bauer, G.M. Sheldrick, U. Nagel and W. Beck, Z. Naturforsch., 40b(1985)1237.

785 V. Alteparmakian, P. Mura, B.G. Olby and S.D. Robinson, Inorg. Chim. Acta, 104(1985)L5.

786 L.F. Rhodes and K.G. Caulton, J. Am. Chem. Soc., 107(1985)259.

787 R.H. Crabtree and M. Lavin, J. Chem. Soc., Chem. Commun., (1985)1661.

788 L. Garlaschelli, S.I. Khan, R. Bau, G. Longoni and T.F. Koetzle, J. Am. Chem. Soc., 107(1985)7212.

789 H. Felkin. T. Fillebeen-Khan, R. Holmes-Smith and L. Yingrui, Tetrahedron Lett., 26(1985)1999.

790 A. Albinati, H. Lehner and L.M. Venanzi, Inorg. Chem., 24(1985)1483.

791 A.L. Casalnuovo, T. Laska, P.V. Nilsson, J. Olofson, L.H. Pignolet, W. Bos, J.J. Bour and J.J. Steggerda, Inorg. Chem., 24(1985)182.

792 A.L. Casalnuovo, T. Laska, P.V. Nilsson, J. Olofson and L.H. Pignolet, Inorg. Chem., 24(1985)233.

793 A.L. Casalnuovo, J.A. Casalnuovo, P.V. Nilsson and L.H. Pignolet, Inorg. Chem., 24(1985)2554.

794 L.F. Rhodes, J.C. Huffman and K.G. Caulton, J. Am. Chem. Soc., 107(1985)1759.

795 A.P. Ginsburg and C.R. Sprinkle, J. Am. Chem. Soc., 107(1985)5550.

796 S. Sakaki, K. Morokuma and K. Ohkubo, J. Am. Chem. Soc., 107(1985) 2686.

797 E.B. Boyar and S.D. Robinson, J. Chem. Soc., Dalton Trans., (1985)629.

798 A. Naito, D.L. Sastry and C.A. McDowell, Chem. Phys. Letters, 115 (1985)19.

799 A.P. Ginsburg, R.L. Harris, B. Batlogg, J.H. Osborne and C.R. Sprinkle, Inorg. Chem., 24(1985)4192.

800 T.T. Johnson, S.D. Phillips and G.A. Crosby, Chem. Phys. Letters, 114(1985)388.

801 R.H. Crabtree, B.E. Segmuller and R.J. Uriarte, Inorg. Chem., 24 (1985)1949.

802 S. Komiya, R.S. Srivastava, A. Yamamoto and T. Yamamoto, Organometallics, 4(1985)1504.

803 M.G. Vinogradov, A.B. Tuzikov and G.I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., (1985)356.

804 T. Nakayama and H. Kanai, Bull. Chem. Soc. Jpn., 58(1985)16.

805 N. Kameda and M. Hattori, Kobunshi Ronbunshu, 42(1985)485 (Chem. Abstr., 103(1985)178692k).

806 A. Yanagawa, Y. Suzuki, I. Anazawa, Y. Tagaki and S. Yada, J. Mol. Catal., 29(1985)41 (Chem. Abstr., 102(1985)184547n).

807 U. Gessner and A. Heesing, Chem. Ber., 118(1985)2593.

808 I. Villax and P. Page, Actas Simp. Iberoam. Catal., 9th, 1(1984)446 (Chem. Abstr., 102(1985)184881s).

809 M. Röper, E.O. Elvevoll and M. Luetgendorf, Erdöl Kohle, Erdgas, Petrochem., 38(1985)38 (Chem. Abstr., 102(1985)133950f).

810 R. Bas, Y. Sasson and J. Blum, J. Mol. Catal., 26(1984)327 (Chem. Abstr., 102(1985)131637k).

811 K. Felföldi and M. Bartok, J. Organometal. Chem., 297(1985)C37.

812 L.I. Zakharkin, N.Yu. Krainova, I.V. Pisareva and V.A. Antonovich, Synth. React. Inorg. Met.-Org. Chem., 15(1985)655 (Chem. Abstr., 104(1986)68912r).

813 R.H. Fish, A.D. Thormondsen and H. Heinemann, J. Mol. Catal., 31 (1985)191 (Chem. Abstr., 103(1985)214508r).

814 I. Minami, I. Shimizu and J. Tsuji, J. Organometal. Chem., 296(1985) 269.

815 J. Podlaha and M. Prochazka, Collect. Czech. Chem. Commun., 50(1985) 1274 (Chem. Abstr., 103(1985)141199d).

816 S. Sato, I. Matsuda and Y. Izumi, Tetrahedron Lett., 26(1985)1527.

817 S. Sato, I. Matsuda and Y. Izumi, Tetrahedron Lett., 26(1985)4229.

818 K. Osakada, K. Matsumoto, T. Yamamoto and A. Yamamoto, Organometallics, 4(1985)857.

819 G. Valentini, G. Sbrana, G. Braca and P. Da Prato, J. Catal., 96 (1985)41.

820 R. Becker, H. Brunner, S. Makboobi and W. Wiegrebe, Angew. Chem. Int. Ed. Engl., 24(1985)995.

821 B.R. James and C.G. Young, J. Organometal. Chem., 285(1985)321.

822 D.A. Evans, M.M. Morrissey and R.L. Dow, Tetrahedron Lett., 26(1985) 6005.