COBALT, RHODIUM AND IRIDIUM

ANNUAL SURVEY COVERING THE YEAR 1980 *

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CONTENTS

INTRODUCTION

The present author intends to retain the major features of the format used previously in this Survey. One change is the addition of a section specifically covering doctoral dissertations. Articles appearing in less-available journals have been covered in abstract form only and are so indicated in the list of references while those reporting only the results of crystal structure studies have not been included. Finally, although most abbreviations will be explained as they occur, because of the prevalence of the π-cyclopentadienyl (η^5-C_5H_5) ligand the abbreviation "cp" for it will be given here.

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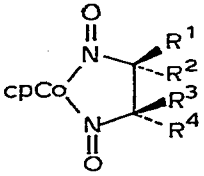
*Previous review see page 1.

A number of reviews dealing at least in part with cobalt, rhodium and iridium have appeared during the course of the year. Besides a general review of complexes of the cobalt group containing metal-carbon σ-bonds (ref. 1) there are discussions of carbon monoxide insertion into M-C bonds (ref. 2) and of complexes containing metallated phosphine ligands (ref. 3). The reactions of carbene complexes (ref. 4) and the synthesis and chemistry of zerovalent isocyanide complexes (ref. 5a) have been covered. The latter review provides a useful update to Malatesta's monograph on the same topic (ref. 5b). A substantial number of reviews on carbonyl compounds have appeared including those covering complexes with μ_2-carbonyl groups (ref. 6), the use of cobalt carbonyls in organic synthesis (refs. 7, 8), the chemistry of metal carbonylate species in liquid ammonia (ref. 9), the synthesis and properties of mixed metal carbonyl clusters (ref. 10), organometallic complexes containing chiral metal atoms (ref. 11), the synthesis and characterization of large carbonyl clusters, particularly those of rhodium (ref. 12), and the chemistry of selected cluster complexes most of which contain mainly carbonyl ligands (refs. 13, 14). Also on this topic but dealing more with complexes containing a variety of ligands besides carbon monoxide are reviews on rhodium and iridium complexes of bulky phosphines (ref. 15), and the photochemistry of hydride complexes (ref. 16).

Under the heading of alkene complexes are reviews of olefin hydroformylation using cobalt and rhodium catalysts (refs. 17-19), homogeneously catalyzed olefin hydrogenation (ref. 20), and metal-catalyzed carbon-carbon bond formation (ref. 21). Also reviewed are cationic rhodium diolefin complexes (ref. 22). Miscellaneous topics reviewed are complexes of multidentate phosphine ligands (ref. 23), the use of trimethylphosphine cobalt complexes as catalysts (ref. 24), the use of boron heterocycles as ligands (ref. 25), cobalt carbaboranes (ref. 26), and organoimido complexes (ref. 27).

DISSERTATIONS

Two dissertations report studies on the chemistry of cyclopentadienyl cobalt alkyl complexes. The compounds $[cpCo(CO)R]_2$ (R = Et, CH_2CF_3) were prepared and on thermolysis produced good yields of dialkyl ketones. Also the reaction of $[cpCo(CO)_2]$ or $[cpCo(NO)]_2$ with olefins in the presence of nitric oxide yielded the dinitroso complexes [1] which on low temperature reduction



[1]

with $LiAlH_4$ gave good yields of the corresponding diamines (ref. 28). The second one reports that $[cpCoMe_2(PPh_3)]$ undergoes substitution of PPh_3 by PMe_3 by a dissociative process. Reaction of the PPh_3 complex with CO yields $[cpCo(CO)(Me)_2]$ which upon thermolysis gives acetone via the intermolecular reaction of the acyl derivative $[cpCo(COMe)(Me)]$. $[cpCoMe_2(PPh_3)]$ undergoes intermolecular exchange of methyl groups and reacts with ethylene to yield propene. Labelling studies demonstrate the transfer of an intact methyl group to the olefin which is interpreted as a confirmation of the generally accepted insertion mechanism for Ziegler-Nalta olefin polymerization and an argument against recently proposed carbene mechanisms. Reactions of $[cpCo(PPh_3)I_2]$ with $Li(CH_2)_4Li$ produces the cobaltacyclopentane complex $[cp\overline{CoCH_2CH_2CH_2C}H_2(PPh_3)]$ (ref. 29).

The reaction of $[RhMeI_2(PPh_3)_2]$ with vinyl, alkynyl, and aryl mercurials occurs stoichiometrically to yield methyl-substituted olefins, acetylenes, and arenes. However $[RhCl(PPh_3)_3]$ catalyzes the reaction of phenylmercuric chloride with vinyl bromide to give styrene. Also $[Rh(CO)_2Cl]_2$ in the presence of LiCl and CO catalyzes the stereospecific formation of divinyl ketones from vinylmercurials (ref. 30).

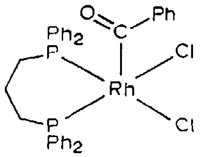
The electrochemical reduction of $[Rh(diphos)_2]^+$ (diphos = 1,2-bis(diphenylphosphino)ethane) in various solvents yields $[RhH(diphos)_2]$ by what was established as an ECE mechanism. The same reaction in the presence of cyclohexane also generated $[RhH(diphos)_2]$ and products derived from the cyclohexyl radical indicating the ability of the Rh(0) complex to activate saturated C-H bonds. The complex $[Co(diphos)_2]^+$ was also studied (ref. 31).

A study of the asymmetric hydrogenation of prochiral olefins using chiral rhodium catalysts has been made. One ligand used was a bidentate phosphinite derived from resolved 1,1'-bi-2-naphthol where the chirality derives from atropisomerism rather than from the presence of a chiral carbon or phosphorus atom (ref. 32). Three studies of the synthesis of a variety of metallocarbaboranes have been reported. Reaction of $[(COD)Ir(PPh_3)_2]^+$ (COD = 1,5-cyclooctadiene) with the nido carbaborane anions $[7\text{-}R\text{-}7,8\text{-}C_2B_9H_{11}]^-$ (R = H, Me, Ph) yields simple salts of the two ions. Thermolysis converts these salts into the hydrido iridium complexes closo-$[3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}1\text{-}R\text{-}3,1,2\text{-}IrC_2B_9H_{10}]$ which are fluxional, the major process appearing to be rotation of the $IrH(PPh_3)_2$ unit about the pentagonal face of the carbaborane cage. Hydrogenation of the salts produces in addition to the closo complexes a second complex in which a cis-$IrH_2(PPh_3)_2$ moiety is attached to a nido-7,8-$C_2B_9H_{10}$ cage via two Ir-H-B bridge bonds (ref. 33). A closely related study of the analogous rhodium carbaboranes closo-$[3,3\text{-}L_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ (L = PMe_2Ph, PEt_3; L_2 = diphos), their fluxional behavior and catalytic properties is also available (ref. 34). The third dissertation describes the synthesis and structures of several cobaltaboranes, -carbaboranes and thiaboranes prepared by metal-atom vapor techniques (ref. 35). The synthesis of the A-frame complexes $[Rh_2(CO)_2(\mu\text{-}Y)(DPM)_2]$ and $[Ir_2(CO)_2(\mu\text{-}S)(DPM)_2]$ (Y = S^{2-}, Se^{2-}, $PHC_6H_{11}^-$; DPM = bis(diphenylphosphino)methane) has been reported. Also in this dissertation is the preparation of $[Rh_2(CO)_2(DPM)_2]$ which is shown to protonate to give $[Rh_2(CO)_2(\mu\text{-}H)(DPM)_2]PF_6$ and to further react with carbon monoxide to give $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2]PF_6$ which also functions as a catalyst for the water-gas shift reaction (ref. 36). Structural and ^{31}P NMR studies on a number of aryldiazo derivatives of rhodium and iridium have been reported (ref. 37). Finally the synthesis of fac- and mer-$[IrH_3(CO)(PPh_3)_2]$ and a study of the interconversion of these isomers has appeared. It is thought this process proceeds via the successive reductive elimination and oxidative addition of dihydrogen. Evidence is presented to suggest the novel trans oxidative addition of dihydrogen (ref. 38).

Metal-carbon σ-bonded complexes

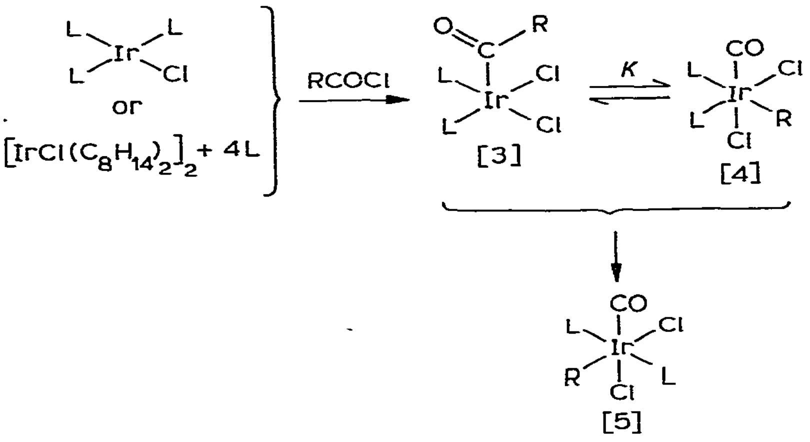
Relatively few reports of simple monomeric complexes of this type have appeared. Reduction of $[Co(acac)_3]$ (acac = acetylacetonate) with triphenylaluminum in the presence of triethylphosphine yields $[CoPh(acac)(PEt_3)_2]$ which is reported to be rather unreactive towards carbon monoxide (ref. 39). A similar complex $[Co(C_6F_5)_2(PEt_3)_2]$ can be got via the "active metal powder" route by treating lithium-reduced cobalt with pentafluoroiodobenzene followed by triethylphosphine (ref. 40). A related reaction of perfluoroalkyl iodides with powdered cobalt and SO_2 in N,N- dimethylformamide provides a route to perfluoroalkyl sulfinates. The reaction is considered to proceed via oxidative addition of the alkyl iodide to a Co-SO_2 complex followed by SO_2 insertion into the Co-C bond (ref. 41).

Thermal decarboxylation of $[Rh(CO)(O_2CR)(PPh_3)_2]$ (R = C_6F_5, C_6Cl_5, C_6F_4H, $C_6F_3H_2$, p-$MeOC_6F_4$) in pyridine yields aryl complexes $[Rh(R)(CO)(PPh_3)_2]$. The reaction rate decreased with decreasing fluorine substitution (ref. 42). The diynes o- and p-$C_6H_4(C\ CH)_2$ undergo oxidative addition to trans-$[Rh(CO)ClL_2]$ (L = PPh_3, $P(C_6H_4F)_3$) followed by loss of HCl in the presence of diethylamine to yield the acetylide complexes trans $[Rh(CO)(C\equiv CR)L_2]$ (R = o- or p-$C_6H_4C\ CH$) in which only one alkyne substituent has reacted (ref. 43). A number of further examples of oxidative addition reactions have been reported. From $[Rh(dppp)_2]Cl$ (dppp = 1,3-bis(diphenylphosphino)propane) and benzoyl chloride at 190°C the pentacoordinate acyl [2] is obtained which shows no tendency to decarbonylate or



[2]

to undergo migration of the phenyl group to the metal in contrast to what has been found for the triphenylphosphine analog. This is thought to be the result of the presence of the chelating diphosphine ligand which prevents an open site *cis* to the acyl from being made available for the migration (ref. 44). An example of this migration is found in the reaction of acid chlorides with $[IrCl(PMePh_2)_3]$ in dichloromethane (Scheme I). For R = Me only the six-coordinate alkyl [4] is seen while for R = Et or Pr^n both acyl [3] and alkyl [4] are observed in solution. Over longer periods, further isomerization to [5] occurs. The observation that the latter process is accelerated by addition of methanol or perchlorate ion suggests that it occurs via rearrangement of a five-coordinate intermediate formed by chloride loss from [4]. Interestingly the product with R = Pr^n can also be formed by reaction of $IrCl(PMePh_2)_3$ with Pr^iCOCl (ref. 45). Paraformaldehyde reacts with $[Ir(PMe_3)_4]PF_6$ to give *cis*-$[IrH(CHO)(PMe_3)_4]PF_6$ which

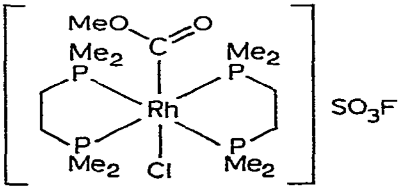


L = $PMePh_2$

R = Me, Et, Pr^n

Scheme 1

on heating in pyridine provides a low yield of $[Ir(CO)(PMe_3)_4]PF_6$ and hydrogen presumably via hydride migration from the formyl ligand to the metal followed by reductive elimination of hydrogen. Reduction of the formyl ligand with BH_3 gives the methyl complex *cis*—$[IrH(Me)(PMe_3)_4]PF_6$. Related formyl complexes *mer*-$[IrH(CHO)Cl(PMe_3)_3]$ and *fac*-$[IrH(CHO)(Me)(PMe_3)_3]$ can be prepared from paraformaldehyde and $[IrCl(cyclooctene)(PMe_3)_3]$ and $[IrMe(PMe_3)_4]$ respectively (ref. 46). In a somewhat different vein, the carbon dioxide complex $[IrCl(CO_2)(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) can be alkylated with methylfluorosulfonate in toluene to give the octahedral complex [6] (ref. 47).



[6]

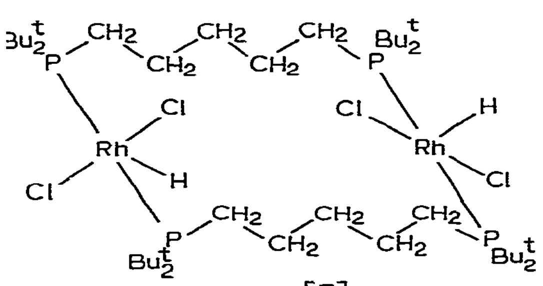
The mechanisms of several reactions involving oxidative addition to Rh(I) and Ir(I) centers continue to be studied. In the decarbonylation of aldehydes by $[RhCl(PPh_3)_3]$, a significant primary isotope effect (k_H/k_D) of 1.86 was observed in the reaction with protio and deuterio phenylacetaldehyde. Crossover experiments using mixtures of $PhCH_2CDO$ and p-tolylacetaldehyde or exo- and endo-5-norbornene-2-carboxaldehyde showed that no crossover occurred. These results indicate that the reaction involves concerted processes which are intramolecular in aldehyde for each step. No evidence for radical processes was found (ref. 48). The reactions of methyl iodide and methyl p-toluenesulfonate with a variety of transition metal nucleophiles including $[Ir(CO)ClL_2]$ (L = PPh_3, PMe_2Ph), $[Rh(CO)Cl(PPh_3)_2]$, $[cpM(CO)PPh_3]$ (M = Co, Rh, Ir) and $[Co(CO)_4]^-$ have been studied. Reasonable linear correlations were observed between log k_{MeI} and log $k_{p\text{-}tolSO_3Me}$ and between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reactions suggesting a common mechanism for both sets. However since a variety of solvents were used and since the corresponding parameters for the reaction of $[Co(CN)_5]^{3-}$ with the same substrates (which is a radical reaction) also fall in the same ranges it is suggested that these results be viewed with caution and that activation parameters alone should not be considered as diagnostic of a particular mechanism in oxidative addition reactions of this sort (ref. 49). Finally, an extensive study of the oxidative addition of alkyl halides to $[Ir(CO)Cl(PMe_3)_2]$ has appeared. Using a variety of optically active substrates it was shown that in all cases, complete loss of stereochemistry at carbon occurred upon oxidative addition. Further studies investigating the effects of traces of oxygen, radical initiators and inhibitors, the structure of the alkyl halide, the identity of the halogen, the electron density on the metal and the presence or absence of light lead to the conclusion that unactivated alkyl halides (except methyl halides), vinyl halides, aryl halides and α-haloesters all react by a radical chain mechanism (Scheme II).

$$\begin{aligned}
R\cdot + Ir^{I} &\longrightarrow R\text{-}Ir^{II}\\
R\text{-}Ir^{II} + RX &\longrightarrow [R\text{-}Ir^{II}\text{-----}XR]\\
[R\text{-}Ir^{II}\text{-----}XR] &\longrightarrow [R\text{-}Ir^{III}\text{-----}XR^{-}]\\
[R\text{-}Ir^{III}\text{-----}XR\cdot^{-}] &\longrightarrow [R\text{-}Ir^{III}\text{-----}X^{-}\text{-----}R\cdot]\\
[R\text{-}Ir^{III}\text{-----}X^{-}\text{-----}R\cdot] &\longrightarrow R\text{-}Ir^{III}\text{-}X + R\cdot
\end{aligned}$$

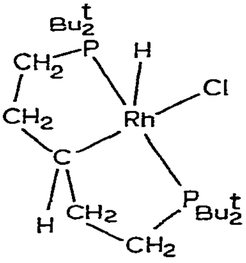
Scheme II

Since the rate depends on X in the order I>>Br>Cl it is thought that the third step is rate determining. Still unresolved is the nature of the initiation step in the absence of oxygen or radical sources. Possible sources of the initiation could be traces of Ir(II) or Ir(0) species. By contrast, the oxidative addition of methyl, allyl and benzyl halides appears not to involve radicals and an S_N2 mechanism is considered to be operative (ref. 50).

In a continuation of studies on complexes of bulky di(tertiary)-phosphines the reaction of 1,5-bis(di-tert-butylphosphino)pentane (L_2) with hydrated rhodium (III) chloride in refluxing ethanol provides a mixture of the ligand-bridged dimer $[RhHCl_2(L_2)]_2$ ([7]), the metallated complex [8] and a complex containing the dehydrogenated ligand [9]. Treatment of [7] with α-picoline converted it to [8] while treatment with CO and sodium methoxide yielded the metallated complex [10]. Complex [8] is fluxional at room temperature and shows no hydride resonance until cooled to -62°C.



[7]



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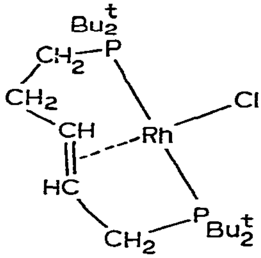

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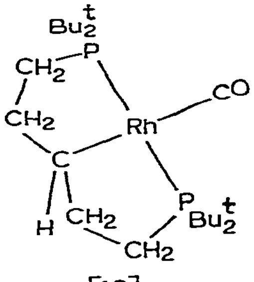
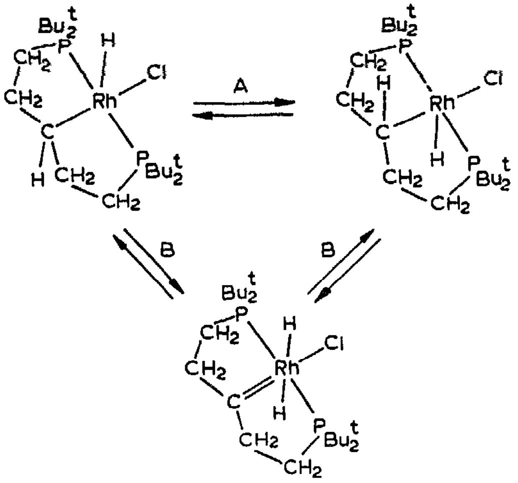


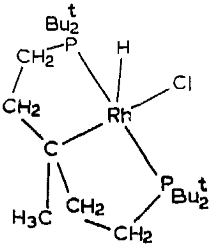
[10]

Two possible processes to explain the fluxionality are detailed in Scheme III. Support for this scheme was obtained from the use of the related ligand 1,5-bis(di-tert-butylphosphino)-3-methylpentane in an analogous reaction. The initial product is the dimeric hydride $[RhHCl_2(L_2)]_2$ with a structure analogous to [7] which exists in six rotameric forms in solution. Treatment

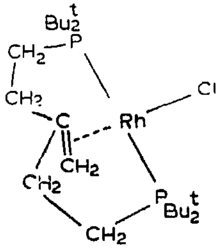


Scheme III

of the dimer with α-picoline gives the metallated complex [11] which is not fluxional and which on refluxing in isopropanol is converted into the exocyclic methylene complex [12]. In contrast, refluxing hydrated rhodium (III) chloride with 1,6-bis(di-tert-butylphosphino)hexane leads directly to the dehydrogenated complex [13]. A small amount of the isomer with *cis* stereochemistry about the double bond is also found. Treatment of [13] with carbon monoxide and sodium tetraphenylborate leads to replacement of chloride by carbonyl with the double bond in the ligand chain remaining coordinated. Finally, reaction of hydrated rhodium (III)

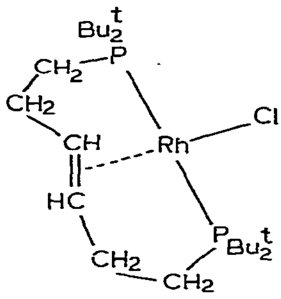


[11]



[12]

chloride with trans-1,4-bis(di-tert-butylphosphino)but-2-ene yields the olefinic complex [14] (ref. 51).



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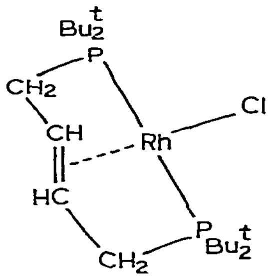
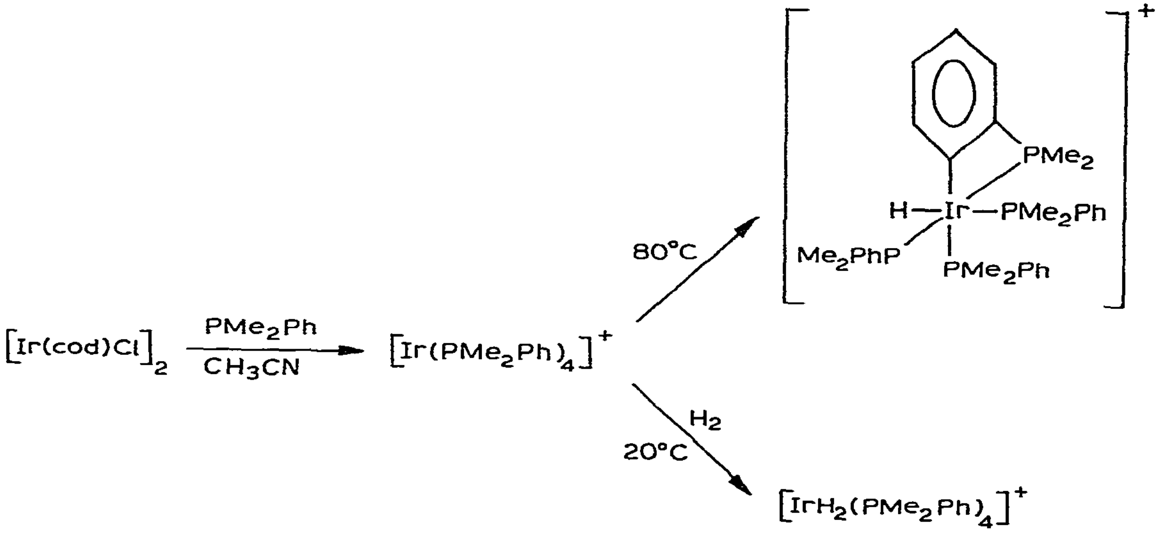


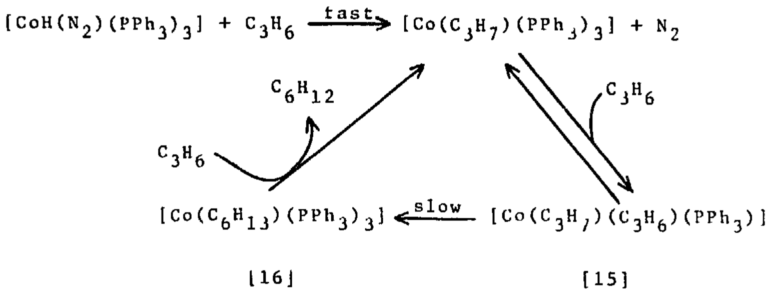
[14]

Ligand metallation is also observed in an iridium system as outlined in Scheme IV (COD = 1,5-cyclooctadiene). The structure of the metallated complex has been determined (ref. 52).

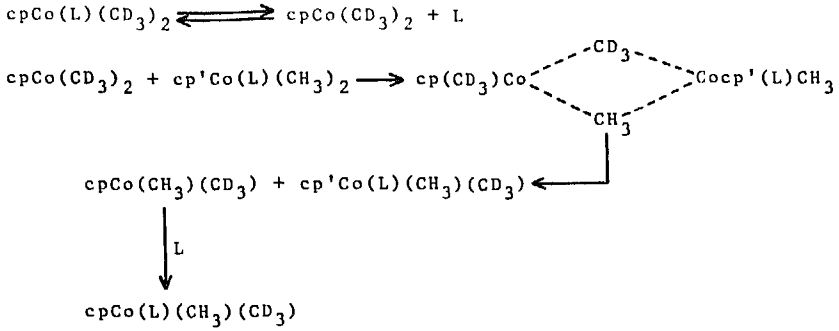


Scheme IV

Several studies in which metal-carbon σ-bonds have been identified or implicated in catalytic or related systems have been described. The dimerization of propene catalyzed by [CoH(N_2)(PPh_3)$_3$] yields a mixture of linear and branched olefinic dimers. The proposed mechanism is depicted in Scheme V. The distribution of products is determined by whether [15] contains an n- or an i-propyl group and the direction of insertion of propene in the conversion of [15]→[16] (ref. 53). In a continuation of work on the chemistry of [cpCo(L)Me_2](L = PPh_3, PMe_3), the mechanism of methyl group exchange between [cpCo(L)(CD_3)$_2$] and [cp'Co(L)(CH_3)$_2$] (cp' = $CH_3C_5H_4$ has been elucidated. Phosphine dissociation from one center has been demonstrated to be a necessary initial step with subsequent steps involving the formation of methyl-bridged dimers (Scheme VI) (ref. 54). A kinetic study of the reaction of [Co(CO)$_4$]$^-$ with



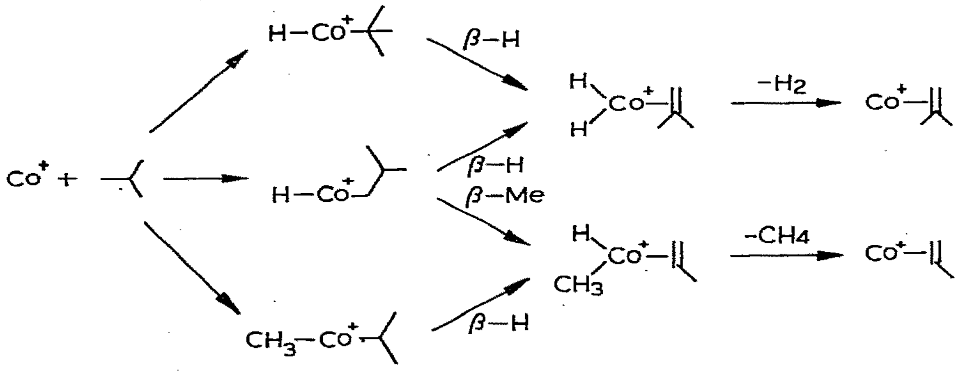
Scheme V



Scheme VI

benzyl chloride, which produces $[PhCH_2Co(CO)_4]$, showed that the rate was very sensitive to the ability of the solvent to solvate the cation and to its ability to assist chloride loss. It was concluded that a tight ion pair, $[N^+,Co(CO)_4^-]$ is a kinetically important species and that solvent assisted chloride loss may be more important than nucleophilic attack by the carbonylate ion (ref. 55). Moderate yields (40-50%) of 2-methylcyclopentanone can be obtained via the cyclization of trans-hex-4-enal mediated by $[RhCl(PPh_3)_3]$ although at high conversion considerable decarbonylation occurs. Under an ethylene atmosphere the system shows modest catalytic activity. By far the major product at low conversion from the reaction with trans-hex-4-enal-1-d is that resulting from syn addition of the aldehyde function to the double bond. The mechanism is proposed to involve oxidative addition of the aldehyde C-H bond to the rhodium followed by hydrogen transfer to C-5 and subsequent expulsion of rhodium from the resulting metallacyclohexanone with accompanying ring closure (refs. 56, 57). A variety of Rh(I) complexes catalyze the conversion of vinyl mercurials and carbon monoxide to divinyl ketones. The most effective system is $[Rh(CO)_2Cl_2]^-$ operating at 25°C and 1 atm. of CO. Yields are 60-96%. Important steps in the proposed mechanism are the oxidative addition of an Hg-C bond to give a vinyl-rhodium species followed by CO insertion to yield an acyl complex. Incorporation of a second vinyl group followed by reductive elimination produces the divinyl ketone (ref. 58). Thermolysis of $[RhClL_3]$ (L = triarylphosphine) yields exclusively 4,4'-biphenyls. Crossover experiments show that the coupling reaction is intermolecular. The insensitivity to radical sources or scavengers and the rate enhancement by electron-donating substituents on the aryl groups are interpreted in terms of a non-radical oxidative addition process. The intermediacy of a Rh-Ar species is suggested by the observation that in the presence of styrene, some arylated styrene is produced (ref. 59). The hydrosilylation of styrene by MeR_2SiH (R = Et, Pr^i, Bu^i) catalyzed by $[RhCl(PPh_3)_3]$ has been studied. Changes in the distribution of the major products, $PhCH(SiR_2Me)CH_3$, $PhCH_2CH_2SiR_2Me$, and trans-$PhCH=CHSiR_2Me$ with changes in R are attributed to the effect of steric factors on the relative stabilities of the intermediates presumed to contain the $MeR_2SiRhCH(CH_3)Ph$ and $MeR_2SiRhCH_2CH_2Ph$ moieties (refs. 60,61).

The unstable species $HCoCH_3$ has been identified in mixtures of cobalt and methane which were codeposited on a cold surface and then irradiated at wavelengths shorter than 360 nm. Tentative evidence for the formation of $Co(CH_3)_2$ following prolonged irradiation was also found (ref. 62). An ion beam study of the reaction of Co^+ with isobutane showed the results presented in Scheme VII.



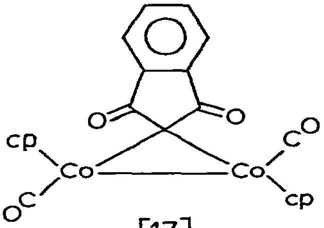
Scheme VII

When isopentane was used, only $CoC_4H_8^+$ and $C_4H_9^+$ were observed which was interpreted to mean that carbene or metallocyclobutane intermediates were unimportant (ref. 63).

A complete single crystal EPR and magnetic susceptibility study of *trans*-$[Co(PEt_2Ph)_2(mesityl)_2]$ has been reported. The results indicate a considerable π-acceptor role for the phosphine ligands (ref. 64).

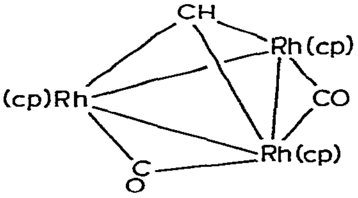
The heterobimetallic complex *mer*-$[IrH(PEt_3)_3(\mu\text{-}H)_2PtPh(PEt_3)]BPh_4$ is formed by treating *trans*-$[PtPh(Cl)(PEt_3)_2]$ with $AgBF_4$ in methanol followed by $[IrH_5(PEt_3)_2]$ and $NaBPh_4$. The structure of the complex was also determined (ref. 65).

Considerable interest has been shown in the chemistry of complexes containing bridging methylene groups. Reaction of $[cpCo(CO)_2]$ with 2-diazo-1,3-dioxoindane in refluxing benzene yields [17] (ref. 66). A similar route has been used to prepare the related rhodium complexes $[cp^*_2Rh_2(CO)_2(\mu\text{-}CRR')]$ ($cp^* = C_5Me_5$; R = R' = H,Ph; R = H, R' = Me, COEt) from $[cp^*_2Rh_2(CO)_2]$ and the corresponding diazo compounds. On heating, $[cp^*_2Rh_2(CO)_2(\mu\text{-}CPh_2)]$ loses CO to form $[cp^*_2Rh_2(\mu\text{-}CO)(\mu\text{-}CPh_2)]$ (ref. 67). The analogous cobalt complex



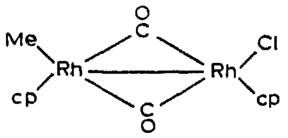
[17]

$[cp^*_2Co_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ was obtained as the unexpected product of an attempt to synthesize $[cp^*_2Co]$ from $CoCl_2$ and Me_5C_5Li in tetrahydrofuran. From control experiments both the methylene and carbonyl ligands were determined to arise from the lithium enolate, $Li^+CH_2CHO^-$, generated by attack of the n-butyllithium used to prepare the Me_5C_5Li, on the solvent (ref. 68). The course of the reaction of $[cp_2Rh_2(CO)_2(\mu\text{-}CH_2)]$ with acids depends on the coordinating ability of the counterion. With HBF_4 at -80°C in ether protonation occurs to give $[cp_2Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CH_2)]BF_4$ which can be deprotonated with methoxide at -80° or tetrahydrofuran at room temperature. On warming to 20°C further reaction occurs to produce hydrogen, methane and the trinuclear methylidyne complex $[cp_3Rh_3(\mu_2\text{-}CO)_2(\mu_3\text{-}CH)]$ ([18]).



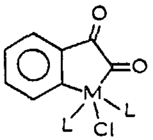
[18]

The last can be reconverted to $[cp_2Rh_2(CO)_2(\mu\text{-}CH_2)]$ by reduction with $LiBHEt_3$. The structure of the methylidyne complex shows the carbonyl groups to form asymmetric bridges and ^{13}C NMR studies indicate rapid CO migration about the triangle of rhodium atoms. If on the other hand, protonation of $[cp_2Rh_2(CO)_2(\mu\text{-}CH_2)]$ is performed with HCl at -80°, the μ-hydrido adduct initially formed reacts on warming to give [19], the structure of which has been determined (refs. 69-71).

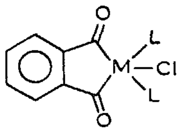


[19]

Another area of significant activity is the synthesis and reactio of metallacycles. Reaction of $[MCl(PPh_3)_3]$ (M = Co,Rh) with benzocyclobutanedione affords [20] which on heating undergoes a rearrangement to [21]. The structure of [21] (M = Rh) has been determined (ref. 72). Reaction of [21] (M = Co) with $AgBF_4$ and a disubstituted

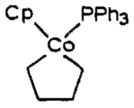


[20]



[21]

acetylene in acetonitrile at 110°C provides a synthesis of 2,3-disubstituted naphthoquinones (ref. 73). Reaction of $[cpCo(PPh_3)I_2]$ with the appropriate dilithium or Grignard reagent forms the metallacycles [22] - [24] while [25] is formed on



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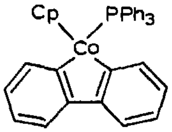

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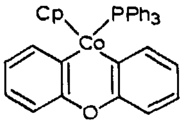

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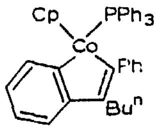
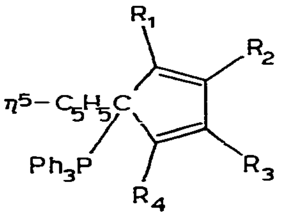


[25]

reaction with a mixture of Bu^nLi and diphenylacetylene. Metallacycles [23] and [25] are stable to 90°C while the others decompose at 25°C. From the fact that the decomposition of [24] is retarded by excess triphenylphosphine it was concluded that phosphine dissociation is the initial step in this process. Reaction of the metallacycles with acetylenes leads to organic products with incorporation of the acetylene in the position originally occupied by the cobalt while reaction with carbon monoxide or isocyanides produces cyclic ketones or cyclic imines respectively (ref. 74). In a related study, it was found that phosphites could replace PPh_3 in [26] (R_1-R_4 = various combinations of Me, Ph, CO_2Me) to



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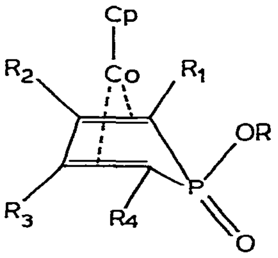
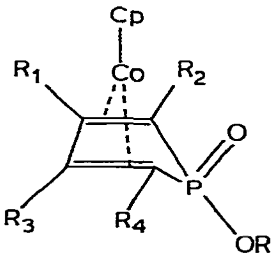
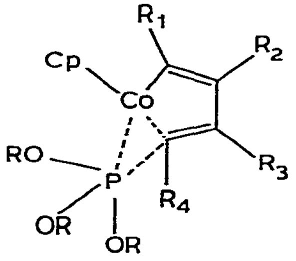


[27]



[28]

yield the simple substitution product which underwent further reaction to give the 1-alkoxyphosphole oxide complexes [27] together with a small amount of the isomeric complex [28]. A kinetic study of the initial substitution reaction indicated it to be a primarily dissociative process while results for the conversion to the phosphole oxide complex suggested that to be intramolecular with electronic effects dominant. Intermediates such as [29] or [30]



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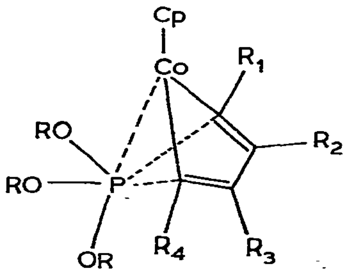
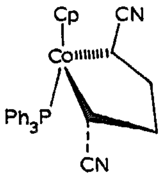


[30]

were proposed (ref. 75). Metallacycles also form on reaction of $[cpCo(CH_2{=}CHCN)(PPh_3)]$ with acrylonitrile at 100°C in benzene. The two isomers [31] and [32] which were formed were separated and their structures determined. Equilibration between [31] and [32] occurs at 100°C but is accompanied by decomposition. Because the plane of the metallacycle is not a plane of symmetry, [32] should exist in two isomeric forms depending on whether the cyano groups are adjacent to the phosphine or to the cyclopentadienyl ring. While only one of these isomers (the latter) is found in the original reaction product, on substitution of PPh_3 by PMe_2Ph, one obtains a small amount of the other cis-isomer together with some of the trans-isomer [31]. On the other hand phosphine substitution in [31] occurs without isomerization of the metallacycle. On heating to 100°, the PMe_2Ph analogs of [31] and [32] equilibrate however [32] converts to the other cis isomer more rapidly than to the trans and more rapidly than [31]→[32]. As PMe_2Ph appears not to be labile, a square planar intermediate is proposed for the interconversion of the cis isomers (ref. 76). A full paper has now appeared giving details of the chemistry of $[cpCo(PPh_3)Me_2$, and derivatives. The kinetics of the conversion to $[cpCo(PMe_3)Me_2]$ indicates this to be a dissociative process. The complex also reacts with carbon monoxide to produce acetone, $[cpCo(CO)_2]$ and $[cpCo(PPh_3)(CO)]$, the ratio of cobalt complexes depending on the amount of CO available. This reaction was shown by crossover experiments to be an intramolecular process as shown in Scheme VIII although in more concentrated solutions (>0.2 M) the crossover experiment was complicated by the occurrence of methyl group exchange between labelled and unlabelled starting materials. This exchange has been described above. Reaction of $[cpCo(PPh_3)Me_2$ with diphenylacetylene produced as the major organometallic product the metallacycle [26] ($R_1 = R_2 = R_3 = R_4 =$ Ph) together with a small amount of $[cpCo(\eta^4\text{-}C_4Ph_4)]$ which presumably is the



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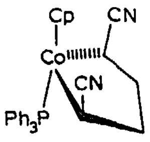
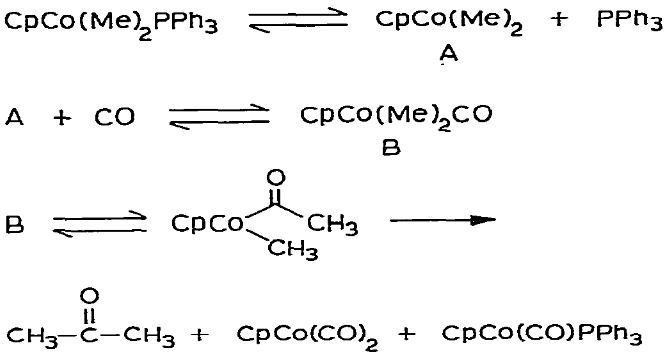
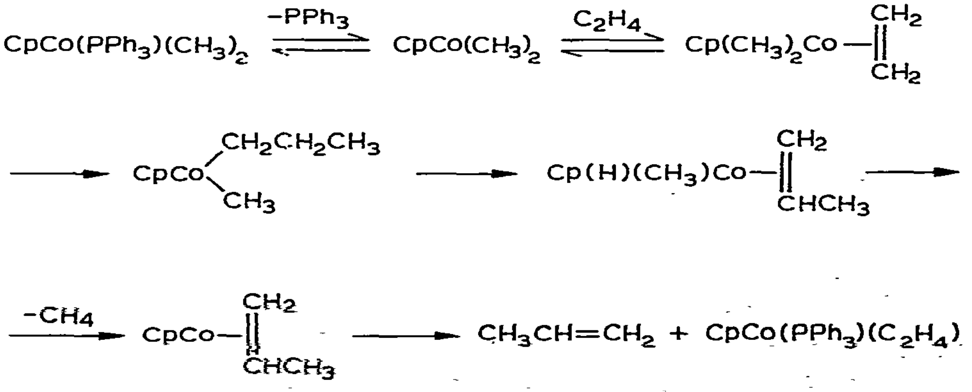


[32]



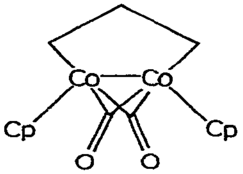
Scheme VIII.

result of thermolysis of the metallacycle. Examination of the organic products showed them to be primarily cis-2,3-diphenylbut-2-ene and 2,3-diphenylbut-1-ene and to account for >95% of the methyl groups in the starting complex. The internal olefin is thought to arise from successive methyl group transfers to a coordinated acetylene while the other presumably arises from the isomerization of the internal olefin via an allyl hydride complex. Perhaps the most significant result of this study is the observation that ethylene reacts with [cpCo(PPh_3)Me_2] at 76°C to yield methane, propene and the rather unstable ethylene complex [cpCo(PPh_3)(C_2H_4)]. Although complicated by methyl group migration to and hydrogen abstraction from the cyclopentadienyl ring, labelling studies were able to confirm that an intact methyl group transfers to ethylene to give propene and that the methane arises from another methyl group with the fourth hydrogen atom coming exclusively from ethylene (Scheme IX).



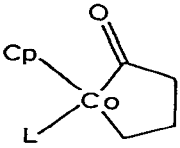
Scheme IX

This argues strongly for alkyl group migration to a coordinated olefin thus supporting the Cossee mechanism for Ziegler-Natta olefin polymerization and arguing against the α-hydrogen abstraction, carbene mechanism proposed earlier by Green and Rooney (ref. 77). Reaction of the radical anion $[cp_2Co_2(\mu\text{-}CO)_2]^{\dot{-}}$ with 1,3-diiodopropane yields [33] which on thermolysis yields propene and cyclopropane by an intramolecular process. Iodine reacts with



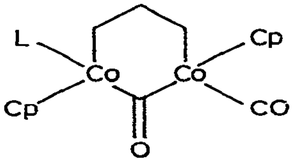
[33]

[33] to give the same hydrocarbons and $[cpCo(CO)_2I]$ while with phosphines or carbon monoxide [cpCoL(CO)] and [34] are obtained



[34]

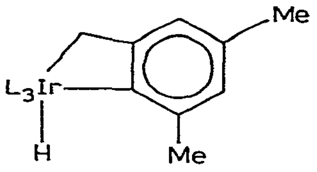
(L = PPh_3, PMe_3, CO). Heating [34] (L = PPh_3) produces cyclopropane and propene while treatment with iodine gives $[cpCoI_2L]$ and cyclobutanone. The initial step of the reaction of [33] with Lewis bases is proposed to involve formation of [35] via



[35]

opening of one carbonyl bridge in [33] with concomitant loss of the Co–Co bond followed by addition of L to the coordinatively unsaturated center (ref. 78). Five-, six- and seven-membered metallacycles of the general formula $[cp^*(PPh_3)M(CH_2)_n]$ (M = Co, Rh, Ir; n = 4. M = Rh, Ir; n = 5. M = Rh; n = 6) have been prepared by the reaction of $[cp^*MX_2PPh_3]$ with $BrMg(CH_2)_nMgBr$. The structures of all three metallacyclopentanes have been determined. For the six- and seven-membered rhodacycles, phosphine dissociation was noted (ref. 79). The possible involvement of metallacyclobutanes in the MCl_3 (M = Rh, Ir)-catalyzed reaction of cyclopropane and benzene to give n- and i-propylbenzene has been reported although no firm evidence for these species was obtained (ref. 80).

Following a crystal structure determination, the iridium complex originally formulated as [36] has now been shown to be [37] (L = $P(OMe)_3$) (ref. 81). Treatment of $[IrCl(COD)]_2$ with norbornadiene (NBD) produces an insoluble species formulated as $[Ir(NBD)_3Cl]_x$. Subsequent treatment with triphenylphosphine displaces the exo-trans-exo dimer of NBD however with more basic phosphines the soluble adducts $[IrCl(L)(NBD)_3]$ (L = PMe_3, PMe_2Ph) are obtained. The crystal structure of the trimethylphosphine adduct has been determined showing it to be the metallacycle [38]. The PMe_2Ph analog of [38] absorbs two molecules of CO and on standing in solution reacts further to give [39] containing three NBD moieties fused in an exo-trans-exo/exo-cis-endo fashion. A species analogous to [38] but containing the acetylacetonate ligand in place of chloride and phosphine is obtained by reaction of $[IrCl(NBD)_3]_x$ with acetylacetone in the presence of sodium carbonate (ref. 82).



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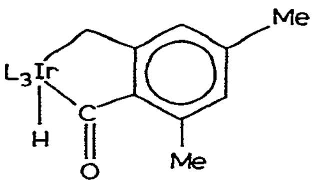

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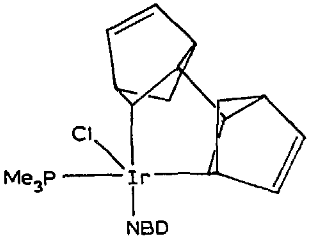

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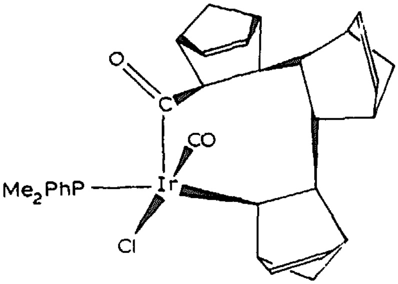


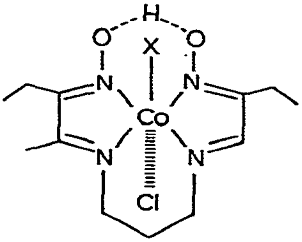
[39]

A large number of studies have appeared on the chemistry of alkyl cobaloximes and related complexes both with respect to their use as agents for organic transformations and for further studies of the mechanisms of action of enzymatic systems involving vitamin B_{12}. Sulfur dioxide inserts into the Co-C bond of cis- and trans-4-methylcyclohexylcobaloxime to give respectively trans- and cis-4-methylcyclohexyl-S-sulfinatocobaloxime indicating that inversion at carbon accompanies the insertion (ref. 83). Heating of a variety of but-3-enyl(pyridine)cobaloximes with carbon tetrachloride or trichloromethanesulfonyl chloride provides 2,2,2-trichloroethylcyclopropanes. A mechanism involving attack of trichloromethyl radical on the δ carbon of the butenyl group followed by cyclization and loss of metal was proposed (ref. 84). In a related study to further explore the thermal and acid-catalyzed interconversions of 1- and 2-methylbut-3-enyl(pyridine)cobaloxime, cis- and trans-2-methylcyclopropylmethyl(pyridine)cobaloxime were prepared. In $CDCl_3$ both rapidly rearrange to a 1:9 mixture of 1- and 2-methylbut-3-enyl(pyridine)cobaloxime implicating the cyclopropyl derivatives as possible kinetic intermediates in the abovementioned rearrangements. Labelling studies indicated the stereospecificity of the rearrangement of the butenyl complexes implying that it proceeds intramolecularly (ref. 85). Reaction of 2,4-dinitrobenzenesulfinyl chloride with a variety of allylic derivatives of pyridinecobaloxime gives moderate yields of 2,4-dinitrophenyl allyl sulfides. The reaction appears to be regiospecific and is considered to involve a heterolytic electrophilic displacement reaction with attack of sulfur on the γ-carbon of the allyl group (ref. 86). If, however, the substrate is styryl(pyridine)cobaloxime no organosulfides are produced. Instead coupling of the styryl and dinitrophenyl moieties is observed (ref. 87). Methyl(dimethylsulfide)cobaloxime reacts with pyridine-N-imine or pyridinium ylides with substitution of the sulfide ligand. A structural study of the imine product indicates that the coordinated imine nitrogen retains its sp^2 character. Reaction of this complex with carboxylic acid anhydride acylates the imine nitrogen and it is proposed that this system provides a means of stabilizing pyridine-N-imines for organic reactions (refs. 88, 89). The structure of the ylide product has also been determined from which it appears that the trans influence of the ylide is larger than that of ligands such as pyridine, imidazoles, triphenylphosphine and water (ref. 90). Reaction of the dimethylsulfide complex with $MeSnCl_3$ at 50°C in dichloromethane showed no transfer of the Co-Me group to tin over several days although NMR evidence for association of the tin atom with this methyl group was seen (ref. 91).

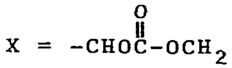
The porphyrin complexes $[Co(N_4)L_2]ClO_4$ (N_4 = octaethylporphyrin (OEP), tetraphenylporphyrin (TPP); L = H_2O) react with ethyl vinyl ether in ethanol-triethylamine solution to yield the five-coordinate Co(III) species $[Co(N_4)CH_2CH(OEt)_2]$ which on chromatography on silica gel is converted to $[Co(N_4)CH_2CHO]$. However when L = pyridine only Co(II) porphyrins are formed (ref. 92). Tosylhydrazones of alkyl aryl ketones react with [Co(TPP)Cl] to give α-styryl derivatives of the [Co(TPP)] moiety (ref. 93).

Several studies of photochemical reactions of alkyl(pyridine) cobaloximes have been reported. In the presence of oxygen, the (-)-R-2-octyl derivative gives racemic 2-octylperoxy(pyridine) cobaloxime (ref. 94). On the other hand, anaerobic photolysis of 4,5-dihydroxypentyl(pyridine)cobaloxime at pH 3 yields a small amount of pentanal. Labelling experiments suggest that homolysis of the Co-C bond occurs on irradiation with the dihydroxyalkyl radical undergoing a 1,5 hydrogen shift followed by an acid-catalyzed conversion to the aldehyde. The system is proposed to be a model for the butane-2,3-diol→butanone conversion catalyzed by diol dehydrase (ref. 95). Base hydrolysis of ethyl(pyridine)cobaloxime yields ethane and ethylene in a 5.6:1 ratio and subsequent photolysis produces no further gases indicating that no base-stable alkyl complexes are formed. When run in aqueous KOD, the ethylene is essentially unlabelled while the ethane is 100% d_1. The ethylene is considered to be formed via an E_2 mechanism however distinction between homolytic and heterolytic Co-C bond cleavage for ethane production could not be made (ref. 96). Photolysis of [PhCo(BAE)] (BAE = dianion of N,N'-ethylenebis(acetylacetonimine)) in the solid state and in benzene solution leads to homolysis of the Co-C bond as determined by EPR measurements which indicate the presence of a [Ph·, $\cdot Co^{II}$(BAE)] caged radical pair (ref. 97).

In another attempt to model the diol dehydrase reaction, [40] was prepared by the oxidative addition of chlorethylene carbonate



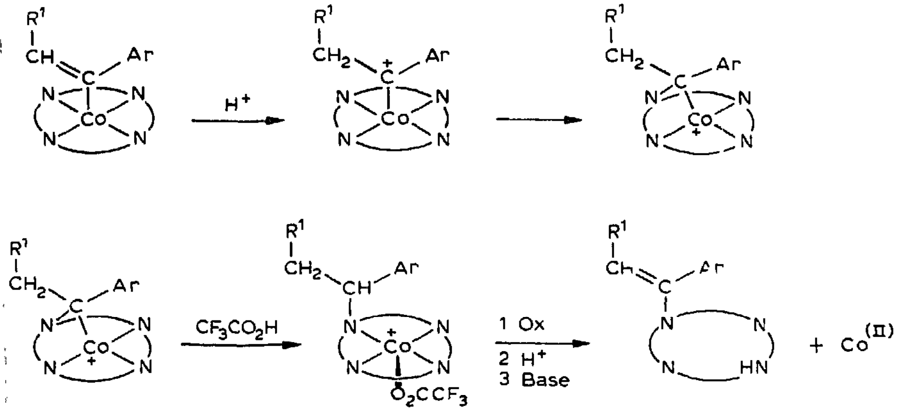
[40]



$X = -CHO\overset{O}{\overset{\|}{C}}-OCH_2$

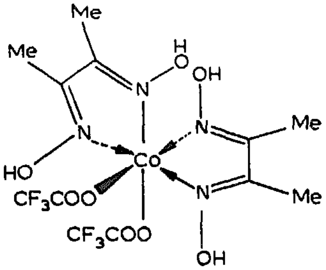
to the corresponding carbonyl Co(I) macrocycle. Reaction of [40] with sodium methoxide in methanol removed the ethylene carbonate group leaving the chloro derivative of the Co(II) macrocycle. The organic products were acetaldehyde, methyl- and dimethylcarbonate in equivalent amounts. The absence of ethylene glycol which can be formed by methoxide attack on free ethylene carbonate was interpreted to indicate that attack of methoxide occurs at the carbonate carbonyl group in the complex. The equivalent amounts of the carbonate esters found suggested possible formation of analogs of [40] with R = $CH_2(OH)CH(OH)-$ or $-CH_2CHO$ as intermediates while the decrease in the amount of acetaldehyde produced when the decomposition is run in the presence of radical traps implicates the formation of radicals (Co–C homolysis) prior to the formation of the Co(II) product (ref. 98).

In these cobalt macrocycles, involvement of the macrocyclic ligand in reactions of the complex can also occur. Thus the reaction of [Co(TPP)Cl] with ethyldiazopropionate at $-50^{o}C$ gives a species proposed to contain a methyl(carboxyethyl)methylene group bridging the cobalt and one of the pyrrole nitrogen atoms. This is thought to arise from formation of cobalt carbene complex with subsequent insertion of the carbene into a Co–N bond. Warming to $-20^{o}C$ leads to rearrangement and isolation of $[Co(TPP)C(=CH_2)CO_2Et]$. Reaction of [Rh(TPP)I] with ethyldiazoacetate in the presence of methanol gives $[Rh(TPP)CH(OMe)CO_2Et]$ (ref. 99). Reaction of [Co(TPP)(styryl)] with trifluoroacetic acid followed by treatment with triethylamine causes transfer of the styryl group to a pyrrole nitrogen of the porphyrin and loss of cobalt from the complex. The color changes observed during this reaction are thought to parallel those observed for the formation of the so-called "green pigments" from cytochrome P450 in the abnormal metabolism of some drugs. The proposed mechanisı is shown in Scheme X (ref. 100). On the other hand reaction of excess trifluoroacetic acid with alkyl derivatives of (pyridine) cobaloxime without subsequent treatment with base yields alkane and the Co(II) complex [41] whose structure has been determined. A mechanism involving initial protonation of an oxime oxygen followed by loss of pyridine, replacement by trifluoroacetate and slower loss of alkane is proposed (ref. 101). The kinetics of axial ligation and hydrolysis of trans-$[CoR(L)(DODOHpn)]ClO_4$ (R = Me, Et, Ph; L = NH_3, H_2O; DODOHpn = diacetylmonoxime diacetylmonoximato propane-1,3-diyldiimino) have been studied. For L = H_2O, titration with hydroxide shows an initial deprotonation of the aquo ligand followed by deprotonation of the macrocyclic ligand. Replacement of water by ammonia proceeds via a conjugate base mechanism involving deprotonation of the macrocycle. The kinetic _trans_ effect in these reactions is Et>Me>Ph which corresponds to the relative donor abilities of these ligands (ref. 102). In



Scheme X

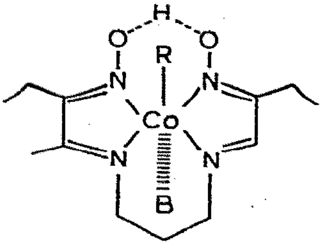
a related study, the equilibrium constants for the replacement of water by other ligands in aryl(aquo)cobaloximes (aryl = $MeO_2CC_6H_4$) were measured together with the rates for base-catalyzed hydrolysis of the carboxymethyl group. Correlation of these latter results via the Taft dual substituent parameter equation indicated considerable resonance interaction of unsaturated axial ligands(e.g. CN^-,SCN^- with the aryl ligand. In general the inductive effect of the axial ligand paralled its proton basicity (ref. 103).



[41]

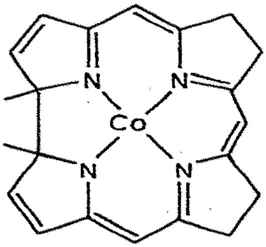
Several electrochemical studies of cobaloximes and related macrocyclic complexes have appeared. In the methyl-bridged electron transfer reactions between $[Co(N_4)(H_2O)Me]^{2+}$ and $[Co(N_4)(H_2O)_2]^{2+}$ (N_4 = (dimethylglyoximate)$_2$, 1,5,8,12-tetraazacyclotetradecane and related macrocycles) and between methyl cobalamin and cobalamin(II), the free energy independent barrier to the reaction was least in the cobalamin system and increased with the bulk of the macrocyclic ligand for the other systems. This barrier was attributed to factors contributing to bond strength in the transition state which was proposed to be a three-center, 3-electron $Co-CH_3-Co$ entity (ref. 104). The effect of methyl iodide on the cyclic voltammogram for the reduction of the Co(II) complex of bis(2-thioformyl-2-phenylvinyl)-trimethylenediamine was interpreted as indicating that the reduced $Co(I)^-$ species reacted with methyl iodide to produce a MeCo(III) complex (ref. 105). With larger alkyl groups decomposition of the Co(III) alkyl intermediates formed in this manner occurs to give olefin and hydrogen. Thus for $[Co^{II}(salen)]$ (salen - N,N'-bis(salicylidene)ethylendiamino) electrogeneration of $[Co^{I}(salen)]^-$ in the presence of tert-butyl halides yields $[Co^{II}(salen)]$, hydrogen, and isobutene. For the bromide the reaction is electrocatalytic. The reaction is presumed to involve oxidative addition of the alkyl halide to the Co(I) complex followed by a slow decomposition via homolysis of the Co-C bond (ref. 106). Stable Co(III) alkyls could be obtained by this route when aquocobalamin or related Co(III)-porphyrin complexes were electrolytically reduced in the presence of ω-bromoalkylcyclohexenones. Further reduction of these species in the presence of Michael olefins led to coupling via 1,4 addition and regeneration of the Co(I) complexes (ref. 107).

Considerable interest has been shown in the determination of factors affecting the stability of the Co-C bond in alkylcobalamin and models for it. From cyclic voltammetric studies it was concluded that [42] is a better model for the electrochemical behavior of vitamin B_{12} than are the more often proposed cobaloxime systems. The apparent stability of the Co-C bond appears from this study to be a function of the concentration of the axial base (ref. 108). To probe the electronic and steric effects on the reactivity at the cobalt center and the properties of axial ligands, B_{12} analogs [43] and]44], containing 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyl-A,D-didehydrocorrin (BDHC) and its tetradehydro analog (TDHC) respectively (only macrocyclic skeletons are shown) were prepared. These differ from the parent corrin complex

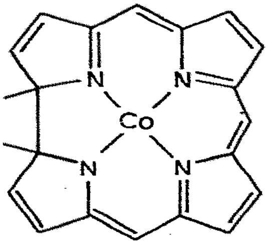


[42]

(vitamin B_{12s}) in possessing greater unsaturation and having one additional angular methyl group between the A and D rings. The electronic absorption spectra of the Co(III) derivatives of [43] and [44] containing a variety of neutral and anionic axial ligands



[43]



[44]

showed that the BDHC species quite resembled the parent corrin in this regard while the TDHC complexes were distinctly different. Cyclic voltammetric studies also showed a difference with the reduced form (Co(I)) of [44] being considerably more stable than that obtained from [43] implying stabilization by the conjugated π system of the former. Reduction of $[Co(CN)_2(BDHC)]$ with sodium borohydride gave $[Co(BDHC)]^-$ which reacted with alkyl halides by an S_N2 process as does the reduced form of vitamin B_{12s} but a significantly greater retardation in rate was observed as the bulk of the alkyl group increased due to the steric effect of the additional angular methyl group. The reduced form of [44] was not reactive towards alkyl halides implying that the conjugated π system is effective in removing electron density from the Co(I) thereby reducing its effective nucleophilicity. Despite the evidence that [43] and its derivatives appear to be good B_{12} models, they do not induce the 1,2 rearrangement of either $-CH_2CH(CO_2Me)_2$ or $-CH_2CH(Me)COSEt$ when these moieties are axial ligands presumably because the steric pressure of the additional angular methyl group prevents the initially formed alkyl fragments from remaining associated with the metal (ref. 109).

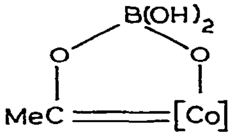
Steric effects on the properties of the Co-C bond have also been investigated in a structural study of isopropyl(triphenylphosphine)-cobaloxime. The Co-C bond is long (2.22(2) Å) and comparison with the corresponding pyridine derivative showed that the cobalt was displaced further from the plane of the ring towards the phosphine. Considerable close contacts between the isopropyl group and the in-plane ligands occur (ref. 110). In an extensive study of the vitamin B_{12a} system itself a large number of alkylated derivatives were prepared and the effect of the alkyl group on the pK_a for the protonation of the axial dimethylbenzimidazole was examined. It was concluded that the main variable affecting the pK_a was the Co-C bond length. A study of the decomposition of the neopentyl derivative by various reagents indicated that it involves homolytic Co-C bond cleavage with the labilization attributed to steric distortion about the α-carbon in the six coordinate complex (ref. 111). A similar conclusion as to the importance of steric effects on the lability of the Co-C bond was reached in study of the action of ethanolamine ammonia-lyase, an adenosylcobalamin-dependent enzyme. Using adenyl residues bound to the cobalt by a $(CH_2)_n$ (n = 2-6) chain it was found that the favored conformational changes accompanying enzyme-coenzyme binding could be blocked by bulky β substituents on the adenyl residue leading to the conclusion that the driving force towards the favored enzyme-coenzyme complex is Co-C cleavage (ref. 112). A review of cobalt corrinoid complexes as models for vitamin B_{12} is available (ref. 113).

A few studies of related rhodium systems have appeared. Reaction of $[Rh(dmgH)_2(PPh_3)]^-$ (dmgH = dimethylglyoximate) with alkyl halides in basic aqueous methanol proceeds via an S_N2 process to give $[Rh(R)(dmgH)_2(PPh_3)]$ R = $PhCH_2$, Bu^n). In aqueous solution $[RhH(dmgH)_2(PPh_3)]$ reacts with these alkyl halides to yield alkane and $[Rh(H_2O)(dmgH)_2(PPh_3)]^-$ which reacts with further starting material to give $[Rh(dmgH)_2(PPh_3)]_2$. The reaction could proceed via a radical process but a hydride transfer reaction is considered more likely (ref. 114). Borohydride reduction of [Rh(OEP)Cl] generates the nucleophilic $[Rh^I(OEP)]^-$ which reacts with heterocyclopropanes and highly strained cyclopropane rings (e.g. nortricyclanone) to form Rh(III) alkyl derivatives with opening of the three-membered ring. With ethyl cyclopropylcarboxylate an NMR study of the $[Rh(OEP)(CH_2)_3CO_2Et)]$ product showed that attack occurred with inversion at carbon (ref. 115). Methyllithium reacts with [Rh(OEP)Cl] to give [Rh(OEP)Me] which on treatment with excess RLi (R = Ph, Bu^n, p-$MeOC_6H_4$) gives products in which the R group substitutes a meso position on the porphyrin ring. A study of the spectral changes accompanying the reaction suggest initial coordination of the carbanion to the open coordination position on the metal prior to migration to the ring (ref. 116). Reaction of the corrin hydrogenobyrinicacid A,C-diamide with $[Rh(CO)_2Cl]_2$ in acetic acid-ethanol followed by treatment with KCN yields $[Rh(CN)_2(corrin)]$ which from a structural study appears to be very similar to the cobalt analog (ref. 117).

Finally, photolysis in the ligand-to-metal charge transfer band of $[Co(NH_3)_5O_2CR]^{2+}$ (R = CH_2Br, CH_2CO_2H, CH(OH)Ph, CH_2Ph) in a frozen matrix gives the alkyls $[Co(NH_3)_5R]^{2+}$. Radicals were detected in some instances (ref. 118).

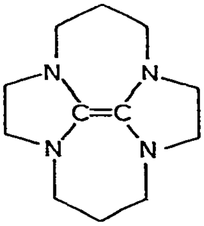
Metal Carbene Complexes

In a significant experiment designed to probe the mechanism of the Fischer-Tropsch reaction, diazomethane was reacted with a cobalt surface in flowing helium. Over the temperature range 25-200° the major product was ethylene which was interpreted to indicate that surface methylene groups were formed and then dimerized. In flowing hydrogen at 210°C, C_1-C_{18} hydrocarbons were formed with the distribution of C_4 species being very similar to what has been observed from CO/H_2 mixtures over a cobalt surface. The possibility of hydrocarbon production by the polymerization of surface methylene groups in the Fischer-Tropsch process was therefore indicated (ref. 119). A mixture of CoI_2 and tributylphosphine is effective for the homologation of methanol by CO/H_2 mixtures to ethanol, acetaldehyde, methyl acetate and ethyl acetate. Methane is also produced. Addition of borates increased the selectivity to ethanol which was attributed to the formation of adducts like [45] in which the resulting enhancement of the carbenoid character of the Co-C bond would favor hydrogenolysis (ref. 120). In a continuation of studies on the formation of carbene complexes from electron-rich olefins, $[Rh(COD)Cl]_2$ was reacted with [46] to yield the bis-(carbene) [47] which was characterized by a structural study.

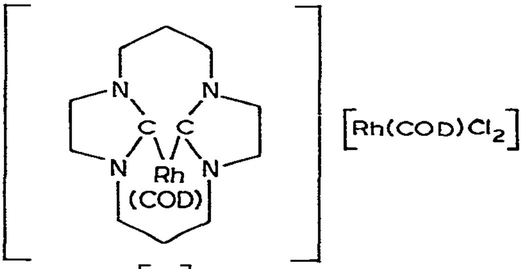


[45]

Reaction of [47] with carbon monoxide gave the dicarbonyl analog (ref. 121).



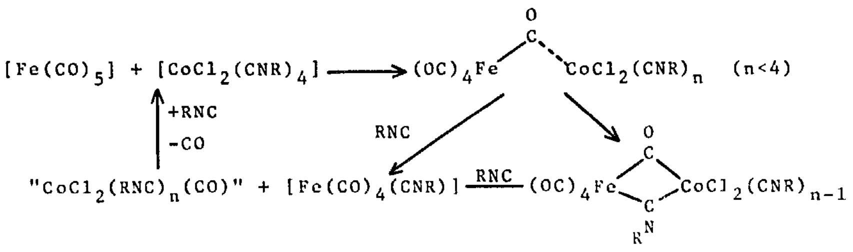
[46]



[47]

Metal Isocyanide Complexes

Reduction of $[Co(CNBu^t)_5]PF_6$ with potassium amalgam gives $[Co_2(CNBu^t)_8]$ which has the same structure as $[Co_2(CO)_8]$ but with a shorter Co–Co bond. The complex is fluxional at room temperature with the rearrangement process which renders all isocyanide ligands equivalent being proposed to involve opening of the isocyanide bridges and rotation about the Co–Co bond. The complex reacts with nitric oxide, carbon monoxide and diphenylacetylene to produce $[Co(NO)(CNBu^t)_3]$, $[Co(CNBu^t)_5][Co(CO)_4]$ and $[Co_2(\mu_2-\eta^2-Ph_2C_2)(CNBu^t)_6]$ respectively (ref. 122). The high yield synthesis of $[Fe(CO)_4(CNR)]$ ($R = 2,6-Me_2C_6H_3$) from $[Fe(CO)_5]$ is catalyzed by $CoCl_2 \cdot 2H_2O$. Using stoichiometric quantities of isocyanide in the reaction affords $[Fe(CO)_n(CNR)_{5-n}]$ ($n = 0-3$; $R = Me, Bu^t$). The cobalt-containing product was identified as $[CoCl_2(CNR)_4]$ and as it also catalyzes the substitution at iron, it is considered to be the active species. The mechanism proposed is shown in Scheme XI. The above reaction is also catalyzed by $[RhCl(PPh_3)_3]$ while $CoCl_2{\cdot}2H_2O$ catalyzed the

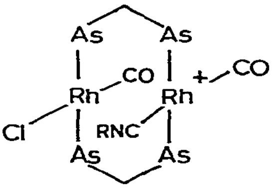


Scheme XI

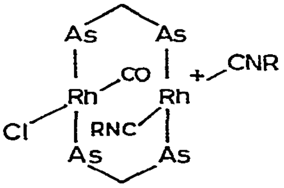
substitution of isocyanides in $[M(CO)_6]$ (M = Cr, Mo, W), $[M_3(CO)_{12}]$ (M = Ru, Os), and $[Ir_4(CO)_{12}]$ (ref. 123). The synthesis of $[Co(CNR)_3(PR'_3)_2]ClO_4$ from $[Co(CNR)_5]ClO_4$ and PR'_3 in dichloromethane (R = Ph, *o*-anisyl, *p*-tolyl, *o*-EtC_6H_4, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, *p*-XC_6H_4 (X = F,Cl,Br,I); R' = Ph, *p*-ClC_6H_4) or from $[Co(CNR)_3(AsPh_3)_2]ClO_4$ and PR'_3 (R = Ph; R' = *p*-ClC_6H_4, *p*-ClC_6H_4O) has been reported. As the bulk of the isocyanide increases there is increasing tendency to produce monosubstitution although in all cases, some monosubstitution product could be seen in the filtrate. In solution $[Co(CNR)_4PR'_3]^+$ tends to disproportionate to $[Co(CNR)_5]^+$ and $[Co(CNR)_3(PR'_3)_2]^+$ (ref. 124, 125). A similar series of $[Co(CNR)_3(L)_2]^+$ complexes (R = Ph, *p*-tolyl, *p*-$MeOC_6H_4$, *p*-$MeOC_6H_4$, *p*-$NO_2C_6H_4$, 2,6-$Me_2C_6H_3$; L = $P(OMe)_3$, $PPh(OEt)_2$) has been oxidized electrochemically at mercury and platinum electrodes. The oxidation is a reversible, one-electron process but the Co(II) species produced rapidly isomerizes to a species thought to have C_{2v} symmetry and further converts to very unstable final product which is thought to be a dimer as it is diamagnetic (ref. 126).

The use of polymer-anchored isocyanide groups to provide supported metal complexes for immobilized catalyst studies has been reported. Functionalization of pendant phenyl groups of a polystyrene-divinylbenzene copolymer with $-(CH_2)_nNC$ (n = 1,2) substituents or the reaction of $(EtO)_3Si(CH_2)_3NC$ with silica gave supports which reacted with $[Rh(CO)_2Cl]_2$ to give ⓅCH$_2$)$_n$NCRh(CO)$_2$Cl (ref. 127). Oxidative addition of Ph_3SnCl to $[Rh(CNBu^t)_4]ClO_4$ gives cis-$[Rh(CNBu^t)_4(SnPh_3)(Cl)]ClO_4$. From solvent effects and activation parameters an asymmetric, 3-center transition state was proposed (ref. 128).

The A-frame complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]BPh_4$ ((L_2 = bis(diphenylphosphino)methane (DPM), bis(diphenylarsino)methane (DAM)) react with $CNBu^t$ to give a variety of adducts and substitution products With one, two and five equivalents of isocyanide the DAM complex gives [48], [49] and [50] respectively (phenyl groups omitted for clarity here and below).

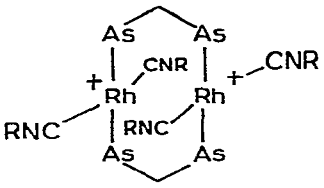


[48]



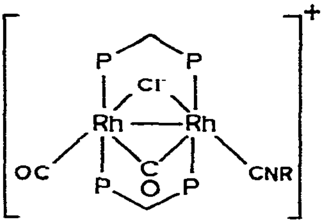
[49]

$R = Bu^t$



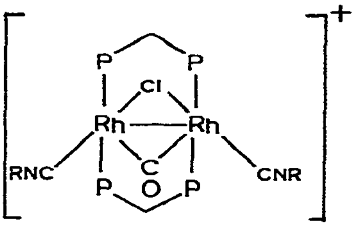
[50]

Carbon monoxide and sulfur dioxide (L) add to [50] to give $[Rh_2(CNBu^t)_4(\mu\text{-}L)(DAM)_2](BPh_4)_2$. The analogous DPM complex forms CO and SO_2 adducts as well. The bridging carbonyl readily dissociates while the SO_2 does not. By contrast, $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BPh_4$ retains the bridging chloride on reaction with one or two equivalents of $CNBu^t$ to give [51] and [52] respectively. Reaction of $[Ir(CO)_2Cl_2]^-$ with DAM under nitrogen gives the face-to-face dimer $[Ir(CO)Cl(DAM)]_2$ which reacts with CO in the presence of $NaBF_4$ to give [53]. Complex [53] loses CO in solution to give $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]BF_4$ which can react with either one or two equivalents of $CNBu^t$ to give



[51]

$R = Bu^t$



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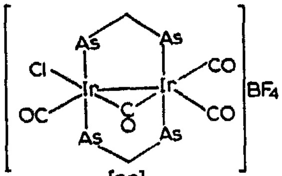
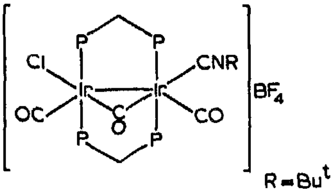
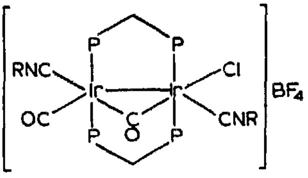


[53]

[54] and [55] respectively. An excess of isocyanide converts [53] to $[Ir_2(CNBu^t)_4(\mu\text{-}CO)(DAM)_2]^{2+}$ which unlike the rhodium analog does not lose CO. The DPM analogs of the last three complexes have also been prepared (ref. 129). A series of interesting two-dimensional polymers have been prepared by the reaction of $[Rh(CO)_2Cl]_2$ with the bridging diisocyanides 1,3- and 1,4-diisocyanobenzene, 4,4'-diisocyanobiphenyl, di(p-isocyanophenyl)methane and 1,4- and 1,5-diisocyanonaphthalene. All have the formula $\{[Rh(bridge)_2]Cl\}_n$ and are quite hygroscopic. X-ray powder data indicate that the interplanar Rh-Rh distance is 3.2-3.4 Å (refs. 130-132). On the other hand, use of diisocyanides such as 1,3-diisocyanopropane (4-br) or 2,5-dimethyl-2,5-diisocyanohexane (TM4-br) affords $[Rh_2(L_2)_4]$-$(PF_6)_2$ (L_2 = 4-br, TM4-br) after treatment with $AgPF_6$. These systems have been intensively studied as potential catalysts for photochemical production of hydrogen. Structures of both these face-to-face dimers have been determined (ref. 133). The 4-br complex contains two eclipsed approximately square planar rhodium moieties showing a slight pyramidal distortion while the TM4-br complex is

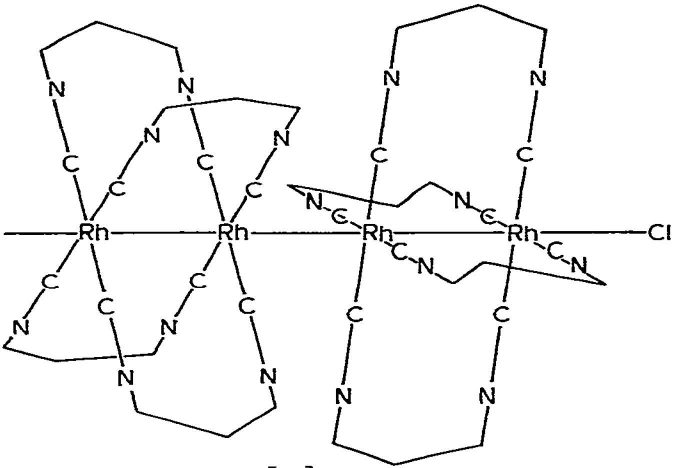


[54]



[55]

staggered by 31° and the rhodium coordination planes show a tetrahedral distortion. Solutions of $[Rh_2(4\text{-br})_4]^{2+}$ in 12 M. HCl liberate hydrogen with the formation of $[[Rh_2(4\text{-br})_4]_2Cl_2]^{4+}$, a derivative of which could be isolated by addition of $CoCl_2 \cdot 6H_2O$. A structural study showed this to be $[(H^+aq)_3][(Rh_2(4\text{-br})_4)_2Cl][CoCl_4] \cdot 6H_2O$, [56].



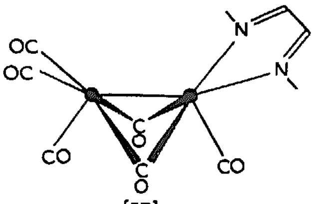
[56]

Photolysis of $[[Rh_2(4\text{-br})_4]_2Cl]^{4+}$ in 12 M. HCl generates further hydrogen and from the structural study it is concluded that [56] perhaps with a second axial chloride ligand is the photoactive species (ref. 135). Further association of $[Rh_2(4\text{-br})_4]$ units in solution has been established. On oxygenation of a solution of $[Rh_2(4\text{-br})_4]^{2+}$ in sulfuric acid $[Rh_2(4\text{-br})_4]_2{}^{6+}$ is formed. This can be oxidized to $[Rh_2(4\text{-br})_4]^{4+}$ with Fe(III) upon irradiation while on reduction with Cr(II) $[Rh_2(4\text{-br})_4]_3{}^{8+}$ is formed. This can be reoxidized to the dimer with Ce(IV). Spectral evidence for $[Rh_2(4\text{-br})_4]_4{}^{10+}$ and $[Rh_2(4\text{-br})_4]_6{}^{16+}$ in the reduced solutions was also found. A detailed study was made of energy and electron transfer processes involving the $^3A_{2u}$ excited state obtained on flash photolysis of $[Rh_2(4\text{-br})_4]^{2+}$. The quenching of this excited state appears to occur by triplet-triplet energy transfer. Oxidative quenching by paraquat or N-methylnicotinamide yielded $[Rh_2(4\text{-br})_4]^{3+}$ while reductive quenching by N,N,N',N'-tetramethyl-p-phenylenediamine or dimethylaniline gave $[Rh_2(4\text{-br})_4]^+$ (ref. 136).

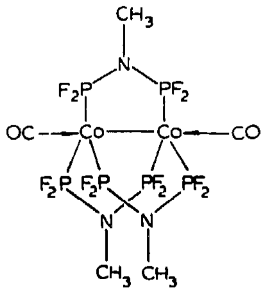
Metal Carbonyl Compounds

a) Homonuclear carbonyl compounds

The chemistry of [$Co_2(CO)_8$] and related complexes continues to attract much interest. Substitution of two terminal carbonyl groups in [$Co_2(CO)_8$] occurs on reaction with the 1,4 diazabutadienes (DAB), RN=CHCH=NR (R = Pr^i, p-tolyl, p-$MeOC_6H_4$, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$) to give air-sensitive products formulated as [$(OC)_3Co(\mu$-$CO)_2(CO)(DAB)$ ([57]). Proton and carbon-13 NMR studies suggest significant π-backbonding to the DAB ligand while the resonance Raman spectrum indicates the presence of a 2-electron Co-Co bond. When warmed in hexane solution, decomposition occurs to give products tentatively identified as [$Co_4(CO)_8(DAB)_2$] although pure compounds could not be obtained (ref. 137). Cyclic voltammetric studies on [58] show that stepwise reduction to the radical anion, [$Co_2(CO)_2(L_2)_3]^{\dot{-}}$, and then to the dianion, [$Co_2(CO)_2(L_2)_3]^{2-}$ (L_2 = $MeN(PF_2)_2$) occurs. The dianion reacts with oxygen to regenerate the radical anion and with methyl iodide although no product was isolated from the latter reaction. When the dianion is generated in the presence of a lithium salt as a supporting electrolyte in place of the Bu_4N^+ salts used



[57]



[58]

in the initial experiments, reoxidation to the neutral dimer occurs in a single two-electron step. This change in electrochemical behavior was attributed to a close association of Li^+ with both metals in the reduced species (ref. 138). The kinetics of CO substitution in $[Co_2(CO)_8]$ by $AsPh_3$, PPh_3 and $PBu_3{}^n$ have been studied. For $AsPh_3$, the rate is relatively slow and is unaffected by the presence of oxygen. This together with the observation of $[Co_2(CO)_7(AsPh_3)]$ as the initial product (the ultimate product is $[Co_2(CO)_6(AsPh_3)_2]$) and the fact that the rate is comparable to that for ^{13}CO exchange suggests the mechanism shown in Scheme XII.

$$[Co_2(CO)_8] \longrightarrow [Co_2(CO)_7] + CO \quad \text{(slow)}$$

$$[Co_2(CO)_7] + AsPh_3 \longrightarrow [Co_2(CO)_7(AsPh_3)] \quad \text{(fast)}$$

Scheme XII

For the phosphines the rate is considerably faster, is strongly inhibited by oxygen and the major product is $[Co(CO)_3L_2][Co(CO)_4]$. These data suggest a radical chain mechanism (Scheme XIII) (refs. 139 140). The pulse radiolysis of $[Co_2(CO)_6(PBu^n)_2]$ is frozen 2-methyltetrahydrofuran yields the radical anion, $[Co_2(CO)_6(PBu_3{}^n)_2]^{\cdot-}$ which

$$[Co_2(CO)_8] + L \rightleftharpoons [Co_2(CO)_8L]$$

$$[Co_2(CO)_8L] \longrightarrow [\cdot Co(CO)_3L] + [\cdot Co(CO)_4] + CO$$

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

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

$$[\cdot Co(CO)_4] \longrightarrow [\cdot Co(CO)_3] + CO$$

$$[\cdot Co(CO)_3] + L \longrightarrow [\cdot Co(CO)_3L]$$

$$[Co(CO)_3L]^+ + L \longrightarrow [Co(CO)_3L_2]^+$$

Scheme XIII

gives an axially symmetric EPR spectrum. Analysis of the spectrum indicates that the unpaired electron resides in an orbital of predominantly Co-Co and Co-P σ^* character which is approximately 65% Co and 23% p in nature (ref. 141). The same complex has been oxidized to give $CoCO_3$, $Bu_3{}^nPO$ and CO with the rate depending on the concentrations of complex and oxygen (ref. 142). A brief report of the oxidation of $[Co_2(CO)_8]$ itself has also appeared (ref. 143). The equilibrium between $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ at 105-145°C and 6-14 atm. of CO has been studied. Further work indicates that in the absence of CO, $[Co_2(CO)_8]$ is thermodynamically unstable at temperatures below 0°C although the decomposition is very slow. Under 1 atm. of CO it is stable up to 5°C (ref. 144).

The decomposition of $[HCo(CO)_4]$ has been the subject of several papers. Photolysis in frozen argon and carbon monoxide matrices leads to H· and $[\cdot Co(CO)_4]$ as the primary photoproducts (ref. 145a), results which indicate that earlier evidence for $[HCo(CO)_3]$ in this reaction is erroneous (ref. 145b). A complication in the study of the photolysis and thermolysis of $[HCo(CO)_4]$ in solution (to give $[Co_2(CO)_8]$ and H_2) is catalysis by $[Co_2(CO)_8]$. This occurs even at the start since traces of the neutral carbonyl seemed always to be present. The proposed mechanism for this catalysis is shown in Scheme XIV (refs. 146, 147). From vapor pressure measurements,

$$[Co_2(CO)_8] \rightleftharpoons 2[\cdot Co(CO)_4]$$

$$[\cdot Co(CO)_4] \rightleftharpoons [\cdot Co(CO)_3] + CO$$

$$[\cdot Co(CO)_3] + [HCo(CO)_4] \rightleftharpoons [\cdot HCo_2(CO)_7]$$

$$[\cdot HCo_2(CO)_7] + [HCo(CO)_4] \longrightarrow [H_2Co_2(CO)_7] + [\cdot Co(CO)_4]$$

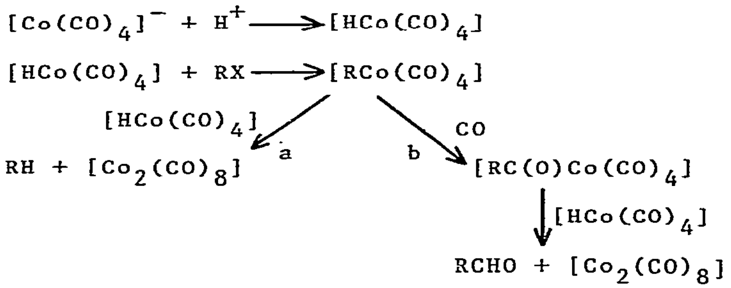
$$[H_2Co_2(CO)_7] \longrightarrow H_2 + [Co_2(CO)_7] \xrightarrow{CO} [Co_2(CO)_8]$$

Scheme XIV

the normal boiling point of $[HCo(CO)_4]$ has been determined to be 47±3°C (ref. 148).

Infrared spectral studies of $Na[Co(CO)_4]$ in ethereal solvents (e.g. tetrahydrofuran (THF) tetrahydropyran (THP) dimethoxyethane (DME) show the presence of anionic sites of several symmetries indicating varying degrees of specific cation-anion interactions. Complexation of the cation with the cryptand C221 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane) converted the entire system to a single (solvent separated) site of T_d symmetry in THF and DME but in THP the single site was only of C_{2v} symmetry suggesting that the anion could still "see" the cation through a "window" in the cryptand (ref. 149). Several systems involving $[Co(CO)_4]^-$

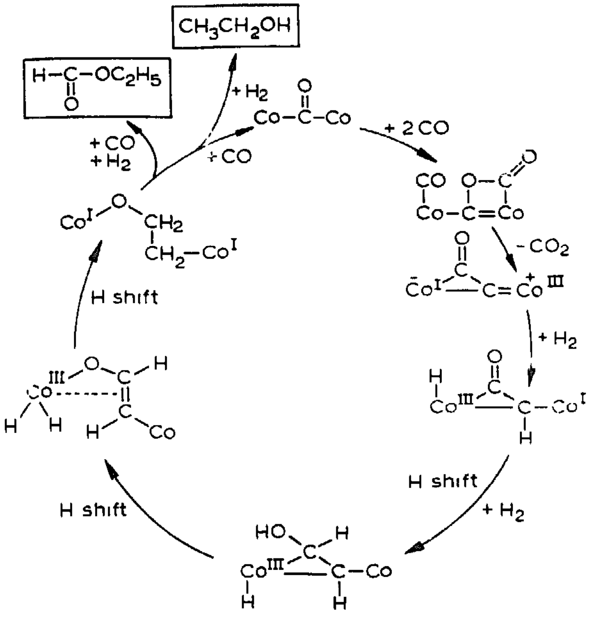
and/or [$HCo(CO)_4$] have been used in organic synthesis. In acidic methanol it is a selective, stoichiometric reducing agent for conjugated carbon–carbon double bonds. In this system, cyclopentadiene was reduced to cyclopentene in 100% yield (ref. 150). The same system has also been used for the hydrogenolysis of carbon-halogen bonds according to Scheme XV. The extent of hydroformylation relative to hydrogenation depends on the rate of step b) relative



Scheme XV

to step a) and is favored by electronegative R groups (ref. 151). Under phase-transfer conditions ($Bu_4{}^nNCl/H_2O/CH_2Cl_2$), [$Co(CO)_4$]$^-$ effects the carbonylation of benzylbromide, the product being [$PhCH_2C(O)Co(CO)_4$] (ref. 152). In these systems the choice of the phase transfer agent can be critical since it has been shown that alkylammonium halides with cation substituents capable of forming stable radicals can react under catalytic conditions. For example the phase transfer system $PhCH_2Et_3NCl/H_2O/NaOH/C_6H_6$ in the presence of [$Co_2(CO)_8$] and methyl iodide produced a 95% yield of $PhCH_2COOH$ upon carbonylation for 5 days at 25°C (ref. 153). A series of 9-alkylidenefluorenes have been stoichiometrically hydrogenated to the corresponding 9-alkylfluorenes by [$HCo(CO)_4$]. The observation that the reaction is much faster than with styrene was interpreted as evidence for a radical pair mechanism on the basis that the fluorenyl radical should be considerably more stable than the styryl radical (ref. 154). [$HCo(CO)_4$] functions as a catalyst or catalyst precursor for the hydrogenation of carbon monoxide to C_1–C_3 alcohols, ethylene glycol, and alkyl formates. A mechanism involving CO insertion into the Co–H bond followed by hydrogenolysis of the resulting formyl to an η^2-formaldehyde species was proposed but the mechanism appears quite speculative (ref. 155). The

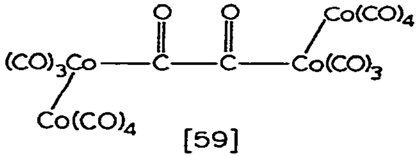
$[Co_2(CO)_8]$-catalyzed carbonylation of methanol to ethanol in the presence of iodide appears to involve $[Co(CO)_4]^-$ as the active species. Presumably the iodide converts methanol to methyl iodide which can then oxidatively add to $[Co(CO)_4]^-$ to give $[MeCo(CO)_4]$ followed by CO insertion and reduction (ref. 156). In a related study, ethanol is reported to be produced with approximately 80% selectivity at a rate of ca. 2.4 x 10^{-3} mol/mol $[Co_2(CO)_8]$/sec. in diglyme at 200°C and 130 atm of CO/H_2 (1:1). Small amounts of C_2-C_3 oxygenated products also are produced and the solvent is largely converted into methyldigol ($MeO(CH_2)_2O(CH_2)_2OH$). The major steps in the proposed primary ethanol production cycle are outlined in Scheme XVI. Although no intermediates have been isolated from this system, one running at



Scheme XVI

150°C and giving substantial yields of hydroxymethyl formate precipitated unstable black crystals on cooling which are thought to be [59], indicating one possible mode of carbon-carbon bond formation in these systems (ref. 157).

The use of $[Co_2(CO)_8]$ as a catalyst precursor for a variety of purposes continues to be studied. In refluxing toluene it is effective for the conversion of 2-thioxo-1,3-dithioles to

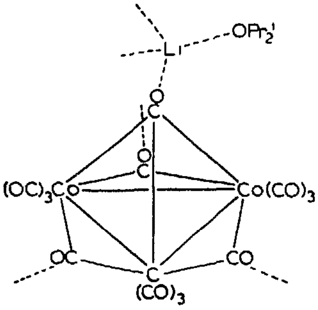


[59]

tetrathiofulvalenes (ref. 158). Although not as active as rhodium, it does provide a catalyst for the hydrosilylation of vinyltrimethylsilane by triethoxysilane (refs. 159, 160). At a ratio of $[Co_2(CO)_8]$/diphos of 1:1 in THF or dioxane, at 150-180°C a catalyst is obtained for the conversion of propene, carbon monoxide and water into good yields of dipropylketones (ref. 161). In toluene at 120°C $[Co_2(CO)_8]$ and diphos are active for the hydroformylation of methylmethacrylate. Other chelating and non-chelating diphosphines give less active catalysts. A possible intermediate is suggested to be $[HCo(CO)_2(diphos)]$ (ref. 162).

An SCF-Xα calculation has been performed on $[Co(CO)_4]^-$ (ref. 163) while an ab initio SCF-MO calculation has been performed on $[Co_2(CO)_6(C_2H_2)]$ as part of a study of the He I and He II photoelectron spectra of a series of $[Co_2(CO)_6(R_2C_2)]$ (R = alkyl or aryl) complexes. The conclusions of this study were that the Co-Co bonding electrons have ionization energies of 7.5-8.0 e.v. with the remainder of the d electrons in near-degenerate orbitals *ca.* 0.5 e.v. lower (ref. 164). The x-ray photoelectron spectra of the phosphine and phosphide clusters $[Co_4(CO)_{10}(PPh)_2]$, $[Co_4(CO)_8(PPh_2)_2]$, $[Co_4(CO)_9(PPh_2)_2(P(OMe)_3)]$ and $[Co_4(CO)_9(PPh_2)_2(PPh_3)]$ have been measured. The phosphorus sp binding energies are all very similar in accord with the lack of reactivity at phosphorus in all these complexes (ref. 165).

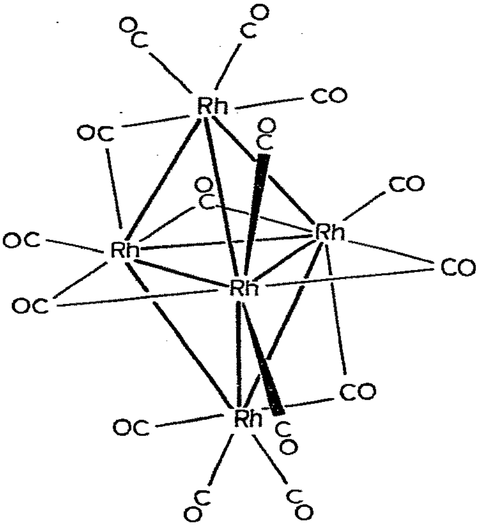
Intense interest in the synthesis and chemistry of carbonyl clusters containing four or more metal atoms continues unabated. Oxidation of $[Co_6C(CO)_{15}]^{2-}$ with iron (III) chloride yields the paramagnetic cluster $[Co_6C(CO)_6(\mu\text{-}CO)_8]^-$. A structural study of the tetramethylammonium salt shows it to be a distorted octahedron of C_{2v} symmetry. The pattern of Co-Co distances together with the disposition of the carbonyl ligands led to the conclusion that the odd electron is largely localized outside one edge of the cluster (ref. 166). Substitution reactions of the tetracobalt cluster have been studied. $[Co_4(CO)_{12}]$ and $[Co_4(CO)_{11}(P(OMe)_3)]$ react with PPh_3 in hexane to yield $[Co_4(CO)_{11}(PPh_3)]$ and $[Co_4(CO)_{10}(P(OMe)_3)(PPh_3)]$ respectively. Inhibition of the latter reaction by CO and first order kinetics indicate a dissociative process. Rather surprisingly the former reaction is very fast (considerably faster than CO exchange) but is unaffected by radical scavengers. Unlike the iridium analog, there appears to be little effect of phosphine substitution on the rate of subsequent substitution reactions (ref. 167). At -70°C, $[Co_4(CO)_{12}]$ reacts with the nucleophiles X^-(X = Br, I, SCN), OR^-(R = Me, Pr^i) and Pr^nNH_2 to give $[Co_4(CO)_{11}X]^-$, $[Co_4(CO)_{11}COOR]^-$, and $[Co_4(CO)_{11}(CONHPr^n)]$ respectively (ref. 168a). The structure of $[Co_4(CO)_{11}I]^-$ has been determined (ref. 168b). On the other hand when $[Co(CO)_4]^-$ (as the Li^+ salt) is the nucleophile, degradation occurs to give $Li[Co_3(CO)_{10}]$ which has been isolated as the diisopropyl etherate and shown to be $Li(OPr_2^i)[Co_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$ ([60])



[60]

In the solid each Li is additionally coordinated by the oxygen atom of the μ_3-carbonyl and those of a μ_2-carbonyl from two additional clusters. However in solution relatively little carbonyl-bridged species is seen. The solid state structure is attributed to the increased acidity of the lithium ion due to poorer solvation in the absence of excess solvent (ref. 169). Reduction of $[Co_2(CO)_8]$ with zinc and carbon monoxide followed by addition of phenyldichlorophosphine gives the tetranuclear cluster $[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ containing a Co_4P_2 unit of approximate octahedral geometry with two opposite Co–Co edges bridged by carbonyl groups. One or two terminal carbonyls can be substituted by PPh_3 (the bis complex has <u>trans</u> phosphines). Both phosphine-substituted complexes have been structurally characterized and the bis complex as well as the parent carbonyl are effective as hydroformylation catalysts for 1- and 2-pentene. Significantly the clusters are fully recoverable at the end of the reaction suggesting that the intact clusters are the active catalysts (refs. 170, 171).

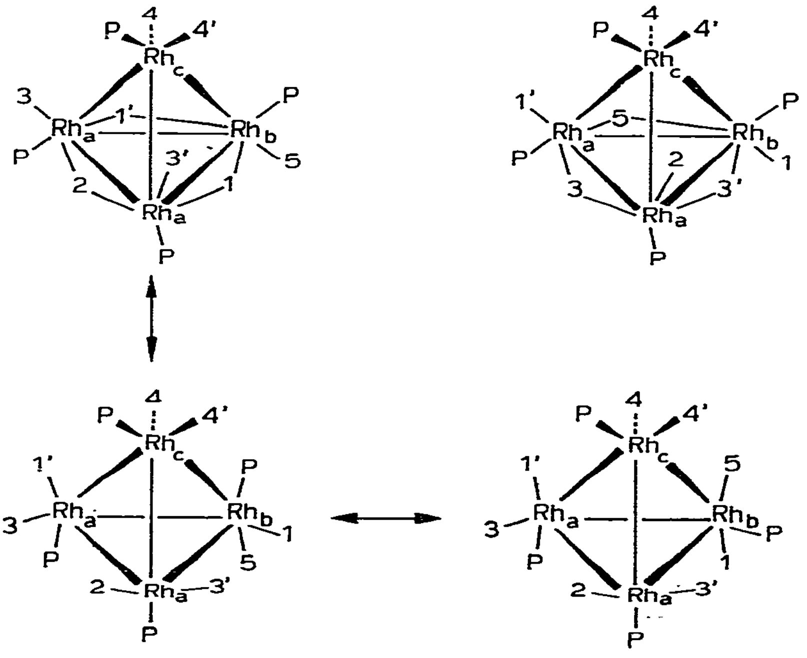
With a significant number of structural studies largely completed, the Italian group has made great progress in understanding the complexities of the rhodium cluster carbonyl system. Reaction of $K_2[Rh_6C(CO)_{15}]$ with $[Cu(NCMe)_4]BF_4$ in methanol gives $[Cu_2(NCMe)_2Rh_6C(CO)_6(\mu\text{-}CO)_9]$ whose structure consists of a C-centered trigonal prism of rhodium atoms with the triangular faces capped by Cu(NCMe) groups and all edges bridged by carbonyl groups. Each rhodium also bears a terminal carbonyl ligand. Because there are no particular steric constraints, the coordination of the copper to the axial faces indicates that these are the most basic sites (ref. 172). Reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with CO at -78°C in THF gives $[Rh_6(CO)_{16}]$ and $[Rh_5(CO)_{10}(\mu\text{-}CO)_5]^-$ (originally thought to be $[Rh_{12}(CO)_{\sim 34}]^-$) whose structure was determined as the PPN^+ salt (PPN = bis(triphenylphosphine)iminium) and shown to be [61]. In solution a ^{13}C NMR study implies either the existence of a D_{3h} structure with six μ_2-carbonyls or a fluxional molecule. The pentanuclear anion can also be prepared in pure form from $[Rh_4(CO)_{12}]$ and $[Rh(CO)_4]^-$ in THF under CO and on flushing the solution with nitrogen regenerates $[Rh_{12}(CO)_{30}]^{2-}$ as well as forming some $[Rh_6(CO)_{15}]^{2-}$ (ref. 173). A high pressure (500-1000 atm) infrared study shows that $[Rh_5(CO)_{15}]^{2-}$ and $[Rh(CO)_4]^-$ do not react in sulfolane between 50 and 200°C in the presence of a 1:1 H_2/CO atmosphere. The same species also appeared to be generated under the same conditions in N-methylmorpholine from $[Rh(CO)_2(acac)]$, $[Rh_6(CO)_{15}]^{2-}$, $[Rh_7(CO)_{16}]^{3-}$, or $[Rh_4(CO)_{12}]$ and cesium benzoate. Under CO pressure the reversible conversion of $[H_{5-n}Rh_{13}(CO)_{24}]^{n-}$ (n = 2,3) to $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ was also noted (ref. 174). The $[Rh_{14}(CO)_{25}]^{4-}$ cluster can be protonated with phosphoric acid in aqueous acetonitrile to give $[HRh_{14}(CO)_{25}]^{3-}$ which was isolated as the tetraethylammonium salt and structurally characterized. From a consideration of the various Rh-Rh distances it was suggested that the hydrogen atom is located on a face bounded by four metal atoms. The complex can also be prepared by reaction of $[HRh_{13}(CO)_{24}]^{2-}$



[61]

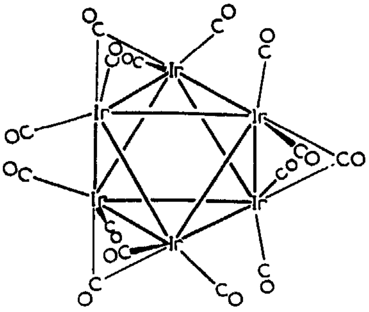
and $[Rh(CO)_2(MeCN)_2]^+$ and can be deprotonated with potassium t-butoxide (ref. 175). Both the hydride and $[Rh_{14}(CO)_{25}]^{4-}$ are fluxional and have been studied by $^{13}C\{^{103}Rh\}$ and ^{103}Rh NMR. For the former complex, the carbonyl and hydride ligands migrate independently with the latter migrating within the metal cage (ref. 176). When $Na_2[H_3Rh_{13}(CO)_{24}]$ (vide infra) (or $[Rh_4(CO)_{12}]$ + NaOH) is refluxed in isopropanol $Na_2[Rh_{14}(CO)_{11}(\mu\text{-}CO)_{15}]$ and $Na_4[Rh_{22}(CO)_{12}(\mu\text{-}CO)_{18}(\mu_3\text{-}CO)_7]$ result. A structural study of the first cluster showed the metal framework to be a combination of body-centered and cubic close-packed fragments. In methanolic base it is converted to $[HRh_{14}(CO)_{25}]^{3-}$ and ultimately to $[Rh_{14}(CO)_{25}]^{4-}$. Hydrogenation in acetonitrile leads to a mixture containing these two Rh_{14} species plus the hydrides $[H_{5-n}Rh_{14}(CO)_{24}]^{n-}$ (n = 2,3) while bromide ion removes one carbonyl to give $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh(CO)_2Br_2]^-$ (ref. 177). The Rh_{22} cluster was studied crystallographically as its propyltriethylammonium salt and is described as a combination of hexagonal and cubic close-packed atoms in a 6/7/6/3 layer arrangement. The cluster appears to contain four electrons less than would be predicted and the possibility that it also contains four interstitial hydrides is raised although no NMR evidence for them has yet been found (ref. 178). The heteroatom clusters $[Rh_6C(CO)_{16}]^{2-}$, $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ and $[Rh_9P(CO)_{21}]^{2-}$, which, unlike the non-heteroatom clusters mentioned above, do not degrade under high pressures of CO/H_2 and may therefore be possible analogies for poisoned heterogeneous catalysts, have been studied by ^{103}Rh NMR. The first shows only one rhodium environment as expected. The second shows three signals in the ratio of 1:8:8 to increasing field. The unique rhodium is extremely deshielded while the highest field resonance is close to that of rhodium metal suggesting a formulation as a Rh(I) disulfide moiety embedded in a largely zerovalent rhodium cage. For the phosphide cluster the spectrum shows one peak at room temperature and three in a 1:4:4 ratio at -80° indicating the Rh skeleton to be fluxional (ref. 179).

On a simpler plane, $^{13}C\{^{1}H, ^{31}P\}$ NMR studies on the fluxional cluster $[Rh_4(CO)_9(P(OMe)_3)_4]$ showed it to have a static structure at -90°C and to equilibrate all carbonyl and all phosphite ligands at 82°C. The lowest energy carbonyl scrambling process involves only the carbonyl ligands in the basal plane and is shown in Scheme XVII (ref. 180).



Scheme XVII

One of the few large clusters of iridium has been synthesized by the reaction of $[Ir(CO)_2Cl_2]^-$ with carbon monoxide at 90°C in aqueous 2-methoxyethanol in the presence of potassium carbonate and formulated as $[Ir_6(CO)_{12}(\mu\text{-}CO)_3]^{2-}$. The structure of the benzyltrimethylammonium salt was determined, showing it to be [62] (ref. 181).



[62]

There is considerable activity in the area of supported clusters as catalysts or catalysts precursors. Judging by the number of references to it, many results were reported recently at a Russian symposium on this topic (ref. 182) although the general availability of the conference report is not known. In the area of heterogenized clusters, $[Rh_6(CO)_{16}]$ has been supported by reaction with silica containing pendent diphenylphosphinopropyl or cyclohexylaminopropyl groups and found to be active for ethylene hydrogenation. Treatment with hydrogen alone led to aggregation to form larger metal crystallites (ref. 183). Carbonylation of the supported phosphine cluster gave a species thought to contain $Rh_6(CO)_{13}$ units which was relatively resistant to CO loss and which on heating to 80° gave a mixture of Rh(I) and Rh(0) species which could be readily interconverted (ref. 189). Reduction of $[Ir(CO)_2(\underline{p}\text{-toluidine})Cl]$ with zinc in 2-methoxyethanol in the presence of the phosphinated silica gave anchored $Ir_4(CO)_{11}$

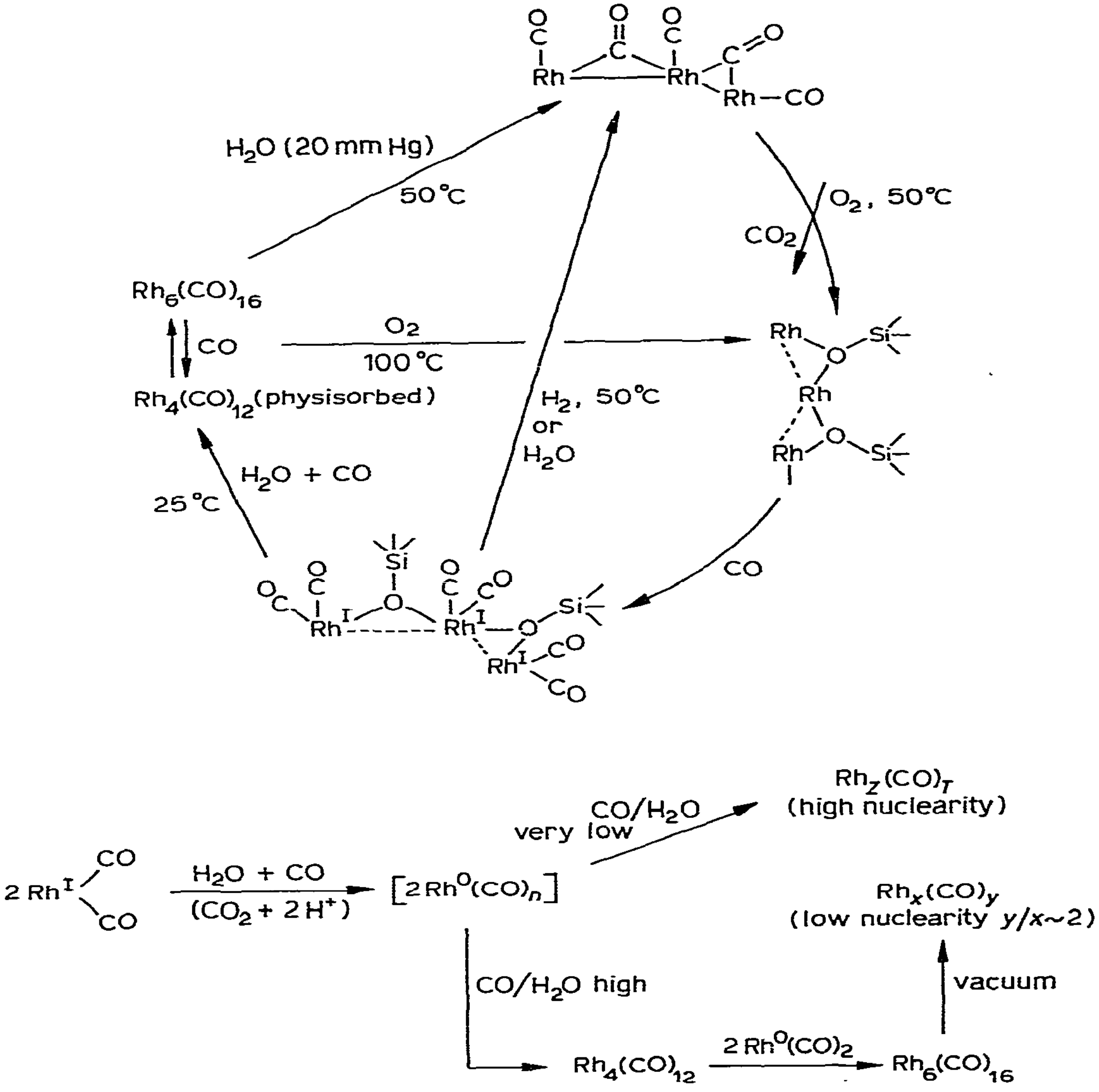
clusters. The phosphinated silica also reacted with preformed $[Ir_4(CO)_{11-n}(PPh_3)_n]$ to give supported $Ir_4(CO)_{10-n}(PPh_3)_n$ (n = 1,2) clusters all of which appeared to retain their integrity up to 80^oC under carbon monoxide and hydrogen. Similar properties were noted for these clusters supported on phosphinated styrene-divinylbenzene copolymer although above 120^oC decomposition and metal aggregation occurred. The supported clusters are catalysts for hydrogenation of ethylene and cyclohexene at 80^oC and maintain good activity up to 5000 turnovers. The kinetics of the hydrogenation reaction are distinctly different from those observed using supported iridium metal suggesting that the intact clusters are the active species. Active site formation via a reversible Ir-Ir bond cleavage is suggested (refs. 185-187). Catalysts for the hydrogenation of carbon monoxide have been prepared from a variety of metal oxides and $[Co_2(CO)_8]$ or $[MnCo(CO)_9]$. The Co-Mn catalyst on alumina was more active and longer-lived than cobalt by itself and gave straight chain C_1-C_{11} hydrocarbons with the maximum at C_6 (ref. 188). On the other hand, the cobalt-alumina system at 175^oC was also reported to give a mixture of straight and branched chain alkanes (68:26) (ref. 189). The use of SiO_2, TiO_2, and ZrO_2 supports gave catalysts more active than those on MgO or Al_2O_3, but the alumina supported system gave the highest yield of lighter alkanes (ref. 190). A more selective catalyst can be obtained by the cadmium vapor reduction of CoA and CoY zeolites. The former yields propene from synthesis gas while the latter gives n-butane plus a mixture of other C_4-C_7 species. An infrared spectrum of the CoA catalyst after use indicated the presence of a cobalt cluster containing only terminal carbonyl ligands (ref. 191). Treatment of a RhY zeolite with carbon monoxide gives a species having an infrared spectrum indicative of an $Rh^I(CO)_2$ species which reacts with methyl iodide to give an Rh(III) acetyl species. Further reaction with carbon monoxide causes the acetyl group to migrate to the support and regenerates the $Rh^I(CO)_2$ species (ref. 192). In studies of the nature of the surface species in systems like these, it was determined that $[Co_2(CO)_8]$ adsorbed on MgO at room temperature produced small carbonyl-containing clusters but on heating these lost carbon monoxide and agglomeration occurred (ref. 193). When adsorbed on silica surfaces containing surface Sn(II) and Sn(IV) species, $Co(CO)_n$ fragments bound to Sn were detected. Most numerous were those with a Co/Sn ratio of 2 (ref. 194).

The thermal decomposition of $[M_4(CO)_{12}]$ (M = Co,Ir) and $[Rh_6(CO)_{16}$ in KBr discs has been studied by infrared spectroscopy. A matrix effect is observed which enhances the thermal stability (ref. 195). A temperature-programmed decomposition study of $[Co_2(CO)_8]$, $[M_4(CO)_{12}$ (M = Co, Rh, Ir) and $[Rh_6(CO)_{16}]$ supported on alumina in a helium atmosphere shows methane to be a significant product. The methane is thought to arise from reaction of the carbonyl ligands with surface hydroxyl groups and the yield is quite insensitive to the nuclearity of the cluster. In the presence of hydrogen a quasi-catalytic reduction of carbon monoxide is observed which is thought to occur directly rather than by decomposition to surface carbide species. The results are interpreted to indicate that clusters are not essential for Fischer-Tropsch catalysis (ref. 196). On the other hand, if $[Rh_6(CO)_{16}]$ on alumina is treated with oxygen at low temperature, the metal cluster remains intact even though all the carbonyls are removed. If sufficient adsorbed water is present, the original carbonyl cluster can be regenerated on carbonylation. This ability is destroyed if the decarbonylated sample is heated above 250°C. The recarbonylation step generates CO_2 but not hydrogen so water-gas-shift catalysis is not operative. Also if $^{18}O_2$ is used in the decarbonylation step, the label appears in the CO_2 produced on recarbonylation. The species formed on treatment with oxygen is proposed to be $[Rh_6(O_2)_6]$ and the recarbonylation reaction is thought to be that shown in Scheme XVIII (ref. 197). Silica-supported $[Rh_4(CO)_{12}]$ is converted to $[Rh_6(CO)_{16}]$, a process which is inhibited by carbon monoxide. Both supported clusters decompose to high nuclearity metal particles in the presence of water and to $Rh^I(CO)_2$ species in oxygen. Regeneration of the clusters can be accomplished by treatment of the $Rh^I(CO)_2$ species with CO + H_2O (Scheme XIX) (ref. 198).

$$[Rh_6(O_2)_6] \xrightarrow{CO} [Rh_6(CO)_{12}(O_2)_6] \xrightarrow{CO} [Rh_6(CO)_{16}] + CO_2$$

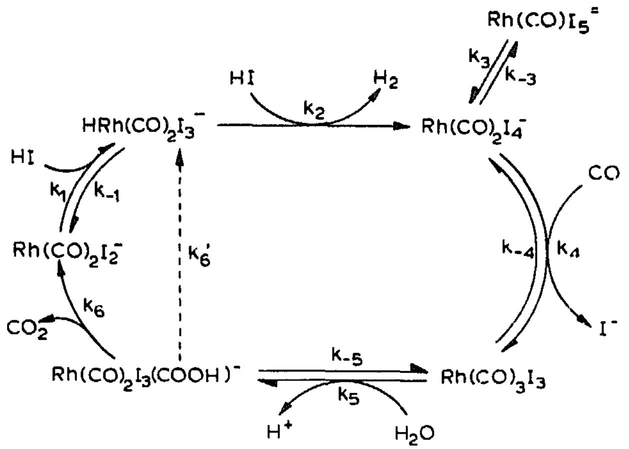
Scheme XVIII

Ethylenediamine solutions of $[Rh_2(CO)_4Cl_2]$, $[Rh_4(CO)_{12}]$ and $[Rh_{12}(CO)_{30}]^{2-}$ catalyze the water-gas-shift reaction and are proposed to be simpler than systems using alcoholic potassium hydroxide (ref. 199). Another effective catalyst precursor for this reaction is $[Rh(CO)_2I_2^-]$ which operates in a mixture of aqueous HI and


H₂O (20 mm Hg)
50 °C
O₂, 50 °C
CO₂
Rh₆(CO)₁₆
CO
O₂
100 °C
Rh₄(CO)₁₂ (physisorbed)
H₂, 50 °C
or
H₂O
H₂O + CO
25 °C
CO
very low
CO/H₂O
Rh_Z(CO)_T
(high nuclearity)
2 Rh^I(CO)₂
H₂O + CO
(CO₂ + 2 H⁺)
[2 Rh⁰(CO)ₙ]
Rhₓ(CO)ᵧ
(low nuclearity y/x~2)
vacuum
CO/H₂O high
Rh₄(CO)₁₂
2 Rh⁰(CO)₂
Rh₆(CO)₁₆

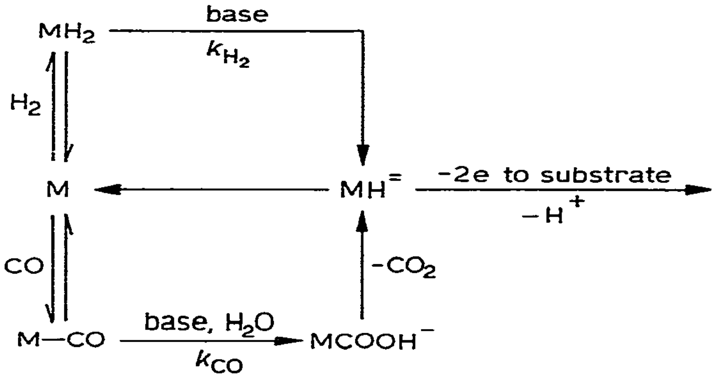
Scheme XIX

glacial acetic acid. The proposed mechanism for this catalyst is shown in Scheme XX. Above 80°C the catalytic reaction shows first order dependence on CO partial pressure and inverse dependence on acid and iodide concentrations while below 65°C the reaction rate is independent of CO pressure and shows second order dependence on iodide and positive dependence on acid concentrations. In the



Scheme XX

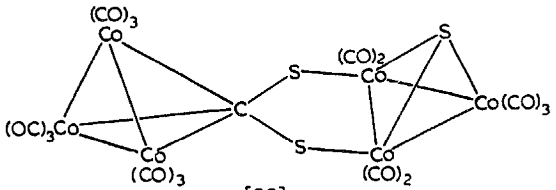
high temperature system, Rh(III) species predominate and the rate limiting step is thought to be CO_2 production (k_6) while at low temperatures, Rh(I) species are the major ones present and the rate limiting step is considered to be that producing hydrogen (k_1 and k_2) (ref. 200). A variation on this system reports the use of $[Ir_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ as catalysts for the reduction of nitrobenzene to aniline by CO/H_2 mixture (Scheme XXI). In this scheme, the species MH^-, in the presence of reducible substrates, can reduce them in preference to generating hydrogen as in the normal water-gas-shift systems. For the rhodium system, the consumption selectivity for hydrogen (upper path) vs carbon monoxide (lower path) is approximately unity over a range of gas composition (CO/H_2) of 1:3 to 3:1 indicating this system can effectively use synthesis gas feedstocks of a range of compositions (ref. 201).



Scheme XXI

A variety of other organic transformations can be accomplished in the presence of carbonyl clusters. Further studies on the oxidation of cyclohexanone in the presence of [$Rh_6(CO)_{16}$] show that the yield of acid increases with increasing carbon monoxide pressure implicating the involvement of species of lower nuclearity in the catalysis. The role of the metal is thought to be to accelerate the decomposition of peroxy species formed in the initial step (refs. 202, 203). In the Reppe modification of the hydroformylation reaction, [$Rh_6(CO)_{16}$] is superior to [$Ir_4(CO)_{12}$] as a catalyst precursor for the conversion of olefins to aldehydes and alcohols. The observation of higher activity at lower catalyst concentrations suggested fragmentation although the nature of the active species was not defined. The proposed mechanism is basically that established for the normal hydroformylation process except that the hydrido species is generated by oxidative addition of water to a low-valent acyl intermediate (ref. 204). At 220°C and high pressures of carbon monoxide, [$Rh_4(CO)_{12}$] catalyzes the addition of disubstituted acetylenes to furan to give up to 80% yields of cis- and trans-2-furanyl olefins and the reduction of p-substituted nitrobenzenes in benzene solution to mixtures of benzanilides and p-substituted anilines (refs. 205, 206). In the presence of small amounts of water, [$Ir_4(CO)_{12}$] is a precursor for a system which at 125-150°C and 100 psi of nitrogen catalyzes the redistribution reaction between triethyl- and tripropylamine. A mechanism involving C-H bond addition to the cluster to give an intermediate imminium complex is proposed (ref. 207).

The chemistry of alkylidynenonacabonyl tricobalt clusters and related complexes continues to attract interest. The reaction of $[Co_2(CO)_8]$ with carbon disulfide produces a large number of products and has been under study for some time. Another of the products has now been characterized as sym-$[(OC)_9Co_3C(CS_2)Co_3(CO)_7S]$, [63] (ref. 208). Reaction of the dichlorocarbene precursor, $PhHgCCl_3$ with $[Co_2(CO)_8]$ at 60°C gives $[ClCCo_3(CO)_9]$ At lower temperatures where no appreciable decomposition of the mercurial occurs the same yield of the alkylidyne cluster is obtained and



[63]

dichlorocarbene can be trapped in both reactions. A mechanism involving direct combination of both reactants either via a 4-center transition state or via oxidative addition of the $Hg-CCl_3$ bond to cobalt was proposed (ref. 209). The synthetic applications of $[XCCo_3(CO)_9]$ (X = Cl, Br) have been further explored. Reaction with aliphatic alcohols or secondary amines give the corresponding esters and amides of $[HO_2CCCo_3(CO)_9]$. In the presence of carbon monoxide and trimethylamine the yields are increased and this system also enables the reaction to be carried out with a variety of phenols and anilines (ref. 210). With alkane thiols, $[BrCCo_3(CO)_9]$ yields $[RSC(O)CCo_3(CO)_9]$ (R = Bu^n, Bu^t, Et) but with thiophenols only low yields of the sulfides $[ArSCCo_3(CO)_9]$ (Ar = Ph, *p*-tolyl) were obtained. For the latter better yields could be realized using $[ClCCo_3(CO)_9]$ or by treating the bromo derivative with the lithium salt of the thiophenol (ref. 211). Reaction of the parent complex $[HCCo_3(CO)_9]$ with R_3GeH (R_3 = Et_3, $Bu^n{}_3$, $ClPh_2$, $ClEt_2$, ClEtPh, Cl_2CH_2Ph) in refluxing benzene under carbon monoxide gave $[R_3GeCCo_3(CO)_9]$ possibly by an addition-elimination process (ref. 212) The hydroformylation of hex-1-ene can be catalyzed by a system based on $[MeCCo_3(CO)_9]$. However the observation of an induction period and an activity very similar to the $[Co_2(CO)_8]$-based system together with infrared evidence for $[Co_2(CO)_8]$ when olefin is absent suggests the active catalyst is probably mononuclear (ref. 213) Iridium analogs of the alkylidynenonacarbonyl tricobalt complexes, $[R{-}EIr_3(CO)_9]$, have been prepared by reaction of $NaIr(CO)_4$ with Cl_3CR, Cl_3SiMe or Cl_3GeMe in THF (R = Me; E = C, Si, Ge; R = Ph; E = C) (ref. 214).

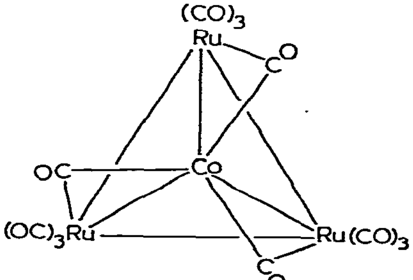
The photoelectron spectra of $[RCCo_3(CO)_9]$ (R = H, Cl, Br, Me) together with those of $[cpCo(CO)_2]$, $[Co_2(CO)_8]$, $[Co(CO)_3NO]$ and $[HCo(CO)_4]$ have been studied as part of an extensive series of carbonyl compounds to determine the extent of charge transfer in the π-backbonding to carbonyl and nitrosyl groups. It was concluded that in the carbonyls, more charge is transferred to carbon than to oxygen while in the nitrosyls it is about equally distributed. Moreover, the core binding energies for carbon, nitrogen and oxygen can be used to assess the extent of π-backbonding (ref. 215). Theoretical treatments of a number of systems of relevance to this section have been made using extended Huckel methods. For the $Co_3(CO)_9^-$ fragment it was concluded that it has bonding properties suitable for bonding to a CH^+ fragment and that in the resulting alkylidyne cluster the Co-C bonding is the major interaction holding it together. It was also determined that the difference in energy between CO-bridged and non-bridged forms was very small (ref. 216). The high-nuclearity rhodium clusters have been studied by determining the bonding capabilities of various close-packed arrays of between six and fifteen metal atoms. The number of cluster valence molecular orbitals was determined to be $6N + X$ where N is the number of atoms and X depends on the geometry of the cluster but is often near seven. The 6N orbitals are primarily metal s and d orbitals and the same number of valence MO's are found as in the bulk metal which is in accord with other data on the large clusters which indicate them to resemble metal fragments (ref. 217). Calculations on species important to the proposed mechanisms for the Co-catalyzed hydroformylation of olefins (e.g. $[Co_2(CO)_8]$, $[Co_2(CO)_7]$, $[HCo(CO)_4]$, $[HCo(CO)_3]$) have been performed. Results include the prediction that the non-bridged form of $[Co_2(CO)_8]$ has a very low barrier for homolysis to $[\cdot Co(CO)_4]$ and also can easily lose an equatorial carbonyl ligand to give $[Co_2(CO)_7]$ (ref. 218). An elaboration on a scheme proposed earlier to systematize the structures and fluxional properties of cluster carbonyls has appeared. The structures of quite a few and the distribution of carbonyl ligands between terminal and bridging modes are rationalized on the basis that the favored arrangement of ligands is that which minimizes non-bonded interactions. This leads to the carbonyl ligands approximating a regular or semi-regular polyhedron within which the metal cluster core resides. Distortions from the ideal arrangement are proposed to be the result of the metal core deviating from approximately spherical average symmetry (ref. 219). An approximate normal coordinate analysis of metal-metal vibrations in clusters such as $[M_4(CO)_{12}]$ (M = Co, Rh, Ir) has been proposed which appears to give reasonably good agreement with much more elaborate treatments (ref. 220).

b) Heteronuclear metal-metal bonded complexes

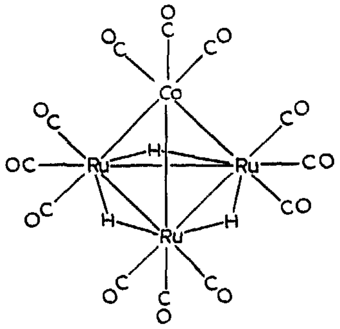
The photochemistry of $[R_3SiCo(CO)_4]$ (R = Et, Ph) in the presence of various substrates has been investigated to determine the relative importance of Co-Si bond cleavage vs. loss of carbon monoxide. The majority of the results indicate that dissociative loss of CO is the primary photoreaction. Thus photolysis in the presence of $P(OPh)_3$ or $P(OPh)_3$ + $HSiEt_3$ gave only $[R_3SiCo(CO)_3(P(OPh)_3)]$ while at -78°C in the presence of pent-1-ene, $[R_3SiCo(CO)_3(\text{pent-1-ene})]$ was the product. Irradiation in the presence of pent-1-ene/$HSiEt_3$ mixtures catalyzes the hydrosilylation and isomerization of the olefin (ref. 221). The dimers $[Co(CO)_3L]_2$ (L = PMe_2Ph, $AsMe_2Ph$, PEt_3, PBu^n_3) react with trifluorosilane to give $[F_3SiCo(CO)_3L]$ but with chlorosilanes decomposition occurred. With $[CoH(CO)_3(PPh_3)]$ at -95°C SiF_3H and $Si(OEt)_3H$ gave $[F_3SiCo(CO)_3(PPh_3)]$ and $[(EtO)_3SiCo(CO)_2(PPh_3)_2]$ respectively while $SiPh_3H$ yielded $[Ph_3SiCoH_2(CO)_2(PPh_3)]$. The last reacted with CO to give $[Ph_3SiCo(CO)_3(PPh_3)]$. Carbon monoxide is replaced by phosphines (L = PPh_3, $PMePh_2$) in $[Ph_3SiCo(CO)_4]$ to give analogous products while with $[Et_3SiCo(CO)_4]$, $[Co(CO)_3(PPh_3)]_2$ and Et_6Si_2 were the products (ref. 222). Reduction of $[Co(CO)_3((S)\text{-}Ph_2PNMeCHMePh)]_2$ with sodium amalgam followed by treatment with $MePh(Ph_3C)SnBr$ gave $[MePh(Ph_3C)SnCo(CO)_3((S)\text{-}Ph_2PNMeCHMePh)]$. The corresponding triphenylphosphine complex was prepared in the same way from $[Co(CO)_3PPh_3]_2$. The racemic products of both reactions were separated into their respective diasteroisomers and the structures determined to give the first examples of the determination of the absolute configuration about tetracoordinate tin.

The related complexes $[RPhMeSnCo(CO)_3L]$ (L = CO, PPh_3; R = $PhMe_2CCH_2$, $PhMeCHCH_2$, Ph) were prepared similarly and their configurational stability assessed (refs. 223, 224). Reaction of $[Co(CO)_4]^-$ with GeH_2ClGeH_2Cl gave $[(OC)_4CoGeH_2GeH_2Co(CO)_4]$ (ref. 225).

In an attempt to stabilize clusters against fragmentation, the tripod ligand $HC(PPh_2)_3$ was reacted with $[Co_2Rh_2(CO)_{12}]$, $[HFeCo_3(CO)_{12}]$ and $[M_4(CO)_{12}]$ (M = Co, Rh, Ir) to give $[HC(PPh_2)_3M_4(CO)_6(\mu\text{-}CO)_3]$ with the ligand coordinated to a face of the metal tetrahedron. For the Co_2Rh_2 cluster the ligand was found to bind to a Rh_2Co face (ref. 226). Several routes to mixed metal clusters have been reported. The reaction of $K[Co(CO)_4]$ with the trinuclear clusters $[Ru_3(CO)_{12}]$ and the mixture $[Ru_{3-n}Os_n(CO)_{12}]$ (n = 1,2) followed by protonation with phosphoric acid gave the monohydrides $[HCoRu_3(CO)_{13}]$ and a mixture of $[HRu_{3-n}Os_n(CO)_{13}]$ (n = 1,2) respectively. Using $PPN[Co(CO)_4]$ in the same reaction without acidification gave $PPN[CoM_3(CO)_{13}]$ from $[M_3(CO)_{12}]$ (M = Fe, Ru) and impure samples of $PPN[CoFe_2Ru(CO)_{13}]$ and $PPN[CoFeRu_2(CO)_{13}]$ from $[FeRu(CO)_{12}]$ and $[FeRu_2(CO)_{12}]$ respectively. Attempts to protonate $[CoFe_3(CO)_{13}]^-$ failed. The structure of $PPN[CoRu_3(CO)_{13}]$ was determined to be [64] (ref. 227). While $[Os_3(CO)_{12}]$ failed to react under these conditions, photolysis of the solution for 48 hrs. provided a 35% yield of $PPN[CoOs_3(CO)_{13}]$ (ref. 228). Hydrogen reacts with $[HCoRu_3(CO)_{13}]$ in refluxing hexane to yield $[H_3CoRu_3(CO)_{12}]$ [65] whose structure has been determined. From low temperature proton NMR studies the presence of a second isomer, thought to be [66] is present in solution. On warming interconversion of isomers and a total averaging of hydride environment occurs



[64]



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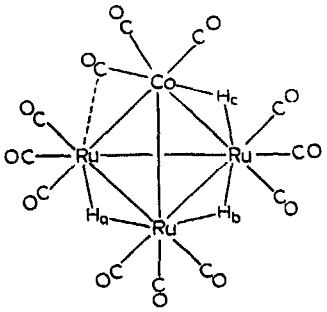
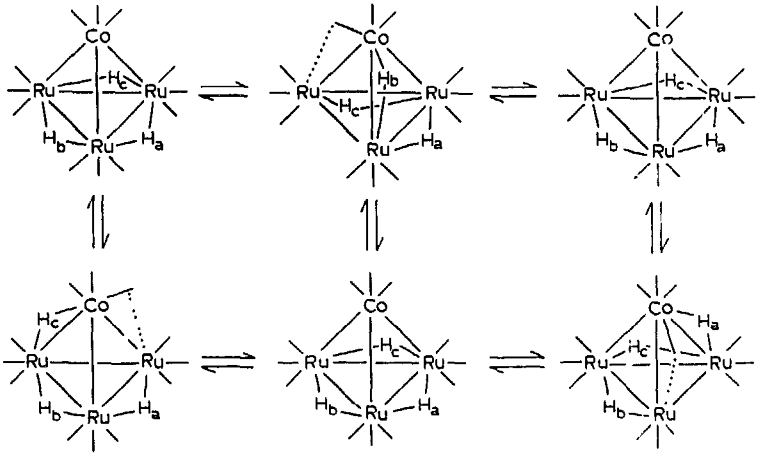


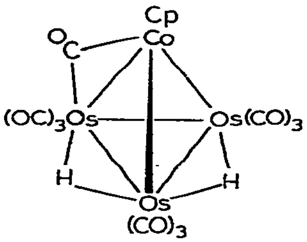
[66]

by a mechanism proposed to be that shown in Scheme XXII (ref. 229). Carbon monoxide reacts readily with $[HCoRu_3(CO)_{13}]$ at 25°C to generate $[Ru_3(CO)_{12}]$, $[Ru(CO)_5]$, hydrogen and uncharacterized



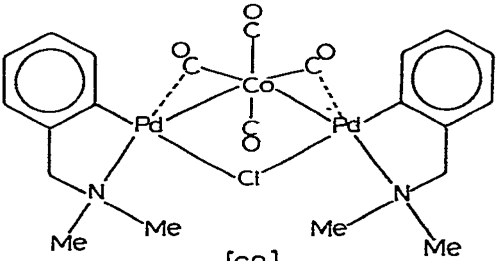
Scheme XXII

cobalt-containing products. By contrast the anion $[CoRu_3(CO)_{13}]^-$ under the same conditions goes to $[Ru_3(CO)_{12}]$ and $[Co(CO)_4]^-$ (ref. 230). An interesting mixed metal species containing both early and late transition series metals can be got from the reactio of $[cp_2NbH_3]$ and $[Co_2(CO)_8]$ in benzene. The structure has been determined and shows it to be $[cp_2Nb(CO)(\mu\text{-}CO)Co(CO)_3]$ (ref. 231). The coordinatively-unsaturated cluster $[H_2Os_3(CO)_{10}]$ reacts with $[cpCo(CO)_2]$ at 90°C in toluene to give the fluxional dihydride [67] (ref. 232).



[67]

One of the few examples of a mixed-metal cluster containing palladium is obtained by the reaction of $[Pd_2Cl_2L_2]$ (L = o-metallated dimethylbenzylamine) with $Na[Co(CO)_4]$. Both *cis* and *trans* isomers of the product are obtained and a crystal structure of the former showed it to be [68] (ref. 233). The electrochemical reduction

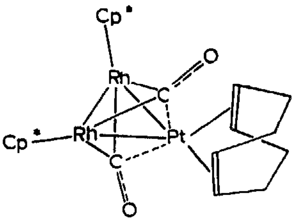


[68]

of the linear trimetallic species $[(OC)_4CoPt(L)_2Co(CO)_4]$ and $[(OC)_4CoPt(L)_2CoL_4]$ (L = cyclohexylisocyanide) at a gold electrode proceeds via an irreversible one-electron step to generate $[Co(CO)_4]^-$. The remaining $[Pt(L)_2CoL'_4]$ species (L' = CO, $C_6H_{11}NC$) is a radical with a half-life of 30 min. (refs. 234, 235). The tin-transition metal species $[SnCl_2M_2]$ (M = $Mn(CO)_5$, $Re(CO)_5$, $cpFe(CO)_2$) react with $Tl[Co(CO)_4]$ to generate the salts $[SnClM_2][Co(CO)_4]$ however with the unsymmetrical derivatives $[SnCl_2(Crcp(CO)_3)M]$ (M = $Mn(CO)_5$, $cpFe(CO)_2$) the neutral complexes $[SnCl(Crcp(CO)_3)(M)(Co(CO)_4)]$ are obtained. From infrared and mass spectral measurements, the Co-Sn bond is the weakest of the three heterometallic bonds. (ref. 236).

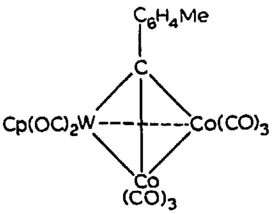
Trimethylphosphite reacts with $[Co_3Rh(CO)_{12}]$ and $[Co_2Rh_2(CO)_{12}]$ to give mono-, di- and trisubstituted clusters plus a variety of fragmentation and rearrangement products. For $[Co_3Rh(CO)_9(P(OMe)_3)_3]$, two ^{31}P NMR signals are observed for the rhodium-bound phosphite suggesting the presence of axial and equatorial substituents at this site. Other products from the first reaction are $[Co_2Rh_2(CO)_{10}L_2]$ $[Co_2(CO)_6L_2]$ and $[Co(CO)_2L_3][Co(CO)_4]$ while from the second these are the latter two plus $[Co_3Rh(CO)_{10}L_2]$ and $[Co_4(CO)_{10}L_2]$ (ref. 237).

The observation that $[cp_2{}^*Rh_2(CO)_2]$ reacts with carbene precursors to give methylene-bridged dimeric products (see section on σ-bonded complexes) suggested the possibility of the insertion of a low-valent metal complex into the Rh-Rh double bond. This proved successful and with $[Pt(COD)_2]$ [69] was obtained. A related complex containing

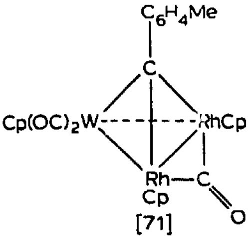


[69]

one CO and one PPh_3 ligand on the platinum was prepared from $[Pt(C_2H_4)(PPh_3)_2]$. The structure of [69] has been determined (ref. 238). The synthesis of novel heterometallic alkylidyne trimetal systems has been achieved using the carbyne complex $[cpW(CC_6H_4Me)(CO)_2]$ Reaction with $[Co_2(CO)_8]$ or $[cp_2Rh_2(CO)_2]$ gave [70] and [71]. Reaction

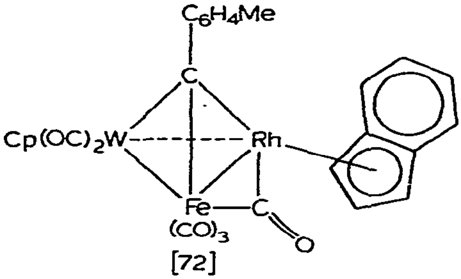


[70]



[71]

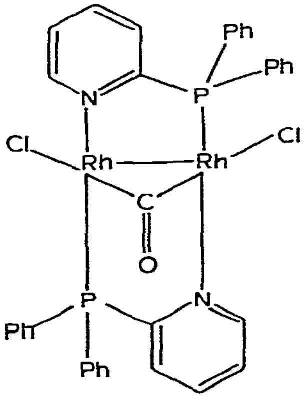
of the carbyne complex with $[(\eta^5\text{-}C_9H_7)Rh(CO)_2]$ gave $[(\eta^5\text{-}C_9H_7)RhW(cp)\text{-}(\mu\text{-}CC_6H_4Me)(CO)_3]$ which reacted further with $Fe_2(CO)_9$ to give [72].



[72]

The structures of these complexes have been determined (ref. 239).

The potentially bridging ligand diphenyl(2-pyridyl)phosphine has been used in that capacity for a stepwise synthesis of homo- and heterobimetallic complexes. With $[Rh(CO)_2Cl]_2$ it binds initially through phosphorus to give the familiar <u>trans</u>-$[Rh(CO)Cl(L)_2]$ complex which on further reaction with $[Rh(CO)_2Cl]_2$ or with $[Pd(COD)Cl_2]$ yields the dimers [73] and [74]. The structures of both have been determined and it is interesting to note that in both cases rearrangement of one ligand has occurred on dimer formation (ref. 240).



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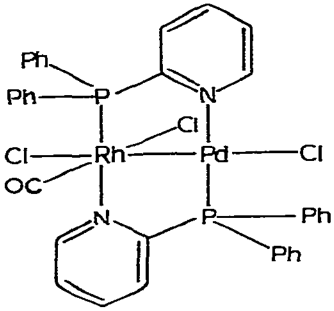
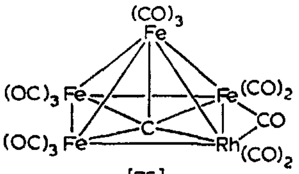


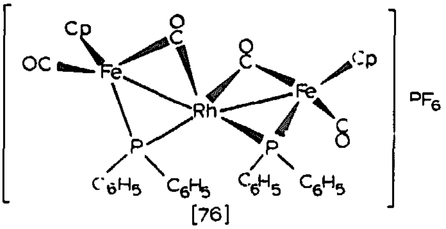
[74]

As part of a rational synthesis of mixed metal clusters, $[Fe_5C(CO)_{14}]^{2-}$ was reacted with $[M(COD)Cl]_2$ (M = Rh, Ir) or $[Rh(CO)_2Cl]_2$ to give the octahedral clusters $[MFe_5C(CO)_{14}(COD)]^-$ and $[RhFe_5C(CO)_{16}]^-$ respectively. Oxidation of the latter complex with Fe(III) removes an iron vertex giving $[RhFe_4C(CO)_{14}]^-$ [75] (ref. 241). A full

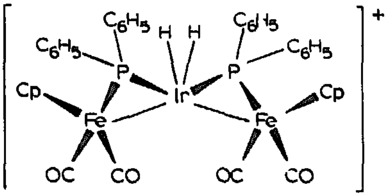


[75]

account has now appeared on the behavior of $[(\eta^5\text{-}C_5H_4R)Fe(PPh_2)(CO)_2]$ (R = H, Me), L, as a ligand. In toluene or benzene, reaction with $[Rh(CO)_2Cl]_2$ or $[M(COD)Cl]_2$ (M = Rh, Ir) produces *trans*-$[M(CO)ClL_2]$ but if methanol is used as a solvent for $[Rh(COD)Cl]_2$, addition of a large counterion such as PF_6^- produces the novel chiral species [76]. In solution [76] readily racemizes via opening of the carbonyl bridges. The iridium analog is only obtainable from $[Ir(COD)(EtOH)_x]BF_4$ and sodium tetraphenylborate in ethanol. Complex [76] is unreactive towards hydrogen but reversible hydrogenation of the iridium complex occurs to give [77].

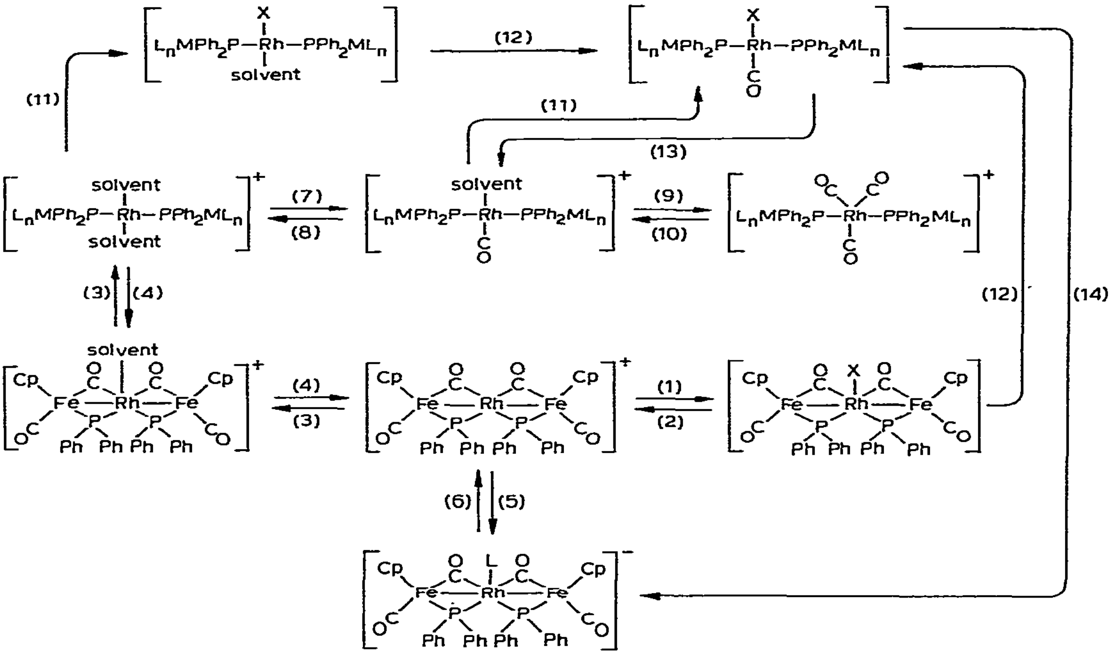


[76]



[77]

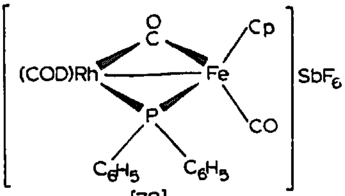
Further chemistry of [76] is given in Scheme XXIII.



(1) X^-(=Cl,Br,I,CN) in CH_2CL_2. (2) BPh_4^-,PF_6^-,SbF_6^- in EtOH. (3) Solv.(=THF,acetone). (4) Solvent loss. (5) L'(=PPh_3,$P(OMe)_3$) in Ch_2Cl_2. (6) Loss of L. (7) CO. (8) Solv.(=THF,acetone). (9) CO in $CHCl_2$. (10) Solv. (=THF,acetone) or heat in CH_2Cl_2. (11) X^-(=Cl,Br,I,CN). (12) (CO). (13) Ag^+ in THF or acetone. (14) L'=$P(OMe)_3$ in CH_2Cl_2.

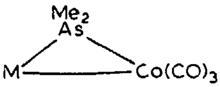
Scheme XXIII

Treatment of $[Rh(COD)Cl]_2$ with $AgSbF_6$ in ethanol followed by a limited quantity of the ligand gave [78]. Analogs of [76] and [78] with the ligands $[cpFe(SBu^t)(CO)_2]$ and $[cpFe(SPh)(CO)_2]$ respectively were also synthesized (ref. 242). One of the larger examples of mixed-metal clusters is $(PPN)_2[NiRh_6(CO)_7(\mu\text{-}CO)_6(\mu_3\text{-}CO)_3]$ which was prepared from $[Rh_6(CO)_{15}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$. The other product of the reaction is $[Rh_7(CO)_{16}]^{3-}$. Treatment of the mixed cluster with CO regenerates $[Rh_6(CO)_{15}]^{2-}$ with the concomitant formation of $[Ni(CO)_4]$. The reaction can be reversed on flushing the solution with nitrogen. A related octahedral cluster, $[NiRh_5(CO)_{15}]^-$ can be prepared from $[Ni_5(CO)_{12}]^{2-}$ and $[Rh_4(CO)_{12}]$ and is converted to $[Ni(CO)_4]$ and $[Rh_5(CO)_{15}]^-$ by CO (ref. 243).

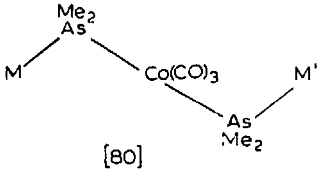


[78]

The construction of open-chain as well as cluster complexes containing several different metal atoms is an area of considerable activity Reaction of [79] (M = $Fe(CO)_4$, $Fe(CO)_3PMe_3$, $cpMn(CO)_2$) with $M'AsMe_2$

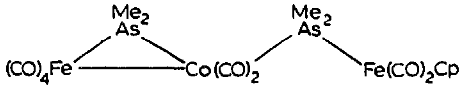


[79]



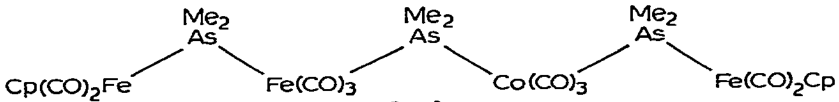
[80]

(M' = $cpFe(CO)_2$, $cpFe(CO)PMe_3$, $cpM''(CO)_3$ (M'' = Cr, Mo, W)) yields [80] (ref. 244). Longer chains can be constructed by the reaction of $[cpFe(CO)_2AsMe_2]$ with $[(OC)_4FeAsMe_2Co(CO)_2(NBD)]$ to give [81]



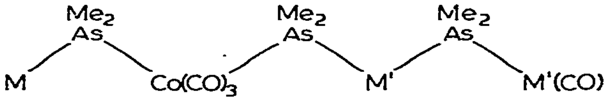
[81]

which on treatment with more [$cpFe(CO)_2AsMe_2$] yields [82]. Similar



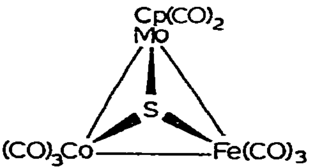
[82]

processes have afforded related species containing three different metals ([83] (M = $Fe(CO)_4$, $cpMn(CO)_2$; M' = $cpCr(CO)_2$, $cpMo(CO)_2$).

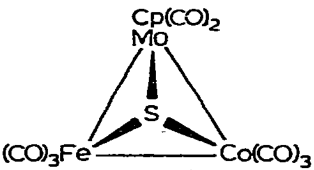


[83]

The structure of the Fe-Co-Cr-Cr complex has been determined (ref. 245) Other routes to related chains have made use of bridging ligands such as Me_2NEMe_2 (E = P, As) and Me_2PPMe_2. Reaction of [79] (M = $Fe(CO)_4$) with these ligands yields [$(OC)_4FeAsMe_2Co(CO)_3L$]. Further reaction of the Me_2PPMe_2 derivative with [79] (M = $Fe(CO)_4$) gives the biphosphine-bridged complex [$(OC)_4FeAsMe_2Co(CO)_3PMe_2PMe_2$-$Co(CO)_3AsMe_2Fe(CO)_4$]. Cleavage of the M-Co bond in [79] (M = $Fe(CO)_4$, $cpMn(CO)_2$) with PMe_2Cl gives [$MAsMe_2Co(CO)_3PMe_2Cl$] which can be hydrolyzed to [$(MAsMe_2Co(CO)_3PMe_2)_2O$] (refs. 246, 247). The first example of the resolution of an optically active cluster has been reported. The racemic mixture [84] reacts with (R)-$PMePr^nPh$ with substitution occurring only on cobalt. The diastereomers were separated by fractional crystallization and reconverted to the corresponding optically active carbonyl clusters by treatment with

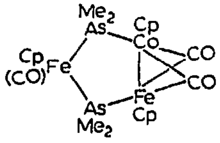


[84a]



[84b]

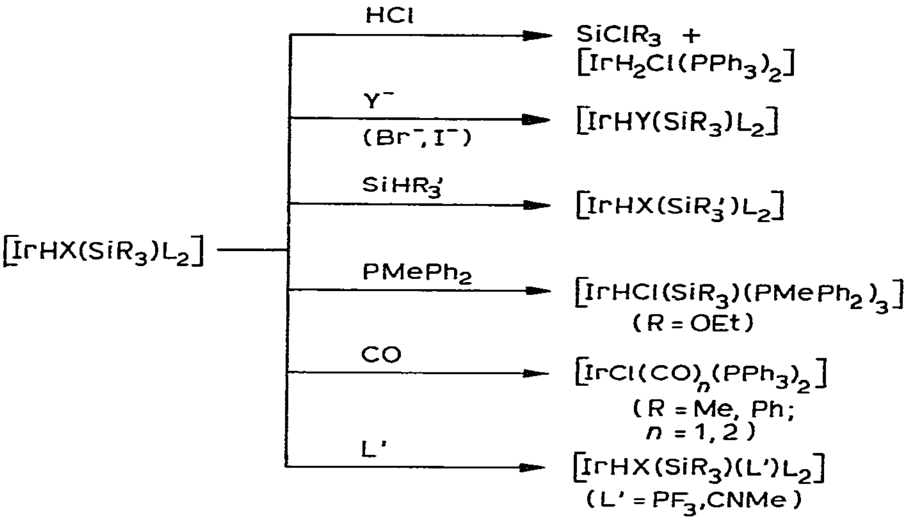
CO in the presence of methyl iodide. The absolute configurations were determined from a crystal structure study of the phosphine derivative of [84b] (ref. 248). Although the majority of the preceeding reactions appear to be quite straightforward, the reacti between [cpFe(CO)$_2$AsMe$_2$] and [cpCo(CO)$_2$], which required forcing conditions, yielded a variety of products. The structure of one of these showed it to be [85] (ref. 249).



[85]

Dimethylsulfoxide solutions of Hg(ClO$_4$)$_2$ are reported to react with [Ir(CO)Cl(PPh$_3$)$_2$] to give [Ir(CO)Cl(PPh$_3$)$_2$)$_n$Hg](ClO$_4$)$_2$ (n = 1-3) while in the presence of Hg(O) ananalogous species with n = 4 can form. The complexes were characterized polarographically (ref. 250). In an exploration of the mechanism of the catalysis of the formation of alkoxy silanes from HSiR$_3$ (R = Et, Ph, OEt) and ethanol or methanol by Ir(I) complexes, the reaction of the silanes with [IrX(N$_2$)L$_2$] or [IrXL'$_2$] (X = Cl, Br; L = PPh$_3$, AsPh$_3$; L' = PPh$_3$, AsPh$_3$, SbPh$_3$, P(cyclo-C$_6$H$_{11}$)$_3$, P(p-tolyl)$_3$, PMePh$_2$) was studied. From both, the complexes [IrHX(SiR$_3$)L$_2$] were formed. Further reactions of these are shown in Scheme XXIV. For R = F, the reaction with CO gave a mixture of four isomers (ref. 251). In the catalytic system it is proposed that [IrHX(SiR$_3$)L$_2$] is the initial species formed and that the coordinated silyl group is attacked by the alcohol to give alkoxy silane and [IrH$_2$XL$_2$] which loses hydrogen to regenerate [IrXL$_2$] for resumption of the catalytic cycle (ref. 252).

In the presence of [HFeCo$_3$(CO)$_{12}$], cis-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] reacts with hydrogen in methanol at 20°C to yield up to 0.32 mol of ammonia per mol of tungsten together with traces of hydrazine. A protonation of tungsten-bound nitrogen by the hydrido cluster is proposed to occur (ref. 253). Finally, a mass spectral study gives the Co-Sn bond dissociation energy in [Me$_3$SnCo(CO)$_4$] as 217kJ/mol (ref. 254).



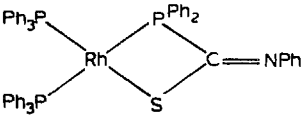
Scheme XXIV

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

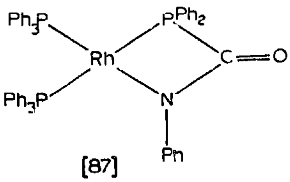
The reaction between $[Co_2(CO)_8]$, triphos (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) and CS_2 gives $[Co(triphos)(\eta^2-CS_2)]$. The unbound sulfur atom can coordinate to other metal atoms and by reaction of this complex with M(THF) (M = $cpMn(CO)_2$, $Cr(CO)_5$) the bimetallic complexes $[Co(triphos)(\mu-CS_2)M]$ were prepared. Reaction of $[Co(triphos)(\eta^2-CS_2)]$ with $[Co(H_2O)_6]^{2+}$ and triphos gave $[Co(triphos)(\mu-CS_2)Co(triphos)]^{2+}$ which could also be prepared from $Co(BF_4)_2 \cdot 6H_2O$, triphos and CS_2 in hot acetone and which could be reduced to $[Co(triphos)(\eta^2-CS_2)]$ with sodium naphthalenide or $NaBH_4$ in the presence of CS_2. Reduction with $NaBH_4$ in the absence of CS_2 gave $[Co(triphos)(\eta^2-CS_2)][Co(triphos)(BH_4)]$. The structures of several of the products were determined (ref. 255). Reaction of $[Co_2(\mu-X)_2(triphos)_2](BPh_4)_2$ with CO or cyclohexylisocyanide (L) gave $[CoX(L)(triphos)]BPh_4$ (X = Cl, Br). The iodo derivative could be got directly by carbonylation of CoI_2 in dichloromethane/ethanol in the presence of triphos followed by addition of $NaBPh_4$. The structure of the chlorocarbonyl complex was determined and it was noted that all complexes are paramagnetic which is unusual for Co(II) carbonyl complexes (ref. 256). The dimer with X = OH reacts with methanethiol in acetone to yield $[Co_2(\mu-SMe)_2(triphos)_2](BPh_4)_2$ and similarly carbonylates to $[Co(SMe)(CO)(triphos)]BPh_4$.

Treatment of the μ-OH complex with H_2S yields $[Co_2(\mu\text{-}S)_2(triphos)_2]BP$ which can be reduced to $[Co_2(\mu\text{-}S)_2(triphos)_2]$ by $NaBH_4$ and oxidized to $[Co_2(\mu\text{-}S)_2(triphos)_2](BPh_4)_2$ by $NOPF_6$. The structures of all but the carbonyl complex have been determined (ref. 257). From $Co(BF_4)_2\cdot 6H_2O$, triphos and P_4 in THF/ethanol the novel complex $[Co(triphos)(\eta^3\text{-}P_3)]$ can be prepared which reacts further with M(CO) (M = $Cr(CO)_5$, $cpMn(CO)_2$) to give $[Co(triphos)(\mu\text{-}P_3)Mn]$ (M = $Cr(CO)_5$, n = 1,2; M = $cpMn(CO)_2$, n = 3). The structures of all complexes have been determined and confirm that the P_3 unit remains η^3-bonded to cobalt while the individual phosphorus atoms act as monodentate ligands towards the second metal atoms (refs. 258, 259).

While $[RhCl(PPh_3)_3]$ reacts with CS_2 in benzene followed by addition of pyridine (py) to give $[RhCl(\eta^2\text{-}CS_2)(py)_2(PPh_3)]$, the heteroallyl complexes $[Rh(XC(Z)Y)(PPh_3)_2]$ (X = Y = S; Z = NEt_2,NMe_2. X = S, Y = NPh; Z = PPh_2, $SPPh_2$) give the thiocarbonyls $[Rh(CS)\text{-}XC(Z)Y)(PPh_3)]$ as the isolated product. The reactions are thought to proceed via an initial η^2-CS_2 adduct however (ref. 260). Further studies of the coordination properties of the related species $XC(PPh_2)NR^-$ (X = S; R = Me, Ph. X = O; R = Ph. X = N-p-tolyl; R = p-tolyl) and $SC(XPPh_2)NPh^-$ (X = O, S) have been made. With the first group of compounds are obtained $[M(XC(PPh_2)NR)(PPh_3)_2]$ (M = Rh, Ir) from $[RhCl(PPh_3)_3]$ and $[IrCl(cyclooctene)_2]_2$ + PPh_3. In all cases, the PPh_2 group is coordinated with either X or NR completing the coordination in the order S>NR>O (e.g. [86], [87]).

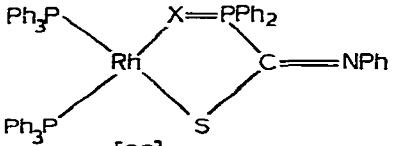


[86]



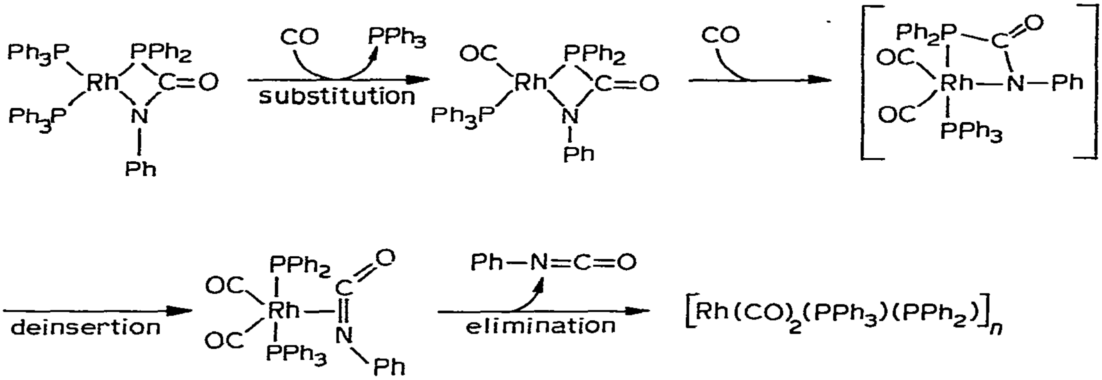
[87]

One triphenylphosphine ligand can be replaced with CO. For the second group, the proposed structure is [88]. An extensive study of the ^{31}P NMR spectra of the complexes was also made (ref. 261). On extended reaction with CO, [87] yields PhNCO and $[Rh(CO)_2(PPh_3)(PPh_2)]_n$ (n thought to be 2) by a process proposed to be that outlined in Scheme XXV. The same reaction with



[88]

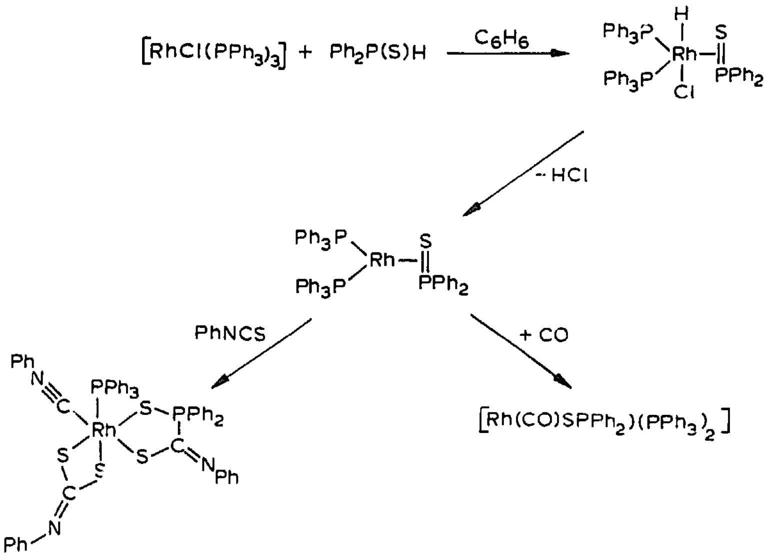
$[Rh(PPh_3)_2(Ph_2PC(N\text{-}p\text{-}tolyl)N\text{-}p\text{-}tolyl]$ yields p-tolyl-N=C=N-p-tolyl. Reaction of $[RhCl(PPh_3)_3]$ with $Ph_2P(S)C(R)NHR'$ (R = O, R' = Ph; R = N-p-tolyl, R' = p-tolyl) initially yields complexes analogous



Scheme XXV

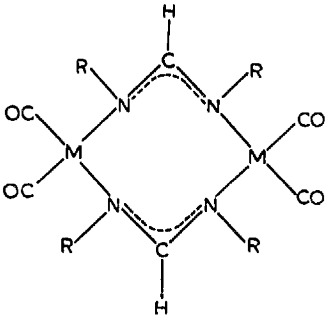
to [88] which decompose to $[Rh(PPh_3)_2(SPPh_2)]$ and R'N=C=R. This product can also be prepared from $[RhCl(PPh_3)_3]$ and $Ph_2P(S)H$ and reacts with CO and PhNCS according to Scheme XXVI (ref. 262). In related work, the formamidine derivatives $Li[CH(NR)_2]$ (R = Ph, p-XC_6H_4 (X = Me, MeO, F, Cl)) react with $[Rh(CO)_2Cl]_2$ or $[Ir(CO)_3Cl]$ to give the dimers [89] (M = Rh, Ir). In the rhodium complex, the formamidino proton is equally coupled to both metals (J = 2.50 H_z) indicating a symmetric structure (ref. 263).

Oxidative addition of RCH_2SO_2Cl (R = Ph, p-tolyl, p-$NO_2C_6H_4$) to $[RhCl(PPH_3)_3]$ and $[Ir(CO)Cl(PPh_3)_2]$ gave the expected sulfonyl complexes but attempts to prepare coordinated sulfines by dehydrohalogenation were unseccessful (ref. 264). The question of the interference of the spin traps nitroso-t-butane and



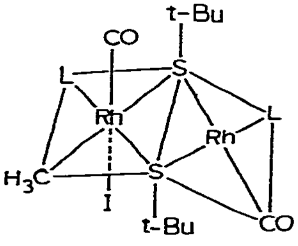
Scheme XXVI

1-nitroso-2,3,5,6-tetramethylbenzene with the search for radical intermediates in the oxidative addition of alkyl halides to $[RhCl(PPh_3)_3]$ and $[Ir(CO)Cl(PPh_3)_2]$ has been further explored. For the rhodium complex reacting with methyl iodide and benzyl bromide no spin adducts were observed for Rh/RNO = 10:1 but a weak

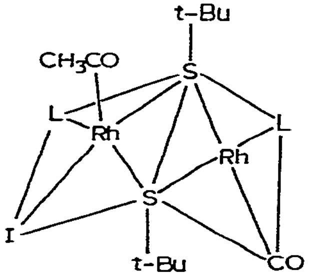


[89]

one was observed in the reaction with Ph_2CHBr. With a large concentration of spin trap (RNO:Rh = 10:1), spin adducts were observed in the alkyl bromide reactions but not with methyl iodide. The same results were observed for the iridium complex. Control experiments in the absence of alkyl halide showed no spin adducts were formed. In separate experiments both metal complexes reacted with trityl chloride to form the trityl radical indicating halogen abstraction had occurred but they did not react with trityl radical generated separately. These results indicate that for these systems, the presence of a spin trap does not induce a radical mechanism; however the question of the extent to which a radical process initiated in other ways contributes to the observed oxidative additions is difficult to assess (ref. 265). Methyl iodide oxidatively adds to only one metal in $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2(PMe_2Ph)_2]$ to give the cis-adduct $[Rh(Me)(I)(CO)(PMe_2Ph)(\mu\text{-}SBu^t)_2Rh(CO)(PMe_2Ph)]$, [90], which rearranges to the corresponding acetyl complex, [91] (ref. 266).



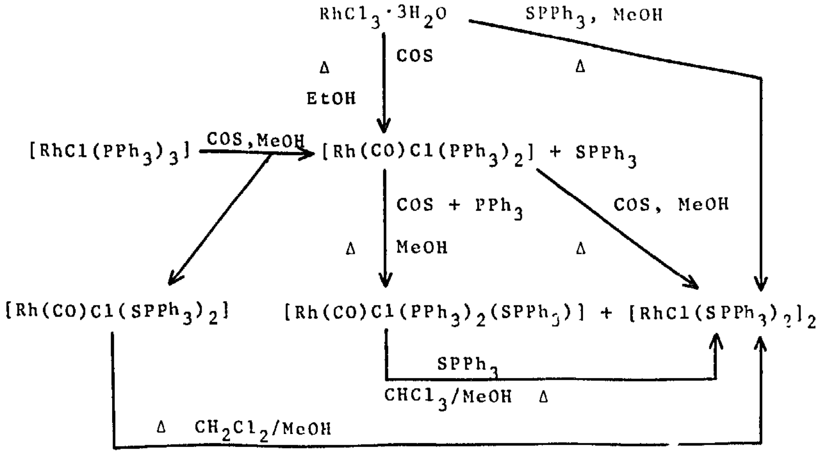
[90]



[91]

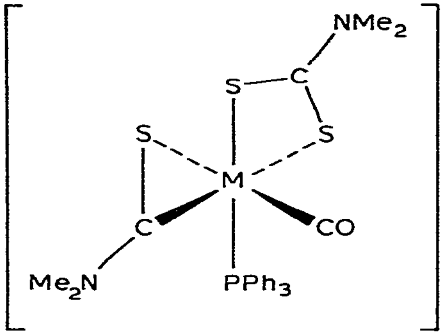
A related series of complexes trans-$[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR)(CO)_2(PBu^t{}_3)_2]$ (R = Pr^i, Bu^n, Bu^t, Ph, p-tolyl) have been synthesized from trans-$[Rh_2(CO)_2Cl_2(PBu^t{}_3)_2]$ and Me_3SiSR. The structure of the complex with R = Bu^t has been determined and has been found to be an active catalyst for olefin hydrogenation, the isomerization of allylbenzene and allyl alcohols, the decarbonylation of benzaldehyde and the conversion of dec-1-ene-3-ol to the corresponding ketone (ref. 267).

Reactions of carbonyl sulfide with a variety of rhodium compounds are detailed in Scheme XXVII (ref. 268). Reduction of hydrated rhodium(III) chloride with CO and ethanol at 80°C and 200 atm pressure in the presence of the tripod phosphines $(Ph_2PCH_2)_3CR(L_3$. R = Me, CH_2PPh_2) followed by addition of hexafluorophosphate gave $[Rh(CO)_2(L_3)]PF_6$ which on treatment with liquid ammonia yielded

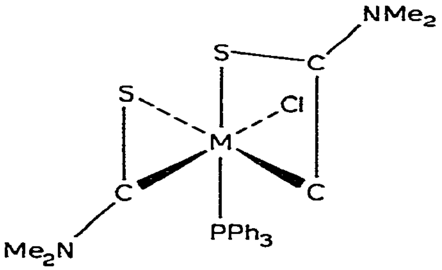


Scheme XXVII

the carbamoyl derivative $[Rh(CO)(CONH_2)(L_3)]$. Further treatment with anhydrous ammonia at 100°C gave the dimer $[(L_3)Rh(\mu\text{-}CO)_2Rh(L_3)]$ while methanolysis gave $[Rh(CO)(COOMe)(L_3)]$ (ref. 269). The oximes salicylaldoxime, α-benzoin oxime, α-furyldioxime, α-benzyldioxime and dimethylglyoxime (L_2) react with $[Rh(CO)_2CL]_2$ to give $[Rh(CO)_2(L_2)$ which with PPh_3, $AsPh_3$ or $SbPh_3$(L') give $[Rh(CO)L'(L_2)]$. The last form 1:1 adducts with tetracyanoethylene (ref. 270). Monomeric rhodium carbonyl complexes containing sulfide and sulfoxide ligands, $[Rh(CO)XL_2]$ (X = Cl, Br; L = R_2SO (R = Me, Pr^n, Bu^n), R'_2S (R' = Me, Et, Pr^i)) have been prepared from $[Rh(CO)_2Cl]_2$. The infrared spectra of the sulfoxides indicate S-coordination (ref. 271). The cationic complexes $[Rh(CO)_2L_3]X$ (L = PPh_3, $AsPh_3$, $SbPh_3$; X = ClO_4^-, BF_4^-) react with substituted *o*-phenanthrolines or biquinoline (N-N) to give $[Rh(CO)(N\text{-}N)_2]X$. They can also be prepared by addition of L to $[Rh(CO)_2(N\text{-}N)_2]X$ in acetone (ref. 272). Tropolone reacts with $[Rh(CO)_2Cl_2]^-$ to give $[Rh(O_2C_7H_5)(CO)_2]$ in which one carbonyl group can be replaced by PPh_3. The structure of the phosphine complex has been determined and shows the tropolonate ligand to be bidentate. It also reacts with thenoyltrifluoroacetone (TTA) to give $[Rh(TTA)(CO)(PPh_3)]$ (ref. 273). Bis(dimethylthiocarbamoyl)sulfide is cleaved on reaction with $[M(CO)Cl(PPh_3)_2]$ (M = Rh, Ir) yielding [92] which lose CO to form [93] (ref. 274).



[92]



[93]

A study of the ligating behavior of diphenyltellurium has been reported and is detailed in Scheme XXVII (ref. 275). Chloride abstraction from $[Rh(CO)ClL_2]$ (L = PPh_3, $AsPh_3$, PMe_2Ph, $P(cyclo\text{-}C_6H_{11})_3$) with $AgClO_4$ followed by addition of a variety of 8- or

$$[RhCl_3\cdot 3H_2O] \xrightarrow[EtOH]{Ph_2Te} [(Ph_2Te)_3RhCl_3] \xrightarrow{CO} [(Ph_2Te)_2Rh(CO)Cl_3]$$

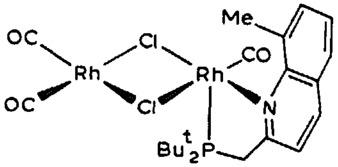
$$[RhCl(C_2H_4)_2]_2 \xrightarrow{Ph_2Te} [(Ph_2Te)_3RhCl] \xrightarrow{CO} \text{Inseparable Mixture}$$

$$[Rh(CO)_2Cl]_2 \xrightarrow{Ph_2Te} [(Ph_2Te)_2Rh(CO)Cl] \xrightarrow{X_2} [(Ph_2Te)_2Rh(CO)ClX_2]$$

$$[RhCl_3\cdot 3H_2O] \xrightarrow[HCHO]{Ph_2Te} [(Ph_2Te)_2Rh(TePh)Cl_2] \xrightarrow{CO} [(Ph_2Te)Rh(CO)(TePh)Cl_2]$$

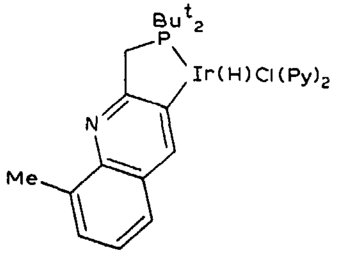
Scheme XVIII

2,8-substituted quinolines (Q) yields $[Rh(CO)L_2(Q)]ClO_4$. The neutral derivatives $[Rh(CO)_2Cl(Q)]$ can be got from $[Rh(CO)_2Cl]_2$ and Q but the yield at equilibrium decreases as the size of the substituents on the ligand increases. The cationic species can also be prepared from 8-alkylquinoline-2-carboxaldehyde-N-methylimine and exist as mixtures of 4- and 5-coordinate species where the stability of the complex of the bidentate, quinoline-derived ligand decreases as the bulk of the alkyl substituent increases (ref. 276). In a related study the ligand 2-di(tert-butyl)phosphinomethyl-8-methylquinoline (mqp) was found to react with $[Rh(CO)_2Cl]_2$ to yield $[Rh(CO)_2(\mu\text{-}Cl)_2\text{-}Rh(CO)(mqp)]$ ([94]). This dimer can be cleaved with CO to give



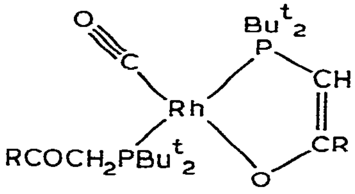
[94]

$[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2Cl(mqp)]$ or with a second equivalent of mqp to give *cis*-[RhCl(CO)(mqp)]. Reaction of this last complex with mqp gives $[Rh(CO)Cl(mqp)_2]$ in which the ligand is bound only through phosphorus. Reaction of mqp with $[IrCl(cyclooctene)_2]_2$ in refluxing pyridine however gives the *o*-metallated species [95] (ref. 277).
A number of complexes of the β-ketophosphines $Bu^t{}_2PCH_2C(O)R$ ($R = Bu^t$, Ph) have been reported. From $[Rh(CO)_2Cl]_2$ can be obtained the



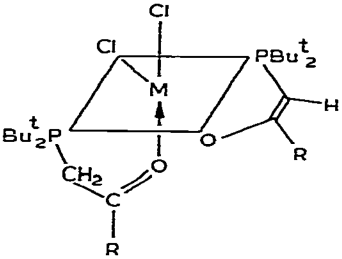
[95]

monodentate complexes *trans*-$[Rh(CO)ClL_2]$ which can be deprotonated with sodium methoxide to give [97]. The octahedral complexes [80] (M = Rh, Ir; R = Ph. M = Ir; R = Bu^t) are obtained from $MCl_3{\cdot}3H_2O$. On deprotonation with methoxide the rhodium complexes give poorly characterized species thought to be [98] while the iridium analog gives the five-coordinate hydride [99] which adds CO trans to the hydride to give an octahedral carbonyl derivative (ref. 278).
Unlike 2-pyridyldiphenylphosphine, tris-(2-pyridyl)phosphine (L)

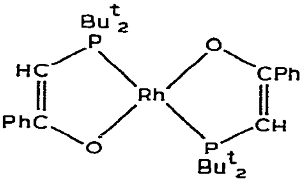


[96]

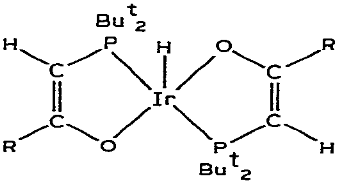
appears to form mainly monomeric complexes. Thus [RhH(CO)L_2(PPh_3)], [Rh(CO)ClL_2], [RhCl(COD)L] and [Rh(COD)L_2]PF_6 can be prepared by



[97]

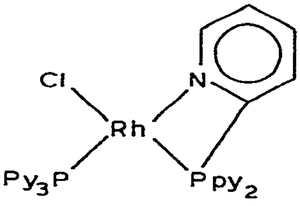


[98]

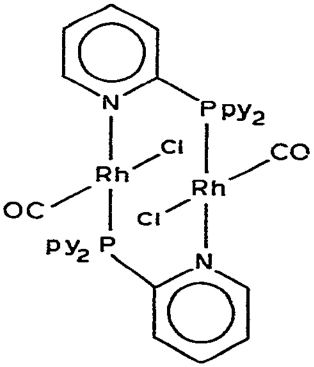


[99]

standard methods. Reaction of $[Rh(COD)Cl]_2$ with an excess of this ligand, however, gives [100] (ref. 279) and in another paper reporting the structure of [Rh(CO)ClL_2], the electronic absorption spectrum



[100]

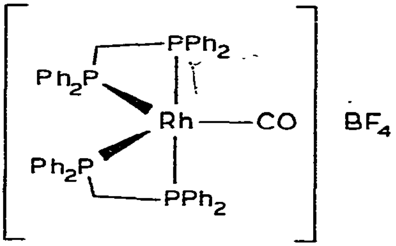


[101]

of the complex in solution shows a low energy band not seen in the solid state. This is proposed to be due to the formation of [101] (ref. 280). Complexes of amino acid anions (AA) and formulated as $[Rh(CO)_2(AA)]$ react with hydrogen halides to give $[Rh(CO)_2X]_2$ (X = Cl, Br) and with tetracyanoethylene (TCNE) to form five-coordinate TCNE adducts (ref. 281).

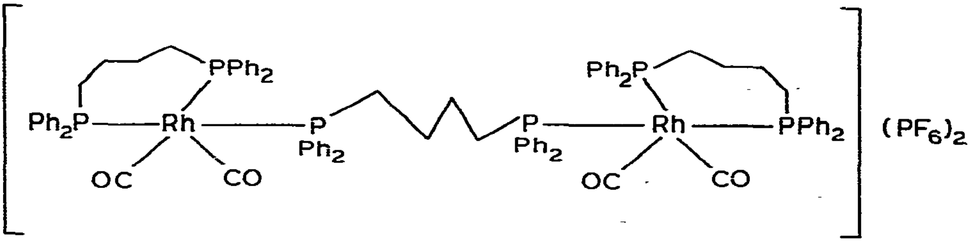
The kinetics of the reaction of $[Rh(CO)_2X_2]^-$ (X = Cl, Br, I) with pyridine in ethanol to give $[RhCl_3py_3]$ have been studied. The observation of a large negative entropy of activation is interpreted to indicate the initial formation of a five-coordinate pyridine adduct of $[Rh(CO)_2X_2]^-$ while the reactivity order $Cl^- < Br^- < I^-$ is thought to indicate that the oxidation to Rh(III) is synchronous with the addition of the first pyridine ligand (ref. 282). Removal of chloride from $[RhCl(CS)(PR_3)_2]$ (R = cyclohexyl) with $AgClO_4$ gives $[Rh(OClO_3)(CS)(PR_3)_2]$ from which the perchlorate ligand can be displaced by a variety of nitrogen-donor ligands e.g. pyridine, 4-methylpyridine, *o*-chlorobenzonitrile (ref. 283).

Several studies of rhodium complexes of poly(tertiary)phosphines and arsines have appeared. The potentially hexadentate ligand *p*-$[(Ph_2As(CH_2)_2)_2PCH_2]_2C_6H_4$ (TDADX) reacts with $[M(CO)Cl(PPh_3)_2]$ (M = Rh, Ir) in refluxing benzene to give the ligand-bridged dimer, $[Rh_2Cl_2(TDADX)]$ or the monomeric [Ir(TDADX)]Cl. The former reacts with CO with displacement of the Ph_2As groups to give $[Rh_2Cl_2(CO)_4(TDADX)]Cl$ while from the latter, [IR(CO)(TDADX)]Cl is obtained. Curiously although this complex is reported to be ionic from conductivity measurements, an Ir–Cl band is said to be observed in the infrared spectrum. This latter observation may be in error since the Ph_2As group often shows substantial absorptions in the metal-chlorine region. Nitric oxide also reacts with [Ir(TDADX)]Cl to give $[Ir(NO)(TDADX)]Cl_2$ (ref. 284). Small molecules react with the complexes $[Rh(L_2)_2]^+$ (L_2 = DPM, diphos, 1,3-bis(diphenylphosphino)propane (DPPP), 1,4-bis(diphenylphosphino)butane (DPPB) and (-)-2,3,-O-isopropylidene-2,3,dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP)). Where L_2 = DPM or DPPP, five-coordinate carbonyl complexes were obtained. The diphos complex was unreactive and mixtures resulted from the others. Oxygen gave 1:1 adducts when L_2 = DPM, diphos and DPPP while the DPPB complex absorbed more than one mol and the DIOP complex was unreactive. Dihydrides resulted with L_2 = DPPP and DIOP while the DPM and diphos complexes failed to react and the DPPB complex gave mixtures (ref. 285). Some of these systems have been studied in more detail by other workers who have determined the structure of $[Rh(CO)(DPM)_2]BF_4$ and found it to be [102]. Because of the small bite of the DPM ligand, the axial



[102]

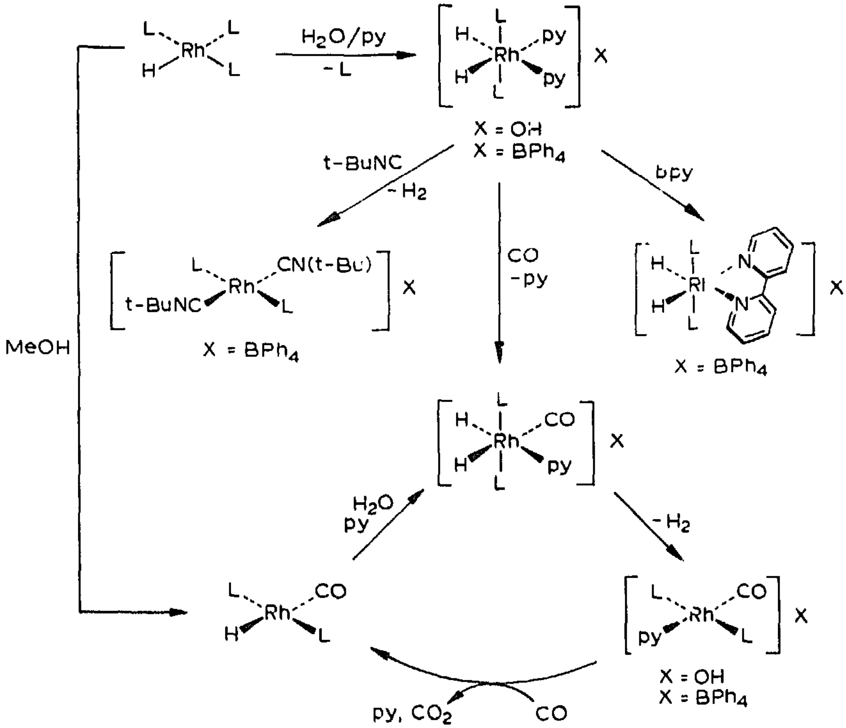
P-Rh-P angle is only 169.3°. Whereas the complex $[Rh(CO)(DPPP)_2]BF_4$ loses CO readily at room temperature, the DPM complex can only be decarbonylated after prolonged reflux in dichloromethane solution. The difference in CO lability is attributed to activation energy differences due to chelate ring strain and it was noted that the DPM complex was fluxional at -80°C (ref. 286). In contrast to the results reported in reference 284, $[Rh(DPPB)_2]PF_6$ has been found to give a well-characterized complex $\{[Rh(CO)_2(DPPB)]_2(\mu\text{-}DPPB)\}(PF_6)_2$ upon reaction with CO. A crystal structure determination showed it to be [103] (ref. 287). The ligand 2,11-bis(diphenylarsinomethyl) benzo[c]phenanthrene(L_2) forms complexes trans-$[M(CO)Cl(L_2)]$ (M = Rh, Ir) in which the ligand spans trans positions in the coordination sphere (ref. 289). The reaction of SO_2 with $[Rh(ttp)(CO)]AsF_6$



[103]

(ttp = bis(3-(diphenylphosphino)propyl)phenylphosphine) gives the square pyramidal adduct [Rh(ttp)(SO_2)(CO)]AsF_6 in which, in contrast to [Rh(ttp)(SO_2)(CO)Cl], the SO_2 ligand is labile. A comparison of the structures of the two complexes shows that the Rh-S bond in the former is longer and the rhodium is very close to the basal plane presumably as the result of the greater π-acidity of CO relative to chloride (ref. 289).

Rhodium complexes of triisopropylphosphine (L) have been investigated in the context of the water-gas-shift reaction and the oxidative addition of water has been established to occur (Scheme XXIX) (ref. 290). Trimethylphosphine displaces all ligands from [RhCl(PPh_3)$_3$

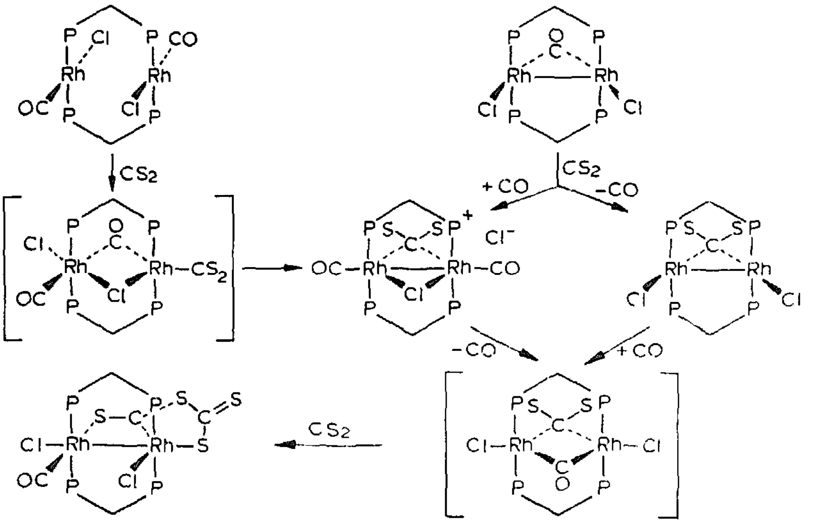


Scheme XXIX

to give $[Rh(PMe_3)_4]Cl$ from which PF_6^- and BPh_4^- salts can be obtained by metathesis. Refluxing the chloride salt in toluene gives the neutral species $[RhCl(PMe_3)_3]$. The original synthesis reported to give this complex (ref. 291) could not be repeated. Both complexes have been structurally characterized as square planar species showing a tetrahedral distortion. They react slowly with diethyl ether, THF, MeOH and EtOH to give $[Rh(CO)Cl(PMe_3)_2]$ and with hydrogen to yield $[RhH_2(PMe_3)_4]^+$. In THF solution $[Rh(PMe_3)_4]^+$ is chlorinated to mer-$[RhCl_3(PMe_3)_3]$ by carbon tetrachloride, chloroform and dichloromethane (ref. 292). Attempts to prepare $[RhH(AsPh_3)_4]$ from hydrated rhodium (III) chloride and $AsPh_3$ by sodium borohydride reduction in ethanol (a route which was successful for the PPh_3 analog) gave a mixture thought to contain hydrido complexes together with species containing o-metallated ligands. However with Na_2IrCl_6 in 2-methoxyethanol, fac-$[IrH_3(AsPh_3)_3]$ could be obtained in good yield. Under the same conditions, $[IrH_2Cl(AsPh_3)_3]$ and $[IrHCl_2(AsPh_3)_3]$ could be synthesized using trimethylamine or N-methyl-N-nitrosotoluene-p-sulfonamide respectively in place of sodium borohydride (ref. 293). Activation of saturated C-H bonds occurs in the electrochemical reduction of $[Rh(diphos)_2]^+$ in benzonitrile with $Bu_4{}^nNClO_4$ as the supporting electrolyte. This is a 2-electron process and yields $[RhH(diphos)_2]$, $Bu_3{}^nN$ and but-1-ene. When carried out in acetonitrile-d_3, a mixture of $[RhH(diphos)_2]$ and $[RhD(diphos)_2]$ result while addition of cyclohexane to the original system gives cyclohexene and bicyclohexyl as the organic products. The results are consistent with reduction of the Rh(I) complex to a Rh(O) species which then abstracts hydrogen from the solvent or supporting electrolyte. The organic products which arise are those resulting from the further reactions of the radicals produced in this step (ref. 294). The decomposition of 1.0 mol $[RhCl(PPh_3)_3(O_2)]$ under anaerobic conditions yields 1.0 mol Ph_3PO, 0.25 mol $[RhCl(PPh_3)_2]_2$ and 0.25 mol $[RhCl(PPh_3)_2(O_2)]_2$. The process was monitored by ^{31}P NMR spectroscopy and $[RhCl(PPh_3)_2O]_2$ was proposed as an intermediate (ref. 295).

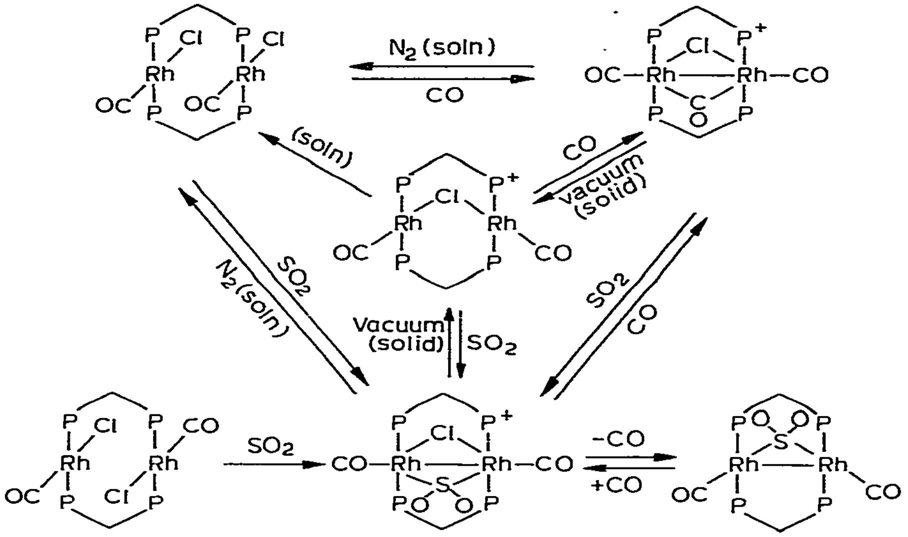
Tetrafluoroboric acid reacts with $[cp^*Rh(CO)_2]$ in ether to give the dimer $[cp_2{}^*Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)]BF_4$ which is deprotonated by sodium methoxide to $[cp_2{}^*Rh_2(CO)_2(\mu\text{-}CO)]$. Photolysis or thermolysis of the latter complex gives $[cp_2{}^*Rh_2(CO)_2]$ which can also be obtained by thermolysis of $[cp^*Rh(CO)_2]$. However carbonylation of $[cp_2{}^*Rh_2(CO)_2]$ leads only to regeneration of the monomers (ref. 296).

The analogous complex $[cp_2Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)]BF_4$ can be got from $[cp_2Rh_2(CO)_2(\mu\text{-}CO)]$ by protonation with HBF_4 in ether at -30°C. The reaction is reversed by treatment with sodium methoxide while in nitromethane solution the hydrido complex disproportionates to $[cp_3Rh_3(\mu\text{-}CO)_3]$ and $[cpRh(CO)_2]$ (ref. 297). Another area of considerable interest is the chemistry of rhodium dimers having the A-frame structure. Carbon disulfide reacts with $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ or $[Rh(CO)Cl(DPM)]_2$ by the route proposed in Scheme XXX to give [104] which has been structurally characterized (ref. 298). The synthesis of $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$ from $[Rh(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$ is facilitated by the presence of chloride. Scheme XXXI details the chemistry of this system. The observation of a band attributable to a bridging carbonyl immediately after addition of SO_2 to trans-$[Rh(CO)Cl(DPM)]_2$ was taken to indicate the presence of an SO_2 adduct analogous to the initial CS_2 adduct shown in Scheme XXX implying that in contrast to the reaction of SO_2 with $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$ attack does not occur directly to both metals (ref. 299). The structure of $[Rh(CO)Cl(DPM)]_2$ has been determined and found to be substantially the same as its DAM analog. Reaction with bromide



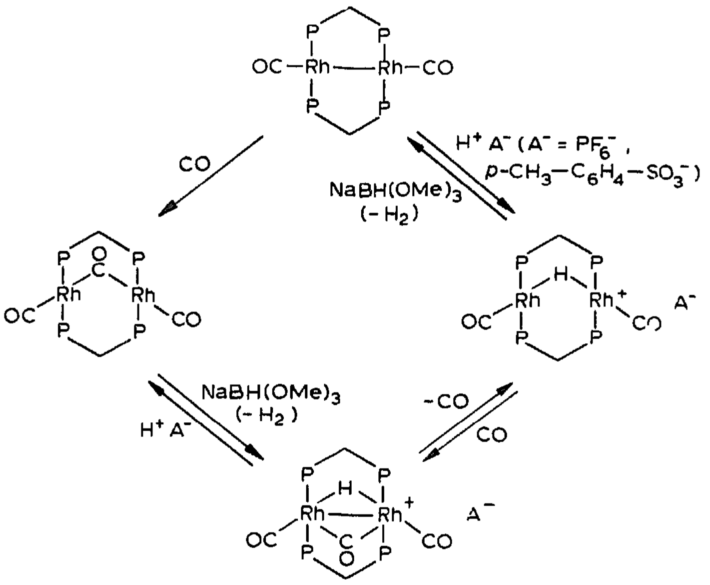
[104]

Scheme XXX



Scheme XXXI

or iodide gives $[Rh_2(CO)X(\mu\text{-}CO)(DPM)_2]X$ (X = Cl, Br) while with $[Rh(CO)Cl(DAM)]_2$ one obtains $[Rh(CO)X(DAM)]_2$, the iodo complex being contaminated with the CO-bridged cationic complex. In solution $[Rh_2(CO)Br(\mu\text{-}CO)(DPM)_2]Br$ rearranges to $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$ whose structure has been determined and which reacts with CO to yield $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Br)(DPM)_2]^+$. The same species together with the iodo analog and those with SO_2 in place of the bridging carbonyl are obtained from $[Rh_2(CO)X(\mu\text{-}CO)(DPM)_2]X$ by treatment with CO or SO_2 (ref. 300). Heating $[Rh_2(O_2CCH_3)_4]$ with CO in anhydrous formic acid gives $[Rh_2(O_2CH)_2(CO)_4]$ which from spectral measurements appears to solvolyze in methanol to give monomeric species (ref. 301). The neutral A-frame complexes $[Rh_2(CO)_2(\mu\text{-}X)(DPM)_2]$ (X = S, Se) can be prepared from $[Rh_2(CO)Cl(DPM)]_2$ and Na_2S or K_2Se in methanol. The related complex $[Rh_2(CO)_2(\mu\text{-}PH(cyclo\text{-}C_6H_{11}))(DPM)_2]PF_6$ is obtained by reaction with $LiPH(cyclo\text{-}C_6H_{11})$ and KPF_6 in dichloromethane. The bridging sulfur in $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$ is susceptible to electrophilic attack and can be converted into $[Rh_2(CO)_2(\mu\text{-}SR)(DPM)_2]PF_6$ (R = H, Et, $PhCH_2$) on reaction with HPF_6, Et_3OPF_6 and $PhCH_2Br$ plus KPF_6 respectively. The original complex adds SO_2 to give $[Rh_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(DPM)_2]$ but with methylisocyanide only replacement of the terminal carbonyls by isocyanide was observed (ref. 302). Reduction of $[Rh(CO)Cl(DPM)]_2$ with sodium borohydride in ethanol gives the Rh(0) dimer $[Rh(CO)(DPM)]_2$ whose reactions are outlined in Scheme XXXII. The structure of [105] has been determined and



[105]

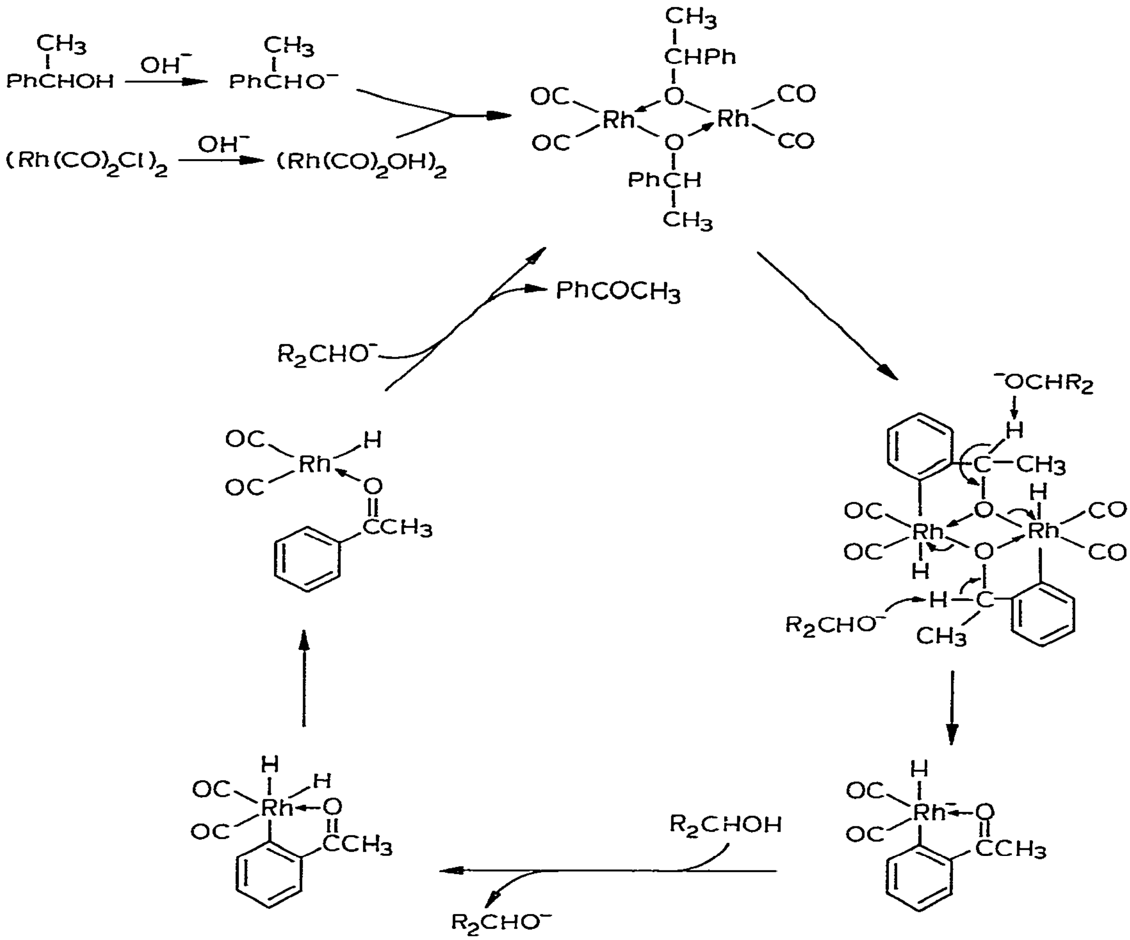
Scheme XXXII

it has also been found to produce an active catalyst system for the water-gas-shift reaction. Acetylene forms an adduct with $[Rh(CO)(DPM)]_2$ which was not isolated but which yielded ethane on exposure to hydrogen. The complex also reacts with methylisocyanide to give $[Rh_2(CNMe)_2(\mu\text{-}CNMe)(DPM)_2]$ (ref. 303). The iridium complex $[Ir_2(CO)_2(\mu\text{-}S)(DPM)_2]$ has been prepared by the same route as the rhodium analog from $[Ir_2(CO)_4Cl(DPM)_2]PF_6$. Addition of CO yields $[Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-}CO)(DPM)_2]$ whose structure was determined to be similar to that for [105]. It reacts reversibly with hydrogen to give an isomeric mixture formulated as $[Ir_2H_2(CO)_2(\mu\text{-}S)(DPM)_2]$ and with $BF_3{\cdot}OEt_2$ to give a 1:1 adduct in which the BF_3 is thought to coordinate to the sulfur. It also is a modest catalyst for the hydrogenation of acetylene, ethylene and propene (ref. 304). Unlike DPM, $(Ph_2P)_2NH(DPA)$ forms primarily monomeric products. Thus on reaction with $[RhCl(C_2H_4)_2]_2$ one obtains $[Rh(DPA)_2]Cl$ which forms 1:1 adducts $[Rh(Y)(DPA)_2]Cl$ ($Y = CO, O_2, S_2, \eta^2\text{-}CS_2$). The dioxygen adduct reacts with SO_2 to give the corresponding sulfate derivative while the carbonyl adduct on treatment with boiling methanol yields a species proposed to be the A-frame complex $[Rh_2Cl_2(\mu\text{-}CO)(DPA)_2]$ (ref. 305).

A number of interesting clusters containing bridging diphenylphosphido groups have been reported. Reaction of two mols of lithium diphenylphosphide with $[Rh(CO)_2Cl]_2$ yields $Li[Rh_4(CO)_5(\mu\text{-}PPh_2)_5]$ which consists of a butterfly arrangement of metal atoms with all five edges bridged by the phosphido groups (ref. 306). Pyrolysis of $[RhH(CO)(PPh_3)_3]$ in refluxing nonane gives $[Rh_3(\mu\text{-}PPh_3)_3(CO)_3(PPh_3)_2]$ containing a triangle of metal atoms bridged by phosphido groups. The cluster is coordinatively unsaturated and reversibly adds CO in solution (ref. 307). If the pyrolysis is carried out under 60 psi of hydrogen and carbon monoxide (1:1), $[Rh_4(\mu\text{-}PPh_2)_4(CO)_3(\mu\text{-}CO)_2(PPh_3)]$ is obtained. Here the metal atoms form an approximately tetrahedral skeleton with the phosphine coordinated to the apical rhodium. The lateral edges are bridged by two carbonyl ligands and one phosphide group while the other three phosphides bridge the basal edges (ref. 308). Using $[Fe(CO)_4(PHPh_2)]$ as a source of the diphenylphosphido group, a variety of compounds have been obtained upon reaction with $[Rh(CO)_2Cl]_2$ in the presence of base, their nature depending on the solvent used and whether or not CO is present. One complex which has been structurally characterized is $[FeRh_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)_3]$. This consists of a butterfly arrangement of metal atoms with the iron at one wingtip. The Fe-Rh edges are occupied by one μ-CO and one $\mu\text{-}PPh_2$ while the hinge is bridged by CO. This complex rearranges to interchange the PPh_2 group on the Fe-Rh edge with the CO bridging the hinge and reacts with CO to give $[Rh(CO)_3(PPh_2)]_2$ which subsequently loses CO and condenses to $[Rh_4(CO)_6(PPh_2)_4]$(ref. 309).

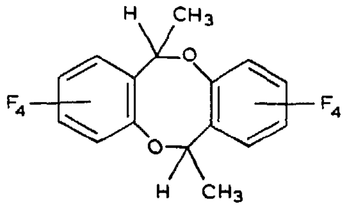
Hydrated rhodium (III) chloride reacts with hydro tris(3,5-dimethylpyrazolyl)borate ion ($HBpz_3^-$) in refluxing methanol to yield $[Rh(HBpz_3)Cl_2]_2$ which on further refluxing is cleaved to $[Rh(HBpz_3)Cl(MeOH)]$. The methanol ligand is labile and is readily replaced by CO, phosphines and other Lewis bases. A new preparation of $[Rh(CO)_2(HBpz_3)]$ from $[Rh(CO)_2Cl]_2$ is also reported as well as studies indicating that earlier reports of the formation of $[Rh_2(CO)_3(HBpz_3)_2]$ and $[Rh(CO)_2(HBpz_3)]_2$ in this reaction are erroneous. Also it was determined that reports that the decomposition observed in this reaction was due to traces of Rh(0) in fact result from borohydride impurities in the ligand (ref. 310).

Many carbonyl-containing complexes have been studied as potential catalysts for a variety of applications. When heated with pyrrolidine, isopropanol or tetralin both $[RhH(PPh_3)_4]$ and $[RhCl(PPh_3)_3]$ but not [$Rh(CO)Cl(PPh_3)_2$] yielded significant quantities of benzene via hydrogen transfer from solvent and hydrogenolysis of the phosphine ligands. No evidence for radicals was found (ref. 311). The dimers [$Rh(\mu$-$SR)(CO)L]_2$ are catalysts for hex-1-ene hydrogenation and that with R = Bu^t and L = phosphite is the most active (ref. 312). The formation of γ-lactams from allylic amines and CO is catalyzed by [$Rh(CO)Cl(PPh_3)_2$] while $RhCl(PPh_3)_3$ or $Rh(acac)_3$ in the presence of iodide catalyzes their formation from allyl halides, primary amines and CO. No mechanism was proposed (ref. 313). A phase transfer catalyst system formed from [$Rh(CO)_2Cl]_2$, benzyltriethylammonium chloride, benzene and aqueous sodium hydroxide efficiently converts secondary alcohols to the corresponding ketones at 50°C. Primary alcohols are less reactive and while [$RhCl(PPh_3)_3$] or [$Rh(CO)Cl(PPh_3)_2$] give catalysts they are less active and render the subsequent workup more difficult. The proposed mechanism is shown in Scheme XXXIII. Support for the formation of the *o*-metallated intermediate is said to derive from the observation that $C_6F_5CH(OH)CH_3$, which cannot form the same species, is not converted to $C_6F_5C(O)CH_3$ by the same catalyst system but instead forms [106] (ref 314). Both pyridine and its hydrochloride form catalyst systems with [$Rh(CO)_2Cl]_2$ and hydrated rhodium (III) chloride which are active for the conversion of nitrobenzenes to the corresponding isocyanates at 205°C and 50 atm of CO. Although the active species was not identified, it is thought to be a Rh(I) carbonyl complex probably containing chloride and pyridine ligands (refs. 315-317). Under milder conditions (120°C, 60 atm) [$RhH(CO)(PPh_3)_3$] also catalyzes this reaction and a rhodium-nitrene intermediate was proposed (ref. 318). Both [$Rh(CO)Cl(PPh_3)_2$] and [$RhH(CO)(PPh_3)_3$] have continued to be studied as olefin hydroformylation catalysts and it is likely that both systems involve the same or very similar active species. For the former with ethylene as the substrate, the rate was a maximum at 110°C and the activation energy was determined to be 33.18 kJ/mol (ref. 319). For the latter with propene as substrate, a kinetic study showed the reaction to be zero order in CO and H_2 the straight/branched chain ratio depended only on the relative amounts of CO and PPh_3 (ref. 320). With time the catalyst degrades markedly and [$Rh(CO)_2PPh_2]_n$, Ph_3PO and Ph_2PrP were identified as decomposition products (ref. 321). In an attempt to identify the active species, *in situ* studies of the hydroformylation reaction were made using high pressure infrared spectroscopy. Using [$Rh(CO)_2Cl]_2$,



Scheme XXXIII

[Rh(py)(CO)$_2$Cl] and [Rh(CO)$_2$acac] as catalyst precursors and C_2H_4/CO/H_2 = 1:1:1, [$Rh_4(CO)_{12}$] and a species thought to be [RhEt(CO)$_4$] were detected. The spectrum attributed to the latter was observed only in the presence of ethylene. Although inactive under normal hydroformylation conditions, [$Rh_4(CO)_{12}$] under 6 atm of ethylene and hydrogen produced an active catalyst when CO was added. From the infrared spectrum of this system in the absence of CO a species tentatively identified as [RhH(C_2H_4)(CO)$_3$] was detected which appeared stable in the absence of ethylene but decomposed to [$Rh_4(CO)_{12}$] on removal of solvent or on reaction with CO (ref. 322). The hydroformylation of methylmethacrylate and



[106]

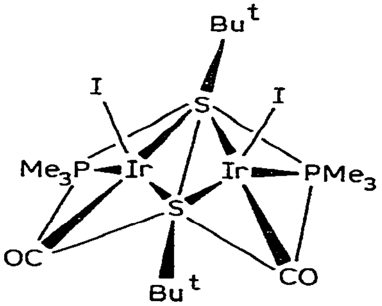
allyl alcohol catalyzed by $[RhH(CO)(PPh_3)_3]$ and related complexes has been studied. For the former system the proportion of branched-chain aldehyde increased on replacing PPh_3 by $(Ph_2PCH_2CH_2)_2PPh$ or phosphinated styrene-divinylbenzene copolymer. This was attributed to an increase in hydridic character of the hydride on increased phosphine substitution leading to a preference for the branched alkyl on olefin insertion (ref. 323). In the latter system, $[RhH(CO)(PPh_3)_3]$ produced good selectivity for straight chain aldehyde at 60°C and a high H_2/CO ratio but hydrogenation was a serious competing process. The best system proved to be the polymer-anchored analog or one using 1,1-bis(diphenylphosphino)ferrocene (ref. 324).

In the presence of $[Rh(CO)_2Cl]_2$ at 140-200°C, cyclopropane and carbon monoxide react to give low yields of propene, cyclobutanone, heptan-4-one and traces of 2-methylhexan-3-one and 2- and 3-methylcyclohexanone. In the presence of ethylene the selectivity to cyclobutanone is somewhat higher whereas at 200°C propene is the major product. It is suggested that activation of cyclopropane occurs via ring-opening on rhodium (ref. 325). Finally, $[RhClL_3]$ ($L = PPh_3, SbPh_3$), $[RhH(CO)(PPh_3)_3]$, $[Rh(CO)Cl(PPh_3)_3]$, $[RhCl(P(CH_2Ph)_3)_3]$, and $[Rh(CO)_2acac]$ have been investigated as catalysts for the hydrosilylation of phenylacetylene. Both *cis* and *trans* addition products were found with the proportion of the latter increasing with increasing chlorine substitution on silicon. However the regioselectivity was not very dependent on the particular system used (ref. 326).

The thermal decomposition of $[Rh(CO)(NO_3)(PPh_3)_2]$ proceeds in two stages. In the first at 168°C substantial amounts of CO_2 and Ph_3PO together with some CO and the nitrogen oxides N_2O, NO and NO_2 are found while at 275°C the remaining CO is liberated.

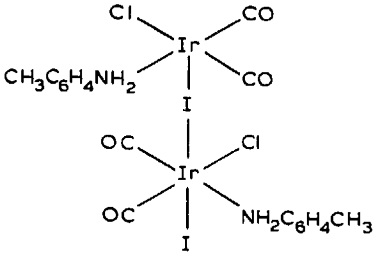
It is suggested that the products of the first stage arise from redox reactions of the ligands while attached to the metal (ref. 327).

Oxidative addition of C_6F_5SSCl to $[Ir(CO)Cl(PPh_3)_2]$ gave the expected $[Ir(CO)Cl_2(SSC_6F_5)(PPh_3)_2]$ (ref. 328). Combination of $[Ir(COD)(L_2)]^+$ (L_2 = o-phenanthroline, bipyridyl) with $[M(CO)_2X_2]^-$ (M = Rh, Ir; X = Cl, Br) gave only dark powders of variable composition. However $[Rh(COD)L_2]^+$ reacted with $[Ir(CO)_2X_2]^-$ to give $[Rh(CO)_3(L_2)][Ir(CO)_2X_2]$ which despite the fact the cation is pentacoordinate appears to show a strong intracomplex metal-metal interaction (ref. 329). Attempts to prepare complexes of $B_3H_8^-$, have met with only limited success. From TlB_3H_8 and $[CoBr(PPh_3)_3]$ or $[Rh(CO)Cl(PPh_3)_2]$ only $B_3H_7PPh_3$ was obtained while with $[Ir(CO)Cl(PPh_3)_2]$ both this and $[IrH(CO)(\eta^3\text{-}B_3H_7)(PPh_3)_2]$ were formed. With $[Ir(CO)(diphos)_2]^+$, $B_3H_8^-$ functioned only as a counter ion but it reacted with $[Ir(diphos)_2]^+$ to give $[IrH_2(diphos)_2]^+$ (ref. 330). The thiolate-bridged dimers $[Ir_2(CO)_4(\mu\text{-}SBu^t)_2]$ react with one and two equivalents of phosphorus ligands to yield $[Ir_2(CO)_3(L)(\mu\text{-}SBu^t)_2]$ (L = PMe_3, $P(OMe)_3$, PPh_3, $P(NMe_2)_3$) and $[Ir_2(CO)_2(L)_2(\mu\text{-}SBu^t)_2]$ (L = PMe_3, $P(OMe)_3$, PPh_3, $P(NMe_2)_3$, PMe_2Ph) respectively. In solution the monosubstituted complexes partially convert into a mixture of the parent and disubstituted complexes. Both $[Ir_2(CO)_4(\mu\text{-}SBu^t)_2]$ and its disubstituted derivatives (L = PMe_3, $P(OMe)_3$, PMe_2Ph) undergo two-center oxidative addition with iodine to give $[Ir_2(CO)_2(L)_2(I)_2(\mu\text{-}SBu^t)_2]$ containing two approximately square pyramidal Ir(II) centers with apical iodines. The PMe_2Ph derivative has been characterized structurally and shown to be the _cis_, _anti_ isomer [107] (refs. 331, 332). Iodine also oxidatively



[107]

adds to [Ir(CO)$_2$Cl(p-toluidine)] yielding trans-[Ir(CO)$_2$ClI$_2$(p-toluidine)] which reversibly associates with starting material to form a binuclear species proposed to be [108] (ref. 333). In a search for a means of generating a readily available site on an



[108]

Ir(I) complex for substrate activation in a catalytic process a number of Ir(I) complexes of bidentate phosphorus-nitrogen ligands were prepared. Reaction of [Ir(CO)$_2$Cl$_2$]$^-$ with the ligands 1-diphenylphosphino-2-dimethylaminoethane (PEN), 1-diphenylphosphino-3-dimethylaminopropane (PPN) and o-diphenylphosphino-N,N-dimethylaniline (PN) gave [Ir(CO)Cl(L$_2$)] (L$_2$ = PEN, PPN, PN). The structure of the PN complex showed it to be square planar with the CO ligand trans to nitrogen and the same stereochemistry was proposed for the others on the basis of ^{31}P NMR data. All three are more effective than [Ir(CO)Cl(PPh$_3$)$_2$] for catalyzing hex-1-ene isomerization but are quite air-sensitive (ref. 334).

A general bonding model for complexes of the type [cp$_2$Rh$_2$(μ-CO)$_2$X] (X = Rh(CO)$_2$, CH$_2$, Pt(COD)) has been proposed. There is a predicted tendency for the μ-CO's to bend towards the X group and thereby become semi-μ_3 bridging as this stabilizes the HOMO. This tendency is quite pronounced in [cp$_2$Rh$_2$(CO)$_2$Pt(COD)] (see ref. 238) (ref. 335). A modified double resonance experiment has enabled ^{103}Rh chemical shifts for Rh(-1) carbonyl complexes to be measured using ^{13}C{^{103}Rh} NMR spectra. The trend in ^{103}Rh chemical shifts has Rh(III) at low field with Rh(I) complexes higher than this and [Rh(CO)$_4$]$^-$ much higher still. From the observation that $^1J_{Rh-C}$ is about the same for [Rh(CO)$_4$]$^-$ as for a variety of square planar Rh(I) complexes it was concluded that this coupling is dominated by the Fermi contact term (ref. 336). Using SCF-Xα-SW calculations, the photoelectron spectra of [Rh$_2$Cl$_2$L$_4$] (L = CO, PF$_3$) have been assigned. The agreement found here supports arguments made earlier from these calculations for the factors which cause the folded structure found for these complexes (ref. 337). A determination of the heats of formation and dissociation as well as M-C and M-M bond energies in Co, Rh and Ir carbonyl clusters has been reported (ref. 338). In an interesting application of optically active complexes, $[Rh(CO)_2-$ (3-trifluoroacetyl-1-(R)-camphorate)] in squalane has been used as the stationary phase in a gas chromatographic procedure which can resolve 3-methylcyclopentene and variously deuterated ethanes (ref. 339). The reaction of alkyl iodides, RI (R = I, H, Me, Et, Pr^n, Pr^i, $PhCH_2$, MeCO) with $[Ir(CO)Cl(PMe_3)_2]$has been followed by titration calorimetry to measure the strength of the Ir–R bond. The results show these to be in the order $H>Me\sim I\sim MeCO>Pr^n>Et>Pr^i>PhCH_2$ (ref. 340).

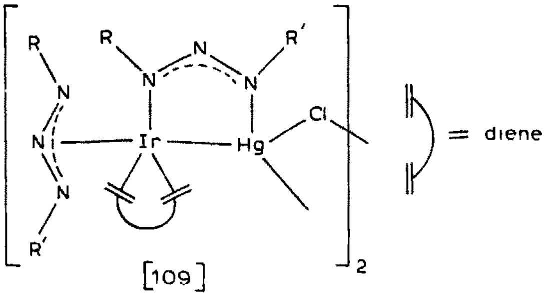
Hydrolysis of $[Rh(CO)Cl(Ph_2P(CH_2)_nSiCl_3)_2]$ (n = 2,8) in aqueous dioxane alone or in the presence of either excess ligand or $MeSiCl_3$ produces polymeric globules having the idealized formulae $\{[O_{1.5}Si(CH_2)_2PPh_2]_3RhCl(O_{1.5}SiMe)_{200}\}_x$ and $\{O_{1.5}Si(CH_2)_8PPh_2]_4Rh_2Cl_2\}_x$ which are active catalysts for olefin hydrogenation (including styrene). Although activity loss occurs on recycling, the latter species is longer-lived presumably because it more closely resembles the homogeneous counterpart (ref. 341). Supporting $[Rh(CO)_2Cl]_2$ on silica which has been modified by Sn, Pb, Mo or W gives a catalyst active for the hydrogenation of benzene, the hydrogenolysis of propane and the conversion of hexane (ref. 342). Finally, $[RhH(CO)-(PPh_3)_3]$ supported on silica or alumina retains catalytic activity for the hydroformylation of propene. A strong complex-support affinity was noted which was attributed to an interaction with surface hydroxyl groups (ref. 343).

Metal nitrosyl and aryldiazo compounds

The complexes $[CoXL_3(NO)]^+$ can be prepared by reaction of NO with $[CoXL_3]^+$ (X = Cl, Br, I; L = $PPh(OMe)_2$, $PPh(OEt)_2$) or $[CoX_2L_2]$ (X = Cl, Br; L = $P(OMe)_3$, $P(OEt)_3$) and isolated as tetraphenylborate salts when L = phosphite. Further reaction with NO gave an equilibrium mixture of $[CoL_2(NO)_2]^+$ and $[CoXL(NO)_2]$, the position of the equilibrium depending on the nature of L and X. Only when L = $PPh(OEt)_2$ and X = I could the neutral species be isolated and in the presence of an excess of $PPh(OEt)_2$, $[Co(PPh(OEt)_2)_3(NO)]$ was formed. The structure of the $[CoX(L)_3(NO)]^+$ complexes is proposed to be square pyramidal with a bent nitrosyl ligand in the apical position. Reaction of $[CoIL_3(NO)]^+$ (L = $P(OMe)_3$, $P(OEt)_3$) with iodid gives $[CoI(L)(NO)_2]^+$ and $[CoL_3(NO)]$ while with CO a mixture of $[CoL_3(CO)_2]^+$, $[CoI(L)_2(CO)_2]$, $[CoI(L)(NO)_2]$, $[CoL_2(NO)_2]^+$ and $[CoL_3(NO)]$ is produced (ref. 344). Electrochemical reduction of $[CoXL_3(NO)]BPh_4$ (X = Cl, I; L = $P(OMe)_3$, $P(OEt)_3$) in acetonitrile gives $[CoL_3(NO)]$ by an e.c.e. type mechanism while oxidation gives $[CoL_2(NO)_2]BPh_4$, $[CoX(L)(NO)_2]$ and other species not containing NO (ref. 345). Sodium bis(2-methoxyethoxy)aluminum hydride has been used as a selective reducing agent at -78°C to convert [cpCo(NO)I] into $[cpCo(NO)]_2$. Although no direct evidence for it was found, [cpCo(NO)H] was suggested as a plausible intermediate (ref. 346). In THF at room temperature the complexes $[Co(NO)(CO)_2L]$ (L = $PBu^t{}_{3-n}(EMe_3)_n$ (n = 0-3, E = Si, Ge, Sn)) are formed from $[Co(NO)(CO)_3]$ (ref. 347) and their ^{59}Co NMR spectra have been measured. For E = Si there is little change in chemical shift over the whole series while for E = Sn there is *ca.* 300 ppm difference between the complexes with L = $PBu^t{}_3$ and L = $P(SnMe_3)_3$. Those with E = Ge show intermediate behavior (ref. 348). Photolysis of a mixture of $[Co(CO)_3(NO)]$ and NO in a pentane matrix at 195 K generates a paramagnetic species believed to be $[Co(CO)_2(NO)_2]$ on the basis of the observed hyperfine splitting and the results using ^{15}NO. The epr spectrum is best simulated by the assumption that the complex is square planar (ref. 349). X-ray photoelectron spectra of $[Co(diars)_2(NO)X]ClO_4$ (X = Cl, Br) and $[Co(diars)_2(NO)](ClO_4)_2$ (diars = 1,2-bis(dimethylarsino)benzene) have been measured and the nitrogen 1s, arsenic 3d and cobalt 2p core binding energies determined. Those of arsenic are independent of the nature of the other ligands and the charge on the complex while those for cobalt reflect the electron-withdrawing effect of the ligand *trans* to NO. The nitrogen 1s core binding energy correlates with the NO stretching frequency but not with the M-N-O angle (ref. 350). At 250-300°C, [Co(TPP)] catalyzes the reduction of NO by hydrogen to give N_2, N_2O and NH_3 (ref. 351).

In refluxing ethanol-dichloromethane, hydrated rhodium (III) chloride reacts with NOCl in the presence of PPh_3 to give $[Rh(NO)_2Cl(PPh_3)_2]$ which on further refluxing or on treatment with HCl is converted to $[Rh(NO)Cl_2(PPh_3)_2]$ (ref. 352). Both $[Rh(NO)X_2(PPh_3)_2]$ and $[Rh(NO)X_3(PPh_3)_2]$ are reported to arise from reaction of NOX (X = Cl, Br) with $[RhCl(PPh_3)_3]$ (ref. 353). Triphenylphosphine is displaced from [Rh(NO)$(PPh_3)_3$] in benzene solution by a variety of bi- and tridentate tertiary phosphines (L_2 and L_3 respectively) to give [Rh(NO)$(L_2)(PPh_3)$] or [Rh(NO)(L_3)]. From ^{31}P NMR studies it was concluded that all had pseudo tetrahedral coordination about the metal with approximately linear nitrosyl groups. From the low-temperature ^{31}P NMR spectrum of the complex with tris(2-diphenylphosphinoethyl)phosphine it was found that the central and only two of the three terminal phosphorus atoms were coordinated. On warming, equilibration of the terminal phosphorus atoms occurred via an associative process involving a five-coordinate intermediate. The phosphorus chemical shifts in the complexes studied varied with the size of the chelate rings and $^1J_{Rh-P}$ decreased with an increase in the number of chelate rings. In chiral systems, the phosphorus chemical shifts appeared to be more sensitive to the chirality of carbon substituents than to chirality at the metal (refs. 354, 355). Reaction of $[Ir(NO)(MeCN)_2(PPh_3)_2]^{2+}$ with 1,2-dihydroxy-3,4,5,6-tetrabromobenzene in methanol containing the stoichiometric quantity of sodium hydroxide yields [Ir(NO)(1,2-O_2-C_6Br_4)$(PPh_3)_2$] which on refluxing in benzene in the presence of chloranil and oxygen gives [Ir(NO)(1,2-$O_2C_6Br_4$)(PPh_3)]. The structural study shows the nitrosyl group to be linear. The observation that the Ir-O bond _trans_ to nitrogen is shorter than that _trans_ to phosphorus, which is a reversal of the usual _trans_-influence series, is attributed to the catecholate ligand functioning as a strong π-donor (ref. 356).

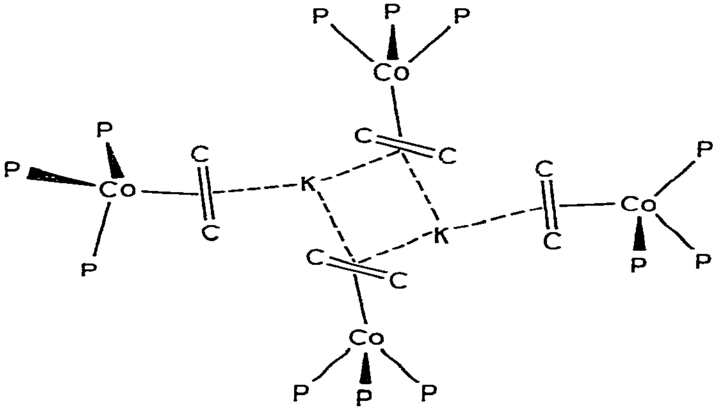
At -70°C in acetone $[Co(CO)_4]^-$ reacts with PhN_2^+ followed by treatment with PPh_3 to yield an unstable oil proposed to be [Co(N_2Ph)$(CO)_2(PPh_3)$] on the basis of infrared spectral measurements (ref. 357). A correlation of the Ir-Cl stretching frequency with ^{31}P chemical shifts in [IrCl(L)$(PPh_3)_2$] (L = CNBu^t, CS, $N_2C_5X_4$ (X = Cl, Br), RN_2^+(R = Ph, _p_-MeOC_6H_4), NO^+, tertiary phosphine, CO , C_2H_4, N_2) has been made and the trends are in accord with the previously established _trans_-influence series. The diazonium ligands show a very low _trans_-influence (ref. 358). A study of the ligand properties of the neutral diazo compounds $C_5X_4N_2$ (X = Cl, Br) shows that they bind only in the η^1 mode. Reaction with [IrCl(N_2)$(PPh_3)_2$] in dichloromethane at 0°C gives the thermally unstable _trans_-[IrCl($N_2C_5Cl_4$)$(PPh_3)_2$] which from a crystal structure study contains a "singly-bent" diazo ligand (ref. 360). The diazo ligand is readily displaced by CO however with other ligands, five-coordinate adducts, $[IrCl(N_2C_5Cl_4)(L)(PPh_3)_2]$, (L = PMe_3, PMe_2Ph, $PMePh_2$, $CNBu^t$) can be prepared at low temperature. Analogs of formula $[IrCl(N_2C_5X_4)(L)_2]$ (L = PPh_3, $P(\underline{p}\text{-tolyl})_3$, $P(\underline{p}\text{-}FC_6H_4)_3$) can also be prepared from $[IrCl(cyclooctene)_2]_2$, L and $N_2C_5X_4$. All are thermally unstable. At 0°C, $[IrCl(N_2C_5Cl_4)(PPh_3)_2]$ reacts with $NOPF_6$ to give the presumably square pyramidal $[Ir(NO)Cl(N_2C_5Cl_4)(PPh_3)_2]PF_6$ while at -78°C, HCl reacts to give $[IrHCl_2(N_2C_5Cl_4)(PPh_3)_2]$ which on treatment with N-methyl-N-nitrosotoluene-p-sulfonamide gives the neutral nitrosyl $[Ir(NO)Cl_2(N_2C_5Cl_4)(PPh_3)_2]$. Attempts to prepare rhodium analogs were unsuccessful presumably as the starting complexes were not sufficiently basic (ref. 359). The SO_2-bridged dimer, $[Ir(CO)_2(PPh_3)(\mu\text{-}SO_2)]_2$, reacts with $\underline{p}\text{-}RC_6H_4N_2BF_4$ (R = Me, MeO, F) in benzene to produce $[(Ir(CO)(PPh_3))_2(\mu\text{-}N_2C_6H_4R)(\mu\text{-}SO_2)]BF_4$ which can be protonated by HBF_4 to give $[(Ir(CO)(PPh_3))_2(\mu\text{-}N{=}NHC_6H_4R)(\mu\text{-}SO_2)](BF_4)_2$. It also reacts with halide ion to give the triply-bridged complexes $[(Ir(CO)(PPh_3))_2(\mu\text{-}X)(\mu\text{-}N_2C_6H_4R)(\mu\text{-}SO_2)]$ (X = Cl, Br, I) (ref. 361). Triazenido complexes [109] have been prepared from $[Ag(RN_3R^1)]_n$ (R = Me, Et, p-tolyl; R^1 = p-tolyl), mercury (II) chloride and $[M(diene)Cl]_2$ (M = Rh, Ir, Diene = COD. M = Rh, diene = NBD) or from $[Ag(RN_3R^1)]_n$ and $[(diene)MCl(HgCl_2)]_n$. The complexes appear to be monomeric in solution and for the rhodium species there is intramolecular exchange of the two triazenido ligands (ref. 362).



[109]

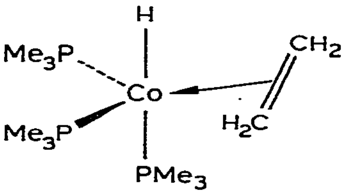
Metal alkene compounds

Reduction of $[Co(C_2H_4)(PMe_3)_3]$ with 0.5 equivalent of potassium in pentane at room temperature yields the metastable "semicobaltate" $K[Co(C_2H_4)(PMe_3)_3]_2$. A portion of the unit cell contents (methyl groups and hydrogen atoms omitted for clarity) is shown as [110]. On standing in solution this disproportionates to $[Co(C_2H_4)(PMe_3)_3]$



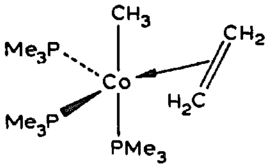
[110]

and $K[Co(C_2H_4)(PMe_3)_3]$. Flushing the solution with nitrogen gives $[Co(C_2H_4)_2(PMe_3)_3]$ and $K[Co(N_2)(PMe_3)_3]$ while with ethylene $[Co(C_2H_4)(PMe_3)_3]$ and $K[Co(C_2H_4)_2(PMe_3)_2]$ are formed (ref. 363). Protonation of $K[Co(C_2H_4)(PMe_3)_3]$ yields [111] which is evidently in equilibrium

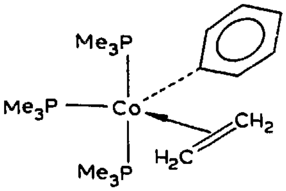


[111]

with $[Co(C_2H_5)(PMe_3)_3]$ since the product when MeOD is used shows a random distribution of deuterium over the metal and the olefin. Pent-1-ene is isomerized to <u>cis</u>- and <u>trans</u>-pent-2-ene in the presence of [111]. Alkylation of $[CoCl(PMe_3)_3]$ with methyllithium or phenyllithium in the presence of ethylene gave [112] and [113] respectively. The structure of [113] has been determined. Insertion of ethylene into the Co-C bond did not occur in either [112] or [113] however on heating [113] gave biphenyl and $[Co(C_2H_4)(PMe_3)_3]$ (ref. 364).

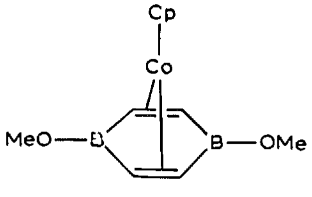


[112]



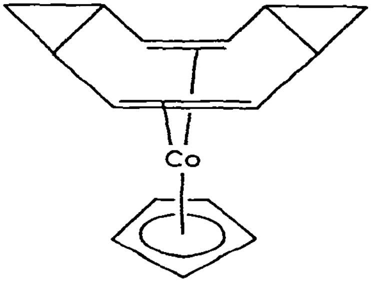
[113]

At 80°C, $[cpCo(CO)_2]$ reacts with 1,4-dimethoxy-1,4-dibora-2,5-cyclohexadiene to give [114] which can be converted into the corresponding dimethyl derivative on treatment with MeMgI. The structure of the latter has been determined and it appears that the major bonding interaction between the metal and the heterocycle involves the



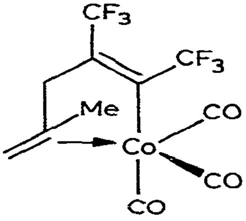
[114]

carbon-carbon double bonds. From cyclic voltammetric studies, the heterocyclic ligand appears to function as a strong acceptor (ref. 365). In the presence of a variety of polyolefins and acetylenes $Co(ClO_4)_2 \cdot 6H_2O$ and triphos form $[Co(triphos)L]ClO_4$ (L = butadiene, isoprene cycloheptatriene (CHT), cyclooctatetraene (COT), PhC≡CH, PhC≡CPh). The structure of the CHT complex has been determined and the CHT ligand found to bind as a 1,3-diene. The same coordination mode is proposed for COT while the acetylenes are proposed to function as 4-electron donors (ref. 366). Methylene generated by the reaction of zinc-copper couple with CH_2I_2 adds to the uncoordinated double bonds of the COT ligand in [cpCo(COT)] to give [115] (ref. 367). Hexafluorobut-2-yne adds to the allyl ligand of $[(n^3\text{-}2\text{-}MeC_3H_4)Co(CO)_3]$ to give the 1:1 and 1:2 adducts [116] and [117]. A polymer derived from the acetylene was also produced (ref. 368). Co-condensation of cobalt vapor with butadiene

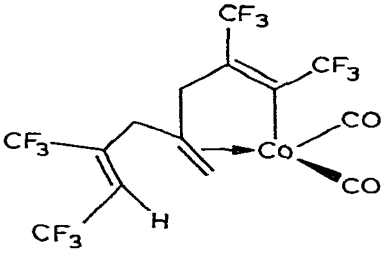


[115]

followed by warming and addition of PEt_3 yielded [118] which catalyzed the cyclotrimerization of PhC≡CH to 1,3,5-triphenylbenzene and which

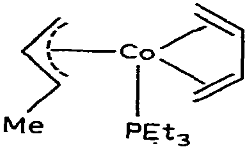


[116]



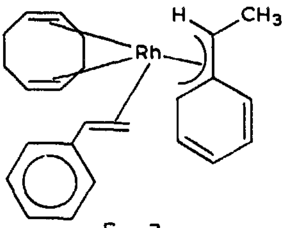
[117]

reacted with ethyl bromide to give COD and 4-vinylcyclohexene. Infrared studies of the original matrix during warmup suggested that up to 0°C the major species was $[Co(\eta^2-C_4H_6)]$. This subsequently



[118]

rearranged to species either containing chelating butadiene or the butadienyl ligand (ref. 369). The reaction of $[Rh(COD)Cl]_2$ with Pr^iMgBr in the presence of olefinic substrates gives a variety of olefin and allyl complexes. From styrene [119] is obtained in which the η^3-benzyl ligand is fluxional. Since the fluxional process occurs without loss of stereochemistry at the benzylic carbon, a σ-bonded benzyl group is proposed as an intermediate (ref. 370). With 4-vinylcyclohexene and 1-methyl-1,4-cyclohexadiene [120] and the isomeric mixture [121] and [122] are obtained respectively.



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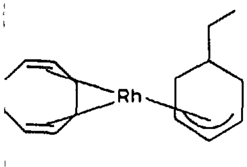

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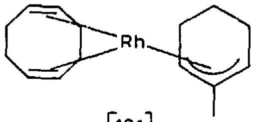

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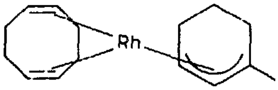
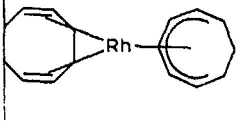


[122]

Complex [120] is also obtained using butyllithium in place of the Grignard reagent. Reaction of $[Rh(COD)Cl]_2$ with butyllithium in the presence of cyclooctatetraene gave [123], [124] and [125]. The mechanism of formation of [120] is shown in Scheme XXXIV (ref. 371). The diene complex $[Rh(TFB)Cl]_2$ (TFB = tetrafluorobenzobarrelene) on reaction with $AgClO_4$ in acetone followed by addition of various ligands gives cationic complexes $[Rh(TFB)L_2]ClO_4$ (L = MeCN, PhCN, py, tertiary phosphines; L_2 = o-phenanthroline, bipyridyl, diphos) which have been studied as olefin hydrogenation catalysts. The fastest rates are seen with the most basic ligands and the systems



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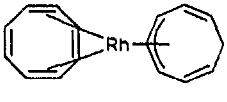

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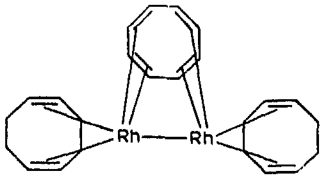
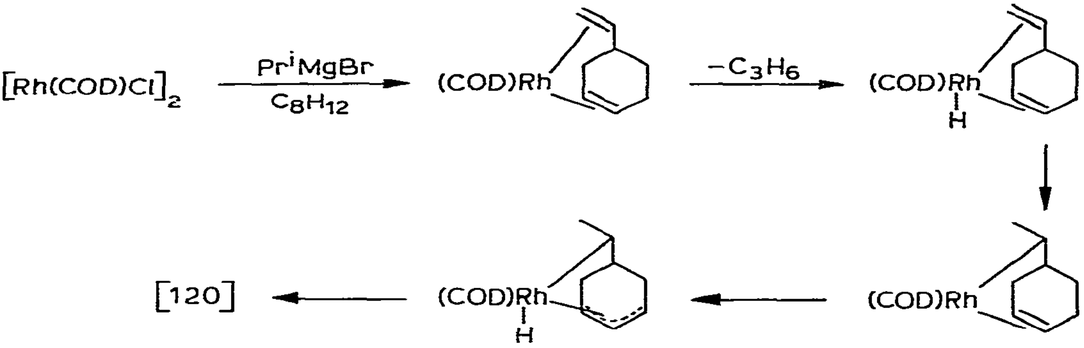


[125]

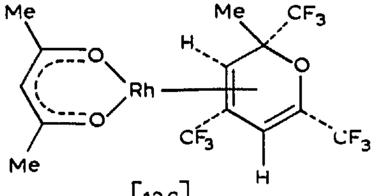


Scheme XXXIV

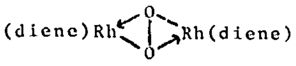
are selective for the hydrogenation of 1,4-cyclohexadiene to cyclohexene (ref. 372). Analogous studies of $[Rh(NBD)L_2]ClO_4$ complexes have also been made but these seem more prone to degradation under catalytic conditions (ref. 373). A reportedly convenient synthesis of $[Rh(CO)_2Cl]_2$ involves reaction of $[Rh(COD)Cl]_2$ with CO in hexane followed by solvent evaporation under CO and sublimation to give 65-75% yield of product (ref. 374). However considering that the synthesis of $[Rh(COD)Cl]_2$ is not a high-yield process it would seem that the direct carbonylation of hydrated rhodium (III) chloride is a more cost-effective route. Amino acids (AAH) react with $[Rh(COD)(O_2CMe)]_2$ in the presence of CO to yield $[Rh(CO)_2(AA)]$ (ref. 375). The bridging chlorides in $[Rh(COD)Cl]_2$ can be replaced by pentafluorophenylthiolate. The NBD analog was also prepared (ref. 376).

While $[Rh(COD)Cl]_2$ reacts with benzothiazole (BT) to give an adduct formulated as $[Rh(COD)(BT)Cl]_2$ which is proposed to retain the chloro-bridged structure with the BT ligand bonded via the S-C-N π-system, $[Rh(C_2H_4)_2Cl]_2$ loses ethylene to give $[Rh(BT)_2Cl]_2$. The latter complex is a catalyst for the dimerization of acetone and benzaldehyde (ref. 377). Replacement of two carbonyl groups in $[Rh(CO)_2(L_2)]$ (L_2 = benzoyltrifluoroacetonate) by COD gives $[Rh(COD)(L_2)]$ whose structure has been determined. It appears that the benzoyl oxygen has the larger trans-influence (ref. 378). In a related reaction, ethylene can be replaced by 2-methyl-2,4,6-tris-(trifluoromethyl)pyran in [Rh(acac)$(C_2H_4)_2$] to give [126] (ref. 379). The schiff-base ligands derived from salicylaldehyde and p-toluidine (SB) or o-phenylenediamine (SB^1) react with $[M(COD)(OMe)]_2$ (M = Rh, Ir) to give [Ir(COD)(SB)] and {$[Rh(COD)]_2(SB^1)$}. The structures of both complexes have been determined (ref. 380).

Dioxygen-bridged dimers [127] (diene = COD, NBD, dicyclopentadiene)



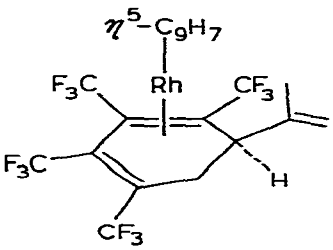
[126]



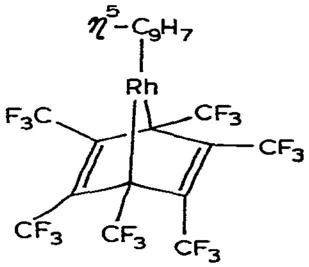
[127]

can be prepared from $[Rh(diene)Cl]_2$ and KO_2. On heating in benzene in the presence of PPh_3 a 97% yield of $OPPh_3$ is obtained. Reaction of the COD complex with ROH (R = H, Me, Et, MeCO) or C_5H_6 yields $[Rh(COD)OR]_2$ and [cpRh(COD)] respectively together with hydrogen peroxide. By contrast $[(\eta^3-C_3H_5)_2RhCl]_2$ yields $[(\eta^3-C_3H_5)_2Rh(\mu-OH)_2-Rh(\eta^3-C_3H_5)_2]$ on reaction with KO_2 although an O_2-bridged dimer analogous to [127] is proposed as an intermediate. Complex [127] (diene = COD) catalyzes the dimerization of acetone (ref. 381).

$[RhCl(C_2H_4)_2]_2$ continues to be a widely used starting point for the synthesis of low-valent rhodium complexes. Reaction with white phosphorus and triphos in dichloromethane produces [Rh(triphos)-(η^3-P_3)] analogous to the cobalt complex described earlier. The iridium analog can be got in a similar fashion from $[Ir(CO)Cl(PPh_3)_2]$. These in turn react with $M^1(BF_4)_2$ (M = Co, Ni) in the presence of triphos to give $[(triphos)M(\mu_2-\eta^3-P_3)M^1(triphos)](BF_4)_2$ (M = Rh, Ir; M^1 = Co. M = Rh; M^1 = Ni). The Rh-Ni complex exhibits paramagnetic behavior which is dependent on the counterion and solvent while the structure shows that the Rh-Ni axis is not coincident with the centroid of the P_3 triangle (ref. 382). Indenyl potassium converts $[RhCl(C_2H_4)_2]_2$ to $[(\eta^5-C_9H_7)Rh(C_2H_4)_2]$ in which the ethylene ligands can be replaced by a variety of other olefinic groups including 1,3-dienes, acrylonitrile, methylenecyclopropane and COT to give the corresponding η^5-indenyl complexes. The derivative with 2-methyl-1,3-butadiene reacts with hexafluorobut-2-yne to give [128] and [129] while that with 1,3-pentadiene gives [129] and [130]. Ethylene couples with hexafluorobut-2-yne on reaction

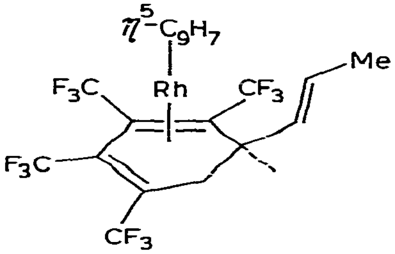


[128]



[129]

of the acetylene with $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ itself giving [131]. The mechanism of Scheme XXXV is proposed for the formation of [128]



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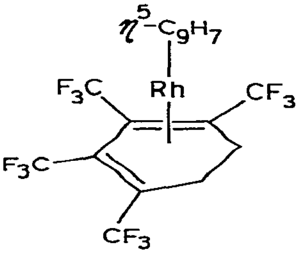
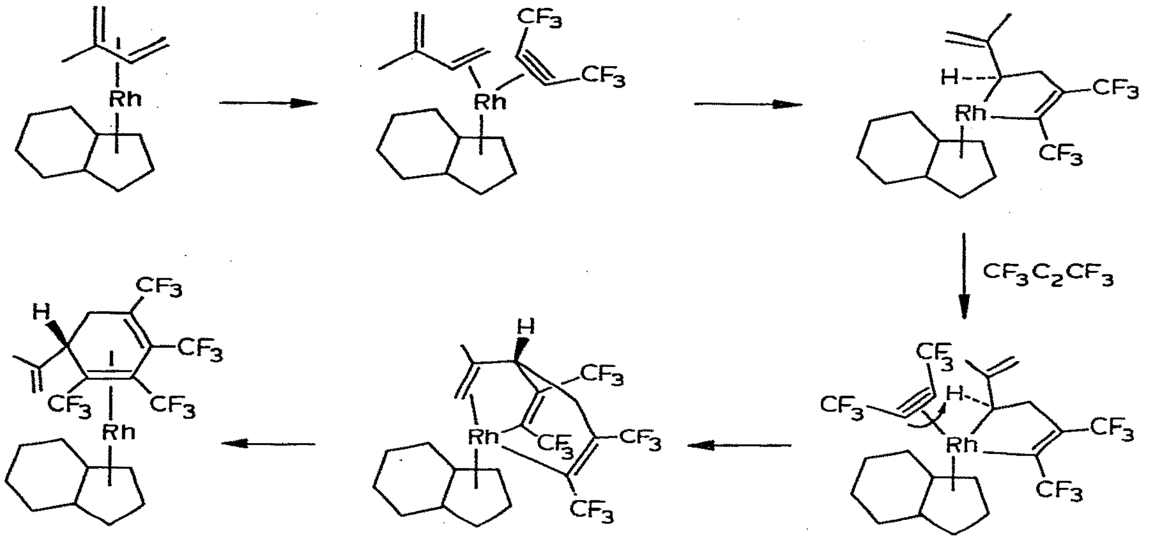


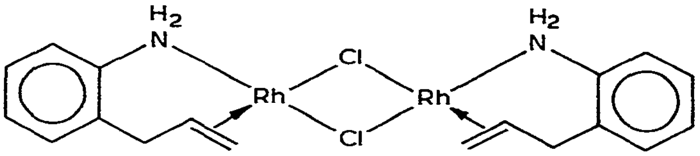
[131]

and presumably analogous processes occur for [130] and [131]. The steps involving acetylene coordination may be aided by a slippage of the indenyl ligand from an η^5- to an η^3-bonding mode. The reaction of $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ with 3,3-dimethylbut-1-yne gave the analog of [131] in which the two acetylene molecules have coupled head-to-head. Also formed were 1,2,4- and 1,3,5-tris(tert-butyl)benzene (10:1) as well as some uncomplexed 1,4-bis(tert-butyl)cyclohexa-1,3-diene. Routes similar to that of Scheme XXXV are proposed to lead to these products (ref. 383). The initial product from the reaction of $[Rh(C_2H_4)_2Cl]_2$ with diphos in toluene is $[Rh(C_2H_4)$-(diphos)Cl]. This loses ethylene, particularly in coordinating solvents to give a solvated [RhCl(diphos)] species which absorbs CO_2 to form $[Rh(CO_2)(diphos)Cl]$. This last complex reacts with oxygen to give a species which although not isolated was proposed from its infrared spectrum and that of the ^{13}C labelled analog to



Scheme XXXV

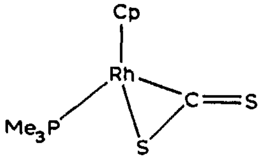
be a carbonate complex. Loss of solvent from the [RhCl(diphos)] species leads to formation of the dimer $[Rh(diphos)Cl]_2$ while reaction with sodium tetraphenylborate gives $[Rh(diphos)(\eta^6-C_6H_5BPh_3)]$ whose structure has been determined. This complex on refluxing in acetone under a CO_2 atmosphere gives the benzoate derivative [Rh(diphos)-(O_2CPh)] which can also be got directly from [Rh(diphos)Cl] and sodium benzoate. When prepared by the former route, mesityl oxide and diacetone alcohol are also formed presumably via a rhodium-catalyzed dimerization of the solvent acetone (ref. 384). The diazadiphosphetidines $(RNPX)_2$ (R = Pr^i, Bu^t; X = F, Cl) react with $[RhCl(C_2H_4)_2]_2$ to give rather insoluble species having the composition $[RhCl(RNPX)_2]$ which are presumed to be polymeric with ligand bridges. The complex with R = Bu^t; X = F reacts with CO to give [RhCl(CO)-$(Bu^tNPF)_2$] which may be dimeric although this was not established. Monomeric complexes $[cpRh((RNPF)_2)_2]$ were obtained from $[cpRh(C_2H_4)_2]$ (ref. 385). The reaction of o-allylaniline with $[Rh(C_2H_4)_2Cl]_2$ yields [132] which on refluxing in dichloromethane in the presence of o-allylaniline gives o-trans-propenylaniline (PA) and $[Rh(PA)_2Cl]_2$. Reaction of N-allylaniline (NAA) with $[Rh(C_2H_4)_2Cl]_2$yields $[Rh_2Cl_2$-$(NAA)_3]$ which rearranges in solution to give a complex proposed to contain an N-phenylazetadine ligand and which on heating with



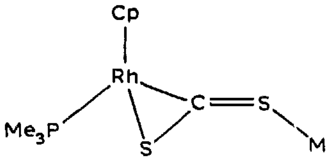
[132]

excess NAA yields propene, aniline, azobenzene and N-propylaniline (both Pr^n and Pr^i groups are present). The formation of the azetidine is thought to arise from electrophilic attack of the nitrogen on the coordinated double bond of the NAA ligand. $[Rh_2Cl_2(NAA)_3]$ also reacts with diphenylacetylene to give 1,2,3-triphenyl-4-methyl-2,5-dihydropyrrole and with methylphenylacetylene to give acetylene dimers and cyclotrimers (ref. 386).

Unlike the lithium formamidinate reactions described earlier $Hg(RNC(Y)NR^1)_2$ (Y = H; R = R^1 = Pr^i, *p*-tolyl. R = Me, Pr^i; R^1 = *p*-tolyl. Y = Me; R = R^1 = *p*-tolyl) reacts with $[Rh(diene)Cl)]_2$ (diene = COD, NBD) to give $[Rh(diene)(RNC(Y)NR^1)HgCl]_2$ with a structure presumed analogous to that for the triazenido complexes [109]. In solution they are also monomeric and fluxional. The iridium analogs could not be prepared (ref. 387). Trichlorostannate ion coordinates to the cations $[Rh(diene)L_2]^+$ (diene = COD, NBD; L_2 = PPh_nEt_{3-n} (n = 0-3); L_2 = diphos) yielding $[Rh(diene)(SnCl_3)L_2]$ which can also be prepared from [Rh(diene)(L)Cl], L and $SnCl_2$ in methanol. Carbon monoxide displaces the diene in the monodentate phosphine complexes yielding $[Rh(SnCl_3)(CO)_2L_2]$ in which both inter- and intra-molecular phosphine exchange processes occur as determined by ^{31}P NMR studies (ref. 388). Related iridium complexes $[Ir(COD)(SnCl_3)L_2]$ (L = PPh_3, $P(p\text{-tolyl})_3$, $P(p\text{-MeOC}_6H_4)_3$, $P(p\text{-FC}_6H_4)_3$; L_2 = diphos, DPPB, DIOP) have been prepared by the second route. The monodentate phosphine complexes yield $[Ir(SnCl_3)(CO)_2L_2]$ and $[IrH_2(SnCl_3)L_2]$ with CO and H_2respectively while the diphos complex also gives a dicarbonyl. In the presence of hydrogen, $[Ir(COD)(SnCl_3)(P(p\text{-tolyl})_3)_2]$ gives a catalyst producing about equal amounts of alkane and internal olefins from hept-1-ene (ref. 389). At 50°C in benzene, CS_2 replaces ethylene in $[cpRh(C_2H_4)L]$ (L = PMe_3, PMe_2Ph) giving $[cpRh(\eta^2\text{-}CS_2)L]$ and, when L = PMe_3, a small amount of [133]. The terminal sulfur atom in $[cpRh(\eta^2\text{-}CS_2)(PMe_3)]$ can



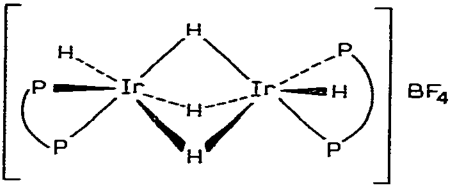
[133]



[134]

be metallated with [M(THF)] (M = Cr(CO)$_5$, cpMn(CO)$_2$) to give [134] (ref. 390).

Iridium-olefin complexes have also been the subject of considerable study. Oxidative addition of HBF$_4$ to [Ir(CO)Cl(PPh$_3$)$_2$] yields trans-[IrH(FBF$_3$)(CO)Cl(PPh$_3$)$_2$] which is proposed to contain a weakly coordinated tetrafluoroborate ion. This can be replaced by ethylene at -40°C and on addition of [Re(CO)$_5$]$^-$, [EtRe(CO)$_5$] and [Ir(CO)Cl-(PPh$_3$)$_2$] are obtained. An intermediate in which the ethylene is coordinated to both metals proposed (ref. 391). Cationic complexes [Ir(COD)L$_2$]X (L = triarylphosphine: X = ClO$_4^-$, BPh$_4^-$) have been prepared from [Ir(COD)Cl]$_2$ and give the expected oxidative adducts with Cl$_2$, I$_2$, MeI and Me$_3$SiCl. However with hydrogen in acetone, hydrogenation of the diene also occurs giving [IrH$_2$L$_2$(acetone)$_2$]BPh$_4$ which reacts with CO to yield [IrH$_2$(CO)$_2$L$_2$]BPh$_4$. This last complex can also be got by treating [Ir(COD)L$_2$]BPh$_4$ with CO to give [Ir(CO)$_3$-L$_2$]BPH$_4$ followed by reaction with hydrogen. In this route the hydrogenation step can be reversed on treatment with CO (ref. 392). The related complex [Ir(COD)(DPPP)]BF$_4$ is obtained from [Ir(COD)Cl]$_2$ and AgBF$_4$ in acetone followed by addition of ligand. On hydrogenation in methanol a mixture of [135] and [136] was obtained. The structures of both have been determined and although the hydrogen atoms were not located crystallographically, low-temperature NMR studies suggested the location shown. For [135] the bridging hydride ligands occur at lower field than the terminal ones which is contrary to most other observations. At ambient temperature the molecule is fluxional, interchanging the nonequivalent bridging hydrogens but not showing any bridge-terminal exchange. For [136] several interconverting isomers are present at ambient temperature. This process, which is more rapid than the interchange of terminal and edge-bridging hydrides was shown to occur via conversion of the μ_3-hydride to a μ_2-hydride by reversible coordination of solvent



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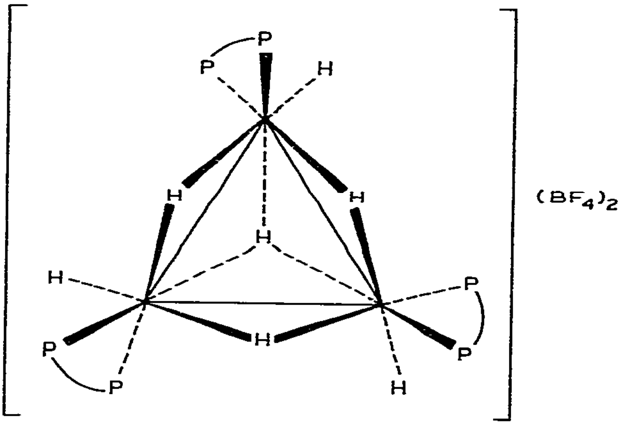
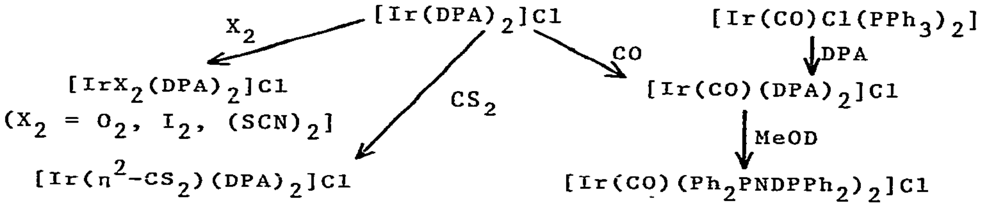
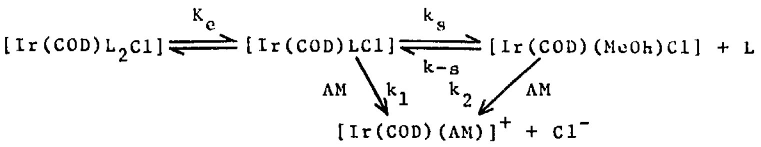


[136]

(ref. 393). The cationic complex $[Ir(DPA)_2]Cl$ is formed from $[Ir(COD)Cl]_2$ and its chemistry is outlined in Scheme XXXVI. The adduct with I_2 is thought to be the cis isomer while that with $(SCN)_2$ is trans (ref. 394). The kinetics of the reaction of $[Ir(COD)(L)Cl]$ (L = α-picoline) with L, bipyridyl and o-phenanthroline (AM) in methanol have been studied and the mechanism depicted in Scheme XXXVII proposed. The activation parameters for the k_s, k_1 and k_2 paths are characteristic of additions to square planar complexes (ref. 395). Tetracyanoethylene adds to

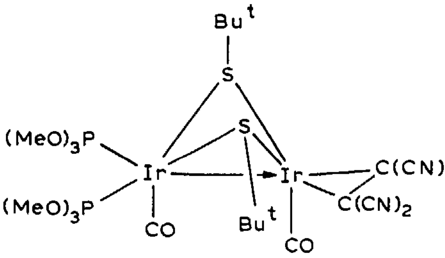


Scheme XXXVI



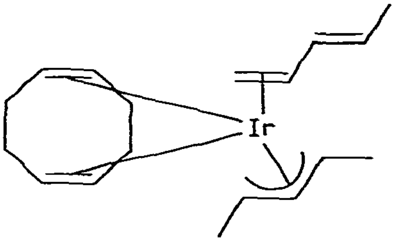
Scheme XXXVII

$[Ir(CO)L(\mu\text{-}SBu^t)_2Ir(CO)L]$ (L = PMe_3, PPh_3, $P(OMe)_3$) to give the the rearranged species $[Ir(CO)L_2(\mu\text{-}SBu^t)_2Ir(CO)(TCNE)]$. The structure of the trimethylphosphite complex is [137]. To account for the short Ir-Ir distance of 2.679(1) Å, a polar metal-metal bond is

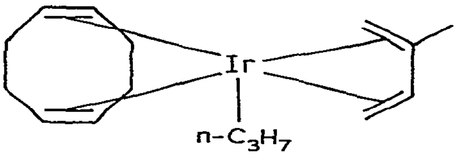


[137]

proposed (ref. 396). A kinetic study of the reaction of oxygen with $[Ir(COD)L_2]Cl$ (L_2 = *o*-phenanthroline) in the presence of iodide to give $[Ir(COD)L_2O_2]I$ has been reported. In methanol the neutral, five-coordinate complex $[Ir(COD)L_2I]$ is favored and appears to react with oxygen about thirty times faster than does the cationic, square planar starting complex. The possibility of end-on coordination of oxygen to the five-coordinate species is suggested (ref. 397). The reaction of $[Ir(COD)Cl]_2$ with Pr^iMgBr in the presence of 1,3-pentadiene and isoprene yields [138] and [139] respectively presumably by a mechanism related to that described earlier in Scheme XXXIV (ref. 398). Abstraction of chloride from $[Ir(cyclooctene)_2Cl]_2$ with AgO_2CCF_3 in pentane gives $[Ir(cyclooctene)_2(O_2CCF_3)]_2$ which on treatment with benzene and trifluoroacetic acid gives the arene complex $[Ir(cyclooctene)_2(\eta\text{-}C_6H_6)][H(O_2CCF_3)_2]$. Solutions of $[Ir(cyclooctene)_2(O_2CCF_3)]_2$ in dichloromethane slowly react to give $[Ir(COD)(O_2CCF_3)]$ and cyclooctane. The same products result if the chloride abstraction is initially carried out in dichloromethane. The mechanism of Scheme XXXVIII is proposed (ref. 399).

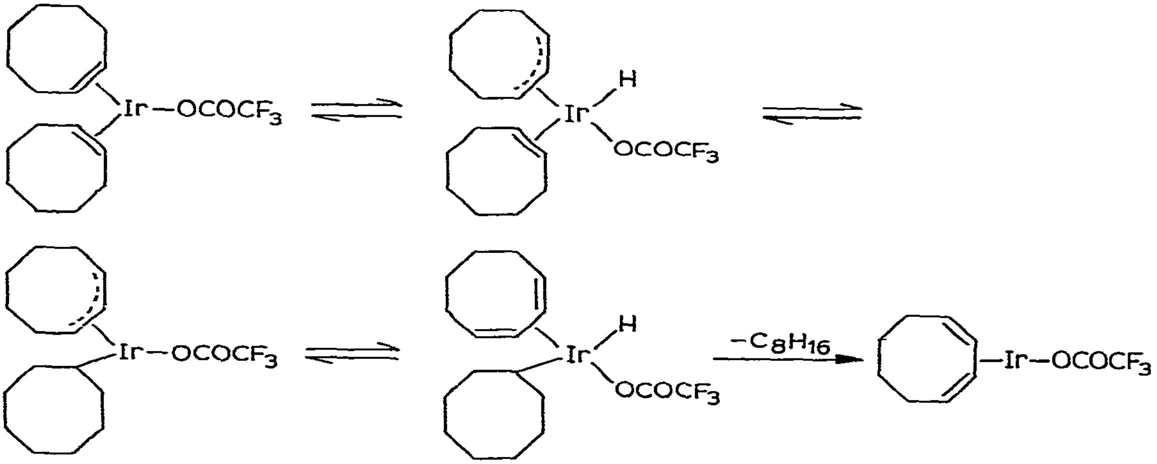


[138]

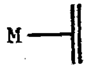


[139]

Complexes of the type $[Ir(COD)L_2]^+$ add hydrogen when L is an electron-accepting ligand such as tertiary phosphines or olefins but not when it is a relatively electron-donating ligand such as pyridine which was interpreted to indicate that in this reaction, the reactive substrates have the metal exhibiting Lewis acid character. This is in contrast to the generally accepted dogma that such addition reactions are favored by increased electron density on the metal. On the basis that the bonding of an olefin to an electron-poor center should be represented by [140] while for an electron-rich center it should resemble [141] it was proposed that the change in chemical shift of the vinylic carbons of the COD ligand on adduct formation ($\Delta\delta = \delta_c$(adduct)$-\delta_c$(starting complex)) could be used to characterize



Scheme XXXVIII

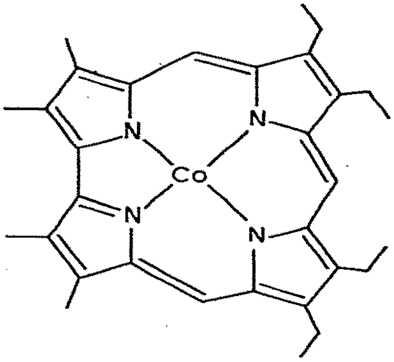


[140]

[141]

the nature of the addition process. Thus $\Delta\delta$ is negative for the adducts with hydrogen, slightly positive for adducts with hydrogen halides and considerably more positive for halogen adducts leading to the conclusion that while the latter two could be characterized as oxidative additions, the first should more properly be called reductive addition (ref. 400).

A wide variety of metal-olefin complexes are involved in catalytic processes either as catalyst precursors or as intermediates in the catalyzed reactions. The corrinoid complex [142] mediates the oxygenation of electron-rich olefins by hydroxide ion to give alcohols or ketones with concomitant reduction to the Co(II) corrin. As the metal can be reoxidized in the presence of oxygen, the system may potentially be catalytic. A mechanism involving coordination of the olefin to the Co(III) corrin followed by hydroxide attack with concomitant reduction of the metal is proposed (ref. 401). Reduction of $[Co(acac)_3]$ with $[Et_2AlCl]_2$ in the presence of diphos gives a catalyst for the cyclocodimerization of norbornadiene with olefins, acyclic 1,3-dienes and acetylenes. A mechanism involving olefin and diene complexes as intermediates is proposed (ref. 402). The addition of ethylene to 4-pentenal is catalyzed by $[Rh(acac)(C_2H_4)_2]$ with the major product (39%) being <u>trans</u>-hept-5-ene-3-one.



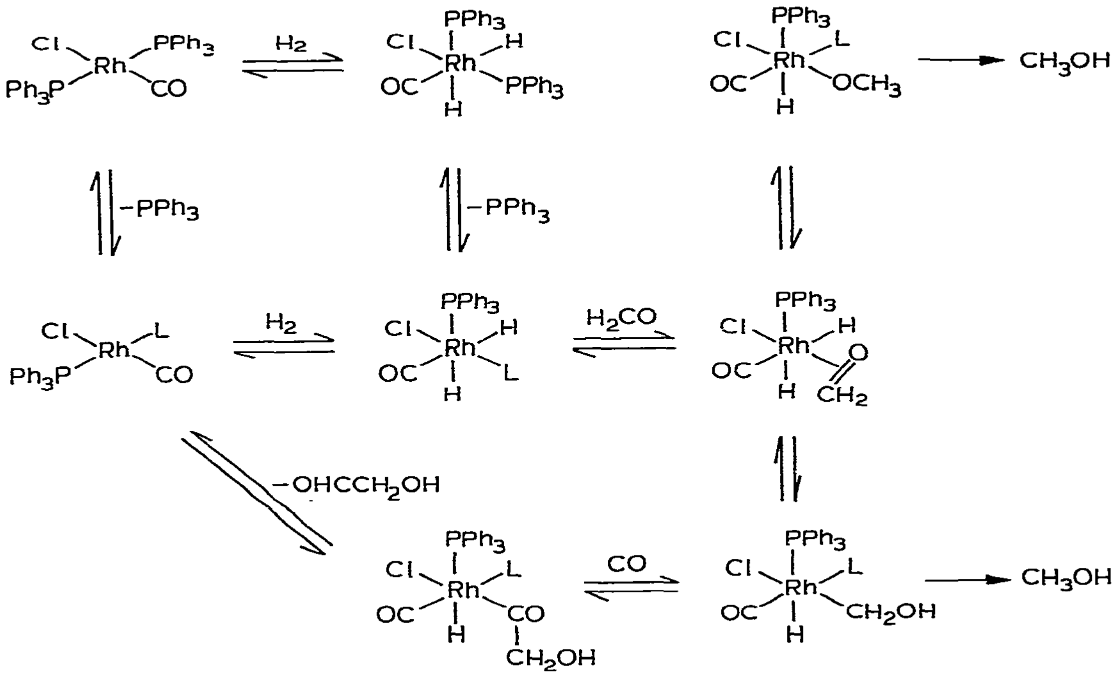
[142]

Small amounts of the cis isomer and hept-6-ene-3-one were also found together with isomers of the starting pentenal. Under the same conditions a mixture of cis- and trans-3-pentenal gave only trans-2-pentenal indicating that the major product of the original reaction resulted from double-bond migration subsequent to coupling with ethylene. A mechanism involving oxidative addition of the aldehyde C-H bond to the metal to give an acyl hydride ethylene complex followed by ethylene insertion into the Rh-H bond and reductive elimination from the acyl ethyl complex was proposed (ref. 403). However with complexes of nominal formula $[RhCl(P(\underline{p}\text{-}RC_6H_4)_3)_2]$ (R = Me, MeO, Me_2N) prepared in situ from $[Rh(cyclooctene)_2Cl]_2$ the coupling reaction is not observed but rather cyclization occurs and for example cyclopentanone can be obtained in good yield from 4-pentenal. Again, oxidative addition of the aldehyde C-H bond is proposed as the initial step but now the hydride produced transfers to the coordinated double bond of the pentenal (ref. 404). Phosphine complexes prepared in situ from $[Rh(NBD)Cl]_2$ are catalysts for the hydrogenation olefins, particularly styrene, in methanol or ethanol. In these systems up to half of the rhodium is converted to $[Rh(CO)Cl(PR_3)_2]$ however none is seen when the reactions are run in benzene, isopropanol or butane-2-one leading to the conclusion that a rhodium-catalyzed hydrogen transfer from the alcohol solvent to the olefin is operative (ref. 405).

Much use continues to be made of $[RhCl(PPh_3)_3]$ and analogs as homogeneous hydrogenation catalysts. Examples include its use for the hydrogenation of the Δ^1 double bond in steroids like androsta 1,4-diene-3,17-dione (ref. 405a), the hydrogenation of squalane precursors with the $P(\underline{p}\text{-}H_2NC_6H_4)_3$ analog (ref. 405b) and the use of the water-soluble analog $[RhCl(PPh_2(\underline{m}\text{-}NaO_3SC_6H_4))_3]$ to hydrogenate double bonds in phospholipid liposomes (ref. 407). Also, $[RhCl(PPh_3)_3]$ supported on cross-linked styrene-divinylbenzene copolymers catalyze the hydrogenation of hex-1-ene, cyclohexene and styrene. Although the rates are lower than for the unsupported catalyst there is a greater selectivity for hex-1-ene over cyclohexene (ref. 408). Related complexes prepared in situ from $[RhCl(cyclooctene)_2]_2$ and PPh_2R (R = Me, $(CH_2)_nSiMe_3$ (n = 1-4)) have been studied as catalysts for hept-1-ene hydrogenation. The silyl-substituted ligands gave more active catalysts presumably because they provide a greater electron density on the metal (ref. 409).

In somewhat different systems [RhCl($(PPh_3)_3$] catalyzes the hydrogen-transfer reduction of azobenzene by isopropanol to give aniline (ref. 410) and in refluxing chloroform in the presence of HCl it catalyzes the conversion of 4,4-disubstituted-1,6-hepta-dienes to the corresponding methylenecyclopentanes (ref. 411). A careful study of its catalysis of the hydrosilylation of propene, hex-1-ene and hex-1-yne showed that catalysis was completely inhibited when all components were rigorously purified but activity could be restored on addition of traces of oxygen or tert-butylhydroperoxide. It was proposed that oxygen or hydroperoxide removed a phosphine ligand by oxidation to $OPPh_3$ thereby generating an open coordination position for olefin coordination (ref. 411). An example of what is termed a "delayed" hydrogen transfer from an alcohol has been found for the reaction of styryl bromide with norbornene mediated by [$RhCl(PPh_3)_3$] in the presence of benzyl alcohol and potassium acetate. The products are exo-styrylnorbornane, benzaldehyde and acetic acid (ref. 413). The direct amination of anthroquinone can be accomplished in the presence [$RhCl(PPh_3)_3$], [$RhCl(C_2H_4)_2]_2$ or [Rh(COD)Cl$]_2$ in refluxing diglyme however the process appears only marginally catalytic. The major product is monosubstituted in the 1-position but some 1,4- and 1,5-disubstitution also occurs (ref. 414).

The hydroformylation of formaldehyde to glycolaldehyde in N,N-dialkylformamide solvents is catalyzed by Rh(I) complexes, in particular [$Rh(CO)Cl(PPh_3)_2$]. In other solvents considerable quantities of methanol result. The mechanism of Scheme XXXIX is proposed and although the precise function of the amide in directing the system to glycolaldehyde formation is unknown it is thought that if its effect is limited to one step then the most likely point of intervention is in promoting the conversion of the hydroxymethyl species to the acyl intermediate (ref. 415). Under phase-transfer conditions (benzyltriethylammonium chloride, aqueous sodium hydroxide, dichloromethane) [$Rh(CO)_2Cl]_2$ catalyzes the conversion of allylic alcohols to ketones. For example hex-1-ene-3-ol is quantitatively converted to hexan-3-one and the mechanism of Scheme XL is proposed (ref. 416). The reduction of ketones by hydrogen transfer from isopropanol is catalyzed by [$Rh(COD)L_2]^+$ (L = tertiary phosphine, L_2 = diphos) and [$Ir(COD)L_2]^+$ (L_2 = bipyridyl, o-phenanthroline) in the presence of aqueous potassium hydroxide. The active species is generated by oxygenation to

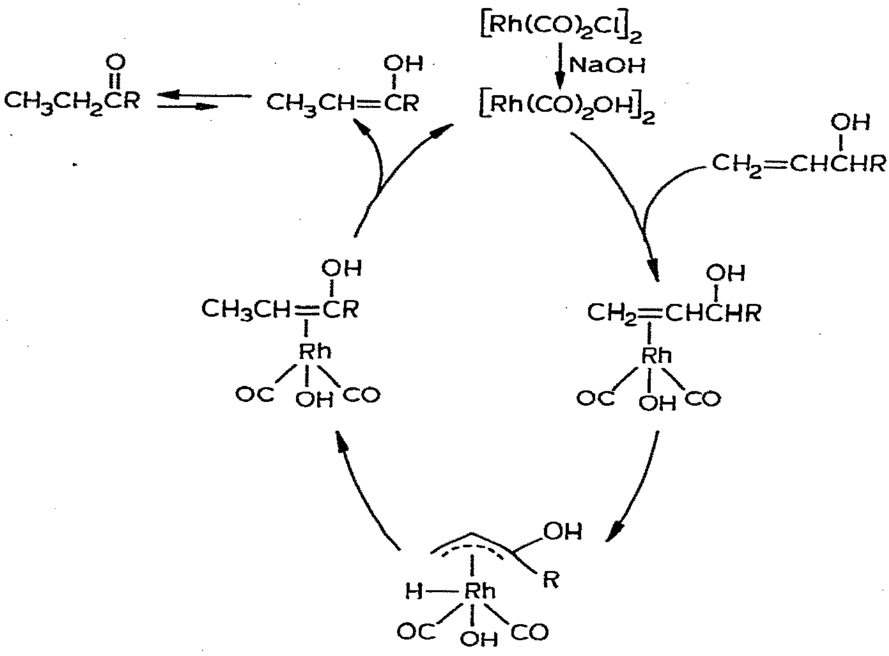


L = amide

Scheme XXXIX

remove the COD ligand with the catalysis then being achieved under argon at reflux. The mechanism of Scheme XLI is thought to be operative for the iridium systems (ref. 417). Up to 60% yields of indoles can be obtained from the condensation of phenylhydrazine with ketones catalyzed by $[Rh(COD)Cl]_2$ in ethanol (ref. 418). The complex $[Ir(COD)L_2]Cl$ (L_2 = 3,4,7,8-tetramethyl-*o*-phenanthroline) is a highly active catalyst for the hydrogen-transfer from isopropanol to α,β-unsaturated ketones such as benzylideneacetone and chalcone in weakly basic media. The olefinic bond hydrogenates first followed by reduction of the carbonyl group (ref. 419).

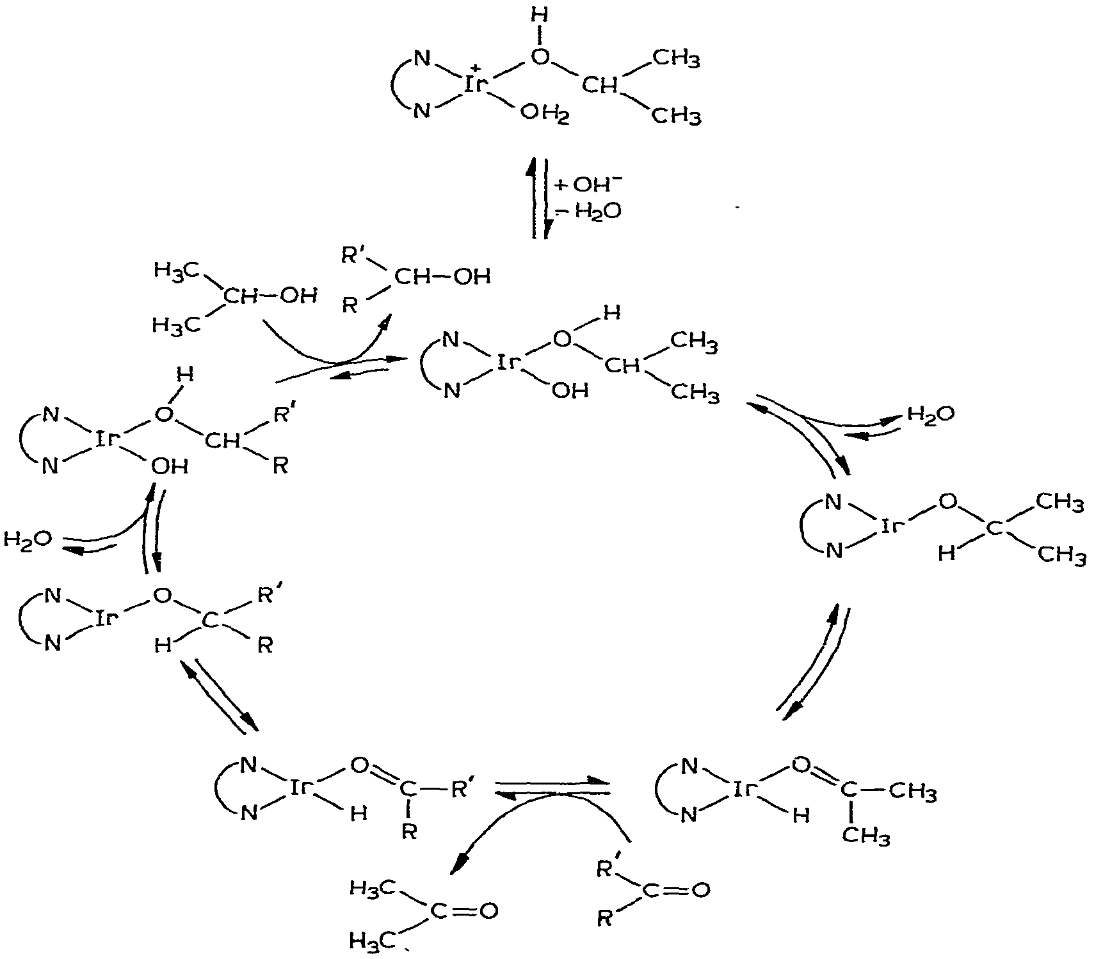
Several rhodium hydrides have been studied because of their involvement in catalytic processes. Triethylphosphine reacts with hydrated rhodium (III) chloride in THF to give an orange material which can be reduced by sodium amalgam in the presence of phosphine to yield $[RhH(PEt_3)_4]$. This loses one phosphine ligand in solution or on heating in vacuo in the solid to give the fluxional complex $[RhH(PEt_3)_3]$. The triisopropyl phosphine analog of this complex



Scheme XL

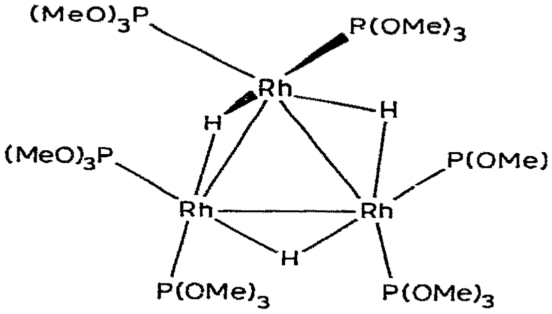
was prepared by the same route and shown to have a planar structure with the two "*trans*" phosphines bent towards the hydride position. From these results, the fluxional process in solution was proposed to involve a trigonal pyramidal intermediate with an apical hydride ligand (ref. 420). The structure of $[Rh_3(P(OMe)_3)_6(\mu\text{-}H)_3]$ [143] demonstrates each metal atom to have approximately square planar coordination. This coordinative unsaturation is presumably the reason for the high activity of the cluster as an olefin hydrogenation catalyst (ref. 421).

Polysiloxanes containing pendant $(CH_2)_nPPh_2$ (n = 2,3) groups have been reacted with $[Rh(cyclooctene)_2Cl]$ to generate supported catalysts analogous to $[RhCl(PPh_3)_3]$. With a 1:1 rhodium to phosphorus ratio quite high rates of hept-1-ene hydrogenation were obtained but these catalysts were rather prone to deactivation. Longer-lived species could be prepared with a higher density of phosphine groups but at the expense of activity (ref. 422). A variety of Rh(I) complexes both homogeneous and supported on silica catalyze the condensation of silanols with mono-, di- and trialkylsilanes to give siloxanes. The mechanism is thought to involve initial oxidative addition



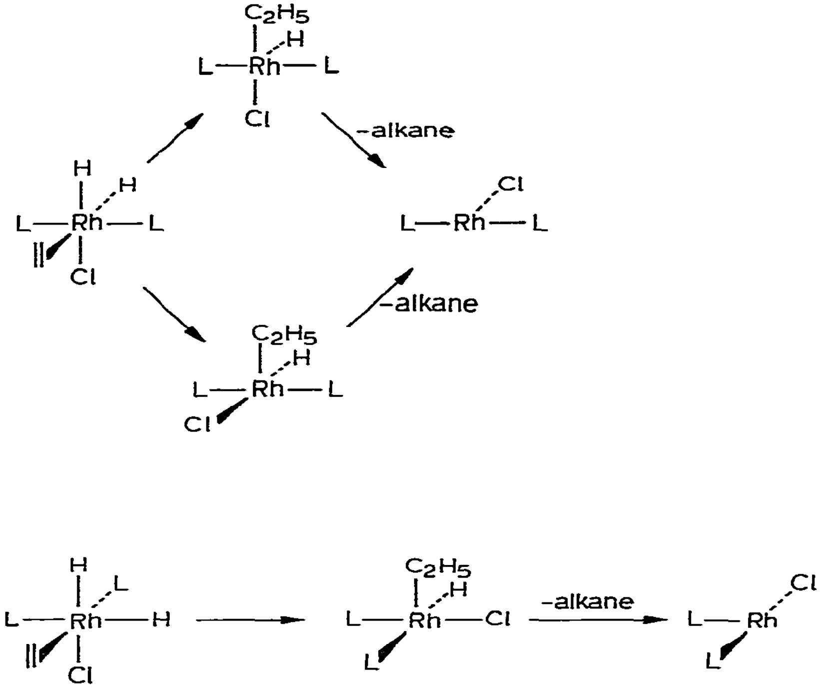
Scheme XLI

of the Si-H bond to rhodium followed by direct nucleophilic attack of the silanol oxygen on the rhodium-boundsilicon. The homogeneous systems were more active than the supported ones (ref. 423). A different approach to polymer-supported metal species has involved the linking of Rh(I) moieties with 1,12-bis(diphenylphosphino)dodecane to form coordination polymers (ref. 424). Finally, [Rh(cyclooctene)$_2$-Cl]$_2$ and [RhCl(PPh$_3$)$_3$] catalyze the oxidation of triphenylphosphine to the oxide by CO$_2$ in refluxing decalin. Although CO is reported to be the reduction product it is surprising that no rhodium carbonyl species could be detected by infrared spectroscopy (ref. 425).



[143]

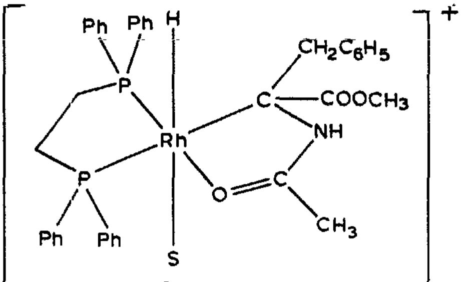
An extensive series of LCAO-MO-SCF calculations has been made to determine the relative stabilities of the most probable isomers (based on minimum total energy) of $[RhClL_2]$, $[RhH_2ClL_3]$, $[RhH_2ClL_2]$ $[RhH_2ClL_2(C_2H_4)]$, and $[RhH_2ClL_2(C_2H_5)]$ ($L = PH_3$) in an attempt to probe the mechanistic details of olefin hydrogenation catalyzed by $[RhCl(PPh_3)_3]$ and related complexes. Although subject to limitations because only idealized geometries were used and because the steric effects of normally-employed phosphine ligands may not have been adequately treated, the agreement of the calculated best geometries for $[RhH_2ClL_3]$ and $[RhH_2ClL_2]$ with their known structures suggested that the results for the others should be valid. It is assumed that hydride formation preceeds olefin complexation and the course of the reaction from this point on is proposed to be that of Scheme XLII. In this scheme, the upper path would be most likely for monodentate phosphine ligands while the lower would be appropriate where chelating phosphines (e.g. diphos, DIOP, etc.) are present. Although, as will be discussed below, α,β-unsaturated acids, their amides and related species when used as substrates do not appear to have this configuration for the hydrido-alkyl intermediate, these systems are complicated because the substrates are capable of coordinating to the metal through the carbonyl or amide groups as well. This is a factor which was not considered in these



Scheme XLII

calculations. Note also that two possible hydrido-alkyl intermediates in the upper path have comparable energies and thus no clear distinction can be made between them. In addition, it was concluded that the addition of the first hydrogen to the alkene is not a simple migration but appears to involve the motion of other ligands as well (ref. 426). In an ion-cyclotron resonance study, the reaction of Co^+ and $Co(CO)^+$ with butane gave mainly $Co(C_2H_4)^+$ and $Co(C_4H_{10})^+$ respectively while with isobutane the major product was $Co(C_3H_6)^+$ and $Co(C_4H_{10})^+$ respectively. Evidently the Co^+ attacks the central C-C bond of butane followed by β-hydride abstraction and elimination of hydrogen. $Co(CO)^+$ on the other hand merely associates with the alkane (ref. 427).

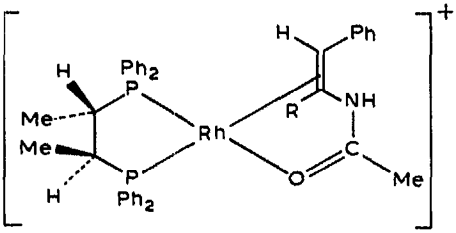
A substantial amount of work has been done to study the mechanism of asymmetric hydrogenation of prochiral olefins using chiral rhodium catalysts and to develop new catalysts of greater selectivity. In a particularly significant study, the hydrido alkyl intermediate in the hydrogenation of methyl-(Z)-α-acetamidocinnamate (MAC) catalyzed by [Rh(diphos)]$^+$ (prepared by addition of H_2 to [Rh(MAC)-(diphos)]$^+$ at -78°C) was characterized by low temperature ^{31}P and ^{13}C NMR studies and shown to have the structure [144]. On warming



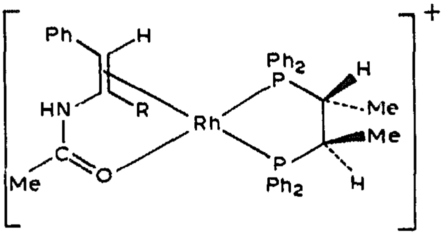
[144]

[S = MeOH]

[144] above -65°C, hydrogen transfer occurs to give N-acetylphenylalanine methyl ester and [Rh(diphos)]$^+$ at a rate comparable to that extrapolated for this step from an earlier kinetic study of the overall catalytic hydrogenation process (ref. 428). The structure of the ethyl-(Z)-α-acetamidocinnamate (EAC) complex of [Rh(S,S-Chiraphos)]$^+$ (S,S-Chiraphos = (2S,3S)-bis(diphenylphosphino)butane) has been shown to be [145] by x-ray crystallography and it is the only species in solution detectable by ^{31}P NMR. Hydrogenation of [145] would be expected to give the ethyl ester of N-acetyl-(S)-phenylalanine however the experiment produced the R isomer in >95% yield leading to the suggestion that in solution there exists a small amount (<5%) of the diastereomeric EAC complex [146] which

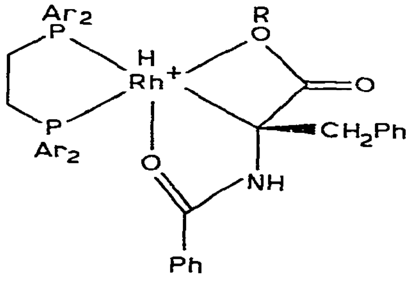


[145]



[146]

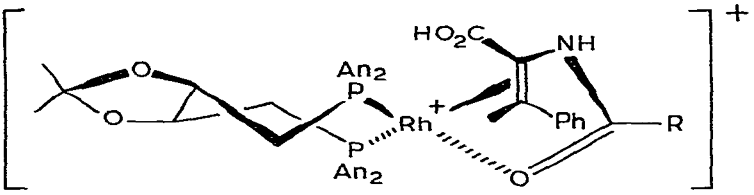
is much more reactive towards hydrogen than is the major diastereomer which was isolated. This implies that the enantioselectivity in this reaction is dominated by the large difference in reactivity towards H_2 of the two diastereomeric EAC adducts rather than by a preferred mode of coordination of substrate. It also explains the inverse dependence of optical yield on hydrogen pressure where at elevated pressure the initial binding of the prochiral olefin becomes the rate determining step (ref. 429). The presence of diastereomeric adducts of N-acyldehydroamino acids and their esters with $[RhL_2]^+$ (L_2 = SS-Chiraphos, R,R-(($\underline{o}$-MeOC_6H_4)PhPCH_2)$_2$(DIPAMP), trans-1,2-bis(diphenylphosphinomethyl)cyclobutane) has also been demonstrated in significant papers by other workers. Variation in the acyl function had more effect on the relative amounts of the two diastereomers for esters than for the parent acids while changes in the ester function affected both the extent of complexation of the prochiral olefin as well as the ratio of diastereomeric adducts generated however there appeared to be no good correlation between the observed diastereomer ratio and the degree of enantioselectivity on subsequent hydrogenation. This presumably reflects the fact that there is no necessary correlation between the relative amounts of the two diastereomeric olefin adducts and their relative reactivities towards hydrogen. With (Z)-N-benzoylamidocinnamic acid or its methyl ester and $[Rh(DIPAMP)]^+$, the kinetic stereoselectivity of the binding of the enamide was low which agrees with the results described earlier concerning the source of the enantioselectivity in these systems not being the initial mode of olefin complexation. In fact with the acid as substrate, hydrogenation at 195 K followed by warming slowly to 220 K gave [147] which again



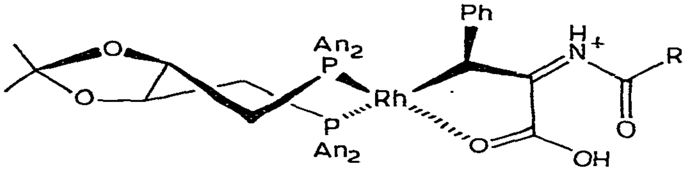
[147]

appeared to be generated from the minor diastereomer formed on initial complexation of the substrate to the metal (refs. 430-432). In an extension of this work comparing the complexation and subsequent hydrogenation of α,β-unsaturated carboxylic acids using $[Rh(DIOP)]^+$

with that for their corresponding esters and amides showed preferential binding of the α-carboxylate group particularly when deprotonated This was found to be necessary for effective asymmetric hydrogenation although again no correlation was found between the percent enantiomeric excess on reduction and the ratio of diastereomeric substrate complexes initially formed. Also in comparison with the corresponding DIPAMP systems it appeared that the DIPAMP complex with its five-membered chelate ring is more effective for the reduction of enamides and other potentially terdentate substrates while the DIOP complex with a seven-membered chelate ring is better for potentially bidentate substrates (ref. 433). The rhodium complex with the o-anisyl analog of the DIOP ligand [Rh(R-PAMPOP)]$^+$ forms the expected adduct [148] with N-acetylamidocinnamic acid at low temperature but on warming an equilibrium mixture of this and [149] is noted.



[148]

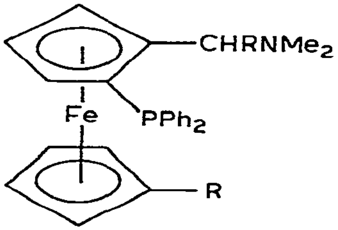


[149] R = Me, An = o-anisyl

Both disappear at the same rate on hydrogenation implying that the rate of equilibration is faster than the rate of hydrogenation. Also unlike the DIOP catalyst system, the PAMPOP complex gives S rather than R products from (Z)-enamides and higher optical yields with esters than with the corresponding acids (ref. 434).

The majority of the remaining reports in the area of asymmetric hydrogenation are primarily concerned with the search for complexes of greater catalytic activity and enantioselectivity. Generally, these are prepared *in situ* from the (usually) bidentate phosphine ligand and [Rh(diene)Cl]$_2$ or [Rh(diene)(S)$_2$]X(diene = NBD, COD; S = MeOH, EtOH; X = BF$_4^-$, PF$_6^-$) in an alcoholic solvent followed by hydrogenation to remove the diene. The commonly used substrates are the α,β-unsaturated acids, their esters and the enamides mentioned above. Two ligands which give quite selective catalysts are

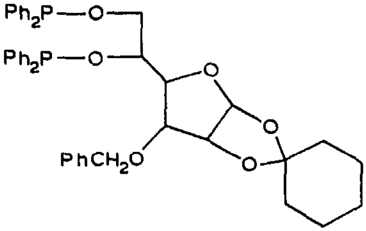
6S-cyano-5R-diphenylphosphino-3R,4S-O-isopropylidene-2-oxabicyclo-[3.2.0]heptane and the R and S forms of 2,2'-bis(diphenylphosphinamino)-1,1'-binapthyl. The former where used in a 2:1 (L:Rh) ratio gave a 92% enantiomeric excess of N-acetyl-(S)-phenylalanine from (Z)-α-acetamidocinnamic acid as compared with only 75% optical yield of the R isomer when DIOP was the ligand (ref. 436). The latter generally gave 85-95% optical yields with the product stereochemistry (R or S) being the same as that of the ligand and unsaturated acids being better substrates than their esters (ref. 437). Two other groups have made use of diphenylphosphinamino groups attached to a cyclohexane or N-alkane backbone for the construction of chiral ligands. Typical ligands are (1R,2R)-bis(diphenylphosphinamino)-cyclohexane, its N-methyl analog and the (1S,2S) isomer. The optical yields achieved were usually in the range 43-93% depending on the substrate and whether a cationic or a neutral catalyst species were used. For acid substrates, the optical yield could be increased by addition of triethylamine which presumably deprotonates the carboxyl group thereby enabling the substrate to bind more strongly. Since the stereoselectivity of the catalyst derived from (2S,3S)-bis(diphenylphosphinamino)butane was about the same as that from the (1S,2S) cyclohexane analog it was concluded that the stereoselectivity arose from the manner in which the most favorable ligand conformation affected the mode of attachment of the substrate (refs. 438-441). Other moderately effective catalysts can be prepared from [150] (R = Me, Pr^i, Ph; R^1 = PPh_2. R = Me; R^1 = H (PPFA)). In all instances, an acylamino or carboxyl group on the substrate was necessary for good optical yields (refs. 442,443). The structure of the racemic catalyst precursor $[Rh(NBD)(PPFA)]PF_6$ has been determined and using models based on these results it was concluded that because of steric constraints, the olefinic substrate could bind in only one fashion. Since the experimentally observed



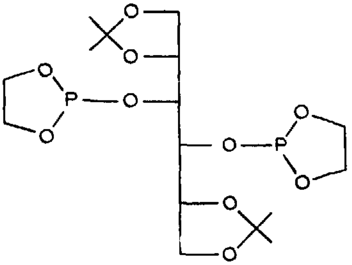
[150]

enantiomer of the product was that expected on hydrogenation of the proposed substrate adduct it was assumed that this was the origin of the stereoselectivity although no direct determination of the stereochemistry of this adduct was made (ref. 443).

A series of interesting but not particularly effective ligands are a variety of phosphines and phosphites derived from α-γ-glucofuranose, mannitol and xylose. Two of the better ones were [151] and [152] but no more than about 50% optical yield could be realized (refs. 444,445). Also examined by one of these groups were catalysts prepared from $[Rh(cyclooctene)Cl]_2$ and the optically active amidines (R) or (S)-PhC(=NR)NHCHMe (R = $PhCH_2$, Ph, Pr^i) or their lithium salts. These were fairly active for the hydrogenation of the usual substrates but gave very low optical yields (ref. 446). New analogs of the DIOP ligand in which the aromatic groups on phosphorus are p-tolyl or o-xylyl have been prepared and purified as the $[CuCl(L_2)]_2$ derivatives. Their rhodium complexes gave 75-85% optical yields from unsaturated amino acids (ref. 447). The same workers have also compared the effectiveness of catalysts derived from ligands where the chirality resides in the carbon backbone (e.g. (R,R)-CHIRAPHOS) with those where it resides at phosphorus (e.g. (R)- or (S)-PMePh-(menthyl)). With (Z)-geranic acid, the first gave only 45% optical yield of R(+)-citronellic acid however with the second ((S) isomer), a 70% optical yield of the same product could be obtained from (E)-geranic acid (refs. 448,449). A catalyst prepared from (R)-1-cyclohexyl-1,2-bis(diphenylphosphino)ethane has been used to

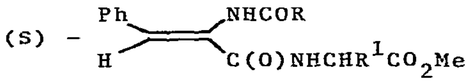


[151]



[152]

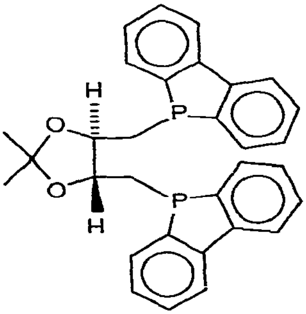
hydrogenate a series of (Z)-α-acetamidoacrylic acids with optical yields up to 95%. Reasonable optical yields could also be obtained in the hydrogenation of the tetrasubstituted olefin β,β'-dimethyl-α-benzamidoacrylic acid. The results indicated that an increased stereorigidity of the catalyst was important in obtaining high optical yields (ref.450). Another novel catalyst system using chiral ligands derived from α-amino acids (e.g. L-(−)-N,N-bis(diphenylphosphinomethyl)alanine) has been studied but proved only moderately successful for asymmetric hydrogenation (ref. 451). Cationic catalysts of DIPAMP and BPPM (BPPM = (2S,4S-N-tert-butoxycarbonyl)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine have been studied for the hydrogenation of a variety of substrates. With (Z)-α-acylaminoacrylic acids the stereoselectivity was found to decrease with increasing hydrogen pressure. The effect was somewhat less for those systems giving S products than for those giving R and in some instances where a 95% enantiomeric excess of the R product could be realized at 1 atm, increasing the pressure to 20 atm gave a 22% enantiomeric excess of the S product. The results were interpreted to indicate that at low pressures, the rate-determining-step is oxidative addition of hydrogen to the catalyst-substrate complex while at higher pressures it is the transfer of the first hydrogen to the olefin (ref. 452). With n-propylpyruvate and ketopentoyl lactone the keto group could be reduced to hydroxyl and the presence of a coordinating solvent was necessary for good optical yields (ref. 453). The same catalysts also proved effective for the asymmetric hydrogenation of the dehydro dipeptides [153] ($R = R^1 = Ph, Me$. $R = Me, R^1 = Ph$). With BPPM



[153]

as the ligand a 95% enantiomeric excess of the R,S dipeptide could be obtained and the presence of the chiral center in the original substrate appeared not to affect the generation of the new chiral center (ref. 454a). Approximately as effective as BPPM were the ligands N-(N'-alkylcarbamoyl)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine (ref. 454b). Several other reports of related systems giving similar results have also appeared (refs. 455–457). In an attempt to determine how essential the α-acylamino group is to asymmetric induction in the hydrogenation of α-acylamino-acrylic acids and related compounds the hydrogenation of 1,1,1-trifluoro-2-acetyloxy-2-propene with a cationic rhodium complex of (R,R)-DIPAMP was investigated. Optical yields of 70–77% were obtained indicating that coordination of a gem functionality to the metal is not essential. Evidently an electronegative substituent which can enhance the binding of the olefin moiety to the metal can also lead to effective asymmetric induction (ref. 458).

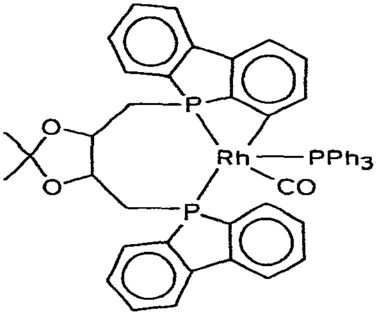
Rhodium–DIOP complexes in the presence of triethylamine are effective for the asymmetric hydrogenation of aryl ketones. It is suggested that the rate-determining step is a nucleophilic attack of an Rh–H moiety on the carbonyl group of the ketone with the selectivity arising from interactions between the aryl group and the phenyl groups on the ligand (ref. 459). Up to 50% optical yields in the hydrosilylation of aryl ketones by related catalyst systems have also been reported (refs. 460,461). A polymer-anchored DIOP-type ligand has been used to form a rhodium catalyst for the conversion of N-allylamides to N-propenylamides. Using $[RhH(CO)(PPh_3)_3]$ in the presence of DIOP or DIPHOL ([154]), N-vinylphthalimide could be hydroformylated to the corresponding α-amido aldehyde in 20–40% optical yield. The chemistry of rhodium complexes of DIPHOL was also briefly studied. Reaction of $[Rh(CO)_2Cl]_2$ with the ligand gave [Rh(CO)Cl(DIPHOL)] which on treatment with butyllithium at −78°C in the presence of PPh_3 gave a species thought to be the o-metallated complex [155] (ref. 462). The $[RhH(CO)(PPh_3)_2]$-DIOP catalyst has also been used to hydroformylate butadiene, isoprene and 2,3-dimethyl-1,3-butadiene. From isoprene a 35% optical yield of (S)-3-methylpentanal was obtained and the enantioselectivity



[154]

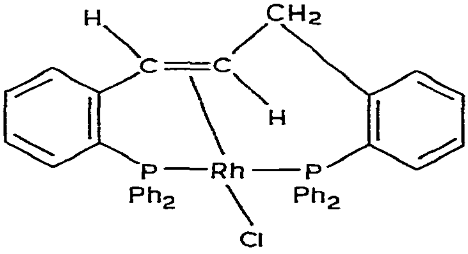
is considered to occur in the hydrogenation of the residual double bond rather than in the hydroformylation step (ref. 463).

On refluxing with $[Rh(COD)Cl]_2$ in toluene, the ligand 1,3-bis(*o*-diphenylphosphinophenyl)propane undergoes dehydrogenation to give the complex [156]. An iridium analog can be prepared similarly.

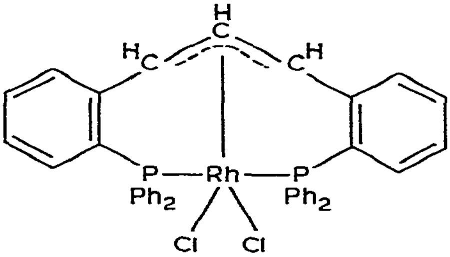


[155]

The new ligand can be isolated by destruction of [156] with cyanide and it reacts with hydrated rhodium (III) chloride in 2-methoxyethanol to give the allylic complex [157] (ref. 464). The binding of $[Rh(COD)Cl]_2$ and $[Rh(C_2H_4)_2Cl]_2$ to several phosphinated polystyrenes has been studied by ^{31}P NMR. Polymer-bound *trans*-$[Rh(C_2H_4)_2Cl]$ and *cis*-[Rh(COD)Cl] moieties were observed respectively (ref. 466). The complexes $[Rh(diene)Cl]_2$ and [Rh(diene)X] (diene = penta-1,4-diene, hexa-1,4-diene, cyclohexa-1,4-diene and their methyl-substituted derivatives; X = acac, cp, $C_5H_4CO_2Me$) undergo thermal isomerization. With acylic dienes mixtures of complexes containing *cis* and *trans* isomers of the corresponding 1,3-dienes result with the *cis*-diene complexes isomerizing to the *trans* isomers at a slower rate. The



[156]



[157]

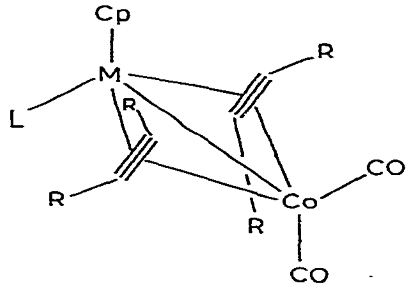
cyclohexa-1,4-diene complexes yield cyclohexa-1,3-diene species. From the kinetics of the reactions as well as the product distributions it appears that the isomerization occurs via the usual allyl-hydride process (ref. 466).

A theoretical analysis of the conversion of bis(olefin) complexes to metallacyclopentanes has appeared. The predicted stereochemical course of the reaction for unsymmetrically substituted olefins is in accord with experiment in a number of systems including the reaction of $[(\eta^5-C_9H_7)Rh(CH_2{=}CHCN)_2]$ with 3,3-dimethylbut-1-yne, the reaction of $[cpRh(\eta^4-C_5H_8)]$ with hexafluoroacetone and the Rh(I)-promoted coupling of fluoroolefins (ref. 467). The infrared and Raman spectra of $[Rh(diene)Cl]_2$ (diene = COD, NBD) have been studied in detail and many band assignments made. In both instances the data indicate that the π-component of the metal-olefin bond is stronger than in the related complexes $[M(diene)Cl_2]$ (M = Pd, Pt) (refs. 468, 469). Photoelectron spectra of the complexes $[M(diketone)L_2]$ (diketone = acac, dipivaloylmethanato, trifluoroacetylacetonato, hexafluoroacetylacetonato; M = Rh, Ir; L = CO, C_2H_4, C_3H_6) have been measured and interpreted in relation to previously reported MO calculations. The observed shifts in the olefin orbital energies over the series are in agreement with the Dewar-Chatt-Duncanson bonding model and indicate an important contribution from the π-backbonding component however for iridium, the σ-component is more important than it is for rhodium (ref. 470).

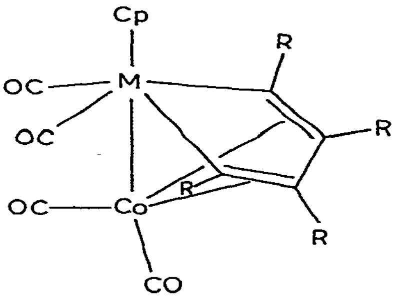
A classification of the types of organometallic reactions possibly involved in ethylene dimerization processes has been generated by computer. A comparison of possible paths for the rhodium trichloride-mediated system with existing experimental data indicated three routes to be consistent of which the authors prefer the one involving a metallacyclopentane (ref. 471).

Metal alkyne compounds

Dicobalt octacarbonyl reacts with $[cpMCl(CF_3C_2CF_3)_2]$ (M = Mo, W) at room temperature to give the acetylene-bridged bimetallic complexes [158] (R = CF_3) which on warming react further to give the metallacycles [159] (R = CF_3). The structures of both have been determined (ref. 472). Cocondensation of cobalt vapor with cyclopentadiene and hexafluorobut-2-yne (HFB) yielded a plethora of products of which ten could be characterized by NMR and mass spectral data following separation by repeated chromatography. Several of these and proposed

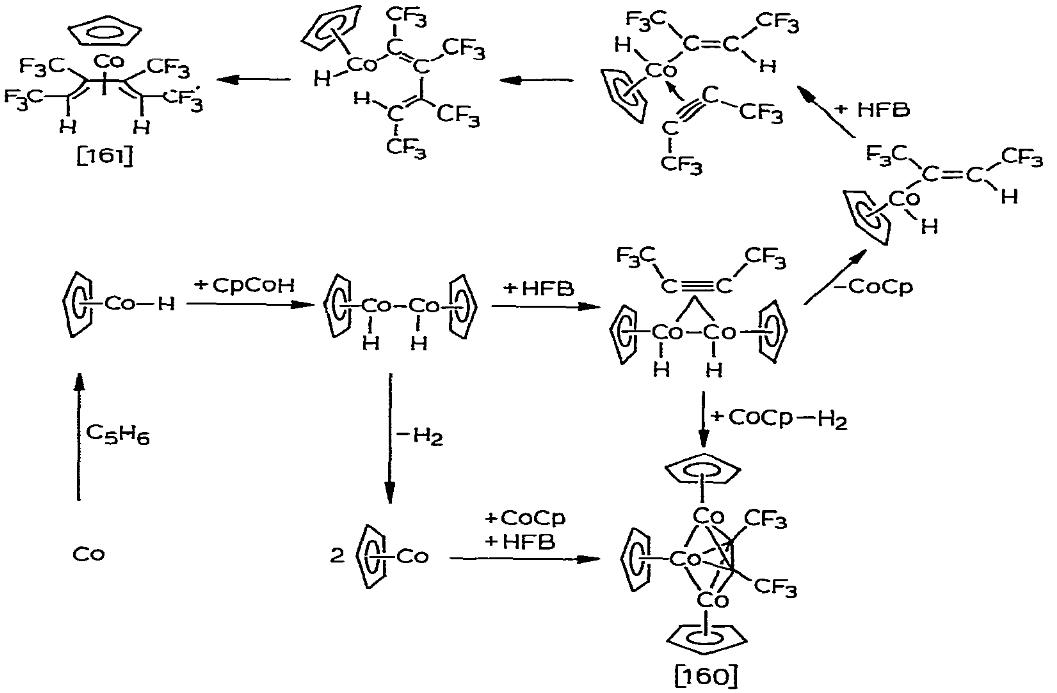


[158]

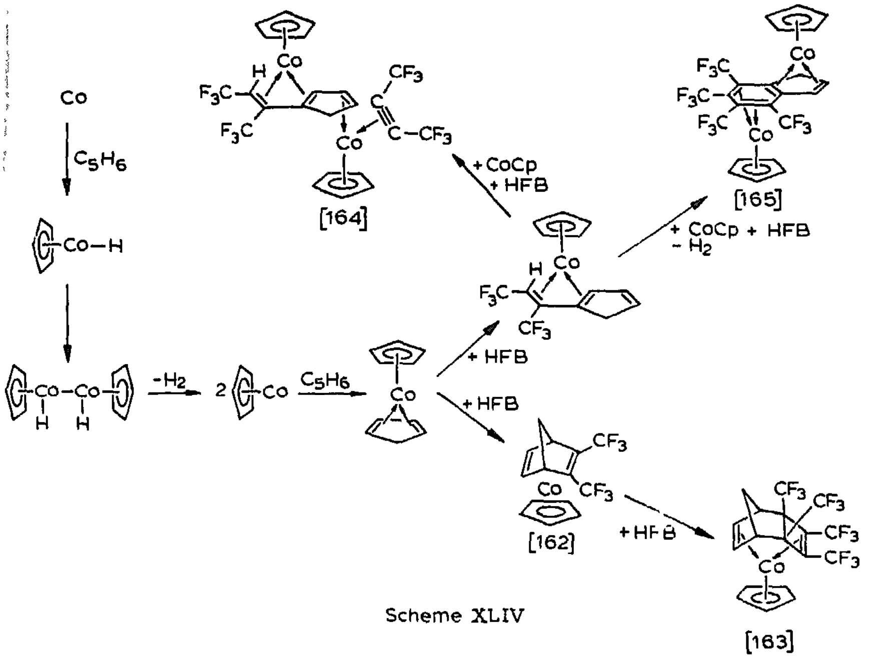


[159]

mechanisms for their formation are depicted in Schemes XLIII and XLIV. Other products from this reaction were [166] - [168]. Similar products although fewer in number were obtained using trifluoropropyne and diphenylacetylene (ref. 473). In refluxing hexane, $[Co_2(CO)_8]$ and $[cp_2Ni_2(Ph_2C_2)]$ or $[Co_2(CO)_6(Ph_2C_2)]$ and this complex, $[cp_2Ni_2(CO)_2]$, or $[cp_2Ni_2]$ or $[cpNiCo_3(CO)_9]$ and diphenylacetylene reacted to form $[cpNi(\mu\text{-}Ph_2C_2)Co(CO)_3]$ as the major product. A related complex was obtained in low yield from $[Co_2(CO)_6(PhC_2Me)]$ and $[cp_2Ni]$ (ref. 474).

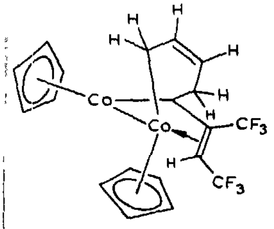


Scheme XLIII

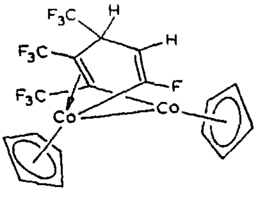


Scheme XLIV

The use of $[cpCo(CO)_2]$ as a catalyst for the cyclocodimerization of acetylenes with α,ω-diynes in order to prepare intermediates for the synthesis of steroids, in particular estrone, has been the subject of an elaborate study. Initial experiments probed the reactions of simple acetylenes and diynes with the complex. Slow addition of



[166]



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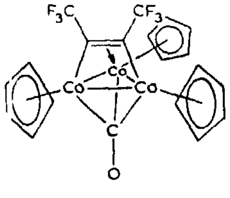
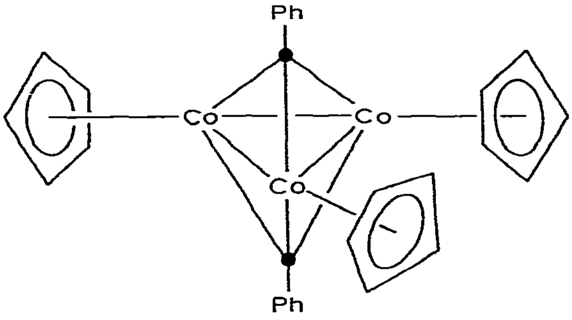


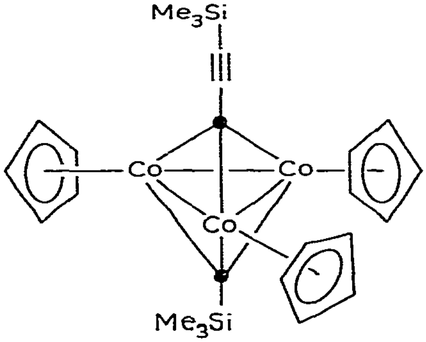
[168]

a 3:1 ratio of $[cpCo(CO)_2]$ and diphenylacetylene in decalin to refluxing decalin gave [169] as the major product rather than the cyclopentadienone complex $[CpCo(Ph_4C_4CO)]$ which is normally obtained when these compounds are refluxed together in more concentrated solution.

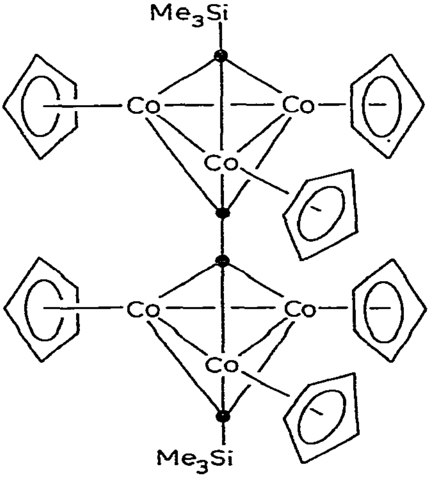


[169]

Analogous species were obtained from dec-5-yne, dimethylacetylenedicarboxylate and trimethylsilylacetylene. From reaction with 1,4-bis(trimethylsilyl)buta-1,3-diyne the major products were [170] and [171] while traces of four other species also containing one or two

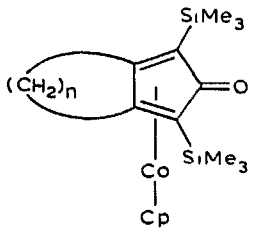


[170]



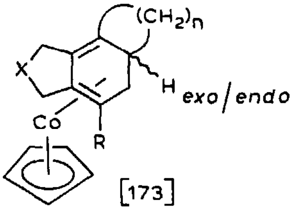
[171]

alkylidyne tricobalt moieties were isolated (ref. 475). On the other hand, photolysis of a mixture of [cpCo(CO)$_2$] and trimethylsilylacetylene at -20^{o}C in THF gave two isomeric cyclopentadienone complexes [cpCo(C$_4$H$_2$(SiMe$_3$)$_2$CO)]. The same reaction with the diynes Me$_3$SiC≡C-(CH$_2$)$_n$-C≡CSiMe$_3$ (n = 2-4) gave the dienone complex [172] which could be oxidized with ceric ammonium sulfate to give the free dienone for further synthetic reactions (ref. 476). This procedure was extended to provide a means of preparing fused tricyclic systems related to steroids. Thus refluxing R-C≡C-X-C≡C-(CH$_2$)$_n$-CH=CH$_2$ (R = H, SiMe$_3$; X = (CH$_2$)$_2$, O; n = 3,4) in isooctane in the presence of [cpCo(CO)$_2$] gave a mixture of the exo and endo isomers of [173]

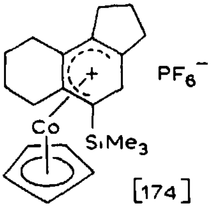


[172]

which for X = $(CH)_2$ and n = 3 reacted with trityl cation to give [174] (ref. 477). Whilst the model study for the $[cpCo(CO)_2]$-catalyzed cyclocodimerization reaction, using $Me_3SiC≡C-OMe$ and hexa-1,5-diyne, gave only [175], with other acetylenes, in particular

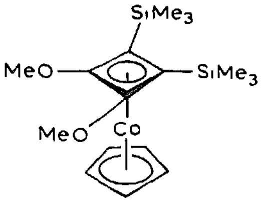


[173]



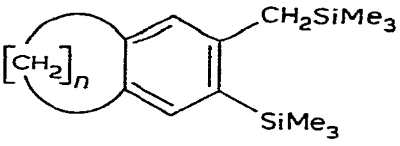
[174]

bis(trimethylsilyl)acetylene (BTMSA) and 1,3-bis(trimethylsilyl)propyne (BTMSP) the desired cyclocodimers were obtained in good yield. Thus slow addition of the diynes $HC≡C(CH_2)_nC≡CH$ (n = 2-4) to



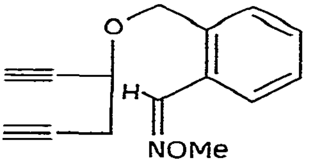
[175]

refluxing BTMSP containing a catalytic amount of $[cpCo(CO)_2]$ gave [176] while in refluxing xylene hepta-1,6-diyne cyclocodimerized with $Me_3SiC≡C-H$ or $Me_3SiC≡CCH_2C(COMe)_2CH_2CO_2Et$ to give analogous bicyclic products (ref. 478). Two of the more interesting syntheses from BTMSA are the catalytic codimerizations with [177] and [178] which yield [179] and [180] respectively. The last on heating undergoes ring-closure to give a fused tetracyclic compound (refs. 479, 480). Presumably, cobalt-alkyne complexes are initially formed in all these reactions.

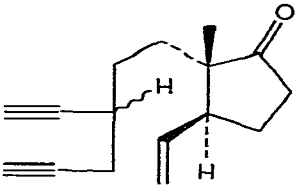


[176]

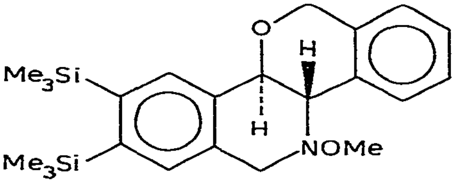
Calculations of the activation energies for the previously proposed paths for the photolytic isomerization depicted in Scheme XLV suggest



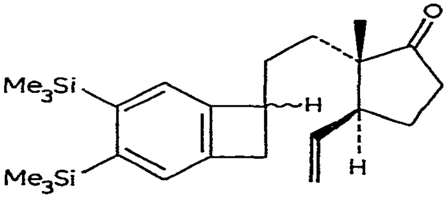
[177]



[178]



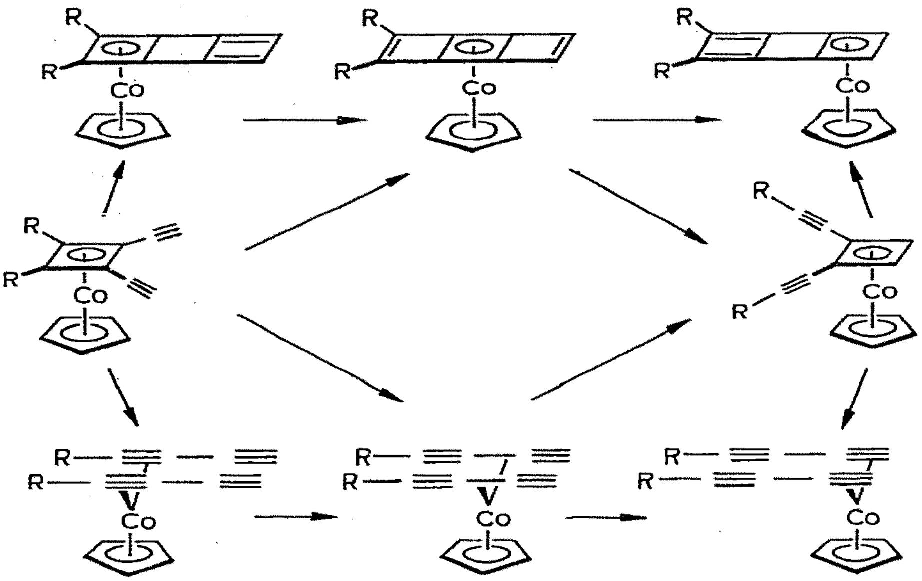
[179]



[180]

that both are improbable. However no more plausible mechamisms were suggested (ref. 481).

A number of isolated cobalt-alkyne complexes have been found useful in organic synthesis. For example, the stabilized propargyl cations $[Co_2(CO)_6(HC{\equiv}CCRR^1)]BF_4$ ($R = R^1 = H$, Me; $R = H, R^1 = Ph$) add readily to ketones, enolacetates, trimethylsilyl enol ethers or allyl silanes with considerable regioselectivity in some instances. Removal of the $Co_2(CO)_6$ moiety by oxidation with $Fe(NO_3)_3$ provides good to excellent yields of the monoalkylated products. In the case of the allyl silane it provides a route to 1,5-eneynes with no elimination or



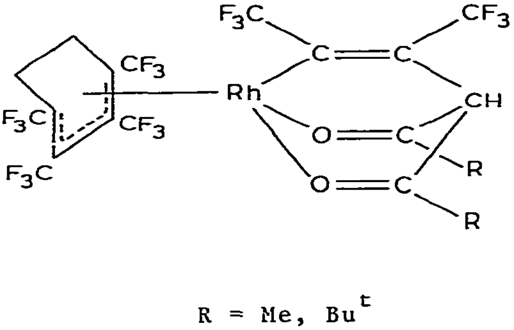
R = SiMe$_3$

Scheme XLV

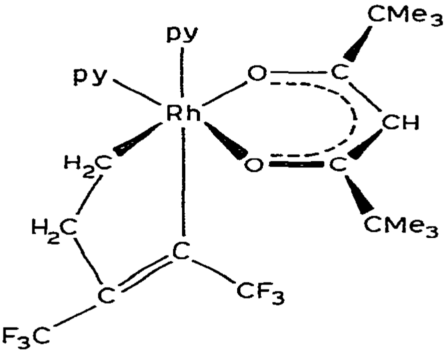
allenic side products (refs. 482, 483). Also by this procedure, oct-2-yn-1-ol and isopropenyl acetate were conveniently converted to undec-5-yn-2-one, an intermediate in the synthesis of dihydrojasmone (ref. 484). The complexes [Co$_2$(CO)$_6$(ac)] (ac = methyl non-8-ynoate, (Z)-methyl non-5-en-8-ynoate) when reacted with ethylene and 8-chlorooct-4-en-1-yne at 160°C provide good yields of cyclopentenone derivatives useful as prostaglandin synthons (ref. 485). The reaction of boron hydrides with acetylenes can be catalyzed by cobalt-acetylene complexes. For example in the presence of [Co$_2$(CO)$_6$-(Me$_2$C$_2$)] pentaborane(9) reacts with but-2-yne to give a 22% yield of 2-(cis-2-butenyl)pentaborane(9) (ref. 486).

The EPR spectra of the electrolytically generated radical cations [Co$_2$(CO)$_6$(RC$_2$R')]$^{\cdot+}$ (R = R^1 = CF$_3$, H, Ph, Bu^t; R = SiMe$_3$; R^1 = Ph, Me, CF$_3$) have been measured. In solution there is equal coupling to both cobalt atoms while in frozen solution a completely anisotropic g tensor is found. Analysis of the spectra indicated that the unpaired electron is in a b$_2$ orbital which is largely Co3d$_z$2 in character with the major axis of the cobalt 3d contribution directed about 20° to the Co-Co axis. To the extent that this orbital is the antibonding counterpart of the Co-Co bonding orbital, the Co-Co bond can be described as bent (ref. 487).

At -78°C, one ethylene molecule in [Rh(C_2H_4)$_2$(diketone)](diketone = acac, dipivaloylmethane (dpm) can be replaced by HFB or by other olefins (e.g. cyclooctene, cycloheptene, propene, but-2-ene when diketone = dpm). In [Rh(acac)(HFB)(C_2H_4)] the ethylene ligand undergoes hindered rotation but with a lower activation energy than for the parent bis(ethylene) complex due to the high π-acidity of the HFB ligand. Reaction of [Rh(diketone)(HFB)(C_2H_4)] with HFB at room temperature gives [181] while with pyridine the dpm derivative yields the metallacycle [182] and with tetramethylallene [183] results.



[181]



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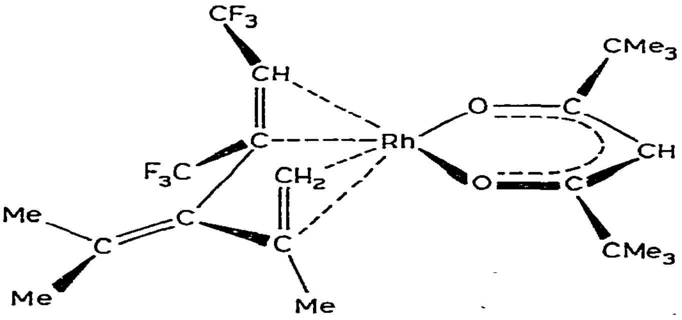
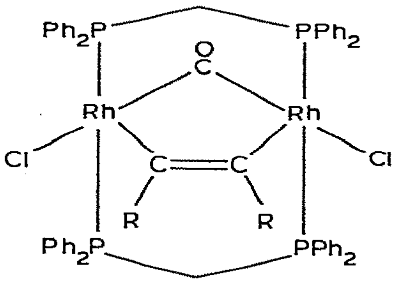


[183]

It is suggested that [182] is a probable intermediate in the formation of cyclohexa-1,3-dienes from one olefin and two acetylene molecules in related systems (refs. 488,489). The acetylenes HFB or dimethylacetylene dicarboxylate (DMAD) react readily with $[Rh(CO)Cl(DPM)]_2$ or $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ to give the vinylidene-bridged complexes [184]. The structure of the complex with R = CO_2Me has been determined and because of the large Rh–C–Rh angle at the bridging carbonyl (116°) and the low C–O stretching frequency (1905 cm^{-1}),



(R = CH_3, CO_2Me)

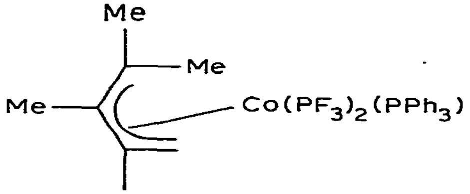
[184]

this ligand is considered to be formally CO^{2-} (ref. 490). Acetylene can be hydrosilylated by $HSiCl_3$, $HSi(OEt)_3$ and $HSiMeCl_2$ to give the corresponding vinyl silanes in 40-80% yield in the presence of $[RhCl(PPh_3)_3]$ or $[RhH(PPh_3)_4]$ as catalysts. However up to 25% of the vinyl silane initially produced is also hydrosilylated (ref. 491).

At room temperature $[Ir(CO)_2(\mu\text{-}SBu^t)]_2$ reacts with HFB or DMAD to give $[Ir_3(CO)_6(\mu\text{-}RC{=}CR)(\mu\text{-}SBu^t)_3]$ (R = CF_3, CO_2Me) while $[Ir(CO)(P(OMe)_3)(\mu\text{-}SBu^t)]_2$ gives only the dimer $[Ir(CO)(P(OMe)_3)(\mu\text{-}SBu^t)_2(\mu\text{-}RC{=}CR)Ir(CO)(P(OMe)_3)]$ (ref. 492).

Metal allyl compounds

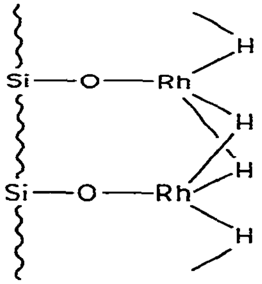
Cobalt allyl complexes have been implicated as intermediates in the polymerization of trans-trans-hexa-2,4-diene catalyzed by diethylaluminum chloride-reduced $[Co(acac)_2]$ but were not characterized (ref. 493). Treatment of $[CoH(PPh_3)_2(\eta^4\text{-}2,3\text{-dimethylbuta-1,3-diene})]$ with PF_3 causes insertion into the Co–H bond to give [185] which reacts further with PF_3 to replace the PPh_3 ligand. This last species can also be got directly from $[CoH(PF_3)_4]$ and trans-2,3-dimethylbuta-1,3-diene suggesting that in the presence of bulky ligands, it may be possible to stabilize diene-hydride complexes (ref. 494). Allyl chloride reacts with $[Rh_6(CO)_{15}]^{2-}$ at room temperature giving $[(\eta^3\text{-}C_3H_5)Rh_6(CO)_{14}]^-$ whose structure was determined as the



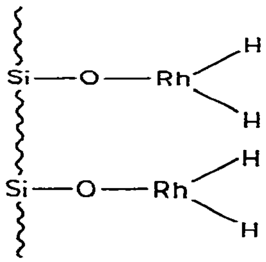
[185]

tetraphenylphosphonium salt. The structure can be thought of as derived from that of [$Rh_6(CO)_{16}$] with the two terminal carbonyl groups on one metal being replaced by the allyl group (ref. 495).

Reaction of [(η^3-C_3H_5)$_3$Rh] with silica yields propene, propane and [(η^3-C_3H_5)$_2$Rh] moieties bound to the surface by Si-O-Rh linkages. Hydrogenation of the modified silica yields propane and supported hydrido rhodium species thought to be [186] and [187]. These are



[186]

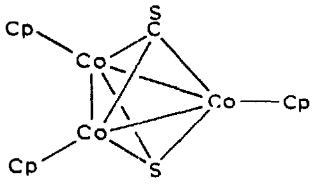


[187]

catalysts for olefin hydrogenation under mild conditions and show a smaller difference in rate between hindered and non-hindered olefins than does [$RhCl(PPh_3)_3$] (ref. 496).

Metal carbocyclic compounds

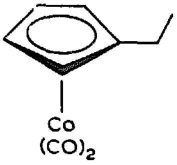
Cobalt carbonate reacts with disodium 2-hydroxy-3,4,5-tris(carbomethoxy)cyclopentadiene-1,4-diolate to yield [Co(η^4-$C_4(OH)(CO_2Me)_3$-CO)]·$3H_2O$ (ref. 497). In refluxing carbon disulfide, [cpCo(CO)(PR_3)] (R = Me, Ph) yields several products of which [cpCo(PR_3)(CS)], [cpCo(PR_3)(η^2-CS_2)] and [cpCo(PR_3)(CS_3)] were characterized. At higher temperatures an appreciable quantity of [$cp_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$], [188], was also obtained. This last complex also resulted from



[188]

thermolysis of [cpCo(PPh$_3$)(η^2-CS$_2$)] in refluxing toluene (ref. 498). Other workers have also obtained this trinuclear species from an attempt to prepare mixed-metal clusters from [cpCo(PMe$_3$)(η^2-CS$_2$)] and [cpCo(PMe$_3$)(μ-CO)$_2$Mn(CO)(η^5-C$_5$H$_4$Me)]. A structural study of [188] showed the μ_3-thiocarbonyl ligand to have a C-S bond length of 1.7 Å implying it to be a single bond. The sulfur atom of the CS ligand is nucleophilic and can be alkylated with alkyl iodides to give [cp$_3$Co$_3$(μ_3-CSR)(μ_3-S)]I (R = Me, Et, Pr^i). It also reacts with [Cr(CO)$_5$(THF)] to yield [cp$_3$Co$_3$(μ_3-CSCr(CO)$_5$)(μ_3-S)] (ref. 499). Refluxing [Co$_2$(CO)$_8$] and norbornadiene in petroleum ether gives [Co(NBD)(CO)$_2$]$_2$ which on further treatment with NaBPh$_4$ and iodine in dimethoxyethane at 85°C yields [Co(NBD)(η^6-C$_6$H$_5$BPh$_3$)] (ref. 500). Tin(II) halides add to [cpCoLX$_2$] to yield [cpCoLX(SnY$_2$X)] (X = Br, I, Y = Cl, Br, I; L = CO, PPh$_3$). In the case of [cpCo(CO)Br$_2$] reacting with SnI$_2$, a novel halogen migration occurs to give [cpCo(I)(SnIBr$_2$)] The corresponding methylcyclopentadienyl complexes react in an analogous manner. The perfluoropropyl complex [cpCo(CO)(C$_3$F$_7$)I] also adds SnY$_2$ to give [cpCo(CO)(C$_3$F$_7$)(SnY$_2$I)] (ref. 501).

Spiro[2.4]hepta-4,6-diene reacts with [Co$_2$(CO)$_8$] on heating to give [189], [190] and [191]. Interestingly no coupling with carbon



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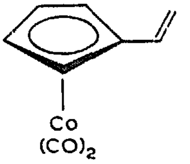

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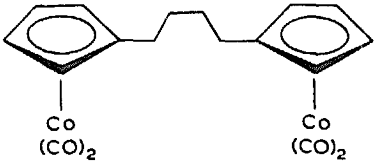
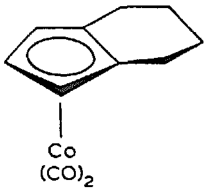


[191]

monoxide was observed. With spiro[4.4]nona-7,9-diene the same reaction produced [192], [193] and [194]. Heating [195] with $[Co_2(CO)_8]$ under CO converts it to [196] (ref.502). Condensation of cobalt atoms with quadricyclane yielded 47% norbornediene and 27% norbornadiene polymers while the same reaction with spiro[4.2]hepta-4.6-diene in the presence of CO gave [189] and [190] (ref. 503)



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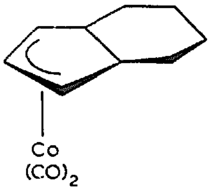

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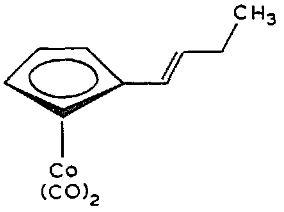

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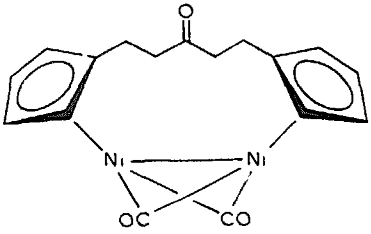
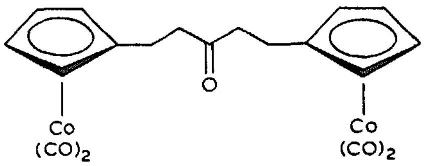
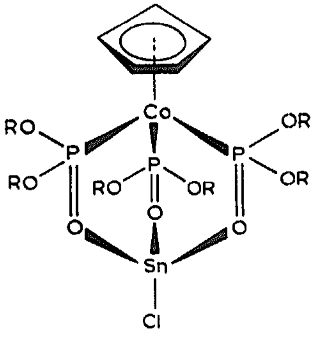


[195]



[196]

In acetonitrile, $[cpCo(CO)Br_2]$ reacts with $AgClO_4$ to give $[cpCo(MeCN)_3](ClO_4)_2$ which on addition of o-aminophenol, sodium maleonitriledithiolate or bipyridyl gives $[cpCo(o\text{-}(NH)OC_6H_4)]$, $[cpCo(S_2C_2(CN)_2)]$ and $[cpCo(bipy)(MeCN)](ClO_4)_2$ respectively. Electrolytic reduction of $[cpCo(MeCN)_3](ClO_4)_2$ gives $[cp_2Co]^+$ and Co(II) (ref. 504). The P=O groups in $Na[cpCo(P(O)(OEt)_2)_3]$ can coordinate to other metal atoms and depending on the amount of $SnCl_2$ used, either [197] or [198] can be formed (ref.505). The related mixed-valence complex [199] shows a temperature-dependent high spin-low spin equilibrium and it was concluded that the process was an intramolecular electron transfer involving primarily inner sphere effects (ref. 506).



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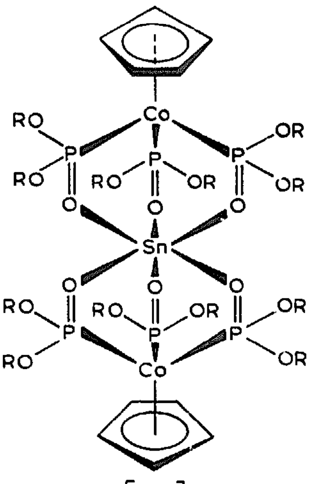
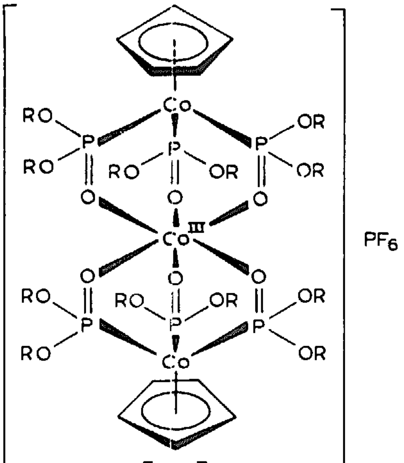


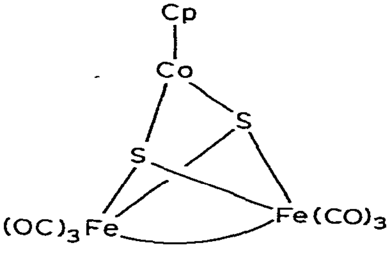
[198]

R = Et

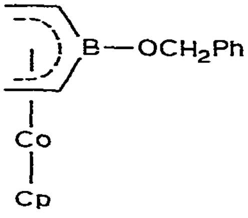


R = Et [199]

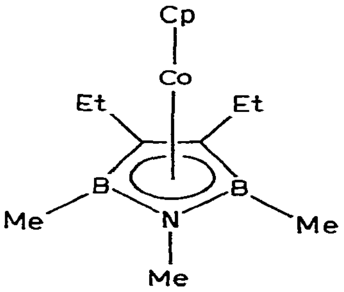
Acylation of sodium cyclopentadienide can be effected by treatmen with esters RCO_2R^1 (R = H, Me, OMe) and the resulting functionalized cyclopentadienide then used to prepare $[(\eta^5-C_5H_4COR)_2Co]$ from $CoCl_2$ or $[(\eta^5-C_5H_4COR)M(CO)_2]$ (M = Co, Rh) from $[Co_2(CO)_8]$ or $[Rh(CO)_2Cl]_2$ respectively. This procedure provides a convenient means of preparing functionalized cyclopentadienyl complexes of metals other than iron (ref. 507). The coordinatively unsaturated complex $[cp_2{}^*Co_2(\mu-CO)_2]$ adds photochemically-generated metal fragments to produce triangular mixed-metal clusters $[MCo_2(cp^*)_2(\mu-CO)_3(\mu_3-CO)]$ (M = $(\eta^6-MeC_6H_5)Cr$, $(\eta^5-C_5H_4Me)Mn$, $(\eta^4-C_4H_4)Fe$) and $[MCo_2(cp^*)_2(\mu-CO)_2(\mu_3-CO)]$ (M = $Fe(CO)_3$, $(\eta^5-C_5H_4Me)Co$). The structures of the complexes have been determined and for the latter pair, the μ_2-carbonyls bridge the Co–Co edge and one of the Co–M edges (ref. 508). Photolysis of a mixture of $[Fe_2(CO)_6(\mu-S_2)]$ and $[cpCo(CO)_2]$ in THF causes insertion of a [cpCo] fragment into the S–S bond yielding [200] (ref. 509). Analogous photochemical procedures using $[cpCo(CO)_2]$ have afforded [201] from chlorodivinylborane followed by hydrolysis with benzyl alcohol (ref. 510), $[cpCo(\eta-Ph_5C_4B)]$ from pentaphenylborole (ref. 511) and [202] from 3,4-diethyl-1,2,5-trimethyl-1,2,5-azadiborolene. However with $[Co_2(CO)_8]$ the azadiborolene binds only through the double bond giving $[Co_2(CO)_4(C_2Et_2B_2Me_2NMe)_2]$ (ref. 512). In a related study, $CoCl_2$ reacts with the 3,4-diethyl-2,5-dimethyl-1,2,5-thiadiborolene complex $Zn[cpFe(C_2Et_2B_2Me_2S)]$ to give the thiadiborolene analog of [202] while reduction of the zinc compound with potassium prior to reaction with $CoCl_2$ gives the "triple-decker" sandwich complex [203] (ref. 513).



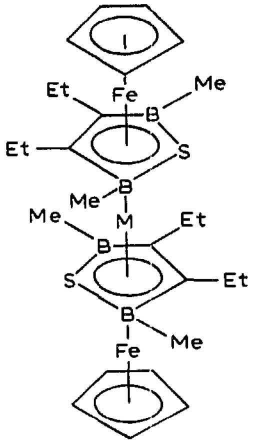
[200]



[201]



[202]



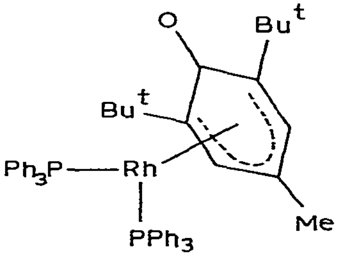
[203]

A convenient synthesis of 1,2-diaminoalkanes involves reaction of an olefin with $[cp_2Co_2(NO)_2]$ and NO at $0^{\circ}C$ to give initially the dinitroso complex [1] (see Dissertations section). Reduction of [1] with $LiAlH_4$ at $-70^{\circ}C$ gave good yields of the diamines. The order of reactivity was determined to be norbornene>cyclopentene>terminal olefins>trans-disubstituted olefins>>cyclohexene>cis-disubstituted olefins (ref. 514). The condensation of terminal acetylenes with alkyl thiocyanates to give approximately equal amounts of 3,6- and 4,6-dialkyl-2-alkylthiopyridines is catalyzed by [cpCo(cyclooctadieny Yields of 24-95% were reported (ref. 515).

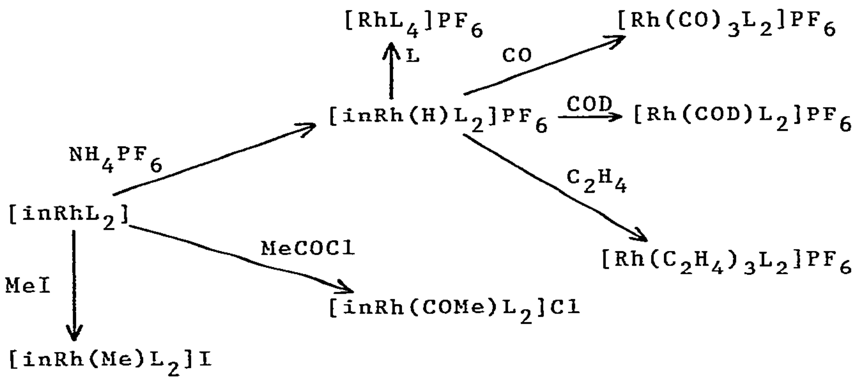
The structure of $[cp^*Co(CO)_2]$ has been determined to ascertain whether the bonding of the cp^* ring to the metal shows a deviation from C_{5v} symmetry as a result of the lower symmetry of the attached $Co(CO)_2$ fragment. Indeed a distortion towards an "ene-yl" bonding mode was noted (ref. 516). Photolysis of $[cpCo(CO)_2]$ at 12 K in dilute CO and N_2 matrices produced $[(\eta^3-C_5H_5)Co(CO)_3]$ and $[cpCo(N_2)(CO)]$ respectively. The fact that the formation of the tricarbonyl was reversible and that photolysis of $[cpCo(CO)_2]$ in dilute Ar and CH_4 matrices gave no evidence for $[cpCo(CO)]$ + CO suggested that substitution reactions of $[cpCo(CO)_2]$ may proceed by an associative process facilitated by the "slippage" of the cp ring from an η^5 to an η^3 bonding mode (ref. 517). The infrared and Raman spectra of $[cp_2Co]^+$ intercalated into MPX_3 hosts (M = Mn, Cd, Zn; X = S, Se) at a level of ca 0.33 $[cp_2Co]^+/MPX_3$ unit have been measured with the conclusion that the host-guest interaction is weak (ref. 518). The band intensities of the Co-H and Co-D stretching vibrations in

$[cp_4Co_4(\mu_3\text{-}H)_4]$ and its deuterated analog show a significant variation with temperature suggesting a criterion for the identification of bridging-hydride vibrations. Although it was possible to assign the symmetric and antisymmetric stretching frequencies in other related complexes, a unique assignment could not be made for the cobalt complex (ref. 519). The complexes $[cpCoL(ArN_3Ar)]PF_6$ (L = PEt_3, PPh_3, $P(OMe)_3$, $P(OPh)_3$; Ar = p-tolyl) have been studied by cyclic voltammetry and all are found to undergo a reversible one-electron reduction. The half-wave potential increases as the basicity of the phosphorus ligand decreases. A one-electron oxidation step is also observed but appears to involve the triazenido ligand rather than the metal (ref. 520).

A toluene solution of $[Rh(N(SiMe_3)_2)(PPh_3)_2]$ reacts with 2,5-di-tert-butyl-4-methylphenol to give the phenoxy complex $[(\eta^5\text{-}C_6H_2\text{-}(Bu^t)_2(Me)O)Rh(PPh_3)_2]$, [204] which was also the subject of a crystal structure determination (ref. 521). Indenyllithium converts either $[Rh(PMe_3)_4]Cl$ or $[RhCl(PMe_3)_2]_2$ to $[(\eta^5\text{-}C_9H_7)Rh(PMe_3)_2]$ whose subsequent chemistry is outlined in Scheme XLVI (ref. 552). Chloride abstraction from $[RhCl(P(OMe)_3)_2]_2$ by $AgClO_4$ in toluene/dichloromethane solution yields $[(\eta^6\text{-}C_6H_5Me)Rh(P(OMe)_3)_2]ClO_4$. The analogous η^6-mesitylene complex can be prepared by the same method or from the toluene complex by arene exchange. Reaction of either the toluene complex or $[RhCl(P(OMe)_3)_2]_2$ with $NaBPh_4$ in methanol gives $[Rh(\eta^6C_6H_5BPh_3)(P(OMe)_3)_2]$. Further reactions of $[(\eta^6\text{-}C_6H_5Me)Rh(P(OMe)_3)_2]ClO_4$ are outlined in Scheme XLVII (ref. 523).

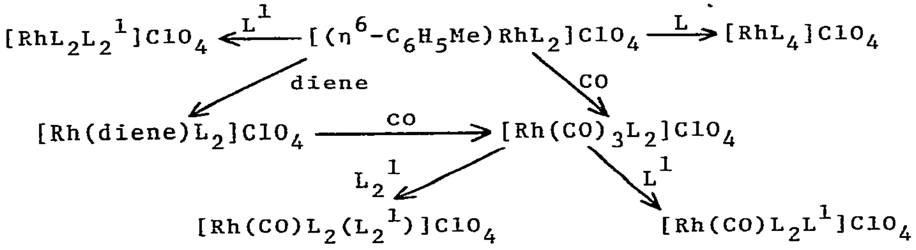


[204]



in = η^5-C_9H_7, L = PMe_3

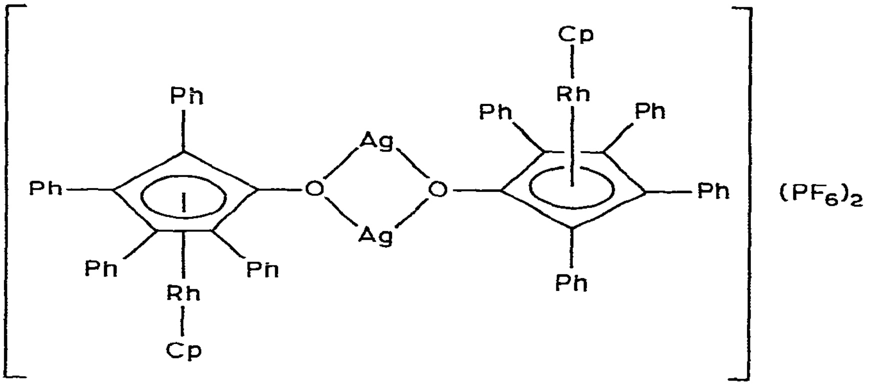
Scheme XLVI



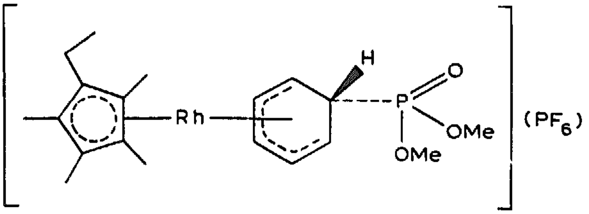
L = $P(OMe)_3$, L^1 = py, ArCN, L_2^1 = bipy, o-phen

Scheme XLVII

Although silver(I) is often used as a mild oxidizing agent, in the case of [cpRh(η^4-C_4Ph_4CO)], $AgPF_6$ reacts without causing oxidation to give [205] (ref. 524). Carbon monoxide displaces the coordinated phenyl group in [Rh(diphos)(η^6-$C_6H_5BPh_3$)] to give [Rh(diphos)$(CO)_2$]-BPh_4. The former complex also causes the polymerization of allene and catalyzes the oligomerization of propyne to linear and branched dimers and trimers as well as cyclotrimers. In the presence of CO_2, the latter reaction gives 4,6-dimethyl-2-pyrone as well as propyne oligomers (ref. 525). Reduction of [(η^6-$C_6Me_6)_2Rh](PF_6)_2$ with zinc in hydrochloric acid gives [(η^6-C_6Me_6)Rh(η^4-$C_6H_2Me_6$)]PF_6. The structure determination showed the two added hydrogen atoms were exo implying that hydrogenation occurred on the zinc. Although exposure to hydrogen causes hydrogenation of the organic ligands, the products are unstable and therefore do not function as arene hydrogenation catalysts (ref. 526). The arene ligand in [(η^5-C_5Me_4Et)Rh(η^6-C_6H_6)]$(PF_6)_2$ can be reduced with $LiAlH(O\text{-}Bu^t)_3$ to give [(η^5-C_5Me_4Et)Rh(η^5-C_6H_7)]PF_6 with exo addition of the hydride. Slow loss of hydride to regenerate the starting arene complex occurs and again it is an exo hydrogen which is involved. Other nucleophiles can attack the arene ring and for example Tlacac and PR_3 (R = Bu^n, Me_2Ph) give [(η^5-C_5Me_4Et)Rh(η^5-$C_6H_6CH(COMe)_2$)]PF_6 and [(η^5-C_5Me_4Et)-Rh(η^5-$C_6H_6PR_3$)]$(PF_6)_2$ respectively in which the nucleophile is in an exo position. The structure of the $P(OMe)_3$ product, [206], has been determined (ref. 527). The benzene complex has also been found to catalyze the conversion of [207] into [208] (R = H; R^1 = H, CH_2OH, o-$C_6H_4(F)CH_2$. R = Me; R^1 = H) in an acetone-nitromethane

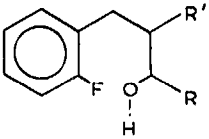


[205]

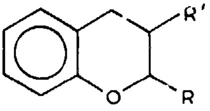


[206]

solvent system at 80°C. Yields are in the range 57-88%. The initial step of the reaction is the replacement of the benzene ligand by the substituted arene (ref. 528). Substitution of iodide for chloride in $[(\eta^5\text{-}C_5Me_4Et)RhCl_2]_2$ occurs with sodium iodide in acetone to give $[(\eta^5\text{-}C_5Me_4Et)RhI(\mu\text{-}I)_2RhI(\eta^5\text{-}C_5Me_4Et)]$ whose structure has been determined.

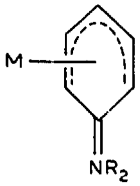


[207]



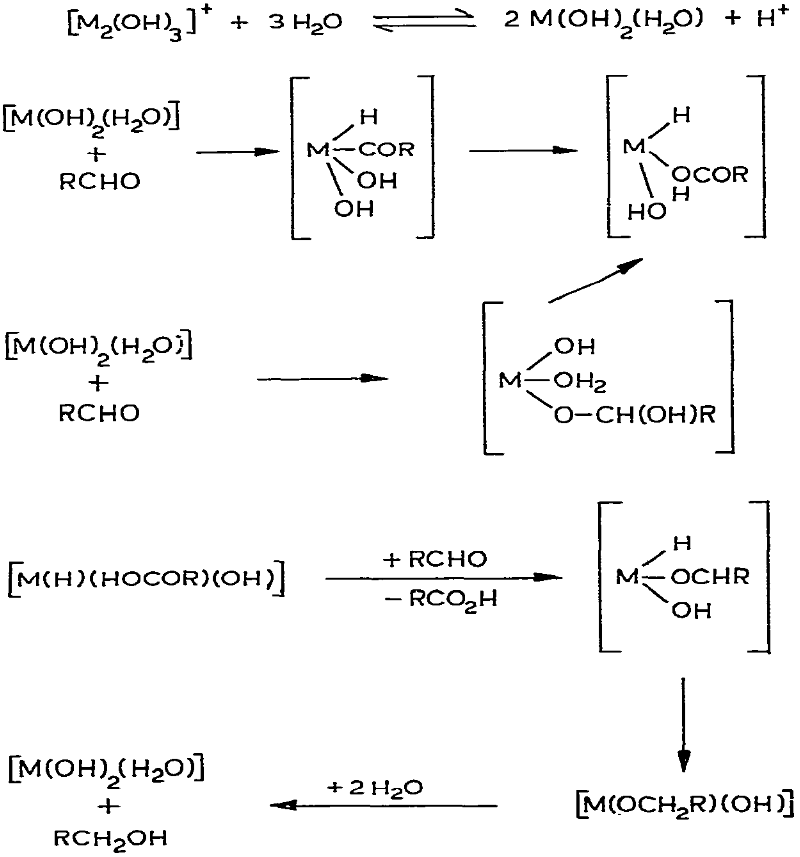
[208]

The chemistry of pentamethylcyclopentadienyl complexes of rhodium and iridium continues to attract attention. In coordinating solvent $[cp_2{}^*M_2Cl_4]$ react with $AgPF_6$ to give $[cp^*M(S)_3](PF_6)_2$ (M = Rh, S = MeCN; M = Ir, S = Me_2CO) which coordinate a series of substituted anilines yielding $[cp^*M(\eta\text{-aniline})](PF_6)_2$. From NMR data it appears that the anilines are bound in an asymmetric fashion such as [209] but the structural study on the rhodium complex of N-methylaniline was unfortunately inconclusive because of disorder. On the other hand, in the analogous anisole complex, the arene ring appears symmetrically bound (ref. 530). The complex $[cp_2{}^*Rh_2(OH)_3]Cl$ is



[209]

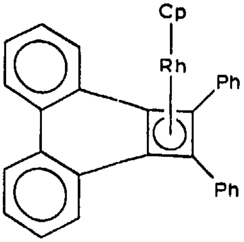
a catalyst for the conversion of aldehydes and water into the corresponding alcohols and carboxylic acids. When the hexafluorophosphate salt was used $[cp_2{}^*Rh_2H(O_2CMe)_2]PF_6$ could be isolated which suggested the mechanism of Scheme XLVIII (ref. 531). If $[cp_2{}^*Rh_2(OH)_3]Cl$ is heated to 45°C in aqueous isopropanol under



Scheme XLVIII

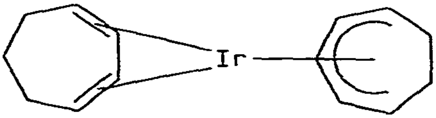
hydrogen, the solution changes from yellow-orange to dark red and upon addition of NH_4PF_6, the trinuclear species $[cp_3{}^*Rh_3(\mu\text{-}H)_3(\mu_3\text{-}O)]$-$PF_6 \cdot H_2O$ was isolated. The structure of the complex was determined and NMR data showed it to be stereochemically rigid (ref. 532).

The reaction of $[cpRh(CO)_2]$ with 2,2'-bis(phenylethynyl)biphenyl in refluxing xylene gave four products, two of which were identified as [210] and the known $[cpRh(\mu\text{-}CO)]_3$ (ref. 533). Sodium nitrocyclopentadienide converts $[Rh(CO)_2Cl]_2$ into $[(\eta^5\text{-}C_5H_4NO_2)Rh(CO)_2]$ whose structure has been determined. Although all the C-C bond distances were equal within experimental error, the substituted carbon was inclined about 10° from the plane of the other four in the cyclopentadienyl ring suggesting a contribution of an η^4-diene structure to the overall bonding description (ref. 534). Oxidation of $[cpCo(PPh_3)_2]$ with $AgBF_4$ gives $[cpCo(PPh_3)_2]BF_4$ however with the rhodium analog, the fulvalene complex $[Rh_2(\eta^{10}\text{-}C_{10}H_8)(PPh_3)_4](BF_4)_2$ results. A second product is $[cpRhH(PPh_3)_2]BF_4$ which can also be obtained as the only product of the protonation of $[cpRh(PPh_3)_2]$ with HBF_4. The fulvalene complex can also be prepared by the reaction of $Li_2C_{10}H_8$ with $[RhCl(PPh_3)_2]_2$ to give $[Rh_2(\eta^{10}\text{-}C_{10}H_8)(PPh_3)_4]$ followed by oxidation with $AgBF_4$. M. O. calculations suggest that the preferred course for a one-electron oxidation of $[cpRh(PPh_3)_2]$ gives a metal-stabilized carbon radical which can then undergo coupling and deprotonation to give the observed products. In a similar fashion, oxidation of $[(\eta^3\text{-}C_3H_5)Rh(P(OMe)_3)_3]$ with $AgPF_6$ gave the hexadiene complex $[(\eta^4\text{-}C_6H_{10})Rh(P(OMe)_3)_2]PF_6$ (ref. 535).



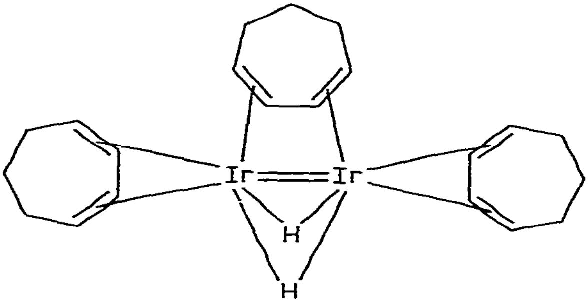
[210]

Organolithium reagents react with $[Ir(diene)_2Cl]$ to yield $[Ir(diene)_2R]$ (diene = cyclohexa-1,3-diene, cyclohepta-1,3-diene; R = Me, Ph). While the hexadiene product decomposes at 45°C, the heptadiene complex reacts to give a product identified as [211]. The same complex can also be prepared from $[Ir(\eta^4\text{-cyclohepta-1,3-diene})_2Cl]$ and sodium carbonate in ethanol. Interestingly, when butyllithium is used in the alkylation of the two diene complexes, the products are $[IrH(\eta^4\text{-cyclohexa-1,3-diene})_2]$ and [211] plus



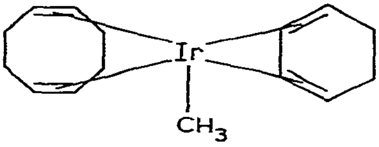
[211]

[212] respectively. Reaction of $[Ir(COD)Cl]_2$ with methyllithium in the presence of cyclohexa-1,3-diene or isoprene gave [213] and



[212]

[214] respectively (ref. 536). However if the reaction is carried out using isopropylmagnesium bromide in the presence of cycloheptatriene or cyclooctatriene, the products are [215] and [216]



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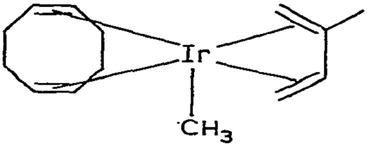
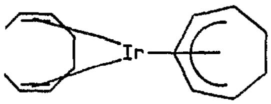
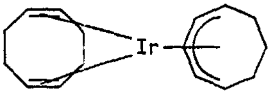


[214]

plus [217] respectively. Treatment of [Ir(COD)Cl] with $Na_2C_8H_8$ followed by hydrolysis gives $[Ir(COD)(C_8H_9)]$ which can be protonated with HBF_4 to yield [218]. NMR studies showed all the products to be fluxional (ref. 537).



[215]



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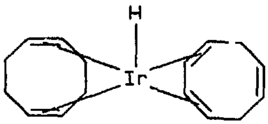
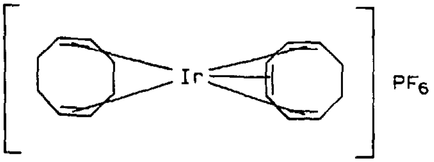
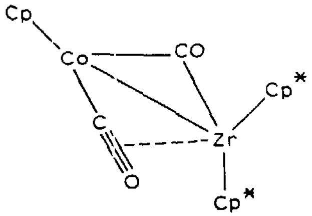


[217]



[218]

A novel mixed-metal dimer has been prepared from [cpCo(CO)$_2$] and [cp$_2^*$ZrH$_2$] or {[cp$_2^*$Zr(N$_2$)]$_2$N$_2$} at -20°C in toluene. The structure has been determined to be [219] in which the unusual μ_2-η^1-η^2 bonding mode occurs for one of the bridging carbonyl ligands (ref. 538).



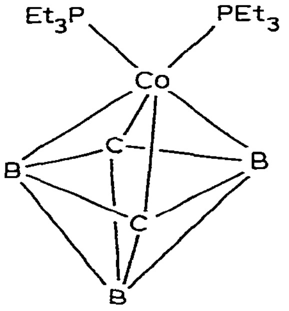
[219]

Reaction of B$_9$H$_9$XSe (X = S, Se) with potassium hydroxide followed by treatment with a mixture of CoCl$_2$, cyclopentadiene and triethylamine yielded the nido cage complex [cpCo(B$_9$H$_9$XSe)]. When X = Se a second product was the closo species [cp$_2$Co$_2$(B$_9$H$_9$Se)] (ref. 539).

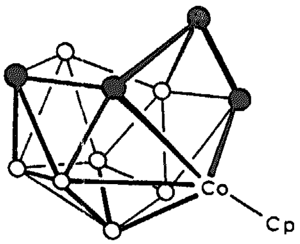
Metal carbaborane complexes

Formaldehyde in aqueous hydrochloric acid converts 7,8-C$_2$B$_9$H$_{12}^-$

into 4,5-$C_2B_7H_{11}$ which reacts with a mixture of $CoCl_2$ and cyclopentadiene in ethanolic KOH followed by oxidation to yield [closo-4,7-$(cpCo)_2$-2,3-$C_2B_7H_9$] (ref. 540). An example of the preparation of a metallacarbaborane by direct insertion of a nucleophilic metal species into a neutral carbaborane is provided by the reaction between closo-1,7-$C_2B_6H_8$ and [$Co(PEt_3)_4$] which gives the hydrido complex [2,2,2-$(H)(PEt_3)_2$-2,1,8-$CoC_2B_6H_8$] as the major product. From the structural study it was noted that the hydride ligand made a close (1.72(6) Å) approach to an adjacent boron atom suggesting a semi-bridging function. A similar reaction of closo-1,5-$C_2B_3H_5$ with [$Co(PEt_3)_4$] gave the paramagnetic complex [2,2-$(PEt_3)_2$-2,1,6-$CoC_2B_3H_5$] as the first example of an octahedral metallacarbaborane ([220] with hydrogen atoms omitted for clarity). Oxidation of [220] with trityl tetrafluoroborate gives [2,2-$(PEt_3)_2$-2,1,6-$CoC_2B_3H_5$]BF_4 which can then be reduced to the hydride [2,2,2-$(H)(PEt_3)_2$-2,1,6-$CoC_2B_3H_5$] with sodium borohydride (ref. 541). Reaction of $Me_4C_4B_8H_8$ with $CoCl_2$ and sodium cyclopentadienide in THF followed by acidification yields [$cpCo(Me_4C_4B_7H_7)$], [$cpCo(Me_4C_4B_8H_8)$] and the previously characterized zwitterionic species σ-$[cpCo(\eta^5\text{-}C_5H_4)]^+[Me_4C_4B_8H_8]^-$. A structural study of the first complex showed it to be [221] with the novel feature of a carbon atom bridging three framework atoms across the open face. It is the fifth distinct type of 12-vertex nido cage systems characterized (ref. 542). In an attempt to prepare a mixed borane-metallacarbaborane, $CoCl_2$ was reacted with a mixture of $[Me_2C_2B_4H_5]^-$ and $[B_5H_8]^-$. The isolated product however was [(2,3-$Me_2C_2B_4H_4$)CoH-(2,3-$Me_2C_2B_7H_7$)] ([222]) (ref. 543). The synthesis of cobaltaboranes and -carbaboranes by the metal-atom vapor technique has been explored. The reaction of cobalt vapor with cyclopentadiene and pentaborane(9)



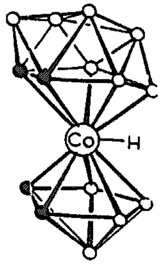
[220]



O - BH ● = CMe

[221]

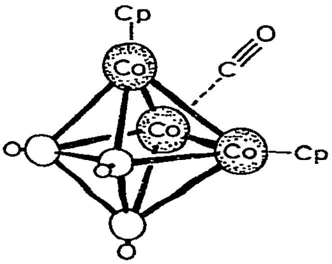
gave thirty products of which the new species characterized were $[1,2,3\text{-}(cpCo)_3B_5H_5]$, $[8\text{-}\sigma\text{-}(C_5H_9)\text{-}1,2,3\text{-}(cpCo)_3B_5H_4]$ and $[(\mu_3\text{-}CO)\text{-}1,2,3\text{-}(cpCo)_3B_3H_3]$ ([223]). The carbonyl group is presumed to come from decomposition of the THF used in the workup of the reaction



O = BH ● = CMe

[222]

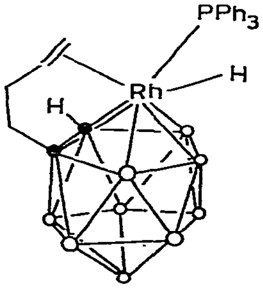
mixture. The same procedure with hexaborane(10) gave the previously reported $[2\text{-}(cpCo)B_9H_{13}]$, $[1,2\text{-}(cpCo)_2B_4H_6]$ and $[5\text{-}(cpCo)B_9H_{13}]$ while with decaborane(14) the new complex $[6\text{-}(cpCo)B_9H_{13}]$ and the known $[5\text{-}(cpCo)B_9H_{13}]$ were obtained. Cocondensation of cobalt atoms with cyclopentadiene, pentaborane(9) and but-2-yne gave $[2,5\text{-}(Me)_2\text{-}1,7,2,5\text{-}(cpCo)_2C_2B_5H_5]$ as the only new species. The same reaction with diphenylacetylene produced $[2,3\text{-}(Ph)_2\text{-}1,7,2,3\text{-}(cpCo)_2C_2B_3H_3]$, $[2,3\text{-}(Ph)_2\text{-}1,2,3\text{-}(cpCo)C_2B_3H_5]$ and $[4,5,7,8\text{-}(Ph)_4\text{-}1,4,5,7,8\text{-}(cpCo)\text{-}C_4B_3H_3]$. The structure of the last complex has been determined (ref. 544b). Finally, cocondensation of cobalt atoms with



[223]

cyclopentadiene, hexaborane(10) and but-2-yne gave [1,2-$(Me)_2$-3,1,2-$(cpCo)C_2B_5H_5$], [6,7-$(Me)_2$-2,5,6,7-$(cpCo)_2C_2B_6H_8$], [6,7-$(Me)_2$-2,4,6,7-$(cpCo)_2C_2B_6H_6$] and three known complexes (ref. 544a).

The chemistry and catalytic properties of a series of rhodium and iridium carbaborane complexes have been the subject of intense study. An assignment of the ^{11}B NMR spectrum of [closo-3,3-$(L)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (L = PPh_3, PEt_3) has been made from analysis of the spectra of specifically deuterated analogs and indicates that the $RhHL_2$ moiety undergoes rotation about an axis passing through the pentagonal face of the dicarbollide ligand (ref. 545). The triphenylphosphine derivative has been found to be an active olefin hydrogenation catalyst and phosphine dissociation to provide a vacant site for olefin coordination has been proposed as an essential feature of the process. To probe this point further, the related complex [224] was prepared from $[RhCl(PPh_3)_3]$ and Cs[7-butenyl-7,8-$C_2B_9H_{11}$] in refluxing methanol



O = BH ● = C

[224]

Indeed [224] was a significantly more active catalyst. Presumably the initial step is the hydrogenation of the butenyl group thereby readily providing a vacant site and this was established by exposing [224] to hydrogen in the presence of PPh_3 whereupon [closo-1-(Bu^n)-3-H-3,3($(PPh_3)_2$-3,1,2-$RhC_2B_9H_{10}$] was obtained. In the absence of added phosphine, hydrogenation gave an air-sensitive purple complex thought to be a dimer (ref. 546). The $RhH(PPh_3)_2$ moiety in these dicarbollide complexes can be readily exchanged between various carbaborane cages in refluxing ethanol. The exchange is most facile when both carbon atoms occupy adjacent vertices in the pentagonal face bound to the metal (ref. 547). Whilst [$IrClL_n$] (L = PMe_2Ph, $AsMe_2Ph$; n = 2. L = PPh_3; n = 3) reacts with $NaC_2B_8H_{11}$ to yield [closo-1,1$(L)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$], with [$RhClL_3$] the products are [nido-9,9-$(L)_2$-9,7,8-$RhC_2B_8H_{11}$] (L = PPh_3, P(p-tol)$_3$) or [nido-9,9,9-$(L)_3$-9,7,8-$RhC_2B_8H_{11}$] (L = $AsMe_2Ph$, $AsMe_3$, $SbMe_3$, PMe_3, PMe_2Ph, PEt_3). For L = PEt_3 one phosphine is lost in solution and partial conversion to a closo species analogous to the iridium complexes results while the P(p-tolyl)$_3$ complex adds CO to yield [nido-9-CO-9,9-(P(p-tolyl)$_3$)$_2$-9,7,8-$RhC_2B_8H_{11}$]. Also, the RhL_3 unit undergoes rotation with respect to the face of the cage. The formation of the closo complexes with iridium is attributed to the greater tendency for Ir(I) to undergo oxidative addition with the acidic bridging hydrogen of the original carbaboranyl ion (ref. 548). The iridium carbaborane [closo-3,3-$(L)_2$-3-H-3,1,2-$IrC_2B_9H_{11}$] can be synthesized from the ion pair [Ir(COD)L_2][nido-7,8-$C_2B_9H_{12}$] and hydrogen in refluxing cyclohexane. At -22°C however, it was also possible to isolate the intermediate species in the above reaction, [nido-3,9-(H_2IrL_2)-3,9-(μ-H)$_2$-7,8-$C_2B_9H_{10}$] (L = PPh_3, P(p-tolyl)$_3$) which on heating converted to the closo complex. The structure of the P(p-tolyl)$_3$ derivative was determined showing it to consist of a $C_2B_9H_{12}$ moiety coordinated to the iridium via the hydrogen atoms of two terminal B-H units. The coordination sphere is completed by two trans phosphines and two cis hydrido ligands (ref. 549). Oxidative addition reactions of the complexes trans[Ir(σ-carb)(CO)L_2] (carb = 2-R-1,2-$C_2B_{10}H_{10}$, 7-R-1,7-$C_2B_{10}H_{10}$ (R = H, Me, Ph); L = PPh_3, $PMePh_2$) have been studied. In the solid state or in non-polar solvents all add gaseous HX (X = Cl, Br, I) to give octahedral species in which cis addition has occurred except for the methyl derivative of the 1,2-dicarbollide complex which gives a trans adduct. In polar media all give mixtures of cis and trans adducts. Oxidative addition of Cl_2 to the solid complexes gives cis adducts while with Br_2 approximately equal quantities of cis and trans adducts result. In solution and in the solid state, the octahedral hydride complexes reductively eliminate H-carb on standing (ref. 550). The hydrosilylation of styrene with $HSiMe_2Ph$ is catalyzed by [closo-3,3-$(PPh_3)_2$-4-py-3,1,2-$RhC_2B_9H_{10}$] to give an 89/11 ratio of $PhCH(SiMe_2Ph)Ch_3$ and $PhCh_2CH_2SiMe_2Ph$. The catalyzed hydrosilylation of phenylacetylene yields a 22/78 ratio of cis- and trans-$PhCH{=}CHSiMe_2Ph$ (ref. 551).

REFERENCES

1 S.D. Robinson, Organomet. Chem., 8(1980)296.
2 E.J. Kuhlmann and J.J. Alexander, Coord. Chem. Revs., 33(1980)195
3 I. Omae, Coord. Chem. Revs., 32(1980)235.
4 F.J. Brown, Prog. Inorg. Chem., 27(1980)1.
5a Y. Yamamoto, Coord. Chem. Revs., 32(1980)193.
5b L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley Interscience, New York, 1969.
6 R. Cotton and M.J. McCormick, Coord. Chem. Revs., 31(1980)1.
7 H. Alper, Pure Appl. Chem., 52(1980)607.
8 D.W. Slocum, Catal. Org. Synth., (1980)296.
9 H. Behrens, Adv. Organometallic Chem., 18(1980)2.
10 W.L. Gladfelter and G.L. Geoffroy, Adv. Organometallic Chem., 18(1980)207.
11 H. Brunner, Adv. Organometallic Chem., 18(1980)152.
12 P. Chini, J. Organometal. Chem., 200(1980)37.
13 S. Takahashi and N. Hagihara, Kagaku (Kyoto), 35(1980)239.
14 E.L. Muetterties, J. Organometal. Chem., 200(1980)177.
15 B.L. Shaw, J. Organometal. Chem., 200(1980)307.
16 G.L. Geoffroy, Progr. Inorg. Chem., 27(1980)123.
17 P. Pino, J. Organometal. Chem., 200(1980)223.
18 H. Siegel and W. Himmele, Angew. Chem. Int. Ed. Engl., 19(1980)178.
19 C. Botteghi, G. Serafino, V. Bellagamba, R. Ercoli, and A. Gamba, Chem. Ind. (Milan) 62(1980)604.
20 J. Halpern, J. Organometal. Chem., 200(1980)133.
21 G.P. Chiusoli, Pure Appl. Chem., 52(1980)635.
22 G.M. Angeles and L.A. Oro, Transition Met. Chem. (Weinheim, Ger.) 5(1980)65.
23 L.M. Venanzi, Pure Appl. Chem., 52(1980)1117.
24 H.F. Klein, Angew. Chem., 92(1980)362.
25 W. Siebert, Adv. Organometallic Chem., 18(1980)301.
26 E.V. Leonova, Uspekhi Khim., 49(1980)283.
27 W.A. Nugent and B. L. Haymore, Coord. Chem. Revs., 31(1980)123.
28 M.A. White, Diss. Abs. Int. B, 40(1980)3179.
29 E.R. Evitt, Diss. Abs. Int. B, 41(1980)195.
30 S.S. Hershberger, Diss. Abs. Int. B, 40(1980)5672.
31 J.A. Sofranko, Diss. Abs. Int. B, 41(1980)191.
32 R.A. DeVries, Diss. Abs. Int. B, 41(1980)959.
33 J.A. Doi, Diss. Abs. Int. B, 41(1980)187.
34 R.T. Baker, Diss. Abs. Int. B, 41(1980)1365.
35 J.G. Zimmerman, Diss. Abs. Int. B, 41(1980)953.
36 C.P. Kubiak, Diss. Abs. Int. B, 41(1980)1763.
37 K.D. Schramm, Diss. Abs. Int. B, 41(1980)2176.
38 J.W. Yorke, Diss. Abs. Int. B, 41(1980)953.
39 A. Yamamoto, K. Maruyama and T. Ito, Transition Met. Chem. (Weinheim, Ger.), 5(1980)14 (Chem. Abstr., 92(1980)181350g).
40 A.V. Kavaliunas and R.D. Riecke, J. Am. Chem. Soc., 102(1980)5944.
41 K. von Werner and H. Blank, Angew. Chem. Int. Ed. Engl., 19(1980)128.
42 G.B. Deacon, S.J. Faulks and J.M. Miller, Transition-Met. Chem. (Weinheim, Ger.), 5(1980)305 (Chem. Abstr., 94(1981)15866b).
43 R. Nast and A. Beyer, J. Organometal. Chem., 194(1980)379.
44 M.F. McGuiggan, D.H. Doughty and L.H. Pignolet, J. Organometal. Chem., 185(1980)241.
45 M. A. Bennett and J. C. Jeffrey, Inorg. Chem., 19(1980)3763.
46 D.L. Thorn, J. Am. Chem. Soc., 102(1980)7109.

47 R.L. Harlow, J.B. Kinney and T. Herskovitz, J. Chem. Soc. Chem. Commun., (1980)813.
48 J.A. Kampemeier, S.H. Harris and D.K. Wedegaertner, J. Org. Chem., 45(1980)315.
49 R.G. Pearson and P.E. Figdore, J. Am. Chem. Soc., 102(1980)1541.
50a J.A. Labinger and J.A. Osborn, Inorg. Chem., 19(1980)3230.
50b J.A. Labinger, J.A. Osborn and N.J. Coville, Inorg. Chem., 19(1980)3236.
51 C. Crocker, R.J. Errington, R. Markham, C.J. Moulton, K.J. Odell and B.L. Shaw, J. Am. Chem. Soc., 102(1980)4373.
52 R.H. Crabtree, J.M. Quirk, H. Felkin, T. Fillebeen-Khan and C. Pascard, J. Organometal. Chem., 187(1980)C32.
53 F. Petit, C. Arzouyan, G. Peiffer and E. Gaydou, J. Organometal. Chem., 202(1980)319.
54a H.S. Bryndza, E.R. Evitt and R.G. Bergman, J. Am. Chem. Soc., 102(1980)4948.
54b R.G. Bergman, Accts. Chem. Res., 13(1980)113.
55 A. Moro, M. Foà and L. Cassar, J. Organometal. Chem., 185(1980)79.
56 R.E. Campbell, Jr. and R.G. Miller, J. Organometal. Chem., 186(1980)C27.
57 R.E. Campbell, Jr., C.F. Lochow, K.P. Vora and R.G. Miller, J. Am. Chem. Soc., 102(1980)5824.
58 R.C. Larock and S.S. Hershberger, J. Org. Chem., 45(1980)3840.
59 M. Lewin, Z. Aizenshtat and J. Blum, J. Organometal. Chem., 184(1980)255.
60 G. Kuncová and V. Chvalovský, Collect. Czech. Chem. Commun., 45(1980)2085.
61 G. Kuncová and V. Chvalovský, Collect. Czech. Chem. Commun., 45(1980)2240.
62 W.E. Billups, M.M. Konarski, R.H. Hauge and J.L. Margrave, J. Am. Chem. Soc., 102(1980)7393.
63 P.B. Armentrout and J.L. Beauchamp, J. Am. Chem. Soc., 102(1980)1736.
64 L. Falvello and M. Gerloch, Inorg. Chem., 19(1980)472.
65 A. Immirzi, A. Musco, P. Pregosin and L. Venanzi, Angew. Chem. Int. Ed. Engl., 19(1980)721.
66 M. Creswick, I. Bernal, W.A. Herrmann and I. Steffl, Chem. Ber., 113(1980)1377.
67 A.D. Clauss, P.A. Dimas and J.R. Shapley, J. Organometal. Chem., 201(1980)C31.
68 T.R. Halbert, M.J. Lenowicz and D.J. Maydonovich, J. Am Chem. Soc., 102(1980)5101.
69 P.A. Dimas, E.N. Duesler, R.J. Lawson and J.R. Shapley, J. Am. Chem. Soc., 102(1980)7787.
70 W.A. Herrmann, J. Plank, E. Guggolz and M.L. Ziegler, Angew. Chem. Int. Ed. Engl., 19(1980)651.
71 W.A. Herrmann, J. Plank, M.L. Ziegler and B. Balbach, J. Am. Chem. Soc., 102(1980)5906.
72 L.S. Liebeskind, S.R. Baysdon, M.S. South and J.F. Blount, J. Organometal. Chem., 202(1980)C73.
73 L.S. Liebeskind, S.R. Baysdon and M.S. South, J. Am. Chem. Soc., 102(1980)7397.
74 Y. Wakatsuki, O. Nomura, H. Tone and H. Yamazaki, J. Chem. Soc. Perkin Trans. II, (1980)1344.
75 K. Yasufuku, A. Hamada, K. Aoki and H. Yamazaki, J. Am. Chem. Soc., 102(1980)4363.
76 Y. Wakatsuki and H. Yamazaki, J. Chem. Soc. Chem. Commun., (1980)1270.
77 E.R. Evitt and R.G. Bergman, J. Am. Chem. Soc., 102(1980)7003.
78 K.H. Theopold and R.G. Bergman, J. Am. Chem. Soc., 102(1980)5694.

79 P. Diversi, G. Ingrosso, A. Lucherini, W. Porzio and M. Zocchi, Inorg. Chem., 19(1980)3590.

80 T.H. Johnson and T.F. Baldwin, J. Org. Chem. 45(1980)140.

81 K. von Deuten and L. Dahlenburg, Transition Met. Chem. (Weinheim, Ger.), 5(1980)222 (Chem. Abstr., 93(1980)186539f).

82 S.A. Bezman, P.H. Bird, A.R. Fraser and J.A. Osborn, Inorg. Chem., 19(1980)3755.

83 J.D. Cotton and G.T. Crisp, J. Organometal. Chem., 186(1980)137.

84 M.R. Ashcroft, A. Bury, C.R. Cooksey, A.G. Davies, B.D. Gupta, M.D. Johnson and H. Morriss, J. Organometal. Chem., 195(1980)89.

85 M.P. Atkins, B.T. Golding, A. Bury, M.D. Johnson and P.J. Sellars, J. Am. Chem. Soc., 102(1980)3630.

86 M.R. Ashcroft, B.D. Gupta and M.D. Johnson, J. Chem. Soc. Perkin Trans. I. (1980) 2021.

87 M. Tada, H. Shinozaki and K. Miura, Bull. Soc. Chem. Jpn., 53(1980) 287.

88 T.Saito, Y. Tsurita and Y. Sasaki, Inorg. Chem., 19(1980)2365.

89 Y. Tsurita, T. Saito and Y. Sasaki, J. Organometal. Chem., 202(1980)91.

90 T. Saito, H. Urabe and Y. Sasaki, Transition Met. Chem. (Weinheim, Ger.), 5(1980)35 (Chem. Abstr., 92(1980)172835s).

91 G. Cros, M.H. Darbieu and J.-P. Laurent, Inorg. Nucl. Chem. Lett., 16(1980)349.

92 H. Sugimoto, M. Nagano, Z. Yoshida and H. Ogoshi, Chem. Lett., (1980)521.

93 H.J. Callot and E. Schaeffer, J. Organometal. Chem., 193(1980)111.

94 J. Deniau and A. Gaudemer, J. Organometal. Chem., 191(1980)C1.

95 B.T. Golding, C.S. Sell and P.J. Sellars, J. Chem. Soc. Perkin Trans. II, (1980)961.

96 K.L. Brown and R.K. Hessley, Inorg. Chem., 19(1980)2410.

97 V.D. Ghanekar and R.E. Coffman, J. Organometal. Chem., 198(1980)C15

98 R.G. Finke and W. McKenna, J. Chem. Soc. Chem. Commun., (1980)460.

99a H.J. Callot and E. Schaeffer, Nouv. J. Chim., 4(1980)307.

99b H.J. Callot and E. Schaeffer, Nouv. J. Chim., 4(1980)311.

100 H.J. Callot and E. Schaeffer, Tetrahedron Lett., 21 (1980)1335.

101 N.W. Alcock, M.P. Atkins, E. H. Curzon, B.T. Goldring and P.J. Sellars, J. Chem. Soc. Chem. Commun., (1980)1238.

102 G. Tauzher, R. Dreos, G. Costa and M. Green, Inorg. Chem., 19(1980) 3790.

103 K.L. Brown and A.W. Awtry, J. Organometal. Chem., 195(1980)113.

104 J.F. Endicott, K.P. Balakrishnan and C.-L. Wong, J. Am. Chem. Soc., 102(1980)5519.

105 R.W. Hay, P.R. Norman and F. McLaren, Inorg. Chim. Acta, 44(1980) L125.

106 A. Puxeddu, G. Costa and N. Marsich, J. Chem. Soc. Dalton Trans., (1980)1489.

107 R. Scheffold, M. Dike, S. Dike, T. Herold and L. Walder, J. Am. Chem. Soc., 102(1980)3642.

108 R.G. Finke, B.L. Smith, M.W. Droege, C.M. Elliott and E. Hershenhart, J. Organometal. Chem., 202(1980)C25.

109 Y. Yurakami, Y. Aoyama and K. Tokunaga, J. Am. Chem. Soc., 102(1980)6736.

110 L. Randaccio, N. Bresciani-Pahor, P.J. Toscano and L.G. Marzilli, J. Am. Chem. Soc., 102(1980)7372.

111a S.M. Chemaly and J.M. Pratt, J. Chem. Soc. Dalton Trans., (1980) 2259.

111b S.M. Chemaly and J.M. Pratt, J. Chem. Soc. Dalton Trans., (1980) 2267.

111c S.M. Chemaly and J.M. Pratt, J. Chem. Soc. Dalton Trans., (1980) 2274.

112 J.S. Krouwer, B. Holmquist, R.S. Kipnes and B.M. Babior, Biochem. Biophys. Acta, 612(1980)153.
113 Y. Murakami, Adv. Chem. Ser., 191(1980)179.
114 T. Ramasami and J.H. Espenson, Inorg. Chem., 19(1980)1846.
115 H. Ogoshi, J.-I. Setsune and Z.-I. Yoshida, J. Organometal. Chem., 185(1980)95.
116 J. Setsune, T. Yazawa, H. Ogoshi and Z. Yoshida, J. Chem. Soc. Perkin Trans. I, (1980)1641.
117 B. Dresow, G. Schlingermann, L. Ernst, W.S. Sheldrick and V.B. Koppenhagen, Liebigs Ann. Chem., (1980)1699.
118 A.L. Poznyak and V.V. Pansevich, Vestsi Akad. Nauk. BSSR, Ser. Khim. Navuk (1980)18 (Chem. Abstr., 92(1980)198517q).
119 R.C. Brady III and R. Pettit, J. Am. Chem. Soc., 102(1980)6181.
120 H. Dumas, J. Levisalles and H. Rudler, J. Organometal. Chem., 187(1980)405.
121 P.B. Hitchcock, M. F. Lappert, P. Terreros and K.P. Wainwright, J. Chem. Soc. Chem. Commun., (1980)1180.
122 W.E. Carroll, M. Green, A.M.R. Galas, M. Murray, T.W. Turner, A.J. Welch and P. Woodward, J. Chem. Soc. Chem. Commun., (1980)80.
123 M.O. Albers, N.J. Coleville, T.V. Ashworth, E. Singleton and H.E. Swanepoel, J. Chem. Soc. Chem. Commun., (1980)489.
124 C.A.L. Becker, Inorg. Nucl. Chem. Lett., 16 (1980)297.
125 C.A.L. Becker, J. Inorg. Nucl. Chem., 42(1980)27.
126 J. Hanzlik, G. Albertin, E. Bordignon and A.A. Orio, Inorg. Chim. Acta, 38(1980)207.
127 J.A.S. Howell and M. Berry, J. Chem. Soc. Chem. Commun., (1980) 1039.
128 R. Kuwae and T. Tanaka, Bull. Chem. Soc. Jpn., 53(1980)118.
129 J.T. Mague and S.H. DeVries, Inorg. Chem., 19(1980)3743.
130 A. Efrati, I. Feinstein, L. Wackerle and F. Frolow, Angew. Chem. Int. Ed. Engl., 19(1980)633.
131 A. Efrati, I. Feinstein, L. Wackerle and F. Frolow, J. Am. Chem. Soc., 102(1980)6341.
132 A. Efrati, I. Feinstein, F. Frolow and A. Goldman, J. Chem. Soc. Chem. Commun., (1980)864.
133 K.R. Mann, J.A. Thich, R.A. Bell, C.L. Coyle and H.B. Gray, Inorg. Chem., 19(1980) 2462.
134 I.S. Siegal, K. R. Mann and H.B. Gray, J. Am. Chem. Soc., 102(1980)7252.
135 K.R. Mann, M.J. DiPierro and T.P. Gill, J. Am. Chem. Soc., 102(1980)3965.
136 S.J. Milder, R.A. Goldbeck, D.S. Kliger and H.B. Gray, J. Am. Chem. Soc., 102(1980)6761.
137 L.H. Staal, P. Bosma and K. Vrieze, Inorg. Chim. Acta, 43(1980)125.
138 A. Chaloyard, N. ElMurr and R.B. King, J. Organometal. Chem., 188(1980)C13.
139 M. Absi-Halabi, J.D. Atwood, N.P. Forbus and T.L. Brown, J. Am. Chem. Soc., 102(1980)6248.
140 N.P. Forbus, R. Oteiza, S.G. Smith and T.L. Brown, J. Organometal. Chem., 193(1980)C71.
141 S. Hayashida, T. Kawamura and T. Yonezawa, Chem. Lett., (1980) 517.
142 V.A. Volkov, N.S. Imyatinov and B.E. Kuvaev, Zh. Prikl, Khim. (Leningrad), 53(1980)1691 (Chem. Abstr., 93(1980)142202m).
143 V.B. Del'nik, M.G. Katsenel'son, A.V. Nogin and B.P. Tarasov, Neftekhimiya, 20(1980)738(Chem. Abstr., 93(1980)249278t).
144 G. Bor and U.K. Dietler, J. Organometal. Chem., 191(1980)295.
145 R.L. Sweany, Inorg. Chem., 19(1980)3512.

146 R.W. Wegman and T.L. Brown, J. Am. Chem. Soc., 102(1980)2494.
147 F. Ungváry and L. Markó, J. Organometal. Chem., 193(1980)383.
148 J.A. Roth and M. Orchin, J. Organometal. Chem., 187(1980)103.
149 W. Edgell and S. Chanjamsri, J. Am. Chem. Soc., 102(1980)147.
150 F. Ungváry, A. Sisak and L. Markó, J. Organometal. Chem., 188(1980)373.
151 F. Ungváry and L. Markó, J. Organometal. Chem., 193(1980)379.
152 H. des Abbeyes and A. Buloup, J. Organometal. Chem., 198(1980)C36.
153 S. Gambarotta and H. Alper, J. Organometal. Chem., 194(1980)C19.
154 T.A. Nalesnik and M. Orchin, J. Organometal. Chem., 199(1980)265.
155 H.M. Feder and J.W. Rathke, Ann. N.Y.Acad. Sci., 333(1980)45.
156 W.R. Pretzer and T.P. Kobylinski, Ann. N.Y. Acad. Sci., 333(1980)58.
157 R.J. Daroda, J.R. Blackborow and G. Wilkinson, J. Chem. Soc. Chem. Commun., (1980)1098.
158 G. LeCoustumer and Y. Mollier, J. Chem. Soc. Chem. Commun., (1980)38.
159 G.K. Magomedov, O.V. Schkol'nik, B.A. Izmailov and S.A. Sigachev, Koord, Khim., 6(1980)761 (Chem. Abstr., 93(1980)131703z).
160 G.K.-I. Magomedov and O.V. Schkol'nik, Zh. Obshch. Khim., 50(1980)1103.
161 K. Murata and A. Matsuda, Chem. Lett., (1980)11.
162 K. Murata and A. Matsuda, Bull. Chem. Soc. Jpn., 53(1980)214.
163 B.D. El-Issa and A. Hinchcliffe, J. Mol. Struct., 69(1980)305 (Chem. Abstr., 94(1980)53312a).
164 H. van Dam, D.J. Stufkins, A. Oskram, M. Doran and I.H. Hillier, J. Electron Spectrosc. Relat. Phenom., 21(1980)47 (Chem. Abstr., 93(1980)228170m).
165 J.A. Kouba, J.L. Pierce and R. A. Walton, J. Organometal. Chem., 202(1980)C105.
166 V.G. Albano, P. Chini, G. Ciani, M. Sansoni and S. Martinengo, J. Chem. Soc. Dalton Trans., (1980)163.
167 D.J. Darensbourg and M.J. Incorvia,Inorg. Chem., 19(1980)2585.
168a G. Longoni, S. Campanella, A. Ceriotti, P. Chini, V.G. Albano and D. Braga, J. Chem. Soc. Dalton Trans., (1980)1816.
168b V.G. Albano, D. Braga, G. Longoni, S. Campanella, A. Ceriotti and P. Chini, J. Chem. Soc. Dalton Trans., (1980)1820.
169 H.N. Adams, G. Fachinetti and J. Strahle, Angew. Chem. Int. Ed. Engl., 19(1980)404.
170 R.C. Ryan, C.U. Pittman, Jr., J.P. O'Connor and L.F. Dahl, J. Organometal. Chem., 193(1980)247.
171 C.U. Pittman, Jr., G.M. Wilemon, W.D. Wilson and R.C. Ryan, Angew. Chem. Int. Ed. Engl., 19(1980)478.
172 V.G. Albano, D. Braga, S. Martinengo, P. Chini, M. Sansoni and D. Strumolo, J. Chem. Soc. Dalton Trans., (1980)52.
173 A. Fumagalli, T.F. Koetzle, F. Takusagawa, P. Chini, S. Martinengo and B.T. Heaton, J. Am. Chem. Soc., 102(1980)1740.
174 J.L. Vidal and W.E. Walker, Inorg. Chem., 19(1980)896.
175 G. Ciani, A. Sironi and S. Martinengo, J. Organometal. Chem., 192(1980)C42.
176 B.T. Heaton, C. Brown, D.O. Smith, L. Strona, R.J. Goodfellow, P. Chini and S. Martinengo, J. Am. Chem. Soc., 102(1980)6175.
177 S. Martinengo, G. Ciani and A. Sironi, J. Chem. Soc. Chem. Commun., (1980)1140.
178 S. Martinengo, G. Ciani and A. Sironi, J. Am. Chem. Soc., 102(1980)7564.
179 O.A. Gansow, D.S. Gill, F. J. Bennis, J.R. Hutchinson, J.L. Vidal and R.C. Schoening, J. Am. Chem. Soc., 102(1980)2449.
180 B.T. Heaton, L. Longhetti, L. Garleschelli and U. Sartorelli, J. Organometal. Chem., 192(1980)431.

181 F. Demartin, M. Manassero, M. Sansoni, L. Garleschelli, S. Martinengo and F. Canziani, J. Chem. Soc. Chem. Commun., (1980)903.

182 A.V. Romanenko, A.P. Shepelin, V.F. Zaikovskii, P.A. Zadin, L.M. Plyasova, V.L. Kuznetsov and Yu.I. Exmakov, Katalizatory, Soderzhasheh. Nansen. Komplexsky, Materialy Simpoz, Tashkent 1980 Novosibirsk, (1980)85 (Chem. Abstr., 94(1981)20947h).

183 E.W. Thornton, H. Knözinger, B. Tesche, J.J. Rafalko and B.C. Gates, J. Catal., 62(1980)117.

184 J.L. Bilhou, V. Bilhou-Bougnol, W.F. Graydon, J.M. Basset and A.K. Smith, J. Mol. Catal., 8(1980)411 (Chem. Abstr., 94(1981) 53511y).

185 T. Castullo, H. Knözinger, J. Lieto and M. Wolf., Inorg. Chim. Acta, 44(1980)L239.

186 Z. Otero-Schipper, J. Lieto, J.J. Rafalko and B.C. Gates, Stud. Surf. Sci. Catal., 4(1980)535(Chem. Abstr., 93(1980)238307a.

187 J. Lieto, J.J. Rafalko and B.C. Gates, J. Catal., 62(1980)149.

188 D. Vanhove, L. Makambo and M. Blanchard, J. Chem. Res. Synop., (1980)335.

189 A.L. Lapidus, A. Yu. Krylova and L.T. Kondrat'ev, Izv. Akad. Nauk SSSR, Ser. Khim., (1980)1432 (Chem. Abstr., 93(1980)167519h).

190 A.S. Lisitsyn, V.L. Kuznetsov and Y.-U. Yermakov, React. Kinet. Catal. Lett., 14(1980)445 (Chem. Abstr., 94(1981)72713x).

191 D. Fraenkel and B.C. Gates, J. Am. Chem. Soc., 102(1980)2478.

192 M. Premet and E. Garbowski, Chem. Phys. Lett., 72(1980)472.

193 E. Guglielminotti, A. Zecchina, F. Boccuzzi and E. Borello, Stud. Surf. Sci. Catal., 4(1980)165 (Chem. Abstr., 93(1980)101845e).

194 A.S. Lisitsyn, V.L. Kuznetsov, E.K. Mamaeva and Yu.I. Ermakov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1980)124 (Chem. Abstr., 93(1980)60185u).

195 R. Psaro, A. Fusi, R. Ugo, J.M. Basset, A.K. Smith, and F. Hugues, J. Mol. Catal., 7(1980)511.

196 A. Brenner and D.A. Hucul, J. Am. Chem. Soc., 102(1980)2484.

197 K.L. Walters, R.F. Howe, T.P. Chojnacki, C.-M. Fu, R.L. Schneider and N.-B. Wong, J. Catal., 66(1980)424.

198 A. Theolier, A.K. Smith, M. Leconte, J.M. Basset, G.M. Zanderighi, R. Psaro and R. Ugo, J. Organometal. Chem., 191(1980)415.

199 K. Kaneda, M. Hiraki, K. Sano, I. Toshinobu and T. Shiichiro, J. Mol. Catal., 9(1980)227 (Chem. Abstr., 94(1981)53521t).

200 E.C. Baker, D.E. Hendrickson and R. Eisenberg, J. Am. Chem. Soc., 102(1980)1020.

201 T. Cole, R. Ramage, K. Cann and R. Pettit, J. Am. Chem. Soc., 102(1980)6182.

202 M.K. Dickson, B.P. Sudha and D. M. Roundhill, J. Organometal. Chem., 190(1980)C43.

203 D.M. Roundhill, M.K. Dickson, N.S. Dixit and B.P. Sudha-Dixit, J. Am. Chem. Soc., 102(1980)5538.

204 R.M. Laine, Ann. N.Y. Acad. Sci., 333(1980)124.

205 P. Hong, B.-R. Cho and H. Yamazaki, Chem. Lett., (1980)507.

206 T. Mise, P. Hong and H. Yamazaki, Chem. Lett., (1980)439.

207 Y. Shvo and R.M. Laine, J. Chem. Soc. Chem. Commun., (1980)753.

208 P.L. Stanghellini, G. Gervasio, R. Rossetti and G. Bor, J. Organometal. Chem., 187(1980)C37.

209 B.L. Booth, G.C. Casey and R.N. Haszeldine, J. Chem. Soc. Dalton Trans., (1980)403.

210 D. Seyferth and C.N. Rudie, J. Organometal. Chem., 184(1980)365.

211 D. Seyferth, C.N. Rudie, J.S. Merola and D.H. Berry, J. Organometal. Chem., 187(1980)91.

212 D. Seyferth and H.P. Withers, Jr., J. Organometal. Chem., 188(1980)329.

213 M. Murata and A. Matsuda, Nippon Kagaku Kaishi, (1980)1077 (Chem. Abstr., 93(1980)185443h).
214 W. Kruppa and G. Schmid, J. Organometal.Chem., 202(1980)379.
215 S.C. Avanzino, A.A. Baake, H.-W. Chen, C. J. Donahue, W.L. Jolly, T.-H. Lee and A.J. Ricco, Inorg. Chem., 19(1980)1931.
216 J. Evans, J. Chem. Soc. Dalton Trans., (1980)1005.
217 G. Ciani and A. Sironi, J. Organometal. Chem., 197(1980)233.
218 V. Bellagamba, R. Ercoli, A. Gamba and G.B. Suffriti, J. Organometal. Chem., 190(1980)381.
219 R.E. Benfield and B.F.G. Johnson, J. Chem. Soc. Dalton Trans., (1980)1743.
220 I.A. Oxton, Inorg. Chem., 19(1980)2825.
221 C.L. Reichel and M.S. Wrighton, Inorg. Chem., 19(1980)3858.
222 R.N. Haszeldine, A.P. Mather and R.V. Parish, J. Chem. Soc. Dalton Trans., (1980)923.
223 M. Gielen, I. Vanden Eynde, F. Polet, J. Meunier-Piret and M. Van Meerssche, Bull. Soc. Chim. Belg., 89(1980)915.
224 M. Gielen and I. Vanden Eynde, Isr. J. Chem., 20(1980)93 (Chem. Abstr., 93(1980)239549t).
225 F.S. Wong and K.M. Mackay, J. Chem. Res. Synop., (1980)109.
226 A.A. Arduini, A.A. Baksoun, J.A. Osborn and C. Voelker, Angew. Chem. Int. Ed. Engl., 19(1980)1024.
227 P.C. Steinhardt, W.L. Gladfelter, A.D. Harley, J.R. Fox and G.L. Geoffroy, Inorg. Chem., 19(1980)332.
228 E.W. Burckhardt and G.L. Geoffroy, J. Organometal. Chem., 198(1980)179.
229 W.L. Gladfelter, G.L. Geoffroy and I. C. Calabrese, Inorg. Chem., 19(1980)2569.
230 J.R. Fox, W.L. Gladfelter and G.L. Geoffroy, Inorg. Chem., 19(1980)2574.
231 K.S. Wong and J.A. Labinger, J. Am. Chem. Soc., 102(1980)3652.
232 J.S. Plotkin, D.G. Alway, C.R. Weisenberger and S.G. Shore, J. Am. Chem. Soc., 102(1980)6156.
233 M. Pfeffer, J. Fischer, A. Mitchler and L. Ricard, J. Am. Chem. Soc., 102(1980)6338.
234 P. Lemoine, A. Giraudeau, M. Gross and P. Braunstein, J. Chem. Soc. Chem. Commun., (1980)77.
235 A. Giraudeau, P. Lemoine, M. Gross and P. Braunstein, J. Organometal. Chem., 202(1980)455.
236 M. Moll, H. Behrens, P. Merbach, K. Görting, G. Liehr and R. Bohme, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 35B(1980)1115.
237 D. Labroue, R. Queau and R. Poilblanc, J. Organometal. Chem., 186(1980)101.
238 N.M. Boag, M. Green, R.M. Mills, G.N. Pain, F.G.A. Stone and P. Woodward, J. Chem. Soc. Chem. Commun., (1980)1171.
239 M. Chetcuti, M. Green, J.A.K. Howard, J.C. Jeffrey, R.M. Mills, G.N. Pain, S.J. Porter, F.G.A. Stone, A.A. Wilson and P. Woodward, J. Chem. Soc. Chem. Commun., (1980)1057.
240 J.P. Farr, M.M. Olmstead and A.L. Balch, J. Am. Chem. Soc., 102(1980)6654.
241 M. Tachikawa, A.C. Sievert, E.L. Muetterties, M.R. Thompson, C.S. Day and V. Day, J. Am. Chem. Soc., 102(1980)1726.
242 J.C.T.R. Burckett-St. Laurent, R.J. Haines, C.R. Nolte and N.D.C.T. Steen, Inorg. Chem., 19(1980)577.
243 A. Fumagelli, G. Longoni, P. Chini, A. Albinati and S. Bruckner, J. Organometal. Chem., 202(1980)329.
244 H.J. Langenbach and H. Vahrenkamp, Chem. Ber., 113(1980)2189.
245 H.J. Langenbach, E. Keller and H. Vahrenkamp, J. Organometal. Chem., 191(1980)95.

246 H.J. Langenbach and H. Vahrenkamp, J. Organometal. Chem., 191(1980)391.
247 H.J. Langenbach, E. Röttenger and H. Vahrenkamp, Chem. Ber., 113(1980)42.
248 F. Richter and H. Vahrenkamp, Angew. Chem. Int. Ed. Engl., 19(1980)65.
249 E. Rottinger, A. Trenkle, R. Muller and H. Vahrenkamp, Chem. Ber., 113(1980)1280.
250 J. Večerník, J. Maček and A. Vlček, Collect. Czech. Chem. Commun., 45(1980)1468.
251 S.N. Blackburn, R.N. Haszeldine, R.V. Parish and J.H. Setchfield, J. Chem. Res. Synop., (1980)170.
252 S.N. Blackburn, R.N. Haszeldine, R.V. Parish and J.H. Setchfield, J. Organometal. Chem., 192(1980)329.
253 H. Nishihara, T. Mori, T. Saito and Y. Sasaki, Chem. Lett., (1980) 667.
254 D.H. Harris and T.R. Spalding, Inorg. Chim. Acta, 39(1980)187.
255 C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, Inorg. Chem., 19(1980)2968.
256 C.A. Ghilardi, S. Midollini, and L. Sacconi, J. Organometal. Chem., 186(1980)279.
257 C.A. Ghilardi, C. Mealli, S. Midollini, V.I. Nefedov, A. Orlandini and L. Sacconi, Inorg. Chem., 19(1980)2454.
258 C.A. Ghilardi, S. Midollini, A. Orlandini and L. Sacconi, Inorg. Chem., 19(1980)301.
259 C. Mealli, S. Midollini, S. Moneti and L. Sacconi, Cryst. Struct. Commun., 9(1980)1017 (Chem. Abstr., 94(1981)75027p).
260 D.H.M.W. Thewissen, J. Organometal. Chem., 188(1980)211.
261 D.H.M.W. Thewissen, H.P.M.M. Ambrosius, H.L.M. van Goal and J.J. Steggerda, J. Organometal. Chem., 192(1980)101.
262 D.H.M.W. Thewissen, J. Organometal. Chem., 192(1980)115.
263 E.W. Abel and S.J. Skittrall, J. Organometal. Chem., 193(1980)389.
264 F. Porta, S. Cenini, P. Del Buttero and S. Maiorana, J. Organometal. Chem., 194(1980)211.
265 T.L. Hall, M.F. Lappert and P.W. Lednor, J. Chem. Soc. Dalton Trans., (1980)1448.
266 A. Mayanza, J.-J. Bonnet, J. Galy, P. Kalck and R. Poilblanc, J. Chem. Res. Synop., (1980)146.
267 H. Schumann, G. Cielusek and J. Pickardt, Angew. Chem. Int. Ed. Engl., 19(1980)70.
268 S. Datta, K.K. Pandey and U.C. Agarwala, Inorg. Chim. Acta, 40(1980)65.
269 H. Behrens, J. Ellermann and E.F. Hohenberger, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 35B(1980)661.
270 K. Goswami and M.M. Singh, Transition Met. Chem. (Weinheim, Ger.), 5(1980)83 (Chem. Abstr., 92(1980)225836b).
271 D.P. Dutta and M.M. Singh, Transition Met. Chem. (Weinheim, Ger.), 5(1980)244 (Chem. Abstr., 93(1980)160449b).
272 D.P. Dutta and M.M. Singh, Synth. React. Inorg. Met. Org. Chem., 10(1980)553 (Chem. Abstr. 94(1981)24216s).
273 J.G. Leipoldt, L.D.C. Bok, S.S. Bosson and H. Meyer, Inorg. Chim. Acta, 42(1980)105.
274 W.K. Dean, J. Organometal. Chem., 190(1980)353.
275 S.A. Gardner, J. Organometal. Chem., 190(1980)289.
276 A.J. Deeming and I.P. Rothwell, J. Chem. Soc. Dalton Trans., (1980)1259.
277 A.J. Deeming, I.P. Rothwell, M.B. Hursthouse and K.M.A. Malik, J. Chem. Soc. Dalton Trans., (1980)1974.
278 H.D. Empsall, S. Johnson and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1980)302.

279 K. Kurtev, D. Ribola, R.A. Jones, D.J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc. Dalton Trans., (1980)55.

280 K. Wajda, F. Pruchnik and T. Lis, Inorg. Chim. Acta, 40(1980)207.

281 D. Dowerah and M.M. Singh, J. Indian Chem. Soc., 57(1980)368.

282 F. Jumeau, J. Indian Chem. Soc., 57(1980)312.

283 P. Lahuerta, R. Uson, D. Carmona and L.A. Oro, Transition Met. Chem. (Weinheim, Ger.), 5(1980)327 (Chem. Abstr., 94(1981)65822e).

284 M.M. TaquiKhan, R. Mohuiddin and M. Ahmed, J. Coord. Chem., 10(1980)1.

285 B.R. James and D. Mahajan, Can. J. Chem., 58(1980)996.

286 L.H. Pignolet, D.H. Doughty, S.C. Nowicki and A.L. Casalnuevo, Inorg. Chem., 19(1980)2172.

287 L.H. Pignolet, D.H. Doughty, S.C. Nowicki, M.P. Anderson and A.L. Casalneuvo, J. Organometal. Chem., 202(1980)211.

288 G. Baliman, L.M. Venanzi, F. Bachechi and L. Zambonelli, Helv. Chim. Acta, 63(1980)420.

289 P.G. Eller and R.R. Ryan, Inorg. Chem., 19(1980)142.

290 T. Yoshida, T. Okano and S. Otsuka, J. Am. Chem. Soc., 102(1980) 5966.

291 G.M. Intille, Inorg. Chem., 11(1972)695.

292 R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse and K.M.A. Malik, J. Chem. Soc. Dalton Trans., (1980)511.

293 A.D. Harris and S.D. Robinson, Inorg. Chim. Acta, 42(1980)25.

294 J.A. Sofranko, R. Eisenberg and J.A. Kampmeier, J. Am. Chem. Soc., 102(1980)1163.

295 M.T. Atlay, L.R. Gahan, K. Kite, K. Moss and G. Read. J. Mol. Catal., 7(1980)31 (Chem. Abstr., 94(1981)75964s).

296 J. Plank, D. Riedel and W.A. Herrmann, Angew. Chem. Int. Ed. Engl., 19(1980)937.

297 W.A. Herrmann, J. Plank and D. Riedel, J. Organometal. Chem., 190(1980)C47.

298 M. Cowie and S.K. Dwight, J. Organometal. Chem., 198(1980)C20.

299 M. Cowie and S. K. Dwight, Inorg. Chem., 19(1980)209.

300 M. Cowie and S.K. Dwight, Inorg. Chem., 19(1980)2500.

301 F. Pruchnik and K. Wajda, Inorg. Chim. Acta, 40(1980)203.

302 C.P. Kubiak and R. Eisenberg, Inorg. Chem., 19(1980)2726.

303 C.P. Kubiak and R. Eisenberg, J. Am. Chem. Soc., 102(1980)3637.

304 C.P. Kubiak, C. Woodcock and R. Eisenberg, Inorg. Chem., 19(1980)2733.

305 J. Ellermann, E.F. Hohenberger, W. Kehr, A. Purzer and G. Thiele, Z. Anorg. Allg. Chem., 464(1980)45.

306 P.E. Kreter, Jr. D.W. Meek and G.G. Christoph, J. Organometal. Chem., 188(1980)C27.

307 E. Billig, J.D. Jamerson and R.L. Pruett, J. Organometal. Chem., 192(1980)C49.

308 J.D. Jamerson, R.L. Pruett, E. Billig and F.A. Fiato, J. Organometal. Chem., 193(1980)C43.

309 R.J. Haines, N.D.C.T. Steen, M. Laing and P. Sommerville, J. Organometal. Chem., 198(1980)C72.

310 S. May, P. Reinsalu and J. Powell, Inorg. Chem., 19(1980)1582.

311 T. Nishiguchi, K. Tanaka and K. Fukuzumi, J. Organometal. Chem., 193(1980)37.

312 P. Kalck, R.Poilblanc, R.P. Martin, A. Rovera and A. Gaset, J. Organometal. Chem., 195(1980)C9.

313 J.R. Knifton, J. Organometal. Chem., 188(1980)223.

314 H. Alper, K. Hachem and S. Gambarotta, Can. J. Chem., 58(1980) 1599.

315 S.S. Novikov, V.I. Manov-Yuvenskii, A.V. Smetanin and B.K. Nefedov, Dokl. Akad. Nauk SSSR, 25(1980)371.

316 V.I. Manov-Yuvenskii, A.V. Smetanin and B.K. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1980)2556 (Chem. Abstr., 94(1981)83245y).

317 V.I. Manov-Yuvenskii, A.V. Smetanin, B.K. Nefedov and A.L. Chimishkyan, Kinet. Katal., 21(1980)1335(Chem. Abstr., 94 (1981)29833s).

318 L.V. Gorbunova, I.L. Knyazeva, E.A. Davydova and G.A. Abakumov, Izv. Akad. Nauk SSSR, Ser. Khim., (1980)1054.

319 M. Polievka, L. Uhlar and V. Macho, Petrochemia, 20(1980)33 (Chem. Abstr., 93(1980)238160x).

320 P. Cavalieri d'Oro, L. Raimondi, G. Pagani, G. Montrasi, G. Gregorio and A. Andreetta, Chem. Ind. (Milan), 62(1980)572 (Chem. Abstr., 94(1981)46710a).

321 G. Gregorio, G. Montrasi, M. Tampieri, P. Cavalieri d'Oro, G. Pagani and A. Andreetta, Chem. Ind. (Milan), 62(1980)389 (Chem. Abstr., 94(1981)30122z).

322 R.B. King, A.D. King, Jr., M.Z. Iqbal and K. Tanaka, Ann. N.Y. Acad. Sci., 333(1980)74.

323 C.U. Pittman, Jr. W.D. Honnick and J.J. Yang, J. Org. Chem., 45(1980)684.

324 C.U. Pittman, Jr. and W.D. Honnick, J. Org. Chem., 45(1980)2132.

325 M. Hidai, M. Orisaku and Y. Ichida, Chem. Lett., (1980)753.

326 V.B. Pukhnarevich, L.I. Kopylova, M. Čapka, J. Hetflejš, E.N. Satsuk, M.V. Sigalov, V. Chvalovsky and M.G. Voronko, Zh. Obshch. Khim., 50(1980)1554.

327 Yu. N. Kukushkin, N.P. Fedyanin, A.I. Mokhov and L.I. Danilina, Zh. Neorg. Khim., 25(1980)784.

328 S.N. Bhattarcharya, C.V. Senoff and F.S. Walker, Inorg. Chim. Acta, 44(1980)L273.

329 P.N.A. Seth, A.E. Underhill and D.M. Watkins, Inorg. Nucl. Chem. Lett., 16(1980)1.

330 N.N. Greenwood, J.D. Kennedy and D. Reed, J. Chem. Soc. Dalton Trans., (1980)196.

331 J.J. Bonnet, P. Kalck and R. Poilblanc, Angew. Chem. Int. Ed. Engl., 19(1980)551.

332 D. de Montauzon, P. Kalck and R. Poilblanc, J. Organometal Chem., 186(1980)121.

333 A.L. Balch and J.R. Yow, J. Am. Chem. Soc., 102(1980)1448.

334 D.M. Roundhill, R.A. Bechtold and S.G.N. Roundhill, Inorg. Chem., 19(1980)284.

335 A.R. Pinhas, T.A. Albright, P. Hofmann and R. Hoffmann, Helv. Chim. Acta, 63(1980)29.

336 C. Brown, B.T. Heaton, L. Longhetti, W. T. Povey and D.O. Smith, J. Organometal. Chem., 192(1980)93.

337 J.F. Nixon, R.J. Suffolk, M.J. Taylor, J.G. Norman, Jr., D.E. Hoskins and D.J. Gmur, Inorg. Chem., 19(1980)810.

338 A.K. Baev, Zh. Fiz. Khim., 54(1980)1 (Chem. Abstr., 93(1980) 121227h).

339 V. Schurig, Chromatographia, 13(1980)263 (Chem. Abstr., 93(1980)88156j).

340 G. Yoneda and D.M. Blake, J. Organometal. Chem., 190(1980)C71.

341a Z.C. Brzezinska and W.R. Cullen, Can. J. Chem., 58(1980)744.

341b Z.C. Brzezinska and W.R. Cullen, Can. J. Chem., 58(1980)750.

342 Yu.I. Ermakov, B.N. Kuznetsov and E.M. Chelganov, React. Kinet. Katal. Lett., 14(1980)37 (Chem. Abstr., 93(1980)238371s).

343 J. Hjortkjaer, M.S. Scurrell and P. Simonsen, J. Mol. Catal., 10(1980)127 (Chem. Abstr., 94(1981)83544v).

344 G. Albertin, E. Bordignon, L. Canovese and A.A. Orio, Inorg. Chim. Acta, 38(1980)77.

345 R. Seeber, G.A. Mazzocchin, G. Albertin and E. Bordignon, J. Chem. Soc. Dalton Trans., (1980)979.

346 B.W. Hames, P. Legzdins and J.C. Oxley, Inorg. Chem.. 19(1980) 1565.

347 H. Schumann and M. Meissner, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 35B(1980)594.

348 H. Schumann, M. Meissner and H.-J. Kroth, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 35B(1980)639.

349 J.R. Morton, K.F. Preston and S.J. Strach, J. Phys. Chem., 84(1980)2478.

350 P. Brant and R.D. Feltham, Inorg. Chem., 19(1980)2673.

351 K. Tsuji, H. Fujitsu, K. Takeshita and I. Mochida, J. Mol. Catal., 9(1980)389 (Chem. Abstr., 99(1981)37037j).

352 K.K. Pandey and U.C. Agarwala, J. Inorg. Nucl. Chem., 42(1980)293.

353 K.K. Pandey and U.C. Agarwala, Indian J. Chem., Sect. A, 19A(1980) 805 (Chem. Abstr., 94(1981)24258g).

354 T.J. Mazanec, K.D. Tau and D.W. Meek, Inorg. Chem., 19(1980)85.

355 D.W. Meek, T.J. Mazanec, and K.D. Tau, Ann. N.Y. Acad. Sci., 333(1980)141.

356 W.B. Shorthill, R.M. Buchanan, C.G. Pierpont, M. Ghedini and G. Dolcetti, Inorg. Chem., 19(1980)1803.

357 W.E. Carroll, F.A. Deeney and E.J.Lalor, J. Organometal. Chem. 198(1980)189.

358 K.D. Schram, T.H. Tulip and J.A. Ibers, Inorg. Chem., 19(1980) 3183.

359 K.D. Schram and J.A. Ibers, Inorg. Chem., 19(1980)2435.

360 K.D. Schram and J.A. Ibers, Inorg. Chem., 19(1980)1231.

361 M. Angoletta and G. Caglio, J. Organometal. Chem., 185(1980)105.

362 P.-I. van Vliet, M. Kokkes, G. van Koten and K. Vrieze, J. Organometal. Chem., 187(1980)413.

363. H.-F.Klein, J. Gross, J.M. Basset and U. Schubert, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 35B(1980)614.

364 H.-F. Klein, R. Hammer, J. Gross and U. Schubert, Angew. Chem. Int. Ed. Engl., 19(1980)809.

365 G.E. Herberich, B. Hessner, S. Beswetherick, J.A. Howard and P. Woodward, J. Organometal. Chem., 192(1980)421.

366 C. Bianchi, P. Dapporto, A. Meli and L. Sacconi, J. Organometal. Chem., 193(1980)117.

367 D.L. Reger and A. Gabrielli, J. Organometal. Chem., 187(1980) 243.

368 M. Bottrill, M. Green, E. O'Brien, L.E. Smart and P. Woodward, J. Chem. Soc. Dalton Trans., (1980)292.

369 H. Nishihara, M. Fujita, H. Takahashi, T. Saito and Y. Sasaki, Transition Met. Chem. (Weinheim, Ger.), 5(1980)98 (Chem. Abstr., 93(1980)26542y).

370 H.-O. Stuhler, Angew. Chem. Int. Ed. Engl., 19(1980)468.

371a H.-O. Stuhler, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 35B (1980)340.

371b H.-O. Stuhler, Z. Naturforsch. B: Anorg. Chem. Org. Chem., 35B (1980)843.

372 R. Usón, L.A. Oro, R. Sariego, M. Valderrama and C. Rebullida, J. Organometal. Chem., 197(1980)87.

373 E. Pinilla, L.A. Oro and R. Sariego, J. Less-Common Metals, 72 (1980) P31.

374 M.Z. Iqbal, Arabian, J. Sci. Eng., 5(1980)121 (Chem. Abstr., 93(1980)87637e).

375 Z. Nagy-Magos, P. Kvintovics and L. Markó, Transition Met. Chem. (Weinheim, Ger.), 5(1980), 186(Chem. Abstr., 93(1980)106168w).

376 R. Salcedo and H. Torrens, Transition Met. Chem. (Weinheim, Ger.) 5(1980)247 (Chem. Abstr., 93(1980)160450v).

377 M. Aresta, Inorg. Chim. Acta, 44(1980)L3.

378 J.G. Leipoldt, S.S. Basson, G.J. Lamprecht, L.D.C. Bok and J.J.J. Schlebusch, Inorg. Chim. Acta, 40(1980)43.

379 A. Christofides, J.A.K. Howard, J.A. Rattue, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1980)2095.

380 R. Bonnaire, C. Potvin and J.M. Manoli, Inorg. Chim. Acta, 45(1980)L255.

381 F. Sakurai, H. Suzuki, Y. Moro-oka and T. Ikawa, J. Am. Chem. Soc., 102(1980)1749.

382 C. Bianchini, M. DiVaira, A. Meli and L. Sacconi, Angew. Chem. Int. Ed. Engl., 19(1980)405.

383 P. Caddy, M. Green, E. O'Brien, L.E. Smart and P. Woodward, J. Chem. Soc. Dalton Trans., (1980)962.

384 P. Albano, M. Aresta and M. Manassero, Inorg. Chem., 19(1980) 1069.

385 J.C.T.R. Burckett St. Laurent, H.E. Hosseini, J. Sinclair and J.F. Nixon, Inorg. Chim. Acta, 44(1980)L17.

386 M. Aresta and M. de Fazio, J. Organometal. Chem., 186(1980)109.

387 P.I. van Vliet, G. van Koten and K. Vrieze, J. Organometal. Chem. 188(1980)301.

388 R. Usón, L.A. Oro, M.T. Pinillos, A. Arruebo, K.A. Ostoja Starzewski and P.S. Pregosin, J. Organometal. Chem., 192(1980) 227.

389 R. Usón, L.A.Oro, M.J. Fernandez and M.T. Pinillos, Inorg. Chim. Acta, 39(1980)57.

390 H. Werner, O. Kolb, R. Feser and U. Schubert, J. Organometal. Chem., 191(1980)283.

391 B. Olgemöller and W. Beck, Angew. Chem. Int. Ed. Engl., 19 (1980)834.

392 R. Usón, L.A. Oro and M.J. Fernandez, J. Organometal. Chem., 193(1980)127.

393 H.H. Wang and L.H. Pignolet, Inorg. Chem., 19(1980)1470.

394 J. Ellerman and L. Mader, Z. Naturforch. B: Anorg. Chem., Org. Chem., 35B(1980)307.

395 W.J. Louw and C.E. Hepner, Inorg. Chem., 19(1980)7.

396 A. Maissonat, J.-J. Bonnet and R. Poilblanc, Inorg. Chem., 19(1980)3168.

397 W.J. Louw, T.I.A. Gerber and D.J.A. de Waal, J. Chem. Soc. Chem. Commun., (1980)760.

398 J. Muller, W. Hähnlein, A. Menig and J. Pickardt, J. Organometal. Chem., 197(1980)95.

399 E. Bianchi, M.C. Gallazzi, L. Porri and P. Diversi, J. Organometal. Chem., 202(1980)99.

400 R.H. Crabtree and J.M. Quirk, J. Organometal. Chem., 199(1980)99.

401 Y. Murakami, Y. Aoyama and M. Hayashida, J. Chem. Soc. Chem. Commun., (1980)501.

402 J.E. Lyons, H.K. Myers and A. Schneider, Ann. N.Y. Acad. Sci., 333 (1980)273.

403 K.P. Vora, C.F. Lochow and R.G. Miller, J. Organometal. Chem., 192(1980)257.

404 R.C. Larock, K. Oertle and G.F. Potter, J. Am. Chem. Soc., 102(1980)190.

405 L. Kollár, S. Tőrös, B. Heil and L. Markó, J. Organometal. Chem., 192(1980)253.

406a N.M. Goncharova and G.S. Grinenko, Khim-Farm. Zh., 14(1980)61 (Chem.Abstr., 93(1980)72076x).

406b J.W. Scott and D. Valentine, Jr., Org. Prep. Proced. Int., 12 (1980)7 (Chem. Abstr., 93(1980)72019f).

407 T.D. Madden, W.E. Peel, P.J. Quinn and D. Chapman, J. Biochem. Biophys. Methods, 2(1980)19.

408 G. Innorta, A. Modelli, F. Scagnolari and A. Foffani, J. Organometal. Chem., 185(1980)403.
409 M. Jakoubková and M. Čapka, Collect. Czech. Chem. Commun., 45(1980)2219.
410 V.Z. Sharf, B.M. Savchenko, V.N. Krutii and L. Kh. Freidlin, Izv. Akad. Nauk SSSR, Ser. Khim., (1980)456 (Chem. Abstr., 93(1980)25569a).
411 R. Grigg, T.P.B. Mitchell and A. Romasubbu, J. Chem. Soc. Chem. Commun., (1980)27.
412 H.M. Dickers, R.N. Haszeldine, L.S. Malkin, A.P. Mather and R.V. Parish, J. Chem. Soc. Dalton Trans., (1980)308.
413 M. Catellani, G.P. Chiusoli, W. Giroldini and G. Salerno, J. Organometal. Chem., 199(1980)C21.
414 K. Mita, T. Yamagishi and M. Hida. J. Chem. Soc. Chem. Commun., (1980)1036.
415 A. Spencer, J. Organometal. Chem., 194(1980)113.
416 H. Alper and K. Hachem, J. Org. Chem., 45(1980)2269.
417 R. Spogliarich, G. Zassinovich, G. Mestroni and M. Graziani, J. Organometal. Chem., 198(1980)81.
418 Y. Watanabe, M. Yamamoto and S.C. Shim, Chem. Lett., (1980)603.
419 A. Camus, G. Mestroni and G. Zassinovich, J. Organometal. Chem., 184(1980)C10.
420 T. Yoshida, D.L. Thorn, T. Okano, S. Otsuka and J.A. Ibers J. Am. Chem. Soc., 102(1980)6451.
421 R.K. Brown, J.M. Williams, A.J. Sivak and E.L. Muetterties, Inorg. Chem., 19(1980)370.
422 V. Kavan and M. Čapka, Collect. Czech. Chem. Commun., 45(1980)2100.
423 Z.M. Michelska, Transition Metal Chem. (Weinheim, Ger.), 5(1980)125 (Chem. Abstr., 93(1980)132552m).
424 R.H. Grubbs, Govt. Rept. Announce. Index (U.S.), 80(1980)1841 (Chem. Abstr., 93(1980)186533z).
425 K.M. Nicholas J. Organometal. Chem., 188(1980)C10.
426 A. Dedieu, Inorg. Chem., 19(1980)375.
427 R.B. Freas and D.P. Ridge, J. Am. Chem. Soc., 102(1980)7129.
428 A.S.C. Chan and J. Halpern, J. Am. Chem. Soc., 102(1980)838.
429 A.S.C. Chan, J.J.Pluth and J. Halpern, J. Am. Chem. Soc., 102(1980)5952.
430 J.M. Brown, P.A. Chaloner, R. Glaser and S. Geresh, Tetrahedron, 36(1980)815.
431 J.M. Brown and P.A. Chaloner, J. Am. Chem. Soc., 102(1980)3040.
432 J.M. Brown and P.A. Chaloner, J. Chem. Soc. Chem. Commun., (1980)344.
433 J. M. Brown and D. Parker, J. Chem. Soc. Chem. Commun., (1980) 342.
434 J.M. Brown and B.A. Murrer, Tetrahedron Lett., 21(1980)581.
435 R. Glaser, S. Geresh and M. Twaik, Isr. J. Chem., 20(1980)102 (Chem. Abstr., 94(1981)3642n).
436 Y. Nakamura, S. Saito and Y. Morita, Chem. Lett., (1980)7.
437 S. Miyano, M. Nawa and H. Hashimoto, Chem. Lett., (1980)729.
438 K. Kashiwabara, K. Hanaki and J. Fujita, Bull. Chem. Soc Jpn., 53(1980)2275.
439 K. Onuma, T. Ito and A. Nakamura, Chem. Lett., (1980)481.
440 K. Onuma, T. Ito and A. Nakamura, Bull. Chem. Soc. Jpn., 53(1980)2016.
441 K. Onuma, T. Ito and A. Nakamura, Bull. Chem. Soc. Jpn., 53(1980)2012.
442 K. Yamamoto, J. Wakatsuki and R. Sugimoto, Bull. Chem. Soc. Jpn., 53(1980)1132
443 W.R. Cullen, F.W.B Einstein, C.-H. Huang, A.C. Willis and E.-S. Yeh, J. Am. Chem. Soc., 102(1980)988.
444 T.H. Johnson and G. Rangarajan, J. Org. Chem., 45(1980)62.
445 H. Brunner and W. Pieronczyk, J. Chem. Res. Synop., (1980)76.
446 H. Brunner and G. Agrifogligo, Monatsh. Chem., 111(1980)275.
447 J.M. Townsend, J.F. Blount, R.C. Sun, S. Zawoiski and D. Valentine, Jr., J. Org. Chem., 45(1980)2995.
448 D. Valentine, Jr., R.C. Sun and K. Toth, J. Org. Chem., 45(1980)3703.
449 D. Valentine, Jr., J.F. Blount and K. Toth, J. Org. Chem., 45(1980)3691.
450 D.P. Riley and R.E. Shumate, J. Org. Chem., 45(1980)5187.
451 K. Kellner, A. Tzschach, Z. Nagy-Magos and L. Markó, J. Organometal. Chem., 193(1980)307.
452 I. Ojima, T. Kogure and N. Yoda J. Org. Chem., 45(1980)4728.
453 I. Ojima and T. Kogure, J. Organometal. Chem., 195(1980)239.

454a I. Ojima and T. Suzuki, Tetrahedron Lett., 21(1980)1239.
454b I. Ojima and N. Yoda, Tetrahedron Lett., 21(1980)1051.
455a D. Meyer, J.-C. Poulin, H.B. Kagan, H. Levine-Pinto, J.-L. Moregat and P. Fromageot, J. Org. Chem., 45(1980)4680.
455b H.B. Kagan, Ann. N.Y. Acad. Sci., 331(1980)1.
456 J. Köttner and G. Greber, Chem. Ber., 113(1980)2323.
457 G. Comisso, M. Mihalić, F. Kajfež, V. Sunjić and G. Snatzke, Gazz. Chim. Ital., 110(1980)123.
458a K.E. Koenig, G.L. Bachman and B.D. Vineyard, J. Org. Chem., 45(1980)2362.
458b K.E. Koenig, M.J. Sabacky, G.L. Bachman, W.C. Christophel, R.B. Friedman, W.S. Knowles, B.R. Stults, B.D. Vineyard and D.J. Weinkauff, Ann. N.Y. Acad. Sci., 333 (1980)16.
459 S. Törös, B. Heil, L. Kollár and L. Markó, J. Organometal. Chem., 197(1980)85.
460 J.-F. Peyronel, J.-C. Fiaud and H.B. Kagan, J. Chem. Res. Synop. (1980)320.
461 I. Kolb and J. Hetflejš, Collect. Czech. Chem. Commun., 45(1980)2224.
462a J.K. Stille and Y. Becker, J. Org. Chem., 45(1980)2139.
462b Y. Becker, A. Eisenstadt and J.K. Stille, J. Org. Chem., 45(1980)2145.
462c J.K. Stille, S.J. Fritschel, N. Takaishi, T. Matsuda, H. Imai and C.A. Bertelo, Ann. N.Y. Acad. Sci., 333(1980)35.
463 C. Botteghi, M. Branca and A. Saba, J. Organometal. Chem., 184(1980)C17.
464 M.A. Bennett and H. Neumann, Aust. J. Chem., 33(1980)1251.
465 A.J. Naktgeboren, R.J.M. Nolte and W. Drenth, J. Am. Chem. Soc., 102(1980)3350.
466 M. Arthurs, C.M. Regan and S.M. Nelson, J. Chem. Soc. Dalton Trans., (1980)2053
467 A. Stocki and R. Hoffman, J. Am. Chem. Soc., 102(1980)2952.
468 D.W. Wertz and M.A. Moseley, Inorg. Chem., 19(1980)705.
469 D.W. Wertz and M.A. Moseley, Spectrochim. Acta, Part A, 36A(1980)467.
470 H. van Dam, A. Terpstra, D.J. Stufkins and A. Oskam, Inorg. Chem., 19(1980) 3448.
471 R. Barone, M. Chanon and M.L.H. Green, J. Organometal. Chem., 185 (1980)85.
472 J.L. Davidson, L. Manojlovic-Muir, K.W. Muir and A.N. Keith, J. Chem. Soc. Chem. Commun., (1980)749.
473 M.B. Freeman, L.W. Hall and L.G. Sneddon, Inorg. Chem., 19(1980)1132.
474 B.H. Freeland, J.E. Hux, N.C. Payne and K.G. Tyers, Inorg. Chem., 19(1980)693.
475 J.R. Fritch and K.P.C. Vollhardt, Angew. Chem. Int. Ed. Engl., 19(1980)559.
476 E.R.F. Gesing, J.P. Tane and K.P.C. Vollhardt, Angew, Chem. Int. Ed. Engl., 19(1980)1023.
477 E.D. Sternberg and K.P. C. Vollhardt, J. Am. Chem. Soc., 102(1980)4839.
478 E.R.F. Gesing, J.A. Sinclair and K.P.C. Vollhardt, J. Chem. Soc. Chem. Commun., (1980)286.
479 R.L. Funk and K.P.C. Vollhardt, J. Am. Chem. Soc., 102(1980)5245.
480a R.L. Funk and K.P.C. Vollhardt, J. Am. Chem. Soc., 102(1980)5253.
480b K.P.C. Vollhardt, Ann. N.Y. Acad. Sci., 333(1980)241.
481 P. Hofmann and T.A. Albright, Angew, Chem. Int. Ed. Engl., 19(1980)728.
482 K.M. Nicholas, M. Mulvaney and M. Boyer, J. Am. Chem. Soc., 102(1980)2508.
483 J.E. O'Boyle and K.M. Nicholas, Tetrahedron Lett., 21(1980)1595.
484 S. Padmanabham and K.M. Nicholas, Synth. Commun., 19(1980)507.
485 R.F. Newton, P.L. Pauson and R.G. Taylor, J. Chem. Res. Synop., (1980)277.
486 R. Wilczynski and L.G. Sneddon, J. Am. Chem. Soc., 102(1980)2857.
487 B.M. Peake, P.H. Rieger, B.H. Robinson and J. Simpson, J. Am. Chem. Soc., 102(1980)156.
488 M.E. Howden, R.D.W. Kemmitt and M.D. Schilling, J. Chem. Soc. Dalton Trans., (1980)1716.
489 C.E. Dean, R.D.W. Kemmitt, D.R. Russell and M.D. Schilling, J. Organometal. Chem., 187(1980)C1.
490 M. Cowie and T.G. Southern, J. Organometal. Chem., 193(1980)C46.
491 H. Watanabe, M. Asami and Y. Nagai, J. Organometal. Chem., 195(1980)363.
492 J. Devillers, J.-J. Bonnet, D. deMontauzon and R. Poilblanc, Inorg. Chem., 19(1980)154.
493 S. Destri, M.C. Gallazzi, A. Giarrusso and L. Porri, Makromol. Chem. Rapid Commun., 1(1980)293.

H. Eshtiagh-Hosseini and J.F. Nixon, J. Organometal. Chem., 192(1980)C9.

G. Ciani, A. Sironi, P. Chini, A. Ceriotti and S. Martinengo, J. Organometal. Chem., 192(1980)C39.

M.D. Ward, T.V. Harris and J. Schwartz, J. Chem. Soc. Chem. Commun., (1980)357

Yu. A. Maletin and I.A. Sheka, Koord. Khim., 6(1980)81 (Chem. Abstr., 92(1980) 120984v).

J. Fortune and A.R. Manning, J. Organometal. Chem., 190(1980)C95.

H. Werner, K. Leonhard, O. Kolb, E. Röttinger and H. Vahrenkamp, Chem. Ber., 113(1980)1654.

D.A. Owen, A. Siegel, R. Lin, D.W. Slocum, B. Conway, M. Moranski and S. Duraj, Ann. N.Y. Acad. Sci., 333(1980)90.

J. Fortune and A.R. Manning, Inorg. Chem., 19(1980)2590.

P. Eilbracht, P. Dahler and G. Tiedtke, J. Organometal. Chem., 185(1980)C25.

A.J.L. Hanlan, R.C. Ugolick, J.G. Fulcher, S. Togashi, A.B. Bocarsley and J.A. Gladysz, Inorg. Chem., 19(1980)1543.

U. Koelle, J. Organometal. Chem., 184(1980)379.

W. Kläui, J. Organometal. Chem., 184(1980)49.

P. Gutlich, B.R. McGarvey and W. Kläui, Inorg. Chem., 19(1980)3704.

W.P. Hart, D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 102(1980)1196.

L.M. Cirjak, J.-S. Huang, Z.-H. Zhu and L.F. Dahl, J. Am. Chem. Soc., 102 (1980)6623.

D. Seyferth, R.S. Henderson and M.K. Gallagher, J. Organometal. Chem., 193 (1980)C75.

G.E. Herberich, E.A. Mintz and H. Muller, J. Organometal. Chem. 187(1980)17.

G.E. Herberich, B. Buller, B. Hessner and W. Oschmann, J. Organometal. Chem., 195(1980)253.

W. Siebert, H. Schmidt and R. Full, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 35B(1980)873.

W. Siebert, C. Bohle and K. Kruger, Angew. Chem. Int. Ed. Engl., 19(1980)746.

P.N. Becker, M.A. White and R.G. Bergman, J. Am. Chem. Soc., 102(1980)5676.

H. Boennemann and G.S Natarajan, Erdoel Kohle, Erdgas, Petrochem., 33(1980)328 (Chem. Abstr., 94(1981)30432a).

L.R. Byers and L.F. Dahl, Inorg. Chem., 19(1980)277.

O. Crichton, A.J. Rest and D.J. Taylor, J. Chem. Soc. Dalton, Trans., (1980)167.

Y. Mathey, R. Clement, C. Sourisseau and G. Lecazeau, Inorg. Chem., 19(1980)2773.

J.A. Andrews, U.A. Jayasooriya, I.A. Oxton, D.B. Cowell, N. Sheppard, P.F. Jackson, B.F.G. Johnson and J. Lewis, Inorg. Chem., 19(1980)3033.

J.E.M. van der Linden, A.H. Dix and E. Pfeiffer, Inorg. Chim. Acta, 39(1980)271.

B. Cetinkaya, P.B. Hitchcock, M.F. Lappert, S. Torroni, J.L. Atwood, W.E. Hunter and M.J. Zaworotko, J. Organometal. Chem., 188(1980)C31.

H. Werner and R. Feser, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 35B(1980) 689.

R. Usón, P. Lahuerta, J. Reyes, L.A. Oro, C. Foces-Foces, F.H. Cano and S. Garcia-Blanco, Inorg. Chim. Acta, 42(1980)75.

P.K. Baker, K. Broadley, N.G. Connelly, B.A. Kelly, M.D. Kitchen and P. Woodward, J. Chem. Soc. Dalton Trans, (1980)1710.

P. Albano and M. Aresta, J. Organometal. Chem., 190(1980)243.

M.R. Thompson, C.S. Day, V.W. Day, R.I. Mink and E.L. Muetterties, J. Am. Chem. Soc., 102(1980)2979.

N.A. Bailey, E.H. Blunt, G. Fairhurst and C. White, J. Chem. Soc. Dalton Trans., (1980)829.

R.P. Houghton, M. Voyle and R. Price, J. Chem. Soc. Chem. Commun. (1980)884.

I.W. Nowell, G. Fairhurst and C. White, Inorg. Chim. Acta, 41(1980)61.

P. Espinet, P.M. Bailey, R.F. Downey and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1980)1048.

J. Cook, J.E. Hamlin, A. Nutton and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1980)144.

532 A. Nutton, P.M. Bailey, N.C. Braund, R.J. Goodfellow, R.S. Thompson and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1980)631.
533 G.M. Reisner, I. Bernal, M.D. Rausch, S.A. Gardner and A.M. Clearfield, J. Organometal. Chem., 184(1980)237.
534 M.D. Rausch, W.P. Hart, J.L. Atwood and M.J. Zaworotko, J. Organometal. Chem., 197(1980)225.
535 R.J. McKinney, J. Chem. Soc. Chem. Commun., (1980)603.
536 J. Muller and H. Menig, J. Organometal. Chem.; 191(1980)303.
537 J. Muller, H. Menig, G. Huttner and A. Frank, J. Organometal. Chem., 185 (1980)251.
538 P.T. Barger and J.E. Bercaw, J. Organometal. Chem., 20(1980)C39.
539 G.D. Friesen, A. Barriola, P. Daluga, P. Ragatz and L.J. Todd, Inorg. Chem., 19(1980)458.
540 J. Plešek, B. Štibr and S. Heřmánek, Chem. Ind. (London), (1980)626.
541 G.K. Barker, M. Green, M.P. Garcia, F.G.A. Stone, J.M. Basset and A.J. Welch, J. Chem. Soc. Chem. Commun., (1980)1266.
542 R.N. Grimes, E. Sinn and J.R. Pipal, Inorg. Chem., 19(1980)2087.
543 N.S. Hosmane and R.N. Grimes, Inorg. Chem., 19(1980)3482.
544a G.J. Zimmerman, L. W. Hall and L.G. Sneddon, Inorg. Chem., 19(1980)3642.
544b G.J. Zimmerman and L.G. Sneddon, Inorg. Chem., 19(1980)3650.
545 W.C. Kalb, C.W. Kreimendahl, D.C. Busby and M.F. Hawthorne, Inorg. Chem., 19(1980)1590.
546 M.S. Delaney, C.B. Knobler and M.F. Hawthrone, J. Chem. Soc. Chem. Commun., (1980)849.
547 T.B. Marder, J.A. Long and M.F. Hawthorne, J. Chem. Soc. Chem. Commun., (1980)677.
548 C.W. Jung and M.F. Hawthorne, J. Am. Chem. Soc., 102(1980)3024.
549 J.A. Doi, R.G. Teller and M.F. Hawthorne, J. Chem. Soc. Chem. Commun., (1980)80.
550 B. Longato, F. Morandini and S. Bresdola, Inorg. Chim. Acta, 39(1980)27.
551 L.I. Zakharkin and T.B. Agakhanova, Izv. Akad. Nauk SSSR, Ser. Khim., (1980)1208 (Chem. Abstr., 93(1980)132547p).