Coordination Chemistry Reviews
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

REACTIONS AND CATALYTIC PROPERTIES OF RHODIUM COMPLEXES IN SOLUTION[1]

B. R. JAMES

Department of Chemistry, University of British Columbia, Vancouver 8, B.C. (Canada)

(Received 25 August 1966)

CONTENTS

ABBREVIATIONS

acac,	acetylacetonate	Ph,	phenyl
Ar,	aryl	phen,	1,10-phenanthroline
bipy,	2,2′-bipyridyl	py,	pyridine
DPE,	1,2-bisdiphenylphosphinoethane	R, R′,	alkyl
dipyam,	di-2-pyridylamine	trien,	triethylenetetramine
en,	ethylenediamine	X, X′,	halogen unless stated otherwise
H_2DMG,	dimethylglyoxime		

A. INTRODUCTION

In recent years there have been a great number of developments in the field of catalysis, notably those concerned with catalytic reactions of transition-metal ions and coordination compounds. Two recent reviews by Halpern[2,3] have concerned themselves with a variety of reactions including homogeneous hydrogenation, hydroformylation, oxidation of olefins, hydration of acetylene compounds and polymerization. The platinum-group metals and their complexes have been found to be exceptionally effective for these types of catalytic reactions and this was the subject of a short review by Bond[4] published in 1964. However, in the past year or so the amount of data published in this field has been quite remarkable and warrants further reviewing. The emphasis of this review will be restricted mainly to the chemistry of rhodium complexes since it is in this particular subject that the expansion of effort has been so considerable; the selection of the catalysis topics, all concerned with homogeneous systems, reflects the reviewer's interests.

Unlike their cobalt(III) analogues, the chemistry of rhodium(III) complexes has been little studied but more recently the study of substitution reactions of rhodium coordination complexes and organometallic species (the latter meaning to include rhodium species containing carbonyl linkages) has been gaining momentum. This is principally due to the preparation of many new rhodium complexes, principally by Basolo and his coworkers[5,6] and Wilkinson and his group[7]. Catalytic methods have been developed for the preparation of rhodium(III) complexes and these methods are intimately concerned with the catalytic properties exhibited by rhodium complexes themselves. A recent paper by Gillard and coworkers[8] briefly surveys the synthetic methods that have been used to date.

The present review will first consider some reactions homogeneously catalyzed by rhodium complexes including hydrogenation, olefin isomerization and polymerization of olefins and acetylenes, and will then deal more generally with recent studies on the solution chemistry of rhodium including addition, substitution, exchange reactions, etc. One section is devoted to carbonyl complexes of rhodium. The classes of reactions to be considered will necessarily lead us somewhat into organometallic chemistry of rhodium although we will not be principally concerned with this. This field itself is rapidly expanding as evidenced in a survey[9] of organometallic chemistry for 1964.

B. HOMOGENEOUS ACTIVATION OF MOLECULAR HYDROGEN IN AQUEOUS SOLUTION AND INTERMEDIATE HYDRIDIC SPECIES

Iguti[10] first reported the activation of molecular hydrogen by rhodium(III) complexes in aqueous acetate solutions at 25° for the reduction of a number of inorganic and organic substrates such as quinone, fumaric acid and sodium nitrite. $[Rh(NH_3)_5H_2O]Cl_3$, $[Rh(NH_3)_4Cl_2]Cl$ and $RhCl_3$ were found to be active, while the "saturated" amine complexes $[Rh(NH_3)_6]Cl_3$ and $[Rh(en)_3]Cl_3$ were inactive. The kinetics were not extensively studied however, and possible mechanisms were not discussed. However, under these experimental conditions, traces of metallic rhodium, a powerful heterogeneous catalyst, are readily formed[11] and H_2-catalyzed substitution reactions have been observed[11, 12] so these early results may not be too reliable. More recently Harrod and Halpern[13] studied the H_2-reduction of ferric ions catalyzed by chlororhodate(III) species in aqueous-acid solutions and this system has been further investigated by James and Rempel[14], after data concerning characterization of the chlororhodate(III) complexes had been published[15]. The determined rate-law is $-d[H_2]/dt = k[H_2][Rh^{III}]$ where, in $3M$ HCl, $k = 2.3 \times 10^{15} \exp[-25{,}000/RT] M^{-1}sec^{-1}$. On comparison with similar and deuterium-exchange studies using chlororuthenate(III) species[16, 17], it seems likely that the mechanism involves heterolytic splitting of H_2 in the rate-determining step, for example

$$RhCl_6^{3-} + H_2 \rightleftharpoons HRhCl_5^{3-} + H^+ + Cl^- \quad (1)$$

the hydride complex then being reoxidized in subsequent rapid reactions with Fe^{III}. Only the anionic, labile chlororhodate(III) species were effective catalysts, the activity of the species increasing with increasing number of coordinated chloride ligands: presumably increasing strength of the metal–chloride bonding in the lower chloro species makes removal of chloride or its replacement by hydride more difficult.

Olefins such as maleic acid were not hydrogenated using this aqueous chlororhodate(III)–H_2 system; H_2 reduced the rhodium(III) to the univalent state, this being stabilized by complexing with the olefin[14],

$$Rh^{III} + H_2 \rightarrow Rh^{I} + 2H^+ \quad (2)$$

$$Rh^{I} + \text{maleic acid} \xrightarrow{\text{fast}} \text{complex} \quad (3)$$

The rate of reduction corresponded to that for reduction of the Fe^{III} substrate, indicating a common rate-determining step such as reaction (1). (Catalytic hydrogenation of certain olefins does occur using a similar chlororuthenate(II) system, the reaction going via a 1 : 1 olefin π-complex[18].) The reduction of ferric species could then equally well involve an intermediate Rh^{I} state rather than the Rh^{III}-hydride species as suggested in reaction (1) through the dissociation

$$Rh^{III}H^- \rightleftharpoons Rh^{I} + H^+ \quad (4)$$

Both $Rh^{III}H^-$ and Rh^{I} can result from a 2-electron reduction of a Rh^{III} species[19]. The extent of the occurrence of reaction (4) will depend partly on the nature of other coordinated ligands, in particular their ability to stabilize the lower oxidation state, for example, a strong π-acceptor.

The proposed unstable intermediate $HRhCl_5^{3-}$ finds close analogues in the more stable hydride complexes, $[RhH(trien)Cl]^+$ and $[RhH(CN)_4H_2O]^{2-}$, isolated by Wilkinson and coworkers[20, 21]; the former is prepared by reaction of $[Rh(trien)Cl_2]^+$ with borohydride and the latter by the action of methanolic

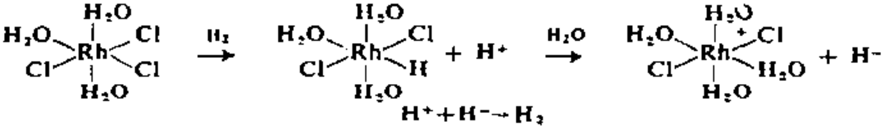
KCN on tetracarbonyl-μ_2-dichlororhodium(I), $[Rh(CO)_2Cl]_2$. The cyanohydrido complex seems remarkably stable considering the strong π-bond capacity of the CN group. Other less-stable hydrides[20,22] were also formed from reaction of borohydride with *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$, $[Rh(NH_3)_5Cl]^+$, *trans*-$[Rh(py)_4Cl_2]^+$ and $[Rh(HDMG)_2Cl_2]^-$. Borohydride reduction of $[Rh(bipy)_2Cl_2]^+$ leads to the production of the rhodium(I) species $[Rh(bipy)_2]^+$; there is evidence of an intermediate $Rh^{III}H^-$ species which decomposes according to reaction (4), the bipyridyl stabilizing the lower valency state[20,23,24]. Reaction with excess borohydride has also given[20,24] the dihydrido species *cis*- and *trans*-$[RhH_2(en)_2]^+$ and *cis*-$[RhH_2(trien)]^+$. None of the above-mentioned isolated hydride species of rhodium(III) complexes containing nitrogen ligands could be obtained by using molecular H_2 as reducing agent, and none activated molecular H_2 for the reduction of olefinic bonds, although they were efficient catalysts for the reduction of aromatic nitro compounds by borohydride through hydrogen-transfer reactions[20].

Excellent reviews concerning hydride complexes of transition metals have recently been published[25,26]. An important conclusion is that hydrogen in such complexes commonly acts effectively as an anionic ligand, occupying a normal coordination position. Generally the hydride behaves as a strong-field ligand[27], but u.v.-spectral studies in the weak-field nitrogen-ligand rhodium hydrides[24] suggest a rather lower ligand-field strength for the hydride, placing it between water and ammonia and more akin to a halide ligand; the hydride ligand also shows a strong trans effect[28a,29]. It is recognized[2] that catalytic activity for homogeneous hydrogenation must be concerned with the stabilities and labilities of hydridometallic species, which must act as intermediates in the catalytic reaction. The intermediate must be labile and its thermodynamic stability lie within narrowly-defined limits. Unless it is sufficiently stable it will not form readily while if its stability is too great, its subsequent transformation to the products will be slow. The structure, type of coordinated ligands and electronic configuration of the catalyst will be important factors, influencing the rate of reaction. Excluding the not too conclusive earlier work of Iguti[10], hydrogenation of olefin or acetylene compounds catalyzed homogeneously by rhodium species in purely-aqueous solution has not been reported. Studies in this medium frequently lead to the presence of rhodium metal, a heterogeneous hydrogenation catalyst[30], which could result from disproportionation or reduction of Rh^I species.

C. CATALYZED SYNTHESIS OF RHODIUM(III) COMPLEXES

A number of interesting reactions of rhodium complexes in solution are thought to involve hydridic species similar to those discussed above and these will now be considered further, since these must be closely related to intermediate hydrides present in catalytic-hydrogenation systems.

Delepine[31, 32] first observed that ethanol and several other alcohols catalyzed the formation of the *trans*-$[Rh(py)_4Cl_2]^+$ cation from aqueous solutions of pyridine and chlororhodate(III), which contain principally[33] 1,2,6-$Rh(py)_3Cl_3$. A kinetic study[6] of this reaction suggested that the mechanism involved a Rh^I species. The reaction was also found to be catalyzed by hypophosphorous acid and molecular hydrogen and an intermediate hydrido complex $RhH(py)_3Cl_2$ was suggested as an intermediate[7, 12, 22]. Similar syntheses involving nucleophilic replacement of halide ions by nitrogen donor ligands, catalyzed by reducing agents such as ethanol, hypophosphorous acid, sodium borohydride, hydrazinium chloride and molecular H_2, have been reported[7, 12, 22, 34–36]. Complexes prepared include *trans*-$[Rh(bipy)_2Cl_2]^+$, *trans*-$[Rh(phen)_2Cl_2]^+$, $[Rh(en)_3]^{3+}$, $[Rh(HDMG)_2Cl_2]^-$, *trans*-$[Rh(dipyam)_2Cl_2]^+$ and substituted pyridine complexes. Both hydrogen[12] and ethylene[11] will also catalyze at room temperature the replacement of chloride ligand by water in the production of the *trans*-$[Rh(H_2O)_4Cl_2]^+$ cation from solutions of rhodium trichloride; at higher temperatures, however, metallic rhodium is formed. A hydridic mechanism is suggested involving heterolysis of hydrogen by the rhodium trichloride, the resultant hydride ion replacing chloride with subsequent displacement of hydride by water:



Evidence that hydride intermediates are being formed, is furnished by the fact that some of these systems do act as catalytic systems for the homogeneous hydrogenation of olefinic bonds (see section E), e.g. ethanolic solutions of $RhCl_3$ or 1,2,6-$Rh(py)_3Cl_3$ containing hex-1-ene, take up molecular H_2, at room temperature and 1 atm, producing n-hexane[12].

Of interest here are polarographic studies with rhodium complexes which, however, have frequently given rise to variable conclusions; most of the work is reported and discussed critically in a recent paper by Wilkinson and coworkers[37]. A number of halogenoammine complexes of Rh^{III} and the hexachlororhodate(III) ion are reduced in 2-electron steps indicating that Rh^{II} is not formed and presenting evidence that the species responsible for the catalytic effects (e.g. the $[RhCl_6]^{3-}$ catalyzed reduction of Fe^{III} by H_2, and the catalyzed synthesis of the rhodium(III)-ammine complexes) are likely to be Rh^{III}–H^- or Rh^I species. Two polarographic waves were observed with *cis*-$[Rh(trien)Cl_2]^+$ each involving a 2-electron step, and this is consistent with the production of the isolated mono- and dihydric species $[RhH(trien)Cl]^+$ and $[RhH_2(trien)]^+$ (section B):

$$\begin{tikzcd}
\textit{cis}\text{-}[Rh(trien)Cl_2]^+ \arrow[r, "2e", "E_{\frac{1}{2}}=-0.38V"'] & {[Rh(trien)Cl_2]^-} \arrow[r, "H_2O"'] & {[RhH(trien)Cl]^+ + Cl^- + OH^-} \arrow[d, "E_{\frac{1}{2}}=-0.75\text{ V}"', "2e"] \\
& {[RhH_2(trien)]^+ + Cl^- + OH^-} & {[RhH(trien)Cl]^-} \arrow[l, "H_2O"']
\end{tikzcd}$$

D. ISOLATED HYDRIDE COMPLEXES OF RHODIUM CONTAINING TERTIARY PHOSPHINES AND RELATED LIGANDS

It is well known that hydrides of transition metals containing tertiary phosphines or arsines as stabilizing ligands, are amongst the most stable of the presently known hydride complexes[25]. The rhodium(III) species[38] $RhHX_2(Ph_2AsMe)_3$, and the rhodium(I) species[39-41], $RhHCO(Ph_3P)_3$, $RhH[C_2H_4(PPh_2)_2]_2$ and[42] $RhH(PF_3)_4$ have been isolated and a $RhHCl_2(Ph_3P)_2$ species has been prepared in chloroform solution[43]. The rhodium(III)-hydride species[41] $[RhHCl(DPE)_2]Cl$ and[44] $RhHCOCl_2(Ph_3P)_2$ have also been mentioned. None of these hydrides are formed using molecular H_2, and the catalytic activity for homogeneous hydrogenation appears to have been little studied although qualitative observations[45] indicate that $RhHCO(Ph_3P)_3$ in toluene solution does act as a catalyst for the hydrogenation of ethylene. The catalytic activity of this species is considered with that of other rhodium complexes in the following section.

The hydrides $RhHX_2(Ph_2AsMe)_3$ undergo an interesting reaction with mercury compounds yielding the complexes $(Ph_2AsMe)_3X_2Rh\text{–}HgY$ (Y = halogen or acetate) containing a rhodium–mercury bond[46].

E. HOMOGENEOUS HYDROGENATION OF OLEFINS AND ACETYLENES (NON-AQUEOUS SOLUTIONS)

Wilkinson and his associates have reported the hydrogenation and hydroformylation of both olefins and acetylenes using a number of rhodium(III) and rhodium(I) complexes as catalysts in ethanol, benzene or ethanol–benzene mixtures[12,21,47,48]. The complexes used include $RhCl_3$, 1,2,6-$Rh(py)_3Cl_3$, the solvated rhodium(I) chlorine-bridged stannous chloride complex, $Rh_2Cl_2(SnCl_2 \cdot EtOH)_4$[49-51], and the triphenylphosphine derivatives, 1,2,3-$RhCl_3(Ph_3P)_3$[52], $RhCl(Ph_3P)_3$[48,53] and $[RhCN(Ph_3P)_2]_2$[21]. The kinetics of these systems have not been reported in detail but the majority are probably quite complex, even for the hydrogenation reactions. Hex-1-ene, for example, a frequently-used olefin substrate, is catalytically isomerized[54] by ethanolic $RhCl_3$, and H_2-catalyzed substitution processes of the type mentioned in section C could be involved. It is also known that reaction of ethanol with the triphenylphosphine-type complexes of the platinum-metal ions can give hydrido- and hydridocarbonyl-type complexes with the metal in a reduced valency state[55,56].

The activity of $RhCl(Ph_3P)_3$ in benzene solution presents a more well-defined system in which a molecular hydride intermediate has been detected during the hydrogenation of ethylene and acetylene[48]. The activity is due, in part, to dissociation of the complex in solution to give a solvated species, $RhCl(Ph_3P)_2(S)$ (where S = solvent), which has a site for coordination of the olefin or acetylene by displacement of solvent, and a crystalline olefin complex, $RhCl(Ph_3P)_2C_2H_4$, containing a very labile ethylene molecule, has been isolated[57]. The benzene solution of $RhCl(Ph_3P)_3$ itself takes up molecular hydrogen and this hydride rapidly reduces any olefin present. The mechanism suggested:

$$\begin{array}{l} RhCl(Ph_3P)_2(S) \xrightleftharpoons{H_2} RhCl(Ph_3P)_2(S)H_2 \xrightleftharpoons{C_2H_4} RhCl(Ph_3P)_2(C_2H_4)H_2 \\ \hspace{22em}\downarrow \\ \hspace{18em} RhCl(Ph_3P)_2(S) + C_2H_6 \end{array}$$

The way in which hydrogen is transferred to the olefin is uncertain.

Very similar type systems for homogeneous hydrogenation are reported by Vaska and Rhodes[45, 58] using the iridium complexes[59] $IrCOCl(Ph_3P)_2$ and[39] $IrHCO(Ph_3P)_3$ which react reversibly with both molecular H_2 and the olefin in benzene solutions:

$$IrCOCl(Ph_3P)_2 + H_2 \rightleftharpoons IrCOClH_2(Ph_3P)_2 \tag{5}$$

$$IrCOCl(Ph_3P)_2 + C_2H_4 \rightleftharpoons IrCOClC_2H_4(Ph_3P)_2 \tag{6}$$

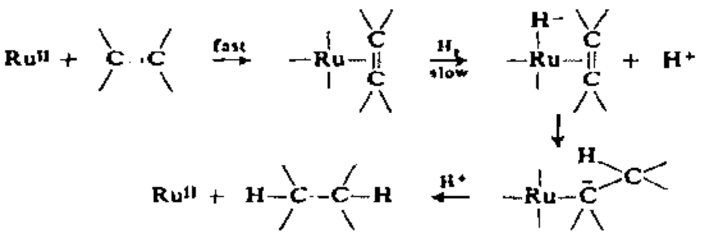
The corresponding rhodium complexes[60, 61] $RhCOCl(Ph_3P)_2$ and[39, 40] $RhHCO(Ph_3P)_3$ also catalyze the hydrogenation of olefins and acetylenes but these complexes themselves show no reaction with hydrogen or olefin[45, 48, 58], indicating the equilibria corresponding to those shown in equations (5) and (6) lie well to the left for the rhodium species. The $RhHCO(Ph_3P)_3$ complex does however act as a catalyst for hydrogen–deuterium exchange (cf. equation (5)) and like the $RhCl(Ph_3P)_3$ complex it does dissociate in solution. The catalytic activity of $RhCOCl(Ph_3P)_2$ is less than that of the $RhCl(Ph_3P)_3$ species[48]; substitution of CO into chlororuthenate(II) complexes has similarly been found to decrease catalytic activity[62]. The $IrCOCl(Ph_3P)_2$ complex also catalyzes the hydrogenation of maleic acid in dimethylacetamide solution[63] and kinetic studies indicate that the maleic acid is activated by coordination to the iridium, this complex then reacting with hydrogen suggesting that the dihydride, $IrCOClH_2(Ph_3P)_2$, may not be directly involved in the hydrogenation mechanism. This system is, incidentally, extremely sensitive to the presence of molecular oxygen, small amounts of which greatly increase the hydrogenation rate indicating that the equilibrium[64],

$$IrCOCl(Ph_3P)_2 + O_2 \rightleftharpoons IrCOClO_2(Ph_3P)_2 \tag{7}$$

can be involved in some way. A maleic anhydride complex has been isolated using benzene solutions of the $IrCOCl(Ph_3P)_3$ species[65].

James and Rempel[11, 14] report that $RhCl_3$ in dimethylacetamide solutions is an efficient homogeneous hydrogenation catalyst for the reduction of olefinic compounds such as maleic and fumaric acids, and ethylene; hydrogen initially reduces the rhodium to the univalent state, this rapidly forming a complex with the olefin substrate (as in the corresponding aqueous system, equations (2) and

(3)). In contrast to the aqueous system, however, the complex undergoes further reaction with hydrogen producing the hydrogenated olefin. The kinetics and mechanism of this stage are not yet fully elucidated but the mechanism is thought to be similar to that reported for the ruthenium(II)-catalyzed hydrogen reduction of maleic acid in aqueous acid chloride solutions[3,18,66]:



The intermediate hydride species is thought to undergo rearrangement, the metal ion and hydride ion adding across the double bond. The mechanisms of olefin hydrogenation reactions are not completely understood, and it is not always clear whether both of the reactants (H_2, olefin) need to be activated by the central metal atom or just the hydrogen; all the reactions must involve intermediate hydride species but it is not known whether coordination of the olefin as a π-bonded ligand (as in the Ru^{II}-catalyzed hydrogenation) is a general feature. These points and general mechanisms of hydrogen activation have recently been discussed by Halpern[2,3].

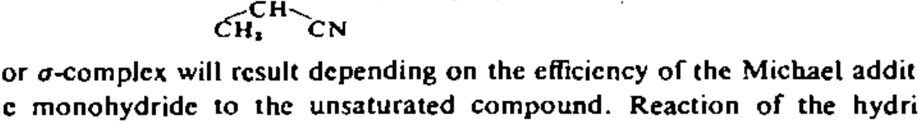
F. RHODIUM OLEFIN- AND ACETYLENE-TYPE COMPLEXES AS POSSIBLE INTERMEDIATES IN HYDROGENATION REACTIONS

If a successful homogeneous hydrogenation reaction involves say, an intermediate olefin–metal complex, then this species must exhibit the correct balance in properties of stability and lability as previously mentioned for intermediate metal-hydride species. Isolation of an olefin complex followed by reaction of it with hydrogen (usually in the presence of excess olefin), and a resulting production of the reduced olefin demonstrates the necessity and existence of the olefin complex as an intermediate in the catalytic hydrogenation. A large number of olefin-type complexes of rhodium have recently been prepared although their role as possible catalytic intermediates for hydrogenation has not in general been studied. These complexes will now be considered.

In the hydrogenation systems considered in section E, intermediate rhodium–olefin complexes (except for the $RhCl(Ph_3P)_2C_2H_4$ species) have not in general been isolated, although in some systems they are clearly present in solution. The ethylene dimer-complex, $[RhCl(C_2H_4)_2]_2$, isolated by Cramer[67], reacts with an ethylene–hydrogen mixture in dimethylacetamide to produce rhodium metal, and so is not considered the likely intermediate in the $RhCl_3$-catalyzed hydrogenation of ethylene in this medium[11]. A reaction closely related to catalytic hydrogenation is the catalytic hydrosilation of olefins for which the ethylene dimer is reported to be an efficient catalyst[68].

Of interest are the recently-reported fluoroethylene complexes of rhodium[69–71] of the type $Rh(acac)(C_2H_4)C_2F_4$ and $[RhCl(C_2H_4)C_2F_4]_2$, where the ethylene can also be displaced by Lewis bases (L) such as phosphines, amines, nitriles or cyanide, to give complexes such as $Rh(acac)(C_2F_4)L_2$, $[Rh(acac)(C_2F_4)L]_2$ and $RhCl(C_2F_4)L_2$. Acetylene complexes such as the hexafluorobut-2-yne derivative $RhCl(Ph_3P)_2C_4F_6$, have also been prepared[69]. Chemical and N.M.R. evidence indicates that the metal–fluoroethylene and –acetylene bonds have considerable π-character, in contrast to the σ-bonded fluoroolefin complexes usually obtained[72]. Bubbling hydrogen through a benzene solution of the $RhCl(Ph_3P)_2C_4F_6$ species results in the production[69] of 1,1,1,4,4,4-hexafluorobutane and the dimer $Rh_2Cl_2(Ph_3P)_4$. The acetylene complex itself is readily prepared by reaction of the hexafluorobut-2-yne with $RhCl(Ph_3P)_3$ and clearly the efficiency of catalytic hydrogenation will depend on the rate of formation and structure of the acetylene (or a corresponding olefin) complex. N.M.R. studies[66,73] indicate that there is no exchange of the coordinated and free fluoroalkyne with the $RhCl(Ph_3P)_2C_4F_6$ complex, and also no exchange of fluoroolefin in the corresponding tetrafluoroethylene complex. $RhCl(Ph_3P)_2C_2F_4$, although the ethylene complexes $RhCl(Ph_3P)_2C_2H_4$ and $Rh(acac)(C_2H_4)_2$ do show rapid ethylene exchange. The complex[74] π-$C_5H_5Rh(C_2H_4)_2$ shows no exchange but it appears that the coordinated ethylene may rotate with the coordinate bond as axis[73].

Olefin-π-complexes of rhodium(I) have frequently been prepared by reduction of rhodium trichloride with the olefin in the presence of ethanol; the ethylene dimer[67], $[RhCl(C_2H_4)_2]_2$, a number of corresponding dimeric diene complexes, $(diene)_2Rh_2Cl_2$, and the monomeric dicyclooctene and dibutadiene complexes, $(C_8H_{14})_2RhCl$ and $(C_4H_6)_2RhCl$, have been prepared in this way[75–78]. A monomeric norbornadiene complex, $(C_7H_8)_2Rh(SnCl_3)$, is isolated when stannous chloride is present in solution[50]. These reactions presumably occur through an intermediate Rh^{III}-hydride again and indirect evidence for this is provided by the fact that a stable σ-rhodium(III) complex can result from a similar system using acrylonitrile[79]. The ethanol-induced reactions have been discussed in terms of the following scheme (L = ligand):



$$\begin{tikzcd}
L_3RhCl_3 \arrow[r, "C_2H_5OH"] & L_3RhHCl_2 \arrow[r] \arrow[d, "CH_2=CH\cdot CN"] & L_3RhCl \arrow[r, "olefin"] & {[(olefin)_2RhCl]_2} \ (\pi\text{-complex}) \\
 & L_3RhCl_2\text{–}CH(CH_3)CN \ (\sigma\text{-complex}) & &
\end{tikzcd}$$

A π- or σ-complex will result depending on the efficiency of the Michael addition of the monohydride to the unsaturated compound. Reaction of the hydride,

$[RhH(CN)_4(H_2O)]^{2-}$, with tetrafluoroethylene similarly gives the σ-bonded $-CF_2 \cdot CF_2H$ complex[21] and likewise the solution of the hydrido species, $RhHCl_2(Ph_3P)_2$, absorbs ethylene and acetylene to give the air-stable ethyl and vinyl complexes of rhodium(III)[43]. Closely related is the finding[80] that tetrafluoroethylene reacts with a platinum–hydride complex to give finally a σ-bonded fluorovinyl compound via an intermediate π-complex:

$$(Et_3P)_2PtHCl + C_2F_4 \rightarrow (Et_3P)_2PtHCl(C_2F_4) \rightarrow (Et_3P)_2PtCl(CF{=}CF_2).$$

The intermediate, isolated in small amounts, is the type sometimes postulated to occur in catalytic hydrogenations (see section E).

No simple olefinic complexes of rhodium(III) have been reported but several cyclopentadienyl compounds are known[81–83].

G. ALLYLIC COMPLEXES OF RHODIUM

An allylic bond can form when a hydride adds to a conjugated double bond of an olefinic substrate, and such allyl complexes could clearly be intermediates in catalytic reactions such as hydrogenation, isomerization (section H) and polymerization (section I). A number of papers have recently reported the first allyl complexes of rhodium. A polymeric π-allylic derivative $C_{12}H_{19}RhCl_2$, dichlorocyclododeca-1,5-dienylrhodium(III), has been prepared via the ethanol-intermediate hydride procedure using *trans,trans,trans*-1,5,9-cyclododecatriene[84] (the compound had been reported previously as π-cyclododeca-1,5,9-trienylrhodium(III) dichloride, $C_{12}H_{17}RhCl_2$)[85]. The compound reacts with Lewis bases giving derivatives such as $C_{12}H_{19}(C_2H_4)_2RhCl_2$, $C_{12}H_{19}(en)RhCl_2$, $C_{12}H_{19}(CO)_2RhCl_2$, etc; these all yield cyclododecane on treatment with borohydride. The preparation of π-allyl-cycloocta-1,5-dienerhodium(I) has recently been described[86].

Addition of allyl chloride to a solution of $RhCl(Ph_3P)_3$ has yielded two compounds of the formula $(Ph_3P)_2Rh(C_3H_5)Cl_2$, in which the allyl group is believed to be π-bonded in one compound and σ-bonded in the other[43]. Similar allylic complexes have been reported by Powell and Shaw[87]; the bridged chloroallylrhodium(III) complex, $[RhCl(C_3H_5)_2]_2$, has been synthesized from the chlorocarbonyl $[RhCl(CO)_2]_2$ and allyl chloride, and derivatives such as $Rh(C_3H_5)_3$, $[Rh(py)_2(C_3H_5)_2]^+$, $Rh(acac)(C_3H_5)_2$, $RhCl(C_3H_5)C_5H_5$ and $Rh(C_3H_5)_2C_5H_5$ are readily formed. N.M.R. evidence indicates that the last named derivative contains one π- and one σ-bonded allyl ligand. The analogous π-crotyl derivatives $RhCl_2(C_4H_7)py_2$ and $RhCl(C_4H_7)C_5H_5$, are also described. A complex $Rh_2Cl_4(C_{12}H_{20})$, isolated from the reaction of rhodium trichloride and butadiene in ethanol, is believed to be $[C_4H_7RhCl_2C_4H_6Cl_2RhC_4H_7]$ containing π-crotyl groups, two bridging and two terminal chlorines and a bridging butadiene ligand[87] (this complex had previously been incorrectly formulated as $Rh_2Cl_4C_{12}H_{18}$)[88].

H. CATALYTIC ISOMERIZATION OF OLEFINS

Of related interest to catalytic hydrogenation reactions is the catalytic isomerization of olefins. Rhodium(III) salts are said to isomerize butenes at 50°, but no details are given[89]. More recently reported are the rhodium trichloride-catalyzed double-bond migration of olefins, studied by Chalk and Harrod[54]; and isomerization of 1,3-cyclooctadiene to 1,5-cyclooctadiene, studied by Rinehart and Lasky[90]. The former workers invoke a mechanism based on reversible addition of a hydrido–metal complex to the olefin while the latter favour a mechanism involving a π-allyl intermediate. Davies[91] rules out both these mechanisms for the Pd^{II}-catalyzed isomerization of olefins and tentatively suggests a mechanism involving a carbene intermediate. The formation of the π-allylic derivative $C_{12}H_{19}RhCl_2$, mentioned in section G, is thought to involve the initial isomerization of the starting olefin (*trans*, *trans*, *trans*-1,5,9-cyclododecatriene), again by the reversible nucleophilic attack on the olefin bond by a hydride[84] $HRhCl_2$, and the isomerization of olefins in the hydroformylation reaction is thought to proceed via a similar mechanism[92,93]. During the preparation[75] of $(C_8H_{12})_2Rh_2Cl_2$ from cycloocta-1,5-diene and $RhCl_3$ all the uncomplexed olefin is converted to the 1,3-isomer[94] and $RhCl_3(PEt_2Ph)_3$ is also reported to be an efficient catalyst for this isomerization[94]. Cramer in a recent important paper[105a] has shown that linear butenes are isomerized by methanolic solutions of $[RhCl(C_2H_4)_2]_2$ or $Rh(acac)(C_2H_4)_2$ in the presence of HCl, and deuterium-tracer studies indicate that the mechanism does involve addition and elimination of a rhodium(III) hydride at the olefin bond.

The isomerization of olefins has been the subject of a recent review by Orchin[95].

I. POLYMERIZATION OF OLEFINS AND ACETYLENES

The polymerization of olefins by Ziegler–Natta-type catalysts continues to be an active field of investigation but one with which we shall not concern ourselves directly. However, there are a number of recent developments in the field of polymerization catalysis that are of interest in the present context.

Rhodium chloride or -nitrate catalyze stereospecifically the polymerization of butadiene in water or alcohol to crystalline *trans*-1,4-polybutadiene[89,96]. Teyssie and Dauby[97] have reported an accelerating effect of reducing agents for the $RhCl_3$-catalyzed butadiene polymerization suggesting the participation of a lower oxidation state, possibly Rh^{I} or alternatively a hydride complex. Natta and coworkers[98] report the $RhCl_3$-catalyzed polymerization of cyclobutene in aqueous emulsion to a crystalline polycyclobutylenamer-2. A mechanistic study has been reported by Bawn and coworkers[99] for the solution polymerization of butadiene to long-chain polymers in the presence of rhodium salts; they conclude that the active species is a π-allylic rhodium(III) hydride rather than a rhodium(I) π-allylic complex. The complex, $Rh_2Cl_4(C_{12}H_{20})$, isolated from a reaction of $RhCl_3$ and butadiene[87] (section G) is not an active intermediate for formation of the long-chain polymers but did convert butadiene to cyclic telomers[99]. The less-stable dibutadiene complex[78] $(C_4H_6)_2RhCl$ could be a possible intermediate.

Closely related are the $RhCl_3$-catalyzed polymerization of phenylacetylenes[100, 101], and the oligomerization of phenylacetylene[102] and hexafluoro-2-butyne[103] catalyzed by dicarbonyl complexes such as $[RhCl(CO)_2]_2$ and π-$C_5H_5Rh(CO)_2$. Metal complexes such as $[(C_6H_5C{\equiv}CC_6H_5)RhCOCl]_n$ and π-$C_5H_5Rh(C_4F_6)_3$ have been isolated. The latter complex, π-cyclopentadienylhexakistrifluoromethylbenzenerhodium, is unusual in that it contains a stabilized non-planar benzene ring[104].

New olefin-to-olefin addition reaction have been found to be catalyzed by rhodium chloride in alcohol solution, although the presence of the solvent is not essential[105b, 106]. These reactions have been referred to in a recent article by Bond[107]. Ethylene can be readily dimerized to linear butenes, the primary product probably being 1-butene, which subsequently isomerizes. Ethylene and propylene can readily be added to dienes giving mainly 1,4-diolefins. The mechanism of the ethylene dimerization in alcoholic HCl solution has been studied by Cramer[105b] and the active catalyst appears to be the anion $[(C_2H_4)_2Rh^{I}Cl_2]^-$. This is oxidized by HCl (possibly via a hydride intermediate) to $[C_2H_5Rh^{III}Cl_3(C_2H_4)S]^-$ where S may be water, ethanol or chloride. At $-15°$ where no dimerization occurs the latter complex loses C_2H_4 and the salt $Cs[C_2H_5RhCl_3(H_2O)]$ has been isolated. Dimerization occurs when the coordinated ethylene in the Rh^{III} derivative inserts itself in a rate-determining step between the C_2H_5 group and the rhodium atom giving the ion $[C_4H_9Rh^{III}Cl_3S]^-$; this loses HCl giving $[C_4H_8Rh^{I}Cl_2S]^-$ from which butene and S are rapidly displaced by C_2H_4 regenerating the Rh^{I} complex ion. Dimerization also occurs only when halide ligands are present. This mechanism involves the following interesting features which are clearly pertinent generally to reactions of coordinated olefins including hydrogenation, isomerization and polymerization:

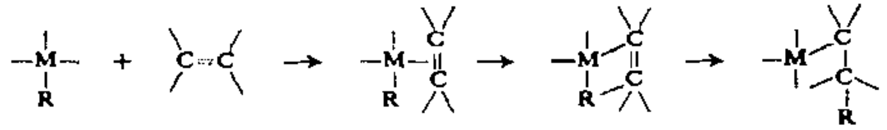
(i) the reversible oxidation of Rh^{I} by a proton acid to give a Rh^{III} hydride,

(ii) the insertion of coordinated olefin between an alkyl group and the metal ion to which it is attached,

(iii) the lability of hydrogen in rhodium(III) alkyl and olefin complexes,

(iv) the importance of appropriate auxiliary ligands to the catalytic effectiveness of rhodium.

Feature (ii) is a specific example of an addition reaction that involves formation of an intermediate π-complex, which rearranges to add the elements of the original complex across the unsaturated bond of the olefin:



where R may be a H atom, an alkyl group, a growing chain etc.

Such a mechanism has been proposed for a wide range of catalytic reactions including hydrogenation (see e.g. section E and F), hydroformylation, hydration, isomerization (see section H) and polymerization[2,3,108,109], and is an example of a much wider class of "insertion"-type reactions recently discussed by Heck[110]. Their role in catalytic reactions has been considered elsewhere[3].

J. CARBONYL COMPLEXES OF RHODIUM

Carbon monoxide insertion reactions are well known[110] and carbon monoxide insertion complexes have been postulated as intermediates in the reduction of metal ions in solution[111–113]. The CO reduction of chlororhodate(III) complexes in HCl solution at 80° and 1 atm. CO pressure, leads to the production of the Rh^I anionic species $[Rh(CO)_2Cl_2]^-$, and probably occurs through such an intermediate[114] (chloride ligands are omitted):

$$\begin{tikzcd}
\mathrm{Rh^{III}{-}OH_2} + \mathrm{CO} \arrow[rr, "k"] & & {[\mathrm{Rh{-}CO{-}OH_2}]} \arrow[d, "\text{fast}"] \\
\mathrm{Rh^I(CO)_2} & \arrow[l, "2\mathrm{CO}", "\text{fast}"'] & \mathrm{Rh^I} + \mathrm{CO_2} + 2\mathrm{H^+} \arrow[l]
\end{tikzcd}$$

The reaction is of interest in that it exhibits autocatalysis, the dichlorodicarbonylrhodate(I) complex catalyzing a further reduction of the chlororhodate(III) species by CO. Addition of triphenylphosphine to the solution of $[Rh(CO)_2Cl_2]^-$ gives a simple preparation of the familiar $RhCOCl(Ph_3P)_2$ complex. Heck[115] has described a similar procedure in methanol solution which, however, requires 1-pentene to reduce the rhodium to the univalent state. It may be that a coordinated H_2O ligand is necessary for CO reduction of rhodium(III) to occur under mild conditions; $RhCl_3$ in some non-aqueous solvents reacts with CO to give apparently Rh^{III} carbonyl derivatives[114]. Hieber and Lagally[116] found that hydrated $RhCl_3$ was much more reactive than the anhydrous material in its reaction with CO and methanol to give the $[RhCl(CO)_2]_2$ dimer[116–118].

A large number of mono- and dicarbonyl derivatives of rhodium(I) have been prepared from the $[RhCl(CO)_2]_2$ dimer. These include the series of complexes $RhL_2(CO)X$, where L = Ar_3P, Ar_3As, Ar_3Sb, $(PhO)_3P$ and X = Cl, I, SCN[60]; the anions $[Rh(CO)_2X_2]^-$ (X = Cl, Br, I) and $[Rh_2(CO)_2X_4]^{2-}$ (X = Br, I)[119,120]; the compounds $[Rh(CO)_2X]_2$ where X is carboxylate, nitrate, thiocyanate, sulphate or cyanide[21,120]; the amine complexes[120] $RhCl(amine)(CO)_2$;

and the complexes[121] (β-ketone)$Rh(CO)_2$. π-$C_5H_5Rh(CO)_2$[122] and its mono- and disubstituted derivatives contining phosphines, phosphites and isonitriles have been synthesized[123].

Reaction of platinum-metal halides with alcoholic solution in the presence of tertiary phosphine-type ligands has given rise to the well-known formation of carbonyl, hydridocarbonyl and hydrido complexes of the metal in a reduced valency state[55, 56, 61, 124] and the complex $RhCOCl(Ph_3P)_2$ has been prepared in this way. This complex has also been isolated by similar decarbonylation of aldehydes and acylhalides[43, 125], and dimethylformamide, dioxan and certain ketones[126] using $RhCl_3$ in the presence of triphenylphosphine or the $RhCl(Ph_3P)_3$ complex itself.

Complexes such as $RhCOCl(Ph_3P)_2$ of d^8 configuration undergo the now familiar oxidative-addition reactions by adding a wide variety of covalent molecules to form hexacoordinated complexes of d^6 configuration[127, 128]. The rhodium complexes are less reactive than their iridium analogues but derivatives with SO_2[128], HCl[44], organic halides[115], and halogens[115, 129] have been prepared, e.g. $RhL_2(CO)X_3$ ($L = Ar_3P$, R_3P, Ar_3As, Ar_3Sb) from the reaction with halogens, and $RRhL_2(CO)XX'$ from the organic halides. One of the latter compounds, chloroiodomethylbis(tri-n-butylphosphine)carbonyl rhodium(III) absorbs CO to give[115] the acyl derivative, $CH_3CORhICl(CO)[P(n\text{-}C_4H_9)_3]_2$. Equilibria such as

$$Rh^{I}COCl(Ph_3P)_2 + O_2 \rightleftharpoons Rh^{III}COCl(Ph_3P)_2O_2 \tag{8}$$

and the corresponding reactions with molecular H_2 and CO, almost certainly exist as well, but the equilibria lie far to the left[130]. Similar oxidative-addition reactions with "saturated" five-coordinate d^8 complexes, such as π-$C_5H_5Rh(CO)_2$, occur with the loss of a neutral CO ligand. The diiodide derivative[131], π-$C_5H_5Rh(CO)I_2$, and perfluoroalkyl-iodide derivatives such as[132, 133] π-$C_5H_5Rh(CO)(C_2F_5)I$, have been prepared in this way. An anionic carbonyl derivative of rhodium(III), $[Rh(CO)I_4]^-$, has been prepared by direct carbonylation of rhodium triodide in the presence of iodide ion[119].

The oxidative-addition reactions are not restricted to the carbonyl derivatives; other examples in rhodium chemistry include the previously-mentioned reactions of HCl and allyl chloride with $RhCl(Ph_3P)_3$ to give the hydride and allyl derivatives, respectively, and the same complex also undergoes addition reactions with[43] CH_3I and O_2.

Although rhodium(I) carbonyls are quite stable thermodynamically they are highly labile, e.g. the CO and Cl in $RhCOCl(Ph_3P)_2$ exchange immeasurably quickly[134, 135]. Exchange of CO in π-$C_5H_5Rh(CO)_2$ is reported to occur readily apparently via a dissociation mechanism[73], but other work has indicated that the exchange results are not reproducible and substitution of CO in this complex by phosphines etc., occurs via a bimolecular displacement reaction[123]. Second-order exchanges of CO with $Rh(CO)_2$(p-anisidine)Cl also indicates an associative process[134]. Comparison of the exchange rates of these square-planar rhodium(I) carbonyl complexes with corresponding olefin complexes (section F) has been discussed by several workers[23, 28b, 136]. The rate of CO exchange in the rhodium(III) octahedral complex $Rh(Ph_3P)_2COCl_3$ is independent of CO and takes place via a dissociative process[137].

Of the rhodium carbonyl derivatives only the $RhCOCl(Ph_3P)_2$ and $RhHCO(Ph_3P)_3$ (prepared by reaction of hydrazine on $RhCOCl(Ph_3P)_2$)[39] have been reported as active catalysts for homogeneous hydrogenation (see section E) and there is clearly scope for further study of the reactions and possible catalytic properties of these types of complexes. Recently a corresponding thiocarbonyl derivative, $RhCSCl(Ph_3P)_2$, has been prepared by the reaction of $RhCl(Ph_3P)_3$ with carbon disulphide and this again undergoes an oxidative–addition reaction with Cl_2 to give[44] $Rh(Ph_3P)_2CSCl_3$.

K. EXCHANGE AND SUBSTITUTION REACTIONS OF NON-ORGANOMETALLIC COMPLEXES OF RHODIUM

The few studies concerning exchange and substitution reactions of the organometallic rhodium complexes have been considered in section F for the olefin complexes and in section J for the carbonyl complexes. Relatively little work has been reported on such reactions with other rhodium complexes but these are of current interest for comparison with corresponding reactions of other related transition metals, in particular, the well-studied Co^{III} complexes and the last member of the triad, iridium, and for a better understanding of the catalytic properties of the complexes.

Quantitative kinetic studies have been reported for the hydrolysis of rhodium(III) pentammines[138–140] and substitution reactions of a more extensive series of rhodium(III) ammines have been studied by a number of workers[34, 141–144]. The data are really not very extensive but both similarities and differences in behaviour of the Co^{III} and Rh^{III} complexes have been considered[139, 141]. A variety of nucleophilic reagents react with *trans*-$[Rh(en)_2Cl_2]^+$ at the same rate[141] indicating that the hydrolysis reaction is rate determining as is known for Co^{III} complexes. The larger Rh^{III} ion leads to steric effects similar to but, as expected, smaller than those reported[145] for Co^{III}, and a retardation in rates of acid hydrolysis with increased chelation for Rh^{III} complexes is similar to the chelation effect of Co^{III} complexes[146]. Important differences between Co^{III} and Rh^{III} systems emerge in that replacement of an amine ligand by chloride for Rh^{III} gives little increase in rates of acid hydrolysis, charge is not as important in Rh^{III} complexes (suggesting S_N2 substitutions), and the stereochemical result of both acid and base hydrolysis of *trans*-$[Rh(en)_2Cl_2]^+$ is complete retention (for Co^{III}, base hydrolysis is generally accompanied by large amounts of isomerization and racemization). Base hydrolysis is much slower for Rh^{III} than for Co^{III} ammines and this has been discussed in terms of the outstanding π-donor ability of the amide ligand and the idea that π-bonding is much less important for the Rh^{III} complexes in hydrolysis reactions[28c, 142]. The replacement of halides from *trans*-RhA_4LX^{n+} (where $A_4 = (NH_3)_4$ or $(en)_2$; L = halide, N_3^-, OH^-, NO_2^-, NH_3 and X = halide) has been used to estimate the kinetic "trans-effect"[147] of the L group[34, 144]. Harris et al.[148] have studied exchange and substitution reactions of the trisoxalatorhodate(III) complex and various chloroaquo–rhodium(III) species. The rates range from rather-high lability in $[RhCl_5(H_2O)]^{2-}$ to rather-extreme stability in $[Rh(H_2O)_6]^{3+}$; this phenomenon has been discussed previously for the ruthenium(III) series of chloroaquo complexes[149] in terms of crystal-field splitting of Cl^- as compared to H_2O. Much work remains to be done in the field of substitution-reaction mechanisms for rhodium complexes, and the developments in the characterization of species present in solution by u.v. and visible spectroscopy should prove particularly helpful[15, 150, 151].

Very little work has been reported on electron-transfer reactions involving rhodium complexes[152, 153]. The reduction of $[(NH_3)_5RhX]^{2+}$ (where X = halide or acetate) by Cr^{II} has been studied[152]; a bridged activated complex is involved, the rate decreasing in the order $Cl > Br > I$ in contrast to those observed in the corresponding reduction of the pentamminecobalt(III) complexes[154]. This is considered due to the class-a acceptor property[155] of Co^{III} with its decreasing halide affinity in the order $F \gg Cl > Br > I$ and the class-b acceptor character of Rh^{III} with opposite affinities. However, Schmidtke[156], by consideration of the formation of thiocyanate complexes which can coordinate through the "soft" sulphur or "hard" nitrogen atom[157], concludes that $[Rh(NH_3)_5]^{3+}$ is class-a whereas the free Rh^{3+} ion is class-b. A similar argument based on consideration of the Rh^{III} sulphamide complex, where bonding to an oxygen of the $SO_2(NH)_2$ group is indicated[158], would suggest, however, class-a character for the free ion.

Poë and coworkers[159, 160] conclude from equilibria and enthalpy data that the $[Rh(en)_2X_2]^+$ species is slightly class-b, and in the π-cyclopentadienyldicarbonylrhodium(I) complex the metal is designated[123] class-b. For lower oxidation states more class-b or softer behaviour is expected. Ahrland, Chatt and Davies[155] had originally classified rhodium as a type-b element but close to the border line of type-a and rhodium species clearly do exhibit characteristics of both types.

L. CONCLUDING REMARKS

This review has shown that research into the chemistry of rhodium is in a very active state. Many new complexes containing particularly hydrido, carbonyl, olefinic, acetylenic, allylic and tertiary-phosphine type groups have been prepared but as yet there has been relatively little study of their reactions and properties. The catalytic properties of rhodium complexes are of great interest but little quantitative data have been reported although it appears qualitatively that groups such as halides, tertiary phosphines, CO, CN^- and $SnCl_3^-$ are particularly effective in activating the platinum-metal ions generally. Presently in this laboratory we are investigating a number of rhodium complexes in solution as homogeneous hydrogenation catalysts in an attempt to find correlations between catalytic activity and structure of the rhodium complexes through systematic variation of the coordinated ligands.

Support of this work by the National Research Council of Canada is gratefully acknowledged.

REFERENCES

1 The survey of literature relevant to this review was concluded in June, 1966.
2 J. Halpern, *Ann. Rev. Phys. Chem.*, 16 (1965) 103.
3 J. Halpern, *Proc. 3rd Intern. Congr. Catalysis, Amsterdam, 1964*, North Holland, Amsterdam, 1965, p. 146.
4 G. C. Bond, *Platinum Metals Rev.*, 8 (1964) 92.
5 S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1 (1962) 925.
6 J. V. Rund, F. Basolo and R. G. Pearson, *Inorg. Chem.*, 3 (1964) 658.
7 R. D. Gillard, J. A. Osborn and G. Wilkinson, *J. Chem. Soc.*, (1965) 1951.
8 R. D. Gillard, E. D. McKenzie and M. D. Ross, *J. Inorg. Nucl. Chem.*, 28 (1966) 1429.
9 D. Seyferth and R. B. King, *Annual Survey of Organometallic Chemistry, Vol. I*, Elsevier, Amsterdam, 1965, p. 268.
10 M. Iguti, *J. Chem. Soc. Japan*, 60 (1939) 1787.
11 B. R. James and G. L. Rempel, unpublished observations.
12 R. D. Gillard, J. A. Osborn, P. B. Stockwell and G. Wilkinson, *Proc. Chem. Soc.*, (1964) 284.
13 J. F. Harrod and J. Halpern, *Can. J. Chem.*, 37 (1959) 1933.
14 B. R. James and G. L. Rempel, *Can. J. Chem.*, 44 (1966) 233.
15 W. C. Wolsey, C. A. Reynolds and J. Kleinberg, *Inorg. Chem.*, 2 (1963) 463.
16 J. F. Harrod, S. Ciccone and J. Halpern, *Can. J. Chem.*, 39 (1961) 1372.
17 J. Halpern and B. R. James, *Can. J. Chem.*, 44 (1966) 671.
18 J. Halpern, J. F. Harrod and B. R. James, *J. Am. Chem. Soc.*, 85 (1961) 753; *ibid.*, in press.
19 A. A. Vlček, *Progr. Inorg. Chem.*, 5 (1963) 371.
20 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1962) 3594.
21 D. N. Lawson, M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, A (1966) 52.
22 B. N. Figgis, R. D. Gillard, R. S. Nyholm and G. Wilkinson, *J. Chem. Soc.*, (1964) 5189.
23 B. Martin and G. M. Waind, *J. Chem. Soc.*, (1958) 4284.
24 J. A. Osborn, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.* (1964) 3168.
25 M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7 (1965) 115.
26 A. P. Ginsberg, *Progr. Transition Metal Chem.*, 1 (1965) 111.
27 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, (1961) 5507.
28 H. B. Gray and C. H. Langford, *Ligand Substitution Processes*, Benjamin, New York, 1966. (a) p. 25, (b) p. 51, (c) p. 93.
29 F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson and B. L. Shaw, *J. Chem. Soc.*, (1961) 2207.

30 H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, 84 (1962) 1495.

31 M. Delépine, *Bull. Soc. Chim. France*, 45 (1929) 235.

32 M. Delépine, *Compt. Rend.*, 236 (1953) 559.

33 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1964) 1224.

34 F. Basolo, E. J. Bounsall and A. J. Poë, *Proc. Chem. Soc.*, (1963) 366.

35 G. C. Kulasingam and W. R. McWhinnie, *J. Chem. Soc.*, (1965) 7145.

36 B. Martin, W. R. McWhinnie and G. M. Waind, *J. Inorg. Nucl. Chem.*, 23 (1961) 207.

37 R. D. Gillard, J. A. Osborn and G. Wilkinson, *J. Chem. Soc.*, (1965) 4107.

38 J. Lewis, R. S. Nyholm and G. K. N. Reddy, *Chem. Ind.*, (1960) 1386.

39 S. S. Bath and L. Vaska, *J. Am. Chem. Soc.*, 85 (1963) 3500.

40 S. J. Laplaca and J. Ibers, *J. Am. Chem. Soc.*, 85 (1963) 3501; *Acta Cryst.*, 18 (1965) 511.

41 A. Sacco and R. Ugo, *J. Chem. Soc.*, (1964) 3274.

42 T. Kruck and W. Lang, *Angew. Chem.*, 77 (1965) 860.

43 M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn and G. Wilkinson, *Chem. Commun.*, (1966) 129.

44 M. C. Baird and G. Wilkinson, *Chem. Commun.*, (1966) 267.

45 L. Vaska, *Inorg. Nucl. Chem. Letters*, 1 (1965) 89.

46 R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, (1965) 5331.

47 J. A. Osborn, G. Wilkinson and J. F. Young, *Chem. Commun.*, (1965) 17.

48 F. H. Jardine, J. A. Osborn, G. Wilkinson and J. F. Young, *Chem. Ind.*, (1965) 560; *Chem. Commun.*, (1965) 131.

49 A. G. Davies, G. Wilkinson and J. F. Young, *J. Am. Chem. Soc.*, 85 (1963) 1692.

50 J. F. Young, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1964) 5176 and refs. therein.

51 D. M. Adams and P. J. Chandler, *Chem. Ind.*, (1965) 269.

52 R. J. Mawby and L. M. Venanzi, *Experimentia Supplementa*, No. 9, Essays in Coordination Chemistry, Birkhauser, Basel, 1964, p. 240.

53 M. A. Bennett and P. A. Longstaff, *Chem. Ind.*, (1965) 846.

54 A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 86 (1964) 1776; *Nature*, 205 (1965) 280.

55 L. Vaska, *J. Am. Chem. Soc.*, 86 (1964) 1943, and refs. therein.

56 J. Chatt, B. L. Shaw and A. E. Field, *J. Chem. Soc.*, (1964) 3466.

57 Unpublished results of J. F. Young, J. A. Osborn, G. H. Jardine and G. Wilkinson, quoted in ref. 69.

58 L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, 87 (1965) 4970.

59 L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, 83 (1961) 2784.

60 L. Vallarino, *J. Chem. Soc.*, (1957) 2287, 2473.

61 J. Chatt and B. L. Shaw, *Chem. Ind.*, (1960) 931; *ibid.*, (1961) 290.

62 J. Halpern, B. R. James and A. L. W. Kemp, *J. Am. Chem. Soc.*, in press.

63 B. R. James, A. McLaughlin and N. A. Memon, to be published.

64 L. Vaska, *Science*, 140 (1963) 809.

65 J. Collman, private communication.

66 J. Halpern and B. R. James, *Abstr. 142nd Meeting Am. Chem. Soc., Atlantic City, 1962*, p. 23N.

67 R. Cramer, *Inorg. Chem.*, 1 (1962) 722.

68 A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 87 (1965) 16.

69 M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, (1965) 6629.

70 R. Cramer and G. W. Parshall, *J. Am. Chem. Soc.*, 87 (1965) 1392.

71 G. W. Parshall and F. N. Jones, *J. Am. Chem. Soc.*, 87 (1965) 5356.

72 P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, 1 (1964) 143.

73 R. Cramer, *J. Am. Chem. Soc.*, 86 (1964) 217; *Inorg. Chem.*, 4 (1965) 445.

74 R. B. King, *Inorg. Chem.*, 2 (1963) 528.

75 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, (1957) 4735.

76 G. N. Schrauzer and K. C. Dewhirst, *J. Am. Chem. Soc.*, 86 (1964) 3265.

77 E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, (1959) 3178.

78 L. Porri, A. Lionetti, G. Allegra and A. Immirzi, *Chem. Commun.*, (1965) 336.

79 K. C. Dewhirst, *Inorg. Chem.*, 5 (1966) 319.

80 H. C. Clarke and W. S. Tsang, *Chem. Commun.*, (1966) 123.
81 M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1959) 3753.
82 R. J. Angelici and E. O. Fischer, *J. Am. Chem. Soc.*, 85 (1963) 3733.
83 M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, 2 (1964) 325.
84 G. Paiaro, A. Musco and G. Diana, *J. Organometal. Chem.*, 4 (1965) 466.
85 G. Paiaro and R. Palumbo, *Angew. Chem. Internat. Edn.*, 2 (1963) 620.
86 A. Kasahara and K. Tanaka, *Bull. Chem. Soc. Japan*, 39 (1966) 634.
87 J. Powell and B. L. Shaw, *Chem. Commun.*, (1966) 237, 323.
88 S. D. Robinson and B. L. Shaw; cited in J. E. Lyndon, J. K. Nicholson, B. L. Shaw and M. R. Truter, *Proc. Chem. Soc.*, (1964) 421.
89 R. E. Rinehart, H. P. Smith, H. S. Witt and H. Romeyn, *J. Am. Chem. Soc.*, 83 (1961) 4864; 84 (1962) 4145.
90 R. E. Rinehart and J. S. Lasky, *J. Am. Chem. Soc.*, 86 (1964) 2516.
91 N. R. Davies, *Nature*, 201 (1964) 490; 205 (1965) 281.
92 M. Orchin and G. L. Karapinka, *J. Org. Chem.*, 26 (1961) 4187.
93 R. F. Heck and R. Breslow, *J. Am. Chem. Soc.*, 83 (1961) 4023.
94 J. K. Nicholson and B. L. Shaw, *Tetrahedron Letters*, 39 (1965) 3533.
95 M. Orchin, *Adv. Catalysis*, 16 (1966) 1.
96 A. J. Canale, W. A. Hewett, T. M. Shryne and E. A. Youngman, *Chem. Ind.*, (1962) 1054.
97 P. Teyssie and R. Dauby, *J. Polymer Sci.*, Pt. B., 2 (1964) 413.
98 G. Natta, G. Dall'Asta and G. Motroni. *J. Polymer Sci.*, Pt. B., 2 (1964) 349.
99 C. E. H. Bawn, D. G. T. Cooper and A. M. North, *Polymer*, 7 (1966) 113.
100 P. Teyssie, F. Tripier, A. Isfendiyaroglu, B. Francois, V. Sinn and J. Parrod, *Compt. Rend.*, 261 (1965) 997.
101 S. McVey, paper presented at 48th C. I. C. Conference, Montreal, June 1965.
102 P. M. Maitlis and S. McVey, *J. Organometal. Chem.*, 4 (1965) 254.
103 R. S. Dickson and G. Wilkinson, *Chem. Ind.*, (1963) 1432.
104 M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, (1963) 365.
105 R. Cramer (a) *J. Am. Chem. Soc.*, 88 (1966) 2272; (b) *ibid.*, 87 (1965) 4717.
106 T. Alderson, E. L. Jenner and R. V. Lindsey Jr., *J. Am. Chem. Soc.*, 87 (1965) 5638.
107 G. C. Bond, *Platinum Metals Rev.*, 10 (1966) 65.
108 *Chem. Eng. News*, April 10th, 1961, p. 43.
109 J. Halpern, B. R. James and A. L. W. Kemp, *J. Am. Chem. Soc.*, 83 (1961) 4097.
110 R. F. Heck, *Adv. Chem. Series, Vol. 49*, Am. Chem. Soc., Washington D.C., 1965, p. 181.
111 J. Halpern and A. C. Harkness, *J. Am. Chem. Soc.*, 83 (1961) 1258.
112 J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, 83 (1961) 4102.
113 J. Halpern and S. F. A. Kettle, *Chem. Ind.*, (1961) 668.
114 B. R. James and G. L. Rempel, to be published.
115 R. F. Heck, *J. Am. Chem. Soc.*, 86 (1964) 2796.
116 W. Hieber and H. Lagally, *Z. Anorg. Chem.*, 251 (1943) 98.
117 L. F. Dahl, C. Martell and D. L. Wampler, *J. Am. Chem. Soc.*, 83 (1961) 1761.
118 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 8 (1965) 211.
119 L. Vallarino, *Inorg. Chem.*, 4 (1965) 161; *Internat. Conf. Coord. Chem., London, 1959*, Chem. Soc. Special Publication 13, London, 1959, p. 123.
120 D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, (1965) 1900.
121 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 3156.
122 E. O. Fischer and K. Bittler, *Z. Naturforsch.*, 16b (1961) 225.
123 H. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, 88 (1966) 1657.
124 R. H. Prince and K. A. Raspin, *Chem. Commun.*, (1966) 156.
125 J. Tsuji and K. Ohno, *Tetrahedron Letters*, (1965) 3969.
126 A. Rusina and A. A. Vlček, *Nature*, 206 (1965) 295.
127 J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, 87 (1965) 4008, and refs. therein.
128 L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, 88 (1966) 1334, and refs. therein.
129 L. Vallarino, *J. Inorg. Nucl. Chem.*, 8 (1958) 288.
130 L. Vaska, *Science*, 143 (1966) 769.

131 R. B. King, *Inorg. Chem.*, 5 (1966) 82.
132 J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, (1964) 4200.
133 M. R. Churchill, *Inorg. Chem.*, 4 (1965) 1734; *Chem. Commun.*, (1965) 86.
134 H. B. Gray and A. Wojcicki, *Proc. Chem. Soc.*, (1960) 358; *Abstr. 141st Meeting Am. Chem. Soc.*, Washington D.C., 1962, p. 32M.
135 A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, 83 (1961) 525.
136 F. Basolo, *Adv. Chem. Series, Vol. 49*, Am. Chem. Soc., Washington D.C., 1965, p. 92.
137 A. T. Brault, E. M. Thorsteinson and F. Basolo, *Inorg. Chem.*, 3 (1964) 770.
138 A. B. Lamb, *J. Am. Chem. Soc.*, 61 (1939) 699.
139 G. W. Bushnell, G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, A (1966) 719.
140 A. V. Belyaev, V. P. Kazakov and B. V. Ptitsyn, *Dokl. Akad. Nauk SSSR*, 160 (1965) 149.
141 S. A. Johnson, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, 85 (1963) 1741.
142 J. A. Broomhead, F. Basolo and R. G. Pearson, *Inorg. Chem.*, 3 (1964) 826.
143 G. Schmidt, *Z. Phys. Chem. (Frankfurt)*, 41 (1964) 26.
144 A. J. Poë, paper presented at the Inorganic Reaction Mechanisms Symposium, Toronto, June, 1966.
145 R. G. Pearson, C. R. Boston and F. Basolo, *J. Am. Chem. Soc.*, 75 (1953) 3089.
146 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1963, p. 115.
147 F. Basolo and R. G. Pearson, *Proge. Inorg. Chem.*, 4 (1962) 381.
148 W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, 87 (1965) 4472, and refs. therein.
149 R. E. Connick, in S. Kirschner (Ed.), *Advances in Chemistry of Coordination Compounds*, Macmillan, New York, 1961, p. 15.
150 C. K. Jørgensen, *Acta Chem. Scand.*, 10 (1956) 500; *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon, London, 1962.
151 H. H. Schmidtke, *Z. Phys. Chem. (Frankfurt)*, 40 (1964) 96; 45 (1965) 305; *Z. Anoeg. Chem.*, 339 (1965) 103.
152 G. T. Takaki and R. T. M. Fraser, *Proc. Chem. Soc.*, (1964) 116.
153 P. Hurwitz and K. Kustin, *Inorg. Chem.*, 3 (1964) 823.
154 H. Taube, *Can. J. Chem.*, 37 (1959) 129.
155 S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, 12 (1958) 265.
156 H. H. Schmidtke, *J. Am. Chem. Soc.*, 87 (1965) 2522.
157 R. G. Pearson, *J. Am. Chem. Soc.*, 85 (1963) 3533.
158 E. G. Torrible, *J. Inorg. Nucl. Chem.*, 28 (1966) 907.
159 H. L. Bott and A. J. Poë, *J. Chem. Soc.*, (1965) 5931.
160 E. J. Bounsall and A. J. Poë, *J. Chem. Soc.*, A (1966) 286.