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TRANSITION METAL HYDRIDES

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CONTENTS

A INTRODUCTION

The four year period between 1968 and 1971 has seen a proliferation of interest in transition metal hydrides which has been accompanied by significant and abundant empirical reports on the catalytic and physical properties of hydrido–metal species. These reports are discussed here.

More than 9 out of every 10 papers dealing with the chemistry of transition metal hydrides have dealt with the catalytic properties of these compounds. For this reason, it can be said that the catalytic activity of transition metal hydrides is their chemistry, and therefore this review begins with catalysis.

The Co and Ni triads in general have received the greatest amount of attention in the form of new complexes, catalytic activity and reaction mechanisms, spectroscopy, and theoretical studies. Out of the numerous review articles on Co, Rh and Ir hydride catalysis have developed rationales for transition metal hydride chemistry which promise to be one of the most unifying and organizing forces for inorganic chemistry since Werner proposed his "coordination theory". For these reasons and because these rationales are based on the coordination properties of d^8 metal systems, we begin the discussion of catalysis with the Co triad.

Following these introductory comments on d^8 metal systems we turn to a systematic application of these comments across the Periodic Table from right to left. When data suggest necessary general modification of the rationales developed for the Co triad such data are introduced and the results applied to the triad at hand. Upon reaching the Ti triad similarities with Zn are seen and the discussion is brought full cycle and partly back to the starting point. At various points material on nitrogen fixation by transition metal hydrides is introduced because of its unique historical and substantive relation to hydride catalysis.

At the end of the discussion of catalysis we turn to general comments on ligand variety and hydride preparation so as to give the reader a feeling for the great variety and versatility of transition metal hydride catalysts.

The unique spectroscopic properties of transition metal hydrides have all but monopolized the physical chemistry and physics of these complexes, so these data are discussed under a separate heading.

Finally, it should be noted that only reports from American, Canadian or British journals were reviewed unless it was clear that more data were necessary to establish a physical or chemical pattern.

B. CATALYSTS

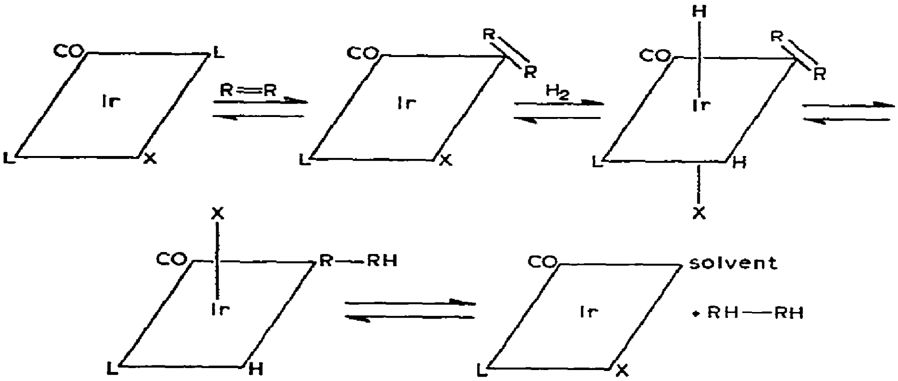
Transition metal catalysis is important to the study of transition metal hydrides because hydrido–metal species are often the active intermediates in many types of catalytic reactions of organic substrates[1,2].

Correlation of, systematization of, and prediction from data on these reactions are achieved by noting several common factors (*a*) the affinity of transition metals and their complexes to be coordinatively saturated[3]; (*b*) the ease and reversibility of H_2 chemisorption by the metals and certain complexes[4,5]; (*c*) the ease and reversibility of redox reactions[6–8], and (*d*) the difference between ligand field stabilization energy and the energy difference between highest occupied and lowest unoccupied metal orbitals These factors are interdependent and thus reflect more fundamental physical phenomena, but serve to organize, rationalize, and predict catalytic activities. Therefore, they are useful in understanding transition metal hydride chemistry, and in suggesting new metal hydrides and reaction pathways.

(i) Co triad

The catalytic activities and reaction mechanisms of Rh and Ir carbonyl–phosphines or halides are the models most often referred to for demonstrating the importance of metal hydride intermediates, and the role of coordinative unsaturation[3]. This is for several reasons: (*a*) they display many catalytically active valence states; (*b*) they catalyze a large number of reactions of organic substrates; (*c*) many of their complexes with organic substrates, and hydrido complexes, are stable and can be characterized, and (*d*) they have been most thoroughly studied in terms of isolation and chemistry of intermediates, and variation of stability, steric effects, and selectivity with change in ligands.

Since earlier reviews of these species[3,7–9], a great deal more literature has appeared on Ir and Rh. Brown et al., Vaska and Tadros, and Strohmeier[10] have studied the rate and equilibrium of alkene hydrogenation catalyzed by Vaska's catalyst, $IrX(CO)L_2$, at 80°C and 1 atm H_2. The mechanism was reported as



This reaction, which is in dynamic equilibrium, is sensitive to R=R and H_2 concentration, temperature, solvent, and X, but not L. The mechanism was deduced from kinetic and equilibrium data on intermediates such as

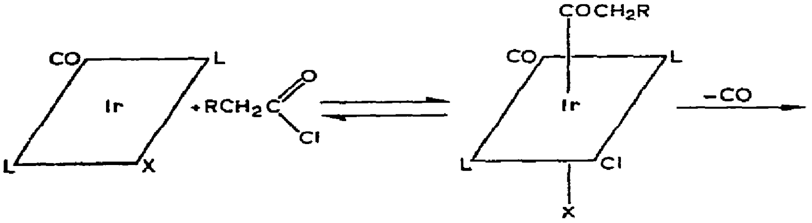
$$IrX(CO)L_2 + H_2 \rightleftharpoons IrX(CO)L_2H_2$$

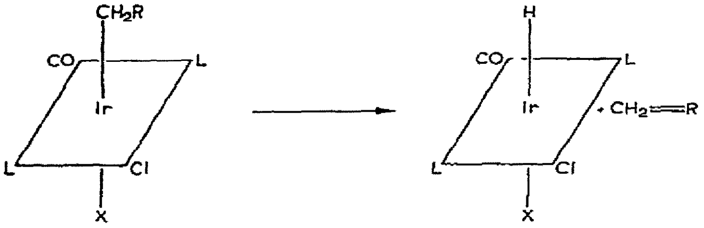
and

$$IrX(CO)L_2 + R{=}R \rightleftharpoons IrX(CO)L_2(R{=}R)$$

Strohmeier and Fleischmann[11] have also studied the selectivity of olefin hydrogenation by $IrX(CO)L_2$ as a function of X and L.

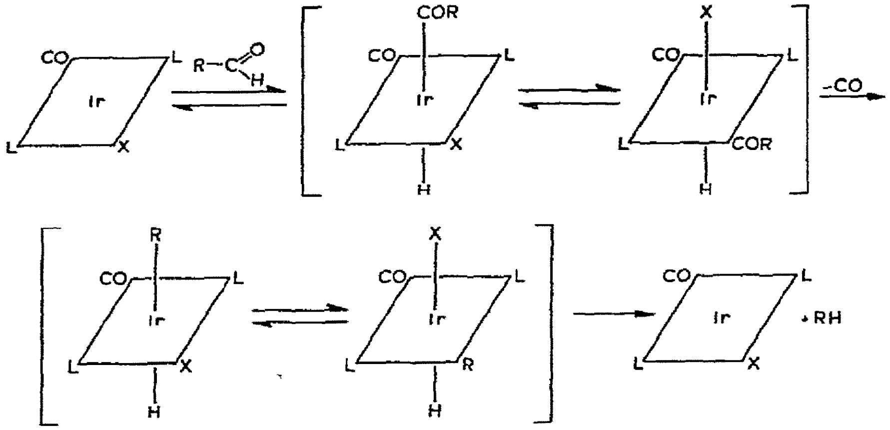
Blum et al.[12] reported decarbonylation–dehydrohalogenation of acyl halides with the same catalyst in the absence of H_2. The mechanism was summarized as





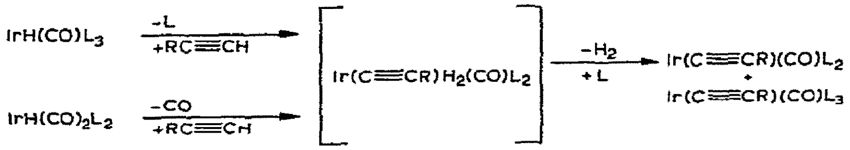
The similarities of the two mechanisms are obvious, the central importance of Ir hydrides apparent.

From these two mechanisms it is possible to predict the reaction between $IrX(CO)L_2$ and aldehydes



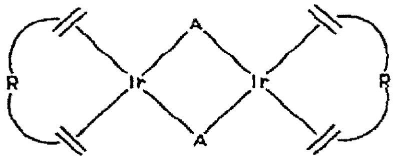
where the first two steps proceed via decarbonylation and the third via hydrogenation. The reverse of this mechanism, under H_2 and CO, represents hydroformylation of olefins.

Brown and Wilkinson[13] have reported the hydroformylation of alkenes and terminal acetylenes catalyzed by $IrH(CO)L_3$ and $IrH(CO)_2L_2$. Their observations are summarized as



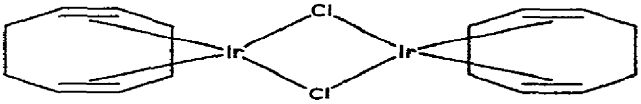
and the similarities with the above mechanisms are again apparent.

A second area of interest has been sandwich-bridged dimers of the general form

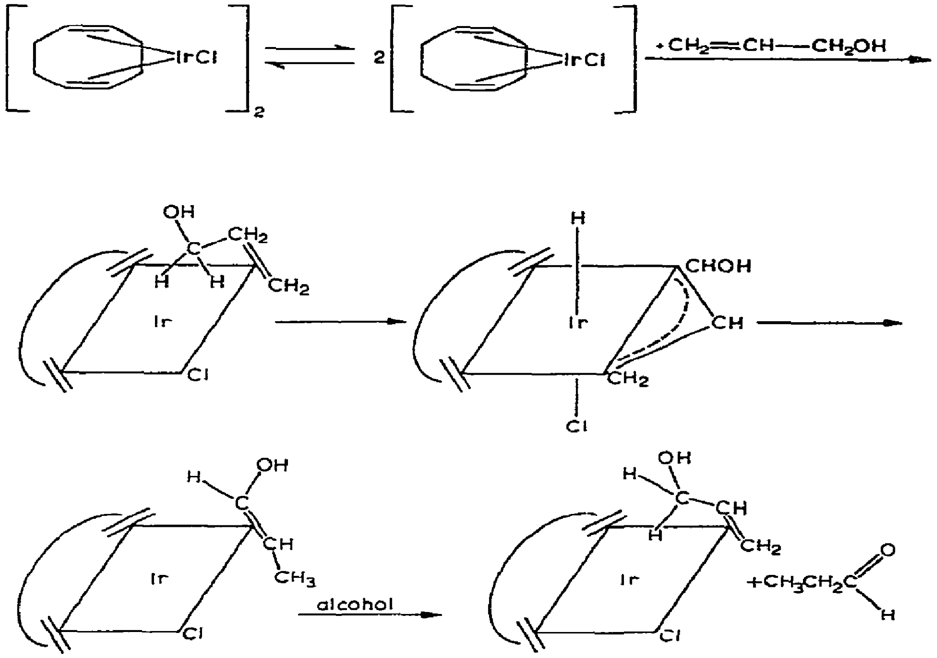


where A is an anion.

Pannetier et al.[14] have reported the catalytic activities and reaction mechanisms of

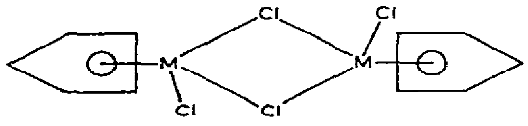


with allyl alcohol to give allyl ethers, propanal and propane. The mechanism for formation of propanal is

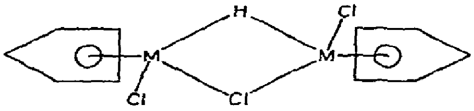


Reactions to give ethers and alkenes involved removal of OH^- rather than H from the alcohol. In the formation of propanal both hydrogenation and dehydrogenation (thus isomerization) and the dependence of products on concentrations are seen. We see that changing the ligands so as to increase the electron-donating ability of Ir decreases the amount of OH^- extraction in favor of H extraction, thus allowing control of products through tailoring of the catalyst

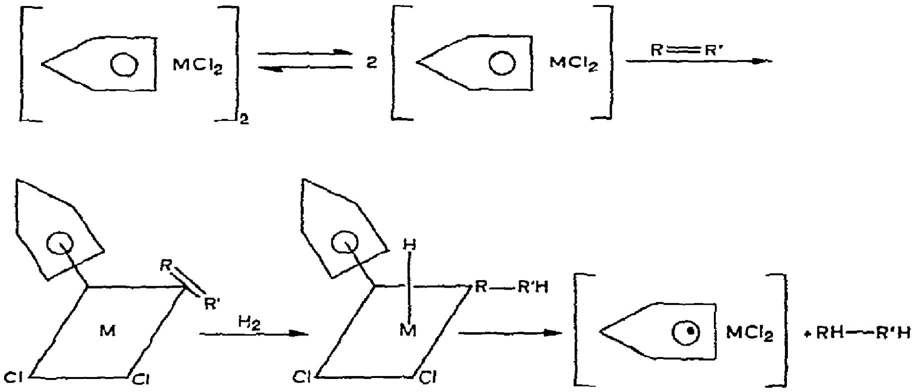
Maitlis and colleagues[15] have reported the use of



where M = Ir or Rh, as a hydrogenating catalyst for olefins. They isolated the hydride

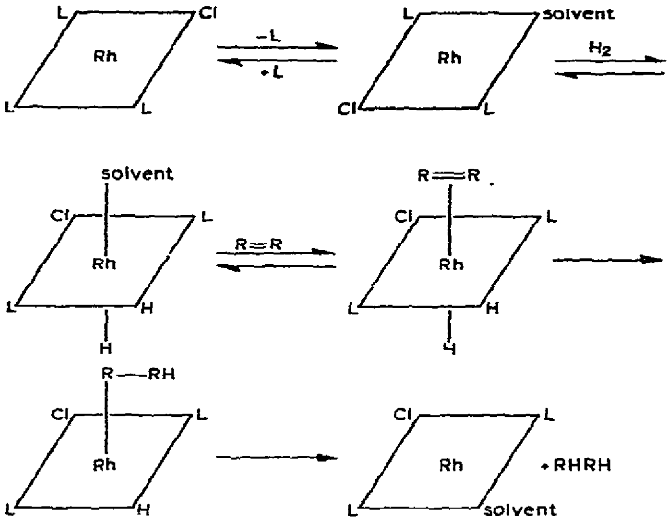


and confirmed its structure by IR deuteration experiments and high-field NMR studies. Both the chloride and hydride species were found to complex with olefins yielding monomeric complexes. Though no mechanism was reported, the work suggests



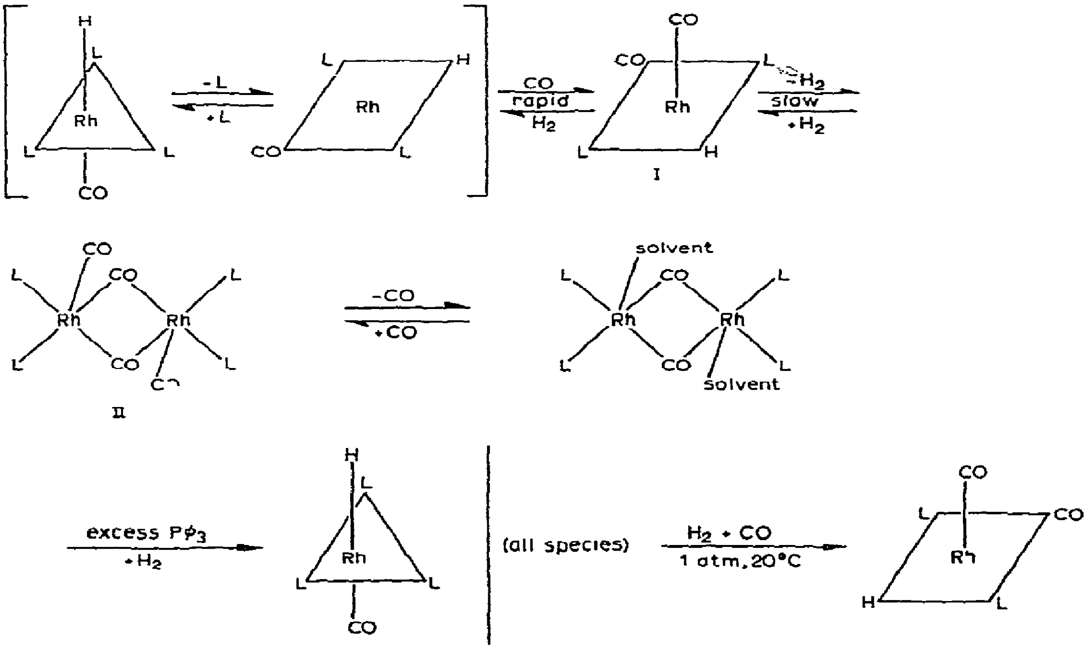
Comparisons of isomerization and hydrogenation reactions of $IrClL_3$ and $RhClL_3$ have been reported by van Gaal et al.[16].

The data for Rh-catalyzed reactions are more complex, but analogous to those for Ir. Most of the mechanistic work has been done by Wilkinson and colleagues. They have reported[17] the hydrogenation of olefins by $RhCl(P\phi_3)_2$ and proposed the mechanism

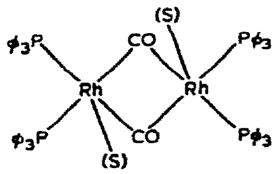


They have studied the effects of varying the halogen and phosphine ligands. In their earliest reports they found the rate of catalysis to increase in the order I > Br > Cl. Later they found the rate to be sensitive to phosphine ligand, the rate being "substantially reduced" for $As\phi_3$ while for $Sb\phi_3$ the complex was "essentially inactive". These trends were related to the ability of the ligands to activate molecular hydrogen via $RhX(PR_3)_2(S)$ intermediates. In this respect they found the olefin complex $RhX(PR_3)_2$(olefin) unable to activate molecular hydrogen. An excess of PR_3 was found to inhibit the rate of hydrogenation and a large excess produced complete inhibition. PR_3 ligands are less effective than $P(aryl)_3$ ligands in catalysis, and this was assumed to be due to less effective transfer of hydrogen atoms in the dihydrido species to the olefin. This explanation was supported by the observation that dihydrido–alkyl phosphine complexes lose H_2 less rapidly than aryl phosphine analogues. These authors have also reported on the steric influence of the phosphine ligands and have shown that alk-1-enes are selectively hydrogenated because of steric interferences of the triphenylphosphine ligands. For $P\phi_3$ complexes the selectivity increases in the order $H_2C{=}CHCH_3 > H_2C{=}CHR > H_2C{=}CR_2 > RHC{=}CR_2 > R_2C{=}CR_2$. Similar observations were made by Haines and Singleton[18] for $IrCl(CO)L_2$, and by Chen and Halpern[19] for the same complex. Chen and Halpern pointed out that $Ir(CO)(PMe_2\phi)_3X$ is more active toward H_2 than $Ir(CO)(P\phi_3)_2X$, which is attributed to a small amount of species with X^- associated with $Ir(CO)(PMe_2\phi)_3^+$ but outside the coordination sphere.

Wilkinson and colleagues[7,8] have also reported on the catalytic properties of $RhH(CO)(P\phi_3)_3$, and its chemistry with CO and H_2, which is more complex than that of the chloride. It was used as a catalyst for hydrogen exchange, isomerization, hydrogenation, and hydroformylation reactions. They reported the reactions in H_2 and CO

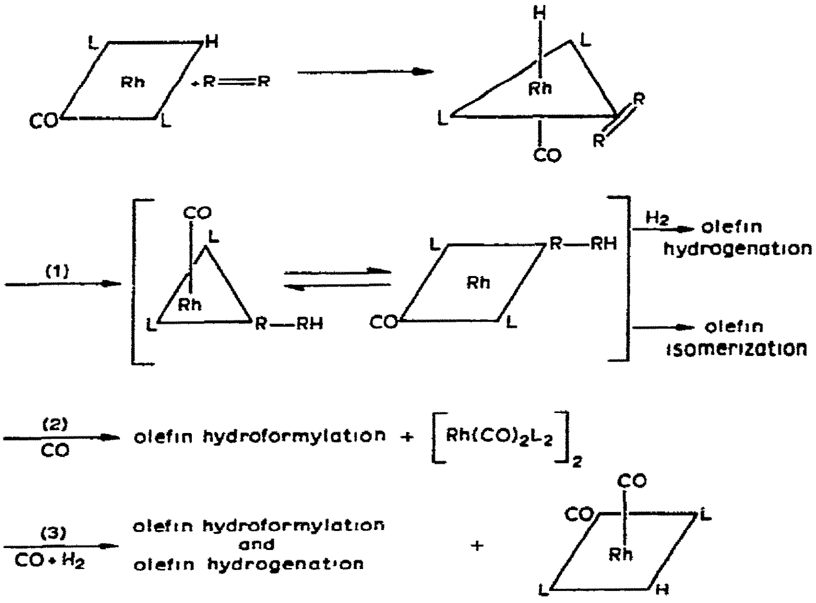


It was also found that $RhHL_2(CO)_2$ but not $RhL_3H(CO)$ reacts with ethylene. The coordination of solvent was supported by the variation in ν_{RhH} and τ_H with solvent and the isolation of



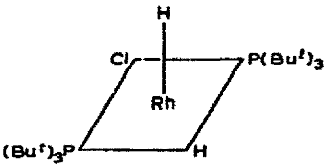
where $S = CH_2Cl_2$ or EtOH. Isolation of the benzene analogue resulted in decomposition of benzene as the solution was concentrated. Species I and II are unstable out of solution in the presence of air, N_2 or vacuum.

Thus a series of catalytic reactions are suggested starting from $RhH(CO)(P\phi_3)_3$

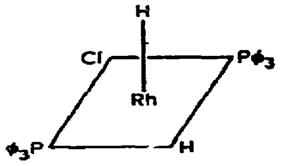


Many of these pathways have been proposed by Wilkinson. Oliver and Graham [20] have reported on Rh–ethylene complexes.

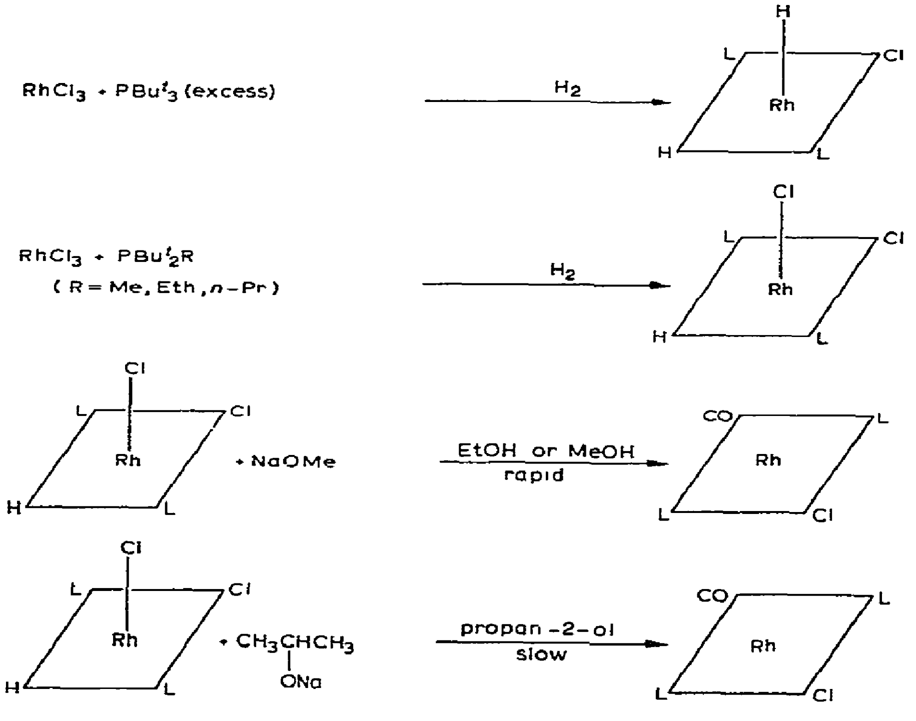
Recently, Shaw and colleagues [21] have examined some higher-valence Rh hydrogenation catalysts, and have isolated

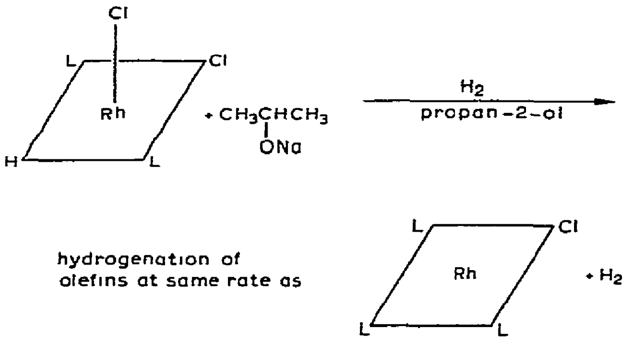


which is recognized as the active intermediate in Wilkinson's mechanism for hydrogenation with $Rh(P\phi_3)_3Cl$ and H_2. Shaw found this dihydrido–Rh complex to be very active itself in hydrogenating olefins. It is interesting to note that only the PBu^t_3 species could be isolated, in agreement with Wilkinson's work on the stabilization of dihydrido complexes by alkylphosphines via slowing the rate at which hydrogens are transferred to the olefins. Shaw also isolated



which is recognized as the Rh^{III} chloride analogue of $Rh(CO)(P\phi_3)_2H$, intermediate in Wilkinson's work with $RhH(CO)(P\phi_3)_3$ in a CO atmosphere. Shaw and colleagues reported that this Rh^{III} hydride is rapidly reduced to $RhCl(CO)(P\phi_3)_2$ in alcohol and base, thus giving the analogue of the compound obtained by Wilkinson and colleagues Shaw also reported that the Rh^{III} hydride catalyzes hydrogenation only in the presence of certain bases The results are summarized





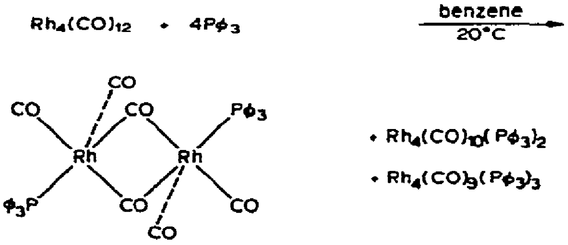
Thus it is obvious that Shaw has isolated the intermediates in Wilkinson's reaction mechanisms, and that the activity of these species and their relationship to $RhH(CO)(P\phi_3)_2$ and $RhCl(P\phi_3)_2$ are explained by Wilkinson's reaction mechanisms A theoretical and empirical investigation of the kinetic hydrogen isotope effect in catalytic hydrogenation of olefins with $RhCl(P\phi_3)_3$ and $RhH(CO)(P\phi_3)_3$ was reported by Siegel and Ohrt[22] and it was pointed out that the overall result of the effect will depend on the kinetic order of hydrogen. Thus its effect can be explained for these complexes on the basis of different overall reaction orders for hydrogen. It is of interest to compare this treatment with Wilkinson's reaction mechanisms. The rate-determining step for $RhCl(P\phi_3)_3$ is of order one with respect to hydrogen while for $Rh(CO)H(P\phi_3)_3$ it is zero.

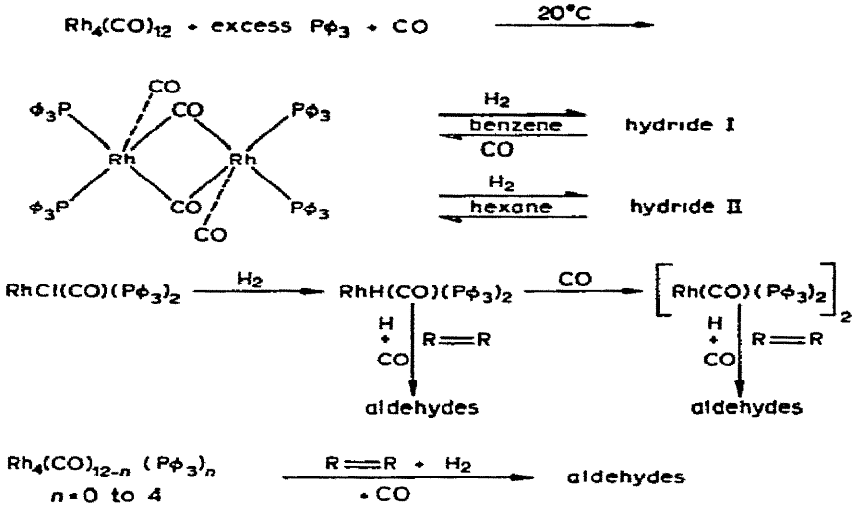
Strohmeier and Rehder-Stirnweiss[6] recently reported the reaction time and conditions for the isomerization of 1-heptene to a 1·1 *cis/trans* mixture catalyzed by $RhH(CO)(P\phi_3)_3$ and $RhCl(CO)(P\phi_3)_2$. The results appear to be in agreement with Wilkinson's mechanism[7–9].

Wilkinson and colleagues[7,13] have also investigated the hydroformylation of alkenes catalyzed by $RhX(CO)(P\phi_3)_2$. The principal catalytic species was found to be $RhH(CO)_2(P\phi_3)_2$. When the reactions start from $RhH(CO)(P\phi_3)_3$ alkenes undergo rapid hydrogenation at 25°C and 1 atm.

Hart-Davis and Graham[23] have reported CO insertion into Rh–C bonds in the reaction of benzyl and allyl halides with $(C_5H_5)Rh(CO)P\phi_3$.

Booth et al.[24] reported the hydroformylation of olefins catalyzed by Rh carbonyl cluster compounds. They isolated $[Rh(CO)_3(P\phi_3)]_2$ and $Rh(CO)_2(P\phi_3)_2$, which catalyzed this hydroformylation. Their observations are summarized



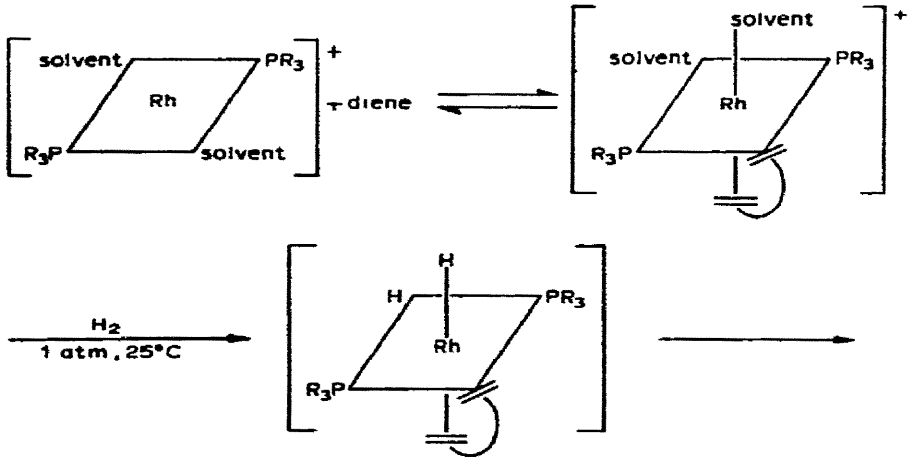


Thus each intermediate in Wilkinson's mechanism for the reaction of $RhH(CO)(P\phi_3)_3$ with CO and H_2 has been isolated and shown to be active in the manner suggested by Wilkinson. It is interesting to note that $RhH(CO)_2(P\phi_3)_2$ appears to be the primary intermediate in that it is more reactive and less stable than other species.

Attridge and Maddock[25] have reported a comparative study of the ring opening ability of various catalysts. Several points are of interest in a discussion of Wilkinson's mechanism: (*a*) second-row transition metals are the most active in a triad while those to the far right of the second row usually give 100% yields; (*b*) $RhH(P\phi_3)_2$ is not active for the group of Rh complexes reported, but $[RhCl(CO)_2]_2$ is the most active of the Rh complexes. Thus it appears that Wilkinson was unable to isolate $[Rh(CO)(benzene)(P\phi_3)_2]_2$ without decomposition of benzene because of the ring opening ability of carbonyl bridge Rh complexes.

Cassar et al.[26] have reported other Rh bridged complexes which cleave the cyclobutane moiety of the cubane molecule.

Schrock and Osborn[27,28] have isolated $[Rh(PR_3)_2]^+PF_6^-$, $Rh(diene)(PR_3)_2^+$ and $[Rh(PR_3)_4H_2]^+[PF_6^-]$. Their observations can be summarized as



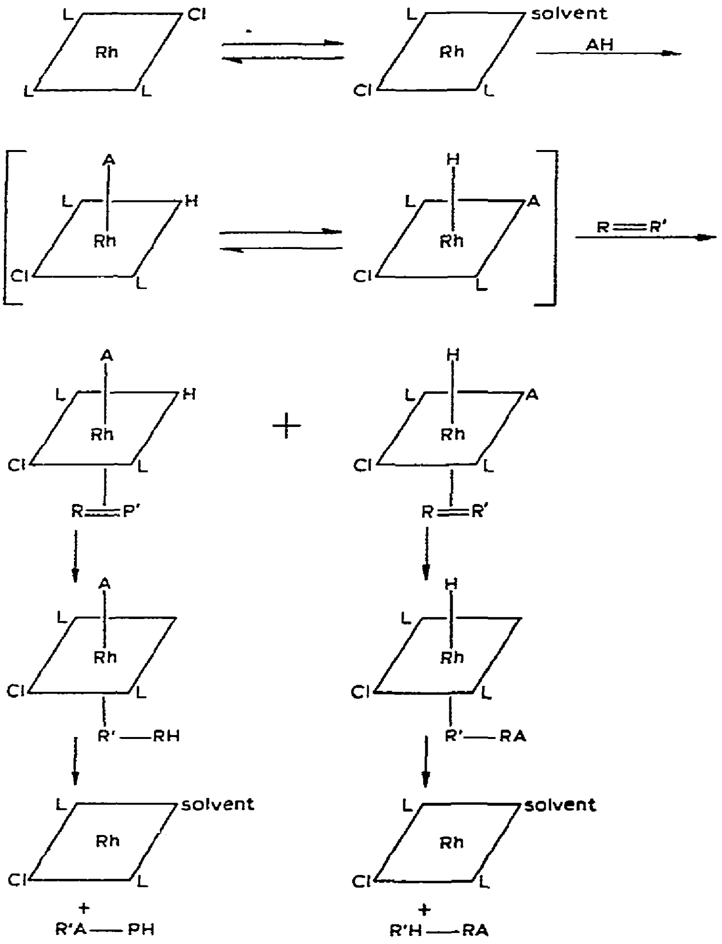
$$\longrightarrow \text{alkene and alkane} + RhH_2(PR_3)_2(\text{solvent})_2$$

$$\xrightarrow{CO} \left[RhL_2(CO)_3\right]^+$$

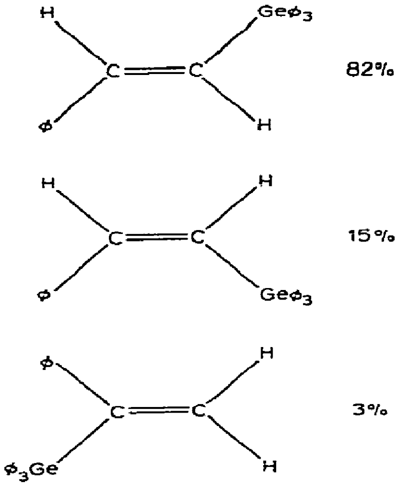
$$\xrightarrow[\text{diene}]{\text{excess}} \text{alkene} + \left[Rh(\text{diene})L_2\right]^+$$

$RhClL_2$(solvent) is totally inhibited from activating molecular hydrogen by addition of alkenes or dienes, while $[RhL_2(\text{diene})]^+$ is active toward H_2 (apparently two non-*trans* sites are necessary for activation) The activity of either species will depend on solvent exchange rates with ligands.

An interesting application of the reaction mechanisms for $RhClL_3$ is found when considering addition of AH to olefins, where A = Si, B, Ge, Al, etc. One would predict in general the following



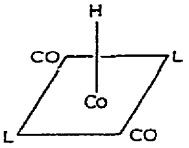
Corriu and Moreau [29] appear to have found this in their studies of hydrosilylation and hydrogermylation of phenylacetylene catalyzed by $RhCl(P\phi_3)_3$. They reported a product yield of

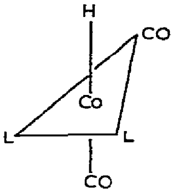


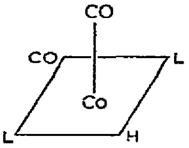
from which it cannot be determined whether A or H adds first to the acetylene or which carbon of the acetylene is bonded to Rh in the intermediate. The actual sequence of events will depend on steric factors of the ligands and substrates as well as on electronic factors, therefore space-filled models will be helpful in solving some of these questions. Of course, isolation of sigma-bonded acetylene intermediates would solve the problem.

Hui and Rempel [30] have reported $[Rh(OCOMe)_2]_2$ as a hydrogenation catalyst The dimer itself is a very active catalyst with easily displaced solvent ligands occupying terminal positions of the dimer. Some isomerization of olefins occurs but the presence of H_2 is required. Oxygen is converted to water by H_2 in the presence of the catalyst. Finally, it is one of an increasing number of H_2-activating catalysts which do not require phosphine or CO stabilizing ligands.

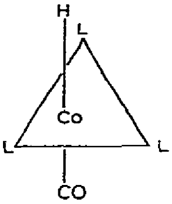
Catalysis by cobalt complexes is similar to that by Ir and Rh but varies somewhat because of lower and fewer oxidation states. Pregaglia et al. [31,32] have reported the hydroformylation, hydrogenation, and isomerization catalytic activities of various cobalt(O) carbonyl phosphine systems It is shown that considerable variation in products occurs with change in reaction conditions They have isolated $CoH(CO)_3PR_3$, $CoH(CO)_2(PR_3)_2$, $CoH(CO)(PR_3)_3$, $[Co(CO)_2PR_3]_m$ and $(\pi\text{-allyl})Co(CO)_2PR_3$ from $Co_2(CO)_8/PR_3$-catalyzed reactions of olefins, and have shown that each is capable of catalyzing reactions between olefins and H_2 or CO with greater stereospecificity than $Co_2(CO)_8$ or $HCo(CO)_4$ Both Pregaglia et al. and Piacenti et al [33] have suggested the greater stereospecificity is due to the bulky phosphine ligands. However, because of the stabilizing effects of phosphine ligands on hydrides and carbonyls the possibility that differences in ligand exchange rates give rise to the stereospecificity cannot be ruled out, especially in light of the fact that the hydrides have been found to undergo rapid H and CO ligand exchange and molecular isomerization. All evidence indicates slow, if any, phosphine ligand exchange. On the basis of NMR and IR data for hydride ligand in $CoH(CO)_2(PR_3)_2$ the complex is assigned three isomers



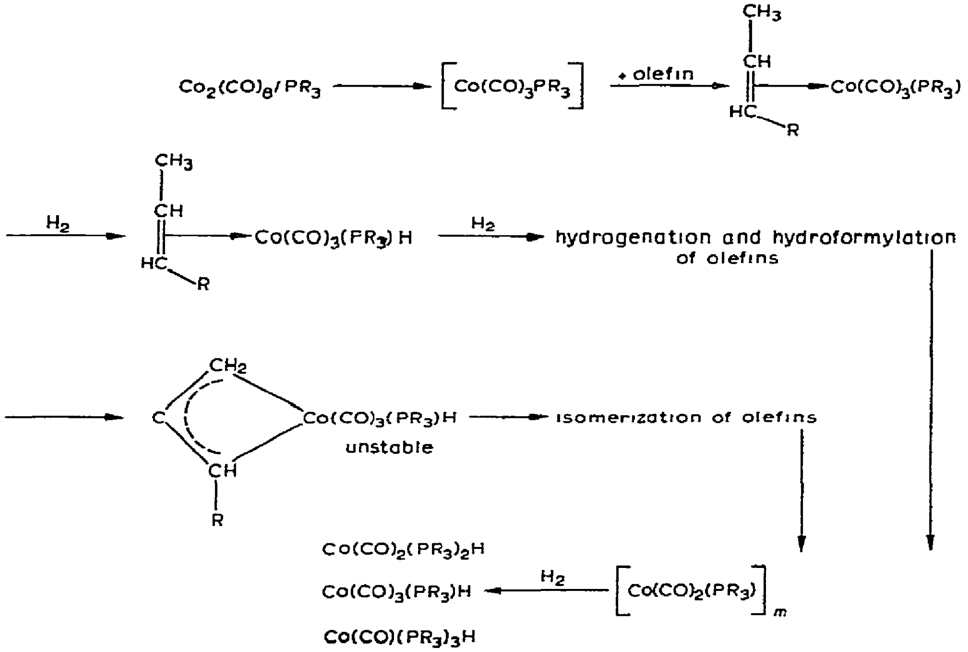




while $CoH(CO)(PR_3)_3$ is assigned



On the basis of variation of products with change in temperature, H_2 pressure, CO pressure, solvent and substrate, and because of the isolation of species discussed above the authors postulated that the reaction mechanisms are very complex for $Co_2(CO)_8/PR_3$ catalysts However, the data suggest the following sequence of events.



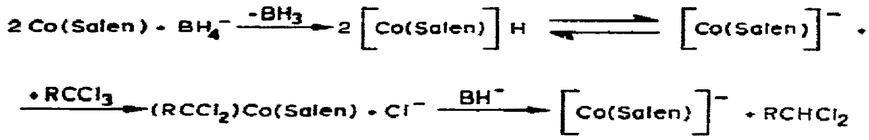
Ono et al.[34] have reported the catalytic hydroformylation of acrylonitrile by $Co_2(CO)_8$ in MeOH.

Taylor and Orchin[35] have studied the isomerization and hydrogenating activities of $HCo(CO)_4$. In order to do this without hydroformylation, they used *cis*-1,2-diphenylcyclobutene, maleate and fumarate, which have been shown to undergo hydroformylation only by about 5%. The rates of the reactions were investigated and the tentative conclusion drawn that hydrogenation of fumarate goes via 1,4 addition while that of maleate goes via 1,2 addition.

Otsuka and Rossi[36] reported the synthesis of $Co(C_8H_{13})(C_8H_{12})$, which is similar in properties to that of the hydrides. The complex, however, showed no high-field NMR activity and no Co—H IR bands. It was concluded that the complex is a convenient source of hydrides but that the complex itself is not a hydride. Further investigation[37] showed that $Co(CO)(C_8H_{13})(C_8H_{12})$ adsorbed CO at –60°C to give the thermally unstable $Co(CO)(C_8H_{13})(C_8H_{12})$, which yielded $CoH(CO)(PR_3)_3$ and $Co(CO)(C_8H_{13})(PR_3)_2$ when PR_3 was added to the solution. The discovery of $CoH(CO)(PR_3)_3$ completed a series of complexes $CoH(CO)_n(PR_3)_{4-n}$ ($n = 0$–4). The authors compared the thermal stability and protonic characteristics of the hydrogen ligand for each member of the series.

Rinze and Noth[38] have studied the reaction between cyclopentadiene and $CoH(N_2)(P\phi_3)_3$ or $CoH_3(P\phi_3)_3$ to give $(\pi\text{-}C_5H_5)Co(P\phi_3)_2$ and various hydrogenation products of cyclopentadiene. Their data[38] on this reaction and reaction of butadiene with $CoH(P\phi_3)_3N_2$ indicate (in agreement with those of Otsuka and Rossi) an ability for Co—phosphine systems to coordinate to delocalized bond systems of substrates, to hydrogenate, and to convert to hydrides and/or N_2 complexes in a dynamic process

A novel catalytic reaction was reported by Levitin et al.[39], whereby trichloroalkanes were reduced by BH_4^- in the presence of bis(salicylidenato)ethylenediamine cobalt at room temperature. The proposed mechanism is unusual in that the hydride ligand does not transfer an electron to the substrate, but reduces the cobalt complex. The mechanism is given as



$$2\,Co(Salen) + BH_4^- \xrightarrow{-BH_3} 2\,[Co(Salen)]H \rightleftharpoons [Co(Salen)]^- + H^+$$

$$\xrightarrow{+RCCl_3} (RCCl_2)Co(Salen) + Cl^- \xrightarrow{BH^-} [Co(Salen)]^- + RCHCl_2$$

Mono- and dichlorides do not react.

Similar equilibria between Co^{I}, Co^{II} and Co^{III} and hydrido—cobalt species appear to be involved with the reduction of vitamin B_{12} and its related complexes. Schrauzer et al.[40] have reported the equilibrium

$$H^+Co^{I} \rightleftharpoons H\text{—}Co^{II} \rightleftharpoons {}^-H\text{—}Co^{III}$$

for various B_{12}-related species.

Wayland and Mohajer[41] have reported the reversible interaction of O_2 and CO with cobaltoporphyrin and vitamin B_{12} derivatives.

Thus the importance of transition metal catalysis to hydride chemistry is apparent. The stoichiometry, accessibility, and reactivity of the intermediates are governed by the characteristics of the metal outlined earlier, and by steric and electronic factors of the ligands.

(ii) Zn triad

The availability of coordination sites is determined by the number of valence electrons and by the relative energies of unoccupied orbitals All transition metals except Zn, Cd and Hg can make use of *ns*, $(n-1)d$ and *np* orbitals. For Cd and Hg only *ns* and *np* orbitals are available for coordination, with the *np* orbitals lying approximately 87 kcal/mole-electron above the valence 5*s* orbitals of Cd^0 and 112 kcal/mole-electron above the valence 6*s* orbitals of Hg^0

Even though there have been several reports during the 1950's of the preparation of hydride species of Cd and Hg, with isolation below −100°C, there have been no definitive spectroscopic data (e g NMR or IR) reported for the products. In light of the energy barriers to the *np* orbitals, it is doubtful that these hydride species did in fact form. Introduction of H^- ligands into the coordination sphere of Cd^{II} and Hg^{II} apparently gives rise to too small a difference between the ligand field stabilization energy and the energy barrier to the *np* orbitals to allow stabilization of the otherwise reactive H^- ligand The energy necessary for use of the *np* orbitals in the coordination sphere of the divalent metal is indicated by the fact that only one *p* orbital is energetically allowed in the coordination sphere of organomercury compounds, and that only stable anionic or neutral ligands form four-coordinate complexes. It should, however, be noted that some evidence exists for the use of more than one *np* orbital in organomercury compounds[42]

With regard to oxidative addition of H_2 by Hg^0 or Cd^0, it has been found that neither metal undergoes chemisorption of hydrogen. Further, a correlation is observed[43,44] between an $xy \rightarrow x^2-y^2$ electron transition energy in $M(\phi_2PCHCHP\phi_2)_2^+$ and the activation energy for oxidative addition of O_2 and H_2 to the species, where M = Co. Rh and Ir. This observation suggests that electron promotion from a filled orbital to an empty orbital precedes oxidative addition, and that the process takes less than 30 kcal/mole-electron for metal complexes to the left of Zn, Cd and Hg in the Periodic Table The hydride chemistry of Cd and Hg is known[45,46] to be associated with a similar process, namely electron excitation to triplet state Cd $[5^3P_1]$ and Hg $[6^3P_1]$. However, the only available orbitals for electron promotion require more than 3 times the energy than for $M(\phi_2PCHCHP\phi_2)_2^+$, which may explain the lack of ground state Cd and Hg hydrides. An interesting possibility which has not been reported would be the reaction of Hg^{II} or Cd^{II} as the PF_6^- or $B\phi_4^-$ salt with molecular hydrogen under conditions of photolysis. In this case the coordination sphere would be an *sd* hybrid into which hydrogen atoms might enter to form $M(H)_2^{2+}$ species with neutral hydrogen ligands

There have been several reports on Cd/Al_2O_3, Cd/M and Hg/M catalysts (where M is another transition metal or its complex) for hydrogenation, isomerization, hydrogen scrambling, etc. of organic substrates, but the role of Cd and Hg is not understood.

The case of zinc is somewhat different. The ease of oxidation and expected lower energy of its 4*p* orbitals raises the possibility of considerable ground state (in contrast to Cd and Hg triplet state) hydride chemistry. The reports by Shriver et al.[47] of $NaZn_2(CH_3)_2H_3$, by Ashby and Beach[48] of K_2ZnH_4 and by Chang and Kokes[49] on the chemisorption of H_2 on ZnO are therefore not totally surprising. It is interesting to note that Chang and Kokes have observed two types of chemisorption; one which is very rapid and completely reversible, and which reacts readily with ethylene, and the other which is irreversible, slow and does not react with ethylene The first might be expected to be associated with *np* coordination where the difference between ligand field stabilization energy and 4*p* orbital energy would be low. The second type might be the result of reaction within the coordination sphere between hydrogen and oxygen to form water and Zn^0 Vaska and Tadros[50] have observed similar reactions for Pt, Ir. Rh and Ru. The Zn^0 would then be oxidized back to ZnO by air or to ZnH_2 by hydrogen.

The importance of ease of metal oxidation (or reduction) is seen not only in the hydride chemistry of Zn, Cd and Hg, but is also obvious in terms of expanding the coordination sphere of the metal catalyst Work by Wilkinson on Rh-catalyzed hydrogenation, and by Grundy et al.[51] on Ru and Os, has demonstrated how the ease of oxidation from a d^{10} to a d^8 to a d^6 metal system gives rise to important variations in the species capable of H_2 activation and elimination of various moieties from organic substrates. It is important, however, to realize that ease of oxidation does not always govern whether the metal will easily undergo "oxidative addition". In this regard Conti, Donati and Pregaglia[62] have pointed out that $PdCl_2$ will bring about isomerization of olefins by hydrogen abstraction from allylic positions, while $PtCl_2$ will not. If the activated complex in the reactions of transition metals with hydrogen is an electron-excited metal species, it cannot a priori be expected that oxidative addition rates would follow the metal oxidation potential in each case. Nonetheless, the overall redox processes are facile enough to be governed in most cases by concentration effects of ligands, substrates, and solvents. Blum and Kraus[12] have indicated such observations for $IrX(CO)L_2$, as have Haines and Singleton[18] for $Rh[P(n\text{-}C_4H_9)_3]_4^+$.

Affinity for coordinative saturation can also be used to explain why most stable valence states during catalytic activity appear to be those which give rise to a d^n, where n is even, configuration. Levitin et al [39], Pregaglia et al.[31] and Chalk[52] have observed this for cobalt It is characteristic to note the oxidative addition of only one ligand to Rh—d^9 complexes compared with oxidative addition of two ligands to Pt—d^{10}, and the preference of the metals for the hydrogen moiety

Coordinative saturation can be used to explain condensation of metal complexes to form cluster compounds Co, Rh and Ir exemplify these properties well. Each has been found to form cluster compounds by condensation. where each metal is bonded to another, thus obtaining coordinative saturation for d^9 systems by forming d^{10} metal dimers or polymers. Systems such as $M_4(CO)_{12}$, where M = Co, Rh and Ir, and $M_3(CO)_{12}$, where M = Fe, Ru and Os, retain their cluster arrangement when CO is replaced by phosphine, and break up only when forced to in the presence of excess phosphine and CO, yielding[15,24] for example $[Rh(P\phi_3)_2(CO)_2]_2$, which is unstable in solution. Wilkinson's[7] observations on the reaction

$$2\,RhH(CO)_2(P\phi_3)_2 \underset{H_2}{\overset{CO}{\rightleftharpoons}} [Rh(P\phi_3)_2(CO)_2]_2$$

are interesting in this respect. The fact that the reaction also occurs when the hydride species is vacuum-pumped or swept with N_2 indicates that condensation occurs because hydrogen is being removed and a Rh–d^9 system is being produced. Similar reversible reactions between hydrido–Ir and Ir carbonyl phosphines were reported by Malatesta et al.[53] and Whyman[54]. Booth et al.[24] and Wilkinson found the Rh dimer to be highly reactive in the solid state and stable only under CO in solution. No magnetic data have been reported for the dimer, such information would allow elucidation of the degree of electron pairing between Rh atoms (i e metal–metal bonding) Even though these d^9 systems are too reactive for isolation, analogous d^7 systems are stable enough to be isolated as the solid in air. White et al.[15] have isolated $[Rh(C_5H_5)Cl_2]_2$, which is unstable in solution but unreactive in the solid state. Undoubtedly the d^7 systems can be isolated because they do not undergo oxidative addition. No magnetic data are available on these compounds either. In the presence of mild reducing agents $[Rh(C_5H_5)ClH]_2$ was isolated. It appears that the dimer is prevented from breaking up to form Rh–d^8 complexes because of the lack of ligands to coordinatively saturate the d^8 system. An interesting Rh–d^7 system was prepared by Masters et al.[21]. A stable $RhCl_2(PR_3)_2$ species was prepared in which the paramagnetism is less than spin-only It appears that the Rh–d^7 is obtaining spin pairing by some means No molecular weight or structural data are available, and the complex was assigned this structure on the basis of comparison of its IR spectrum with that of an "analogous" Pd–d^8 system. Interestingly, Rose and Wilkinson[55] reported an Ru^{II} anion cluster, $Ru_5Cl_{12}^{2-}$, which shows magnetic behavior consistent with one unpaired electron per cluster.

Correlation of chemical activities of other transition metal groups with those of Co, Rh and Ir is possible within the framework of coordinative saturation. It is of interest to examine first some energy considerations of the ability of a metal to chemisorb H_2. Bond[4] has reviewed the reactions

$$2\,M + n\,H_2 \rightleftharpoons 2\,MH_n$$

and showed that except for Cd and Hg they are all exothermic with the heat of adsorption decreasing from left to right across the transition series. Bond points out that heats of adsorption are true measures of the metal's contribution to hydrogen activation chemistry, while rate and equilibrium data for reactions other than simple hydrogen addition to metals cannot give a clear, unambiguous picture of metal–hydrogen reactivity. These other reactions are rate-controlled by processes which occur after initial adsorption (for complexes the rate-determining step may be before or after), and equilibrium-controlled by steric factors These observations are in agreement with a number of papers on homogeneous catalysis by transition metals. In this regard it is important to note that several authors have proposed that the most significant stabilizing effect of ligands such as PR_3 is that they prevent substrates from occupying coordination sites or prevent coordination sites from extracting hydrogen or CO from substrates by occupying the site itself.

The question of which ligands are involved in a necessary dissociation step to activate substrates[56] is far from total elucidation. There is evidence that for species such as MX_2L_2 in some cases L is displaced and in others X^- may be displaced[57–65]. There is also evidence that organic substrates need not enter the coordination sphere to undergo catalytic reaction[66–68].

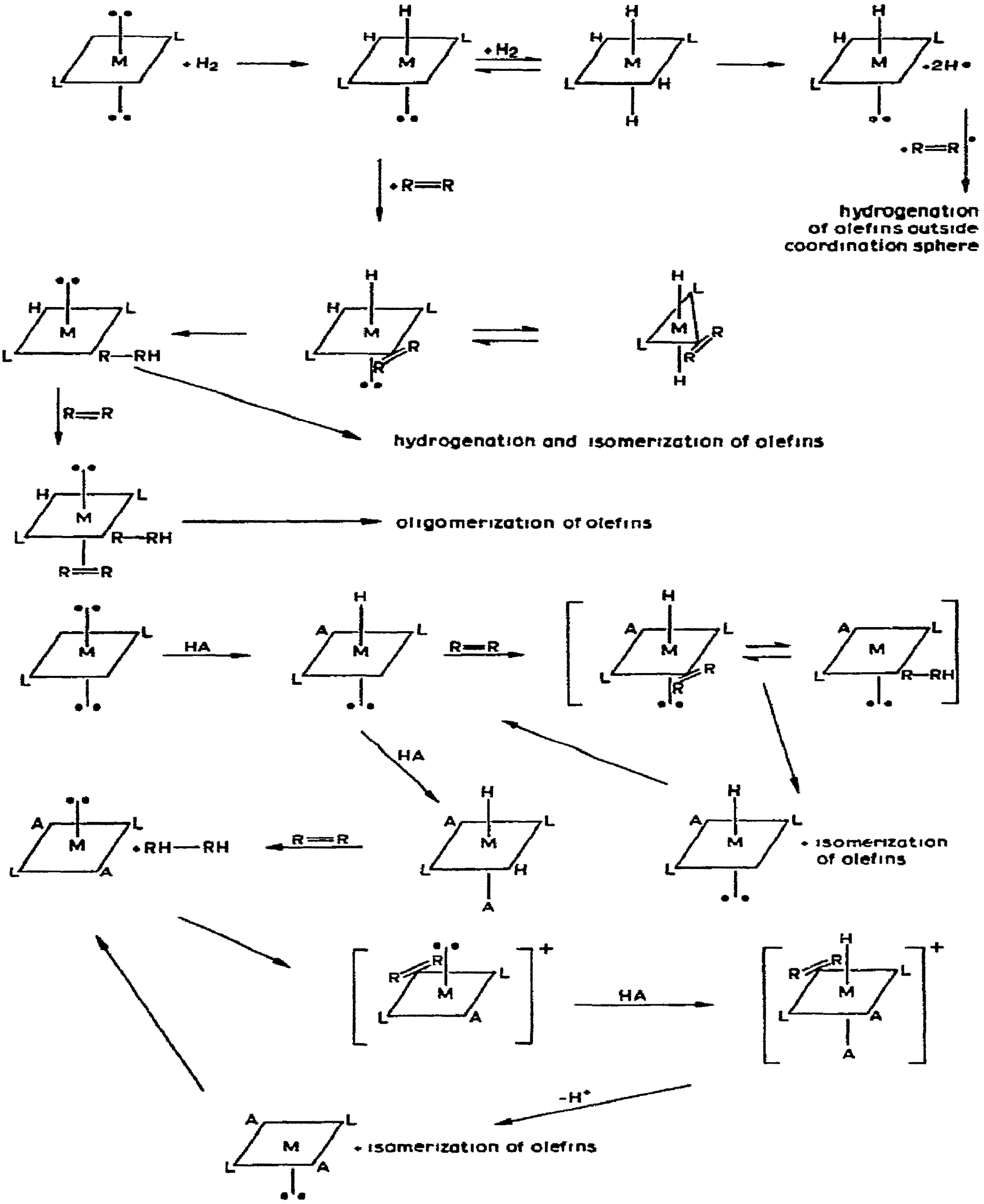


Fig 1. Oxidative addition to d^{10} metal systems

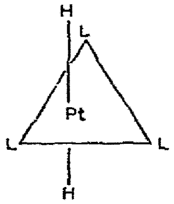
(iii) Ni triad

Catalysis by Ni, Pd and Pt differs from that by Co, Rh and Ir in that the Ni hydrides are more stable than those of the Co triad. This was also observed by Bond[4], who found the heat of adsorption of H_2 to be approximately 10 kcal/mole greater for the Ni triad than for the Co triad. This increased metal–hydrogen bond energy appears to be responsible (or vice versa) for the ability of Ni^0, Pd^0 and Pt^0 to undergo two-electron oxidative addition as well as the one-electron oxidative addition found for Co^0, Rh^0 and Ir^0. It is interesting to note the affinity for either H^+ or $H\cdot$, indicating that it is the hydrogen nucleus for which the metals have their affinity. This of course is what would be expected from a simple electrostatic model, or from a quantum-mechanical electron repulsion model

Two examples of possible d^{10} reaction mechanisms suffice to display how these metal systems can give rise to differences in catalytic activity and still be organized under the concept of coordinative unsaturation (Fig 1).

The first mechanism appears in part to have been observed by DePasquale[69] for $Ni(P\phi_3)_2$. The reversible addition of H_2 to Ni^0 has been reported by Gasser et al.[72], while Green et al[130] have isolated stable Ni hydrides, as has Tolman[2]. Green et al. have pointed out that the thermal stability order for the Ni triad hydrides is Pt > Pd > Ni, which follows the order of energy separation between the lowest empty molecular orbital and highest occupied orbital, and that stable Ni hydrides were the result of bulky ligands which prevent geometric deformation. Five-coordinate Ni hydrides were isolated by Schunn[71] from addition of H^+ to Ni^0L_4, in contrast to Pt and Pd which form four-coordinate species. The existence of π-bonded olefins is supported by IR and quantum-mechanical studies on the chemisorption of olefins at Ni^0 surfaces by Shopov et al[70], while the existence of alkyl–Ni complexes is supported by Matsumoto et al.[68] in their studies of hydrogenolysis of hexanes by Ni^0 and Pt^0.

Gerlach et al.[77] have reported that H_2 readily adds to PtL_3 to form five-coordinate species which are thermally unstable even at –40°C in hydrocarbon solvents. The NMR spectrum is consistent with the structure



The same PtL_3 reacts with H_2O and ROH to give $HPtL_3^+$ in a reversible (for $L = PEt_3$) reaction. Clark and Puddephatt[78] have reported isolation and reactions of Pt σ- and π-bonded hydrocarbons.

The second mechanism appears to be that observed by Miller et al.[73] for $Ni(PR_3)_2(C_2H_4)$. In this respect it should be noted that van der Linde and de Jongh[60] observed that $PdL_2(C_2H_4)$ easily loses ethylene to give PdL_2, while Leites et al[61] have observed that for $PdCl_2(\pi\text{-}R{=}R)$ systems the Pt–Cl rather than the Pt–R=R bond breaks when treated with DMSO or $P\phi_3$. Further, Conti et al [62] have reported that DMSO stabilizes π-allyl Pd^{II} systems. Nelson et al [76] have shown that $PtL_2(RC{\equiv}CR')$ is square planar, with loss of acetylenic triple bond character, stabilized by bonding of Pt to two carbons on the acetylene. Clark and Kurosawa [63] indicated that for Pt HXL_2 hydrogenation of $R{=}R$ the olefin replaces X *trans* to H followed by hydrogen migration. These observations and those of Tolman [2] indicate that the stability of ligands with respect to substitution increases in the order $H > P >$ alkene $> A^-$ for the Ni triad, following the *trans*-effect order. Tripathy et al. [79] have pointed out that $Pt^0L_2(R{\equiv}R)$ converts to PtL_2A_2 in the presence of HA during hydrogenation of the acetylene.

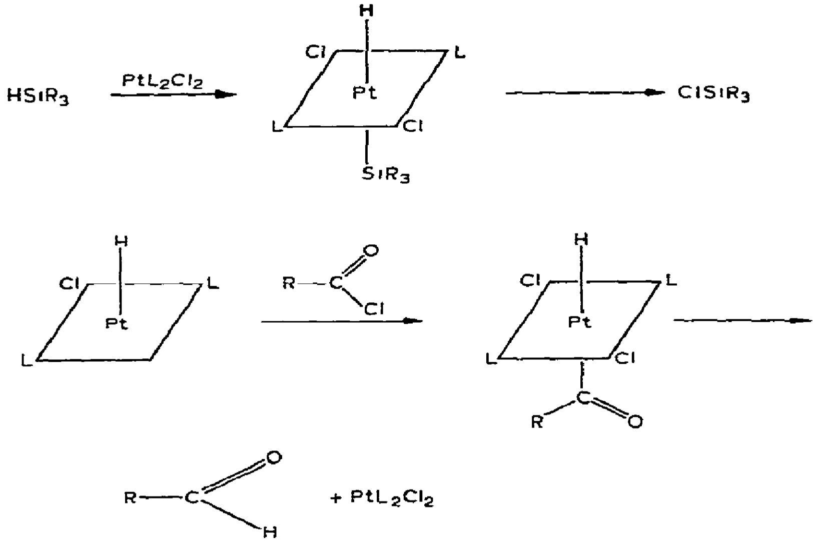
It is important to point out that hydrogen adds *cis* to the acetylene [80] in $PtL_2(R{\equiv}R)$, and not *trans* as reported earlier.

The oxidative addition of HX to Pd^0 complexes has been discussed by Kudo et al. [81].

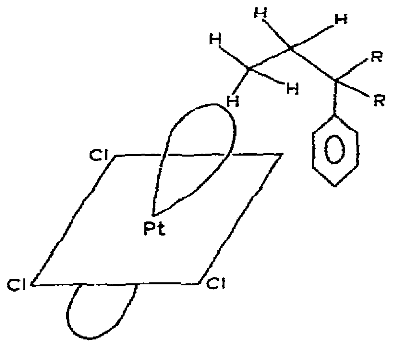
LaMonica et al. [83] noted that the reactivity of actual d^{10} Pt^0 systems with small gaseous molecules and that of formal d^{10} systems such as $M(NO)L_3$, where M = Rh or Ir, and $M(NO)_2L_3$, where M = Ru or Os, was similar, particularly with respect to H_2 and HCl.

The similarities between the second mechanism and hydrosilation of olefins are known [74]. Bennett and Orenski [75] have reported hydrosilation by Ni^0 and Ni^{II} complexes with the observation that square planar species are more active than tetrahedral ones. Hara et al [131] have reported that Pd^0 and Pd^{II} phosphines are active hydrosilylation catalysts Yamamoto et al [82] have discussed hydrosilation with Pt^0 complexes.

An interesting variation was reported by Dent et al. [132] for reaction between $HSiR_3$ and RCOCl in the presence of Pt^{II}. The results can be summarized as



Garnett and Kenyon [84] have examined the steric effects on hydrogen exchange catalyzed by Pt^{II}, and found selectivity to be determined by steric factors. They have proposed species such as



for hydrogen exchange on substituted benzenes. Lukas and Blom[85] have observed that allyl chlorides of more than three linear carbons disproportionate, giving hydrogenation products, and did not isolate the π-allyl Pt complexes which were found with shorter carbon chains.

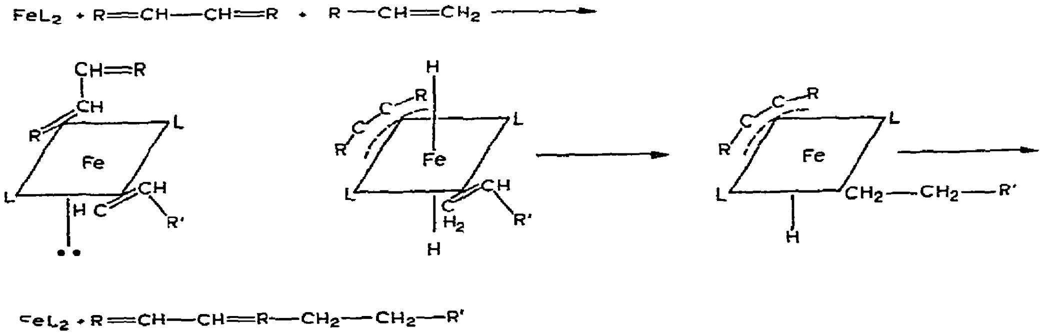
An interesting application of Pt^0 affinity toward activation of H_2 was reported by Pri-Bar and Buchman[86] who used platinum black for general labeling of organic compounds by catalytic exchange with gaseous tritium.

Finally, Pd–hydrides are often the end products of reactions catalyzed by Pd complexes. Graziani et al.[88] have observed this for carbonylation of ethanol by $PdCl_2$, while Heck[89] made the same observation for arylation and carbomethoxylation of olefins by $Pd(OAc)_2$.

(iv) Fe triad

For transition metal groups to the left of the Co triad it becomes difficult to apply the concept of coordinative unsaturation. This arises because of the increasing number of vacant *d* and *p* metal orbitals. Fe^0, Ru^0 and Os^0, being the last d^8 systems, appear to follow the hydrido and catalytic chemistry of the metals to their right.

Greco et al.[87] have reported the co-oligomerization of mono- and di-olefins by bis(cyclooctatetraene)Fe^0, for which the reaction mechanism



was suggested, in which the similarities to previously discussed d^8 mechanisms are obvious. Alper et al.[90] have shown that $Fe(CO)_5$ converts non-conjugated dienes to conjugated dienes via an alkyl hydrido–iron complex as expected for d^8 systems, and Goodsel and Blyholder[91] have found H_2, CO and R=R to be adsorbed on metallic iron surfaces in a manner expected for oxidative addition of H_2. An interesting application of variation in metal d electron configuration to catalytic inversion of configuration of organic substrates was reported by Johnson and Pearson[92]. They reported the reactions

$$\text{D-(+)-BuBr} + Fe(CO)_2(C_5H_5)^- \longrightarrow \text{L-(–)-BuFe}(CO)_2(C_5H_5) + Br^-$$

$$\xrightarrow{P\phi_3} \text{L-(–)-BuCOFe}(CO)(P\phi_3)(C_5H_5)$$

$$\xrightarrow{Cl_2,\,H_2O} \text{L-(–)-BuCO}_2H$$

$$\xrightarrow{Br_2} \text{L-(–)-BuBr} + Br^+$$

in contrast to $IrCl(CO)(P\phi_3)_2$, where both R· and X· add to the metal in a concerted addition with retention of configuration at the carbon atom.

Within the framework of coordinative unsaturation, it is not a priori obvious what reaction would take place (if any) between H_2 and d^6 metal systems such as Fe^{II}, Ru^{II} and Os^{II}. For example, electron-unoccupied d and p metal orbitals could act independently of the valence electrons by showing an affinity for only two electron-donating ligands (e.g $Ru^{II} + 2H^- \rightarrow Ru(H)_2$), or the valence electrons could act in conjunction with the vacant orbitals for one-electron oxidative addition (e.g. $Ru^{II} + H_2 \rightarrow Ru(H)_2{}^{2+}$).

Wilkinson and colleagues[93] settled this question in 1968 with the discovery that $RuCl_2L_3$ does not activate H_2 in benzene solution, instead finding that a hydrido species was formed in the presence of alcohol and H_2. They summarized the reaction as

$$RuCl_2L_3 + H_2 + \text{base} \rightarrow RuClHL_3 + \text{base.HCl}$$

The Ru^{II} activates H_2 in the presence of base by abstracting an H^- ligand. James and Markham[94] have reported similar results and indicated that the hydride species is a potential hydroformylation and hydrogenation catalyst because it coordinates CO and R=R to form octahedral complexes. Ellades et al.[95] have isolated RuH_2L_3 and found it to be even more reactive toward coordination of CO and N_2 than the hydrido–chloride complex. Thus the electrons of these d^6 metal systems and the empty orbitals appear to be independent of one another for reactions with H_2. This trend is followed in other reactions; Sneeden and Zeiss[96], for example, reported that alkyl iron (and chromium) compounds react in the absence of H_2 with olefins, dienes or acetylenes to give hydrogenation products where there is a transfer of hydrogen from the alkyl group bonded to the metal to the complexed olefin, diene or acetylene. They summarized the observations as

$$(R{-}CD_2{-}CH_2)_3Fe(S)_3 \longrightarrow DFe(RCD_2{-}CH_2)_2 + RCD{=}CH_2$$

$$\xrightarrow{\text{olefins}} DFe(RCD_2CH_2)_2(\text{olefin}) \rightarrow$$

$$Fe(RCD_2CH_2)_2(\text{alkyl}) \longrightarrow Fe(RCD_2CH_2) + \text{deuterated olefin and } RCD{=}CH_2$$

from which it appears that only ligand electrons are involved, and D^- is transferred Su and Wojcicki[98] reported similar observations Nishiguchi and Fukuzumi[97] reported an interesting study where dihydroxy-benzenes were found to be better hydrogen donors in homogeneous hydrogenations catalyzed by FeX_2L_2 than were alcohols. The order of increasing activity for the catalysts was $Fe^{II} > Co^{II} > Ni^{II}$ and $Cl^- > Br^- > I^-$ for X. The implication of these observations is not clear with respect to what has been discussed above. An observation which is clearly in disagreement with the apparent (relative) unreactive nature of valence electrons in these M^{II} systems (as compared to the Ni triad) is the protonation of $(C_5H_5)_2Fe^{II}$ to give $(C_5H_5)_2FeH^+$. However, it appears that protonation of the metal does not occur, but that $[(C_5H_5)(C_5H_6)Fe]^+$ is formed. Besides the fact that the high-field NMR shows a peak only at 2.09 p p m. while other protonic hydrides peak at much higher fields for transition metal complexes, Hawthorne et al[99] have found that no high-field NMR is observed for analogous systems which cannot undergo protonation of the ligands

Blackmore et al[100] have recently discussed catalytic polymerization of olefins, and have indicated that for $RuHL_2(C_5H_5)$ and acetylenes the reaction may be

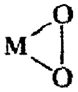
$$\begin{tikzcd}
(C_5H_5)RuHL_2 \arrow[r, "-L", "+R\equiv R"'] & (C_5H_5)RuHL(\pi\text{-}R\equiv R) \\
\rightleftharpoons (C_5H_5)Ru^+HL(\sigma\text{-}R{=}R)^- \arrow[r, "R\equiv R"] \arrow[d, shift right, "+L"'] & (C_5H_5)Ru^+HL(\sigma\text{-}R{=}R{-}R{=}R)^- \rightarrow \text{etc} \\
(C_5H_5)RuL_2(\sigma\text{-}R{=}R) \arrow[u, shift right, "-L"'] &
\end{tikzcd}$$

rather than by the mechanism for olefins

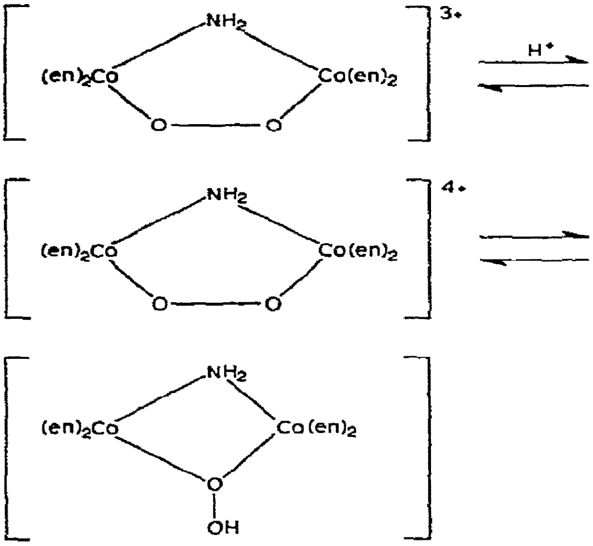
$$L_nM(R) + R'{=}R'' \rightarrow L_nMR(\pi\text{-}R'{=}R'') \longrightarrow L_nM(R'{-}R''{-}R)$$

One question which has not been answered with regard to these d^6 systems is how $RuCl_2(P\phi_3)_3$ isomerizes olefins if a coordinatively saturated $RuCl_2L_3(R{=}R)$ is formed It is interesting to note that Lyons[101] has found that the usual 2% isomerization of olefins was increased to approximately 31% isomerization for 4-vinylcyclohexene when O_2 was bubbled through the pure olefin before addition of $RuCl_2L_3$ Further, the isomerization yield increased to 63–75% when a hydroperoxide was added to the reaction, and to 99% when an olefin solution contaminated with accumulated hydroperoxides from air was used. It appears that the isomerization proceeds via olefin, O_2 or peroxide coordination to Ru^{II}, followed by H· abstraction from the olefin to the oxygen ligand. In this regard several observations are of interest

Khan et al.[102] have reported the activation of O_2 by $RuCl_2(As\phi_3)_3$ at room temperature and 1 atm to give $RuCl_2(As\phi_3)_3(O_2)$, the oxygen complex being paramagnetic with two unpaired electrons. This is in contrast to the d^8 and d^{10} systems, which form diamagnetic complexes with O_2. On passing H_2 through the oxygen complex the O_2 ligand is displaced to give a hydride, the reaction being reversible, while CO displaces O_2 irreversibly. Collman et al.[103] have pointed out that O_2 adds via oxidative addition to Pt, Co and Ir complexes to give diamagnetic species with metal–O_2 structures such as



Thus it appears that for $RuCl_2L_n(O_2)$ this triangle structure is lost, that the M species has not been fully oxidized, and that the O_2 ligand activates hydrogen abstraction from the olefin. Davies et al.[104] have reported an analogous reaction



The use of Ru^I and Os^I catalysts for hydrogenation is known[105], and their activity is more like that of Rh^I than Ru^{II}.

A question which remains is why the O_2 ligand does not become an active oxidizing species This has been shown by Collman et al[103] for d^8 and d^{10} systems, and by James and Ng[106] for Rh^I catalytic oxidation of CO ligands to CO_2, by Graham et al.[107] for O_2 oxidation of $P\phi_3$ to $P(O\phi)_3$ in $Ru(O_2)X(NO)(P\phi_3)_2$, and by Kiji and Furukawa[108] for catalytic oxidation of CO by O_2 in the presence of $RhCl(CO)L_2$. Calligaris et al[109], however, have indicated that for Co complexes bridged by O_2 the metal centers change gradually from oxygenated to oxidized forms, depending on the ligands bonded to cobalt

(v) Nitrogen fixation

As well as having an affinity for O_2, coordinatively unsaturated metal systems have been found to coordinate N_2. These molecular nitrogen complexes are of interest to hydride chemistry for several reasons: (*a*) the similarity of N≡N, CO and olefins, (*b*) N_2-coordinated complexes are believed to be reaction intermediates in metal hydride formation in the presence of hydrazine or NH_3, and (*c*) it has been postulated that conversion of N_2 to NH_3 must proceed through a hydrido–molecular nitrogen metal complex

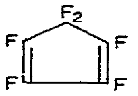
The similarities between N_2 and CO and their possible relation to the chemistry of coordinatively unsaturated metal species has been recently treated by Darensbourg[110].

One of the most informative studies of the bonding in N_2 has been reported by Leigh et al.[111]. They studied the electron density distribution in the N_2 ligand by electron emission spectra from the 1*s* nitrogen orbital. Their results indicate that for $Re^{I}-N_2$ complexes there is a 0.4 atomic charge unit difference between the metal-bonded nitrogen and terminal nitrogen, with the terminal nitrogen being negative. In the case of $Re^{II}-N_2$ complexes the charge difference has decreased to 0 2 atomic charge units and both nitrogens are more positive than in the Re^{I} case Also shown was a correlation between $\nu_{N\equiv N}$ (i.e. molecular nitrogen stability) and charge difference of the two nitrogens The $Re^{I}-N_2$ complex was 80 cm^{-1} lower in energy than the $Re^{II}-N_2$ complex, indicating that for non-bridged $M-N_2$ species the lower the $\nu_{N\equiv N}$, the more negative (i.e. basic) the terminal nitrogen. Maples et al.[112] have reported that the ease of N_2 displacement from $Os^{II}-N_2$ complexes by S_N1 reactions increases as the $\nu_{N\equiv N}$ increases and that both increase as the basicity of other ligands decreases. They also point out that ligands *cis* to N_2 have approximately ten-fold more effect on $\nu_{N\equiv N}$ than those *trans*. These observations are in agreement with those of Darensbourg, who found the group dipole moment derivatives for N_2 in Os^{II} complexes to decrease with decreasing basicity of the other ligands. Also in agreement with Leigh et al.[111], it has been found[113] that Os–d^6 molecular nitrogen complexes are more stable toward N_2 elimination than Os–d^5 systems, and Ru–d^6 is more stable than Ru–d^5. It has also been observed[114] that for Re–d^5 systems $\nu_{N\equiv N}$ is approximately 80 cm^{-1} greater than values for Rd–d^6 systems, as well as for Os, but more interesting was the observation that $\nu_{N\equiv N}$ decreased from approximately 1930 cm^{-1} to as low as 1630 cm^{-1} by forming a N_2 bridged complex between the Re^{I} species and an acceptor molecule which has vacant *d*-orbitals available to accept bonding π-electrons of the di-nitrogen molecule. Thus two methods of weakening the N≡N bond have been reported. (*a*) increasing the negative charge on the metal and thus increasing the ability of the metal to back-donate electrons (via π-bonding) to the N_2 antibonding orbitals, and (*b*) formation of N_2-bridged complexes which allow vacant metal orbitals to overlap with N≡N π-electron density. The first method is of interest in hydride chemistry because it may lead to a sufficiently negative terminal nitrogen for transfer of hydrogen from the metal to nitrogen via simultaneous molecular nitrogen bond rupture. Even though a number of hydrido–metal complexes of N_2 has been isolated[115], facile reduction of N_2 to NH_3 has been limited to reactions involving Ti comple› where both mechanisms (*a*) and (*b*) may be involved. Chatt et al.[116] have shown, contrary to previous reports, that neither mono- nor di-nuclear $Ru^{II}-N_2$ complexes catalyze facile reduction of N_2 to NH_3 by common reducing agents in aqueous solution.

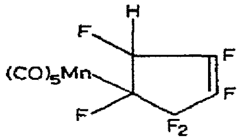
The M–N≡N structure has been proposed and demonstrated by a number of reports, among them the recent X-ray study by Davis and Ibers[117]. Hydrido–metal–N_2 systems have also been known for some time, with that of Yamamoto et al.[118] being among the more recent reports Finally, speculation as to the relationship of "lab bench" fixation of N_2 and in vivo fixation of N_2 has gone on for some time. Rudler et al.[119] have discussed this concept recently, and perhaps their most important comment was that in vivo N_2 fixation occurs under conditions compatible with hydrogenation. With regard to Fe, which is present for in vivo systems of N_2 fixation, Bancroft et al.[120] found the order of N_2 bond weakening by coordination to the metal to be greatest for Fe and least for Ru, in the Fe triad. A similar order of 1st > 3rd > 2nd for other metal triads was also observed *(vi) Mn and Cr triads*

Perhaps the most complex group of metals from a catalytic and hydrido chemistry point of view is the Mn triad. Here it is not clear from the concept of coordinative unsaturation which of three possibilities, viz (*a*) as for Fe^{II}, the vacant *d*-orbitals act independently of the valence electron system and the electrons are relatively inert with respect to H_2; (*b*) as for other odd electron systems (e.g. Rh^0), the Mn^0 and Mn^{II} systems activate H_2 by completing their coordination sphere through electron pairing with H·; (*c*) a combination of (*a*) and (*b*), is responsible for the hydride chemistry of Mn^0 and Mn^{II}.

Tamura and Kochi[121] have examined the catalytic decomposition of R_2Mn species and found evidence that alternative (*c*) is most applicable The fact that MnHR, MnR_2 and MnH_2 species exist indicates that electron pairing to obtain coordinative saturation is not the overwhelming energetic requirement. The unpaired electron of Mn^0 and Mn^{II} may act as a catalyst for activation of H_2 but the equilibrium will be profoundly affected by temperature and the energy required to produce H·. They have found all HMnR and RMnR′ (as well as MnH_2) to decompose to Mn^0. Of particular interest were their observations that hydrogen elimination from R depended on the basicity as well as steric character of the substrate, and the fact that transition metals such as Fe, Pd, Co and Ni shortened the induction period for activation of H_2 and elimination of H· from R by Mn. These factors indicate a need for revaluation of heats of adsorption of H_2 on metal surfaces in order to have a metal by metal comparison of each transition metal's affinity for hydrogen. Booth and Hargreaves[122] observed that $HMn(CO)_5$ adds H—Mn across the triple bond of MeCO—C≡Cϕ, and Lever and colleagues[123] observed that the hydride reacts with



to give



Dobbie[124] found the main reaction between $PX(CF_3)_2$ and $HMn(CO)_5$ gives halogen substitution of hydrogen. DeJong et al.[125] found the favored product of neutron-irradiated $C_5H_5Mn(CO)_3$ was $HMn(CO)_5$.

One question which is unresolved is the stereospecificity of Mn triad catalytic reactions. There are several indications that in hydrogenation, for example, the metal plays a significant role while ligands play a secondary role. Bennett and Watt[133] have found that Mn—hydrido—olefin complexes undergo intramolecular hydrogenation of the olefin via Markownikoff addition while Re complexes go via anti-Markownikoff addition.

For the Cr triad, the valence electrons appear to be even more independent of the empty *d* orbitals with regard to hydride formation than for Fe^{II}. Hydrogenation by

$(C_5H_5)_2Cr^{II}$ has been achieved only by thermal processes, and more recently by photoinduction[126] with $Cr(CO)_5$. In contrast, hydrido species of Mo have been achieved in the presence of base[127]. The reaction

$$(C_5H_5)_2WMe_2 + 2\,HCl \rightarrow (C_5H_5)_2WCl_2 + 2\,CH_4$$

has been reported, which is contrasted with the protonation of W and Mo dihydrides. It has also been pointed out that W reacts via four-coordinate species, indicating increase in energy between valence electron orbitals and vacant orbitals relative to metals further to the right of the Periodic Table The fact that these metals form unstable molecular oxygen complexes[129] may, however, open new possibilities for hydrogenation by a mechanism similar to that for Ru.

(vii) Ti triad

In coming to the V and Ti triads, we return to metal systems which are very active toward H_2. This is usually explained by the greater ease of oxidation of these metals. A comparison of H_2 adsorption by metals with that of their zero-valent complexes makes it apparent that both ease of oxidation and relative energy differences between valence electron orbitals and vacant, coordinating orbitals contribute to the reactivity of these metals toward H_2. Further, it appears that the ease of oxidation is more important for metals to the left of the Periodic Table while lower energy differences between vacant orbitals and valence electron orbitals is more important for metals to the right of the Periodic Table.

The early transition metals have received less attention than the later metals This is due to the strong oxygen affinity which the metals of the Sc, Ti and V triads display This affinity has limited the aqueous chemistry to various oxides or fluorides, has made physical and chemical data on the metals questionable, and has complicated the role of solvents in Sc, Ti and V organometallic chemistry. The restrictions on the Ti triad chemistry are reflected by the heats of formation given in Table 1.

TABLE 1

Heats of formation of Ti triad compounds (kcal/mole)

	Ti	Zr	Hf
(MO_2)	−218	−258	−271
(MF_4)	−370	−445	
(MCl_4)	−179	−230	
Ionization potential	+158	+158	+160

However, in the absence of oxygen and fluoride species these metals have complex physics and chemistry This arises from the ease of oxidation and the abundance of vacant valence orbitals which the metals display. For example, both *3d* and *4p* Ti orbitals, as well as *4s*, are energetically accessible by ligand and metal electrons. This is demonstrated by the existence of some octahedral titanium complexes in which symmetry requires the use of 4s, 3$d_{x^2-y^2}$, 3d_{z^2}, 4p_x, 4p_y, 4p_z metal orbitals in bonding to ligands Thus complexes such as $Li_2(C_5H_5)_2Ti(\sigma\text{-}C_6H_5)_4$. as well as K_2TiF_6, have both p and d metal orbitals energetically accessible at room temperature. In examining the tetrahedral symmetry requirements (most Ti complexes are tetrahedral), it is seen that both 4s, 4p_x, 4p_y, 4p_z and 4s, 3d_{xy}. 3d_{xz}, 3d_{yz} are symmetry-allowed metal orbital configurations, and it is usually assumed that both configurations contribute to the actual bonding situation.

It is obvious, therefore, that coordinative saturation is not as easily determined for the early transition metals as for d^8 systems. Whether a tetrahedral ligand arrangement or an octahedral one represents "coordinative saturation" for Ti metals will be determined in first order by electrostatic energy considerations (i e. electron–electron repulsion, electron–nuclear shielding, and electron–nuclear penetration) which in turn will be affected by metal oxidation state and ligands. It is important to point out that oxidation effects are not the same for the early metals as for the later metals With the later metals, addition and elimination of metal electrons affects coordinative saturation via a "matter effect" by making available empty orbitals, while for the early metals the addition and elimination of metal electrons affect coordinative saturation via an "energy effect" by removal of orbital degeneracy.

The best known consequences of the many energetically accessible vacant metal orbitals are the magnetic properties of these metals and their complexes. The magnetic susceptibility of titanium metal, for example, is +153.0 × 10^{-6} cgs units at 293°K and +150.0 × 10^{-6} cgs units at 90°K, which is greater than that of rhodium metal at +111.0 × 10^{-6} cgs units (298°K). This expected paramagnetic character of Ti^0 may be as important to the activation of H_2 on titanium metal as the ease of oxidation, if the actual reaction mechanism is

$$\mathrm{Ti}(s^2d^2) \rightarrow \mathrm{Ti}(s^1 d_{z^2}^1 d^2) \xrightarrow{H_2} \mathrm{Ti}(d^2)(\mathrm{H})_2$$

Unfortunately, the existence of interfering and tenacious oxide, carbide and nitride surface coatings on titanium metal makes comparison of kinetic data (particularly activation energy) with other transition metals difficult. In most cases activation of H_2 by Ti metal has been studied at or above 300°C, and it appears that this temperature is necessary because of surface coatings The chemisorption of H_2 on Ti metal has been reviewed through 1968 by Mueller et al [135]. They indicated that one study was carried out between 24 and 360°K and that $H_f^0(TiH_2) = -29.5$ kcal/mole at 298°K These data, however, appear not to relate to chemisorption of H_2. Hall and Hope [134] have studied the adsorption of H_2 on Ti film and sponge at 76–154°K and found the thermodynamic data to suggest a "physical adsorption". They postulate that chemisorption is prevented by surface coatings on the metal Further, Bond[4] has indicated that the heat of adsorption of H_2 on Ti metal is in excess of –50.0 kcal/mole, which indicates that the –29.5 kcal value is too low for chemisorption by the metal. However, since both H_2 and N_2 are "physically adsorbed" by film and sponge at 76–154°K, it becomes difficult to define "physical adsorption" in terms other than chemical bonding. In this regard it is interesting to note that TiO_2 has a magnetic susceptibility of +5.9 × 10^{-6} cgs units at room temperature and TiC +8.0 × 10^{-6} cgs units. Further, "pure" Ti metal proceeds to adsorb H_2 and form TiH_2 via a number of non-stoichiometric metal/hydrogen ratios. Thus studies of H_2 adsorption on Ti suffer from poorly defined chemical systems and the possibility of H_2 chemisorption by TiO_2 or TiC. Adsorption by TiO_2 is strongly reminiscent of H_2 chemisorption on ZnO.

Nonetheless, the contamination of freshly prepared Ti metal by hydrogen as well as oxygen and nitrogen is indicative of the affinity for H_2 which the metal displays.

Like the metal, Ti^{II} has two unpaired electrons in 3*d* orbitals and displays paramagnetic susceptibilities as indicated in Table 2

TABLE 2

Magnetic susceptibility of Ti^{II} species[285]

	Susceptibility (cgs units × 10^{-6})	Temperature (°K)
$TiBr_2$	+ 640 0	288
$TiCl_2$	+ 570 0	288
TiI_2	+1790 0	288

Since magnetic susceptibility data for Ti metal are subject to the same chemical problems as thermodynamic studies of H_2 chemisorption on Ti metal, it is interesting to compare the magnetic susceptibilities of various oxygen–Ti systems (Table 3) with that for the metal (153 × 10^{-6} cgs units).

TABLE 3

Magnetic susceptibility of Ti–oxygen systems[285]

	Susceptibility (cgs units × 10^{-6})	Temperature (°K)
Ti_2O_3	+152.0	382
Ti_2O_3	+125 0	298
TiO_3 (peroxide)	+132 4	248
TiO_2	+ 5 9	298
Metal	+153.0	298

Hydrido–Ti chemistry has been mainly an "afterthought" of work on nitrogen fixation (to be discussed later) by low-valent organometallic Ti complexes Clark[136] has reviewed the organometallic chemistry of Ti up to 1968. There appears to be no report of Ti^0 organometallic chemistry, while most work has been connected with $(C_5H_5)_2Ti^{II}$. This compound has been reported as the product of a number of reactions. Clark reviews the following four

$$TiCl_2 + 2\,NaC_5H_5 \xrightarrow{THF} (C_5H_5)_2Ti + 2\,NaCl \tag{1}$$

$$(C_5H_5)_2Ti(CH_3)_2 + H_2 \xrightarrow{hexane} (C_5H_5)_2Ti + 2\,CH_4 \tag{2}$$

$$(\mathrm{C_5H_5})_2\mathrm{TiCl_2} + 2\,\mathrm{NaHg} \xrightarrow[50^\circ\mathrm{C}]{\text{toluene}} (\mathrm{C_5H_5})_2\mathrm{Ti} + 2\,\mathrm{NaCl} + \mathrm{Hg} \tag{3}$$

$$(\mathrm{C_5H_5})_2\mathrm{TiCl_2} + 2\,\mathrm{NaC_{10}H_8} \xrightarrow{\text{THF}} (\mathrm{C_5H_5})_2\mathrm{Ti} + 2\,\mathrm{C_{10}H_8} + 2\,\mathrm{NaCl} \tag{4}$$

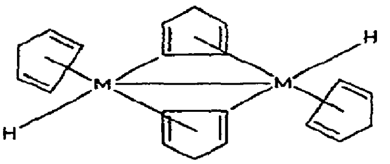
while Brintzinger[137] discusses the following two, as well as the above four.

$$\begin{aligned}(\mathrm{C_5H_5})_2\mathrm{TiH_2} &\xrightarrow[\text{at room temp}]{\text{spontaneous}} \mathrm{H{-}Ti(C_5H_5)_2{-}[(H{-}Ti(C_5H_5)_2]_{\mathit{x}}{-}H}\\ &\xrightarrow{\text{ether solvent}} (\mathrm{C_5H_5})_2\mathrm{Ti} + \tfrac{1}{2}\,\mathrm{H_2}\end{aligned} \tag{5}$$

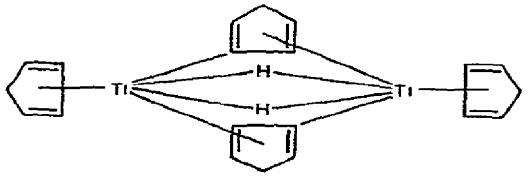
$$\begin{aligned}\mathrm{H{-}Ti(C_5H_5)_2{-}[H{-}Ti(C_5H_5)_2]_{\mathit{x}}{-}H} &\xrightarrow{\text{toluene}} [(\mathrm{C_5H_5})_2\mathrm{Ti}]_2 + \tfrac{1}{2}\,\mathrm{H_2}\\ &\xrightarrow[100^\circ\mathrm{C}]{\text{toluene}} [(\mathrm{C_5H_5})(\mathrm{C_5H_4})\mathrm{TiH}]_2\end{aligned} \tag{6}$$

The product from reaction (4) can be sublimed at 10^{-2} mm Hg between 100 and 140°C, and is a dark-green pyrophoric, diamagnetic material, with a decomposition point at 200°C. It is reported to be a dimer in benzene and a catalyst for polymerization of olefins. It also releases $\mathrm{H_2}$ from water and forms 1:1 etherates of two forms, a green paramagnetic form and a brown diamagnetic one.

Brintzinger and Bercaw[166] more recently have shown that the product from reaction (3) should be formulated as $[(\mathrm{C_5H_5})(\mathrm{C_5H_4})\mathrm{TiH}]_2$ rather than $[(\mathrm{C_5H_5})_2\mathrm{Ti}]_2$. The hydride structure was confirmed by its chemistry in the gas and liquid phases, while solid state IR showed a $\nu(\mathrm{Ti}{<}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{Ti})$ band at 1230 $\mathrm{cm^{-1}}$. No NMR data were given. The hydride hydrogen is shown to arise from an α-hydrogen extraction of $(\mathrm{C_5H_5})$ ring hydrogen, which merely puts this Ti complex on the long list of transition metal complexes which undergo intramolecular rearrangement to hydrides However, this may not be the reason for the rearrangement. Tebbe and Parshall[163] have prepared the Nb and Ta analogues and Guggenberger and Tebbe[165] have determined the crystal structures. The structure of the Nb and Ta complexes is



and by analogy, that for Ti would be



The dihydride bridge for the Ti complex and terminal hydride structure for the Nb and

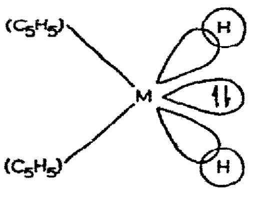
Ta complexes is supported by their ν_{M-H}, which for Ti is 1230 cm^{-1} and for Nb is 1680 cm^{-1}

Brintzinger[138] has reported a similar Ti^{III} hydride, $[Ti(C_5H_5)_2H]_2$, produced according to the reaction

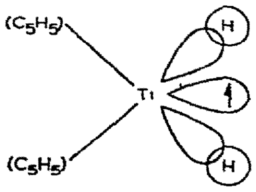
$$[(C_5H_5)_2TiCl]_2 + 2\,RMgX \xrightarrow{\text{ether}} 2(C_5H_5)_2TiR + MgXCl$$

$$(C_5H_5)_2TiR \xrightarrow[\text{ether and excess RMgX}]{\text{spontaneously,}} [(C_5H_5)_2TiH]_2 + \text{olefin}$$

However, Brintzinger[137] reassigned the structure as $(C_5H_5)_2TiH_2^-$ on the basis of EPR spectra. Thus the hydride is contrasted with the chloride $[(C_5H_5)_2TiCl]_2$, which is in thermal equilibrium with its monomer. Brintzinger points out that the hydride is expected to display structural similarity with $(C_5H_5)_2MoH$ and $(C_5H_5)_2WH_2$



M = W or Mo



where the metals are assumed to have formal tetrahedral symmetry The two species differ, however, in that the two electron systems of W and Mo have been reported to react with H$^+$ to give $(C_5H_5)_2MH_3^+$, while the one-electron system of Ti^{III} releases H_2 In these reactions to form Ti^{III} hydride, Brintzinger points out that the solvent plays an important coordination and hydrogen donation role For example, etherates or alkoxy complexes of Ti^{II} are formed in ether solvents, and catalytic cleavage of ether solvents is the source of hydrogen for hydrides in the absence of RMgX. Unfortunately, no NMR data are available for these hydrides because of paramagnetic degradation and side reaction products. Spectral characterization therefore has been limited to EPR and IR work.

Kenworthy et al.[139], in resolving the EPR spectrum of the Ti^{III} hydride, confirmed the structure as $[(C_5H_5)_2TiH_2]^-$ and located the unpaired electron in a $3d_{z^2}$ atomic metal orbital lying along the symmetry axis between the (C_5H_5) ligands and bisecting the TiH_2 angle. They also detected the counter-ions, M^{n+}, and found that on going across the series from Na to Al the TiH_2 angle steadily decreases. This was explained in part by postulating that the preferred cation site for Li$^+$ and Na$^+$ is well off the z axis and close to one or the other hydride ligand, with rapid exchange between hydride sites. On the other hand, Mg^{2+} and Al^{3+} are close to the z axis.

Brintzinger and Bercaw[140] more recently reported that $[(C_5H_5)_2TiH]_2$ could be prepared from $Ti(C_5H_5)_2(CH_3)_2$ and H_2 in solid state reactions, while in the presence of solvent the dark-green $[(C_5H_5)(C_5H_4)TiH]_2$ is formed instead of the violet Ti^{III} dihydride. The violet product is of marginal stability and oxidizes explosively in air. With contact of hexane or toluene solvent it decomposes to a brownish solution at room temperature. As a solid, the violet product is stable under Ar or below room temperature. The solid will slowly convert to a green product, which may be accelerated by contaminates When heated in vacuo at 150°C it loses H_2 per 2 Ti and is converted to the dark-green $[(C_5H_5)(C_5H_4)TiH]_2$ species.

Marvich and Brintzinger[141] reported that reactions (5) and (6) lead to $[(C_5H_5)_2Ti]_2$, the product in ether solvents being a nondescript dark color with no indication of the intense green color of $[(C_5H_5)(C_5H_4)TiH]_2$. The IR spectra obtained in toluene show no $\nu(\mathrm{Ti}{<}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{Ti})$ band and instead give a simple spectrum with two strong bands at 790 and 1010 cm^{-1} When the toluene solution is heated to 100°C $[(C_5H_5)(C_5H_4)TiH]_2$ is obtained The product in ether solution reacts with CO irreversibly to give $(C_5H_5)_2Ti(CO)_2$ and reversibly with H_2 at 1 atm. The amount of H_2 adsorbed is not stoichiometric. When either the toluene or ether solution is left in contact with D_2 for several hours at room temperature, a complete scrambling of deuterium and ring hydrogens occurs. The product of reactions (5) and (6) is unusual in that it does not rearrange to $[(C_5H_5)(C_5H_4)TiH]_2$, and that it does not react with ether solvents As well as Brintzinger's discussion of the reactivity of Ti complexes toward etheral solvents, van Tamelen et al.[142] have shown that Ti^{II}, Ti^{III} and Ti^{IV} species react with carboxy compounds such as alcohols initially to form alkoxy–Ti compounds and finally to form TiO_2 and organic free radicals. Ichiro et al.[143] have reported the reaction between $TiCl_4$ and $ZrCl_4$ and cyclic ethers to give Ti and Zr alkoxides

Marvich and Brintzinger's formulation of the product from reactions (5) and (6) was, no doubt, based in part on Bercaw and Brintzinger's[144] observations for $[(C_5(CH_3)_5)_2Ti]_2$. In attempting to further confirm that $[(C_5H_5)_2Ti]_2$ rearranges to $[(C_5H_5)(C_5H_4)TiH]_2$ via α-hydrogen extraction, the authors produced the penta-methyl derivative by the reaction

$$[C_5(CH_3)_5]_2TiCl_2 + 2\,LiCH_3 \rightarrow [C_5(CH_3)_5]_2Ti(CH_3)_2 + 2\,LiCl$$

$$[C_5(CH_3)_5]_2Ti(CH_3)_2 \rightarrow C_{10}(CH_3)_{10}CH_2Ti + CH_4$$

$$C_{10}(CH_3)_{10}CH_2Ti + H_2 \rightarrow [C_4(CH_3)_5]_2Ti + CH_4$$

The red-brown crystalline product cannot be kept at room temperature under Ar without decomposition, and is light sensitive. Toluene solutions of the product readily and irreversibly absorb 2 moles of CO to give $[C_5(CH_3)_5]_2Ti(CO)_2$. The IR spectrum shows the Ti center to be a better electron-donating species than in $(C_5H_5)_2Ti(CO)_2$. The red-brown product absorbs H_2 reversibly[286] giving a product with $\tau_H = 9.72$ p.p.m. The hydride loses H_2 at room temperature under vacuo but not at −80°C. The stoichiometry of these species is supported by mass spectral results

Analogous, if not identical, hydride species appear to be involved in the catalytic conversion of N_2 to NH_3 by Ti complexes. Vol'pin et al[145] have shown that $(C_5H_5)_2TiCl_2$ catalyzes this reduction in the presence of Mg and MgI_2. A kinetic study[145] indicates that Ti^{IV}, when mixed with Mg and MgI_2, is reduced to $(C_5H_5)_2TiX$ and then to $(C_5H_5)_2Ti$ in a benzene–ether solution. $(C_5H_5)_2Ti$ then reacts with excess Mg to give $[(C_5H_5)_2Ti]^-$, which rearranges to a hydride The $[(C_5H_5)_2Ti]^-$ species is proposed as the active catalyst for N_2 fixation. A later study[146] showed that a hydride forms from $(C_5H_5)_2TiCl_2$ when Mg and MgI_2 is added in the absence of N_2, and that the hydride ligand is extracted from the (C_5H_5) ring and not from the solvent. The evidence indicated that a species of the type $(C_5H_5)(C_5H_4)TiH^-$ is formed. It is also interesting to note that Vol'pin and Shur[147] reported that both $TiCl_4$ and $(C_5H_5)_2TiCl_2$ are capable of reducing N_2 after reaction with RMgX

Van Tamelen et al.[148] have reported the following

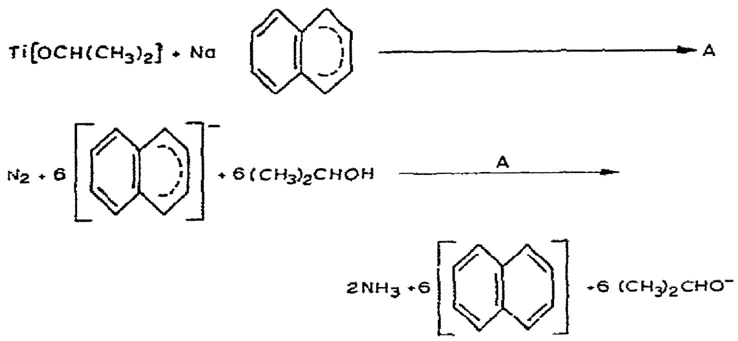
$$TiCl_4 + 2\,KOCH(CH_3)(CH_2CH_3) \rightarrow TiR_2Cl_2 + KCl$$

$$TiR_2Cl_2 + K \rightarrow TiR_2Cl$$

$$\xrightarrow[\text{ether solvent}]{N_2} TiR_2Cl + NH_3$$

Various potassium alkoxy systems were used with no change in the reaction. However, when the reaction was carried out in xylene rather than ethereal solvents the NH_3 production dropped by an order of magnitude Thus it was concluded that the ethereal solvent is the source of hydrogen in production of NH_3 Further, the alkoxy species was just as essential to NH_3 production as Ti, N_2 or K. Without it no NH_3 was produced.

Van Tamelen et al.[149] have also reported the following.



Most important is the fact that reduction of N_2 occurs even in the presence of O_2. Using air as the source of N_2, the yield of NH_3 was reduced to half, but was still appreciable at 21–44% conversion. Thus it appears that either A resists attack by O_2 or that a new, less (but still) active, oxy–Ti species is produced.

The $[(C_5H_5)(C_5H_4)TiH]_2$ system has been examined by van Tamelen et al.[150], and found to absorb N_2 reversibly to form a molecular nitrogen-bridged Ti dimer. Similar behavior was observed for $Ti(OR)_2$, but when R was unsaturated the reaction did not take place This was attributed to internal coordination of Ti with the π-electron systems of R. Treatment of the Ti–N_2 dimer with excess Na naphthalide and subsequent hydrolysis gave NH_3. The IR spectrum of the Ti–N_2 system gave $\nu_{N\equiv N} = 1960\ cm^{-1}$. Finally, the source of hydrogen for NH_3 when using $Ti(OR)_x$ has been confirmed as the ethereal solvent.

Zucchini, Albizzati and Giannini[151] have discussed $Ti(CH_2C_6H_5)_4$ and $Zr(CH_2C_6H_5)_4$. These compounds show unusual thermal stability, with the Zr system more stable than Ti. The thermal stability of halogen-substituted benzyl–Ti derivatives decreases on going from Br to F, while the stability increases with substitution by alkoxy ligands. In fact the stability is dramatic, with a 20-fold increase in decomposition rate for the tetra-benzyl compound on heating from 25 to 60°C while there is no increase in decomposition for the di-alkoxy derivative. Both Ti and Zr tetra-benzyl complexes activate H_2 at or above 50°C to release toluene, but the Zr complex is far more reactive in this respect. Both catalyze hydrogenation of olefins at 0°C and 1 atm H_2, which are conditions under which no noticeable reaction with hydrogen of the complexes alone occurs Most surprising is the absorption of two moles of CO_2 at room temperature to give phenylacetic acid and tribenzylcarbinol after hydrolysis It was proposed that reaction occurs by addition of Ti—C or Zr—C across the C=O bond in a manner similar to RMgX addition to carboxylic acids. However, a six-coordinate metal species $M(R)_4(CO_2)_2$ cannot be ruled out at this time. This reaction is faster with Zr A similar reaction between Pd and CO_2 was reported by Atkins et al.[152] These tetra-benzyl complexes and their derivatives are known to catalyze polymerization of olefins, and both Ti and Zr species are active toward isomerization of olefins For isomerization, however, the Zr species requires photoinduction. The actual catalyst is shown to be a tribenzyl Zr hydride which requires photoinduction It is assumed that a more easily formed and more reactive hydride is involved in catalysis by Ti. Exposure of tetra-benzyl Zr to light gave a diamagnetic tribenzyl Zr hydride even at —70°C in toluene. The structure of the hydride was determined by analytical data with no detectable Zr—H bond in the IR or NMR spectra. Irradiation of the Ti species at —78°C gave a Ti^{III} species without detection of a hydride intermediate.

James et al [153] have investigated hydrido and bromo-hydrido derivatives of $(C_5H_5)_2M^{IV}$, where M = Ti, Zr or Hf. The Ti^{IV} complex reacts with $LiBH_4$ to give violet $(C_5H_5)_2TiBH_4$. The physical data suggest that it should be formulated as $[(C_5H_5)_2TiH_2]^-$ $[BH_2]^+$, while Zr^{IV} and Hf^{IV} are not reduced but yield non-ionic hydrogen-bridged $(C_5H_5)_2M(BH_4)_2$. The Zr—borohydride reacts immediately with trialkylamines to give $(C_5H_5)_2Zr(H)BH_4$ + $(CH_3)_3N \cdot BH_3$ and $[(C_5H_5)_2ZrH_2]_n$ + $2(CH_3)_3N \cdot BH_3$, while the Ti species fails to react in this manner. $(C_5H_5)_2Zr(H)BH_4$ is volatile, air-sensitive and slightly soluble in nonpolar solvents $[(C_5H_5)_2ZrH_2]_n$ acts like a polymer, being nonvolatile, decomposing above 120°C, not air-sensitive, and insoluble in nonpolar solvents. These hydrido species are diamagnetic but no high-field NMR of hydrogen was observed except for the boron—hydride at 0.20 p p.m above TMS. The only unassigned NMR peak was at 4.53 p.p m below TMS and was assumed to belong to the hydrido ligand. This low-field shift is explained by the absence of *d* electron diamagnetic shielding However, d^0 Nb and Ta hydrido systems have been observed at $\tau_H > 10$ p.p.m.; thus this troublesome point of the lack of high-field NMR for Ti, Zr and Hf hydrides has not been settled No NMR data were obtained for $[(C_5H_5)_2ZrH_2]_x$ because of insolubility. $(C_5H_5)_2Zr(H)(BH_4)$ shows a sharp, intense band at 1945 cm^{-1} for ν_{Zr-H} and $[(C_5H_5)_2ZrH_2]_n$ shows a strong, broad band at 1540 cm^{-1} for ν_{Zr-HZr}. The authors point out that within the Ballhausen—Dahl[154] molecular orbital scheme for tetrahedral Ti, $[(C_5H_5)_2ZrH_2]_n$ forms because as a monomer a vacant symmetry-available orbital remains on the metal while polymerization allows this orbital to share H^- from another metal Plato and Hedberg[155] have reported an electron diffraction investigation of $Zr(BH_4)_4$ vapor and found, in agreement with X-ray and NMR data, that the metal is formally tetrahedral with three bridging hydrogens between it and each boron.

Wailes and Weigold[156] have reported the reactions

$$[(C_5H_5)_2ZrCl]_2O + LiAlH_4 \rightarrow 2(C_5H_5)_2ZrH_2 + LiCl + AlOCl_2 \quad (7)$$

$$[(C_5H_5)_2ZrCl]_2O + 4\,LiAl(OBu^t)_3H \rightarrow (C_5H_5)_2ZrH_2 \quad (8)$$

$$[(C_5H_5)_2Zr]_2O + 2\,LiAl(OBu^t)_3H \rightarrow [(C_5H_5)_2ZrH]_2O{\cdot}(C_5H_5)_2ZrH_2 \quad (9)$$

$$(C_5H_5)_2ZrCl_2 + \tfrac{1}{4}\,LiAlH_4 \rightarrow (C_5H_5)_2Zr(H)Cl \quad (10)$$

$$+ \quad LiAlH_4 \rightarrow (C_5H_5)_2Zr(H)Cl$$

$$(C_5H_5)_2ZrCl_2 + Mg \rightarrow (C_5H_5)_2Zr(H)Cl \quad (11)$$

$$(C_5H_5)_2Zr(H)Cl + LiAlH_4 \rightarrow (C_5H_5)_2Zr(H)AlH_4 \quad (12)$$

$$(C_5H_5)_2Zr(Cl)CH_3 + LiAlH_4 \rightarrow (C_5H_5)_2Zr(H)CH_3 \quad (13)$$

The IR data indicate that all these Zr–hydrides are polymeric (Table 4).

TABLE 4

Cyclopentadiene zirconium hydride infrared data

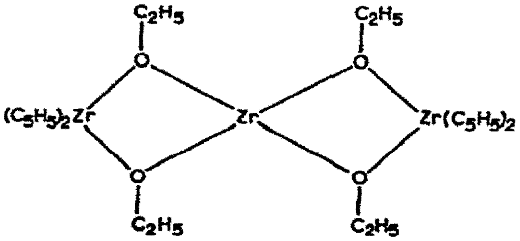
	M–H	M–D
$(C_5H_5)_2ZrH_2$	1520, 1300	1100, 960
$[(C_5H_5)_2ZrH]_2O\ (C_5H_5)_2ZrH_2$	1510, 1385, 1240	1075, 1025, 905
$(C_5H_5)_2Zr(H)Cl$	1390	1020
$(C_5H_5)_2Zr(H)AlH_4$	1425	1055
AlH_4	1790, 1700	1310, 1260
$(C_5H_5)_2Zr(H)CH_3$	1500, 1310	1090, 965

These hydrides are heat- and light-sensitive, but decomposition occurs without loss of Zr–H moiety and appears to involve the (C_5H_5) ligands. They react with chlorinated solvents, exothermally in the case of CCl_3H and slowly in the case of CCl_2H_2, replacing H by Cl. Thus quantitative measurement by NMR of CH_2Cl_2 or CH_3Cl products has been useful for analysis of the hydrides.

Wailes and Weigold[157] have discussed the reaction of $(C_5H_5)_2ZrH_2$ with carboxylic acids to form acylates or alkoxides. With excess acid the acylate, III, is formed and with excess hydride reduction of acids occurs to give bridging alkoxides IV

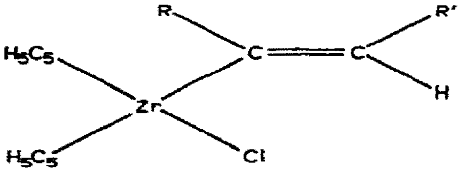
$(C_5H_5)_2Zr(OCOCH_3)$

III

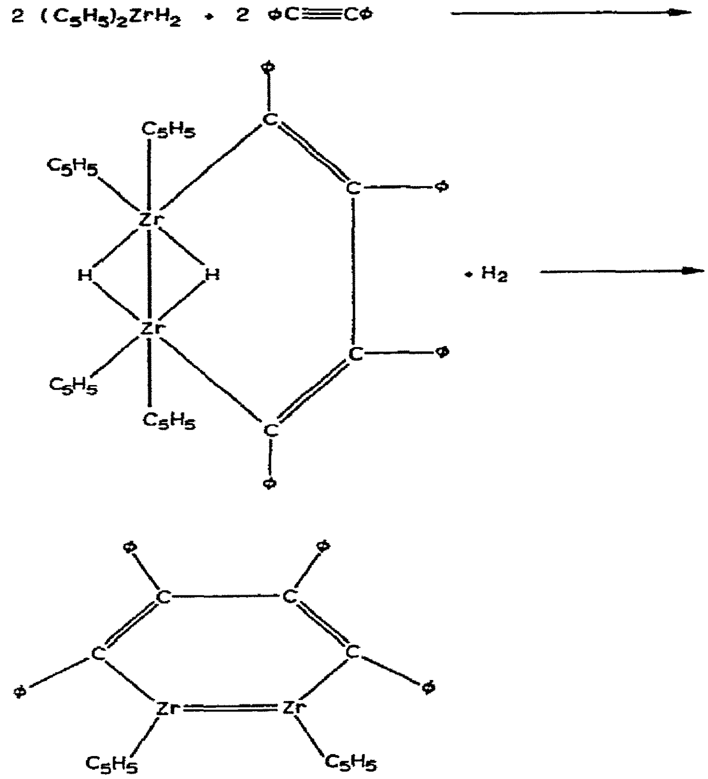


IV

Wailes et al.[158] have reported the reaction of $(C_5H_5)_2Zr(H)Cl$ with acetylenes by addition of Zr–H across the triple bond. The products are generally of the form



while for $(C_5H_5)_2ZrH_2$ the products are usually di-alkenes. However, when the dihydride reacts with diarylacetylenes hydrogen is evolved and the process postulated as



where a double bond is postulated as existing between the metal centers in order to satisfy the metal coordination number.

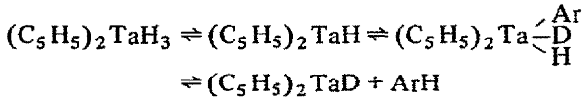
Thus it appears that in going down the triad from Ti to Hf the activation energy for M–H formation increases, the M–H bond becomes more covalent and the M–H bond shows increasing thermal and chemical stability.

(viii) V triad

Less has been reported for the range of V triad catalytic activities than for Ti, Zr and Hf. However, the natures of hydride intermediates for V-, Ta- and Nb-catalyzed reactions are better defined because these hydrido complexes exhibit high-field NMR and both IR and NMR studies have been less troubled by stability problems than have the analogous Ti, Zr and Hf complexes.

As with the Ti triad metals, Ta and Nb bis-cyclopentadienyl complexes have received considerable attention. In 1961 Green et al.[159] first reported $(C_5H_5)_2TaH_3$ in detail and analogous Re, Mo and W hydrides This d^0 Ta system was found to have hydride NMR peaks at 11.63 and 13.02 p.p.m. above TMS, and a rough correlation between increasing τ_H and increasing number of d electrons was established. The observation that the Ta d^0 hydride exhibits $\tau_H > 10$ p.p.m. is of both practical and theoretical importance.

Barefield et al.[160] have reported that $(C_5H_5)_2TaH_3$ as well as L_2IrH_5 catalyze exchange between D_2 and benzene, by oxidative addition of the C—H bond to a coordinatively unsaturated metal intermediate. For Ta the reaction mechanism is assumed to be



$$(C_5H_5)_2TaH_3 \rightleftharpoons (C_5H_5)_2TaH \rightleftharpoons (C_5H_5)_2Ta\begin{smallmatrix}Ar\\D\\H\end{smallmatrix} \rightleftharpoons (C_5H_5)_2TaD + ArH$$

Of particular interest is the observation that heating $(C_5H_5)_2TaH_3$ in benzene with excess PEt_3 yields $(C_5H_5)_2Ta(H)(PEt_3)$, with $\tau_H = 19.48$. It appears that five-coordinate (including metal lone pairs) Ta is a coordinatively saturated metal species. However, it must be noted that work on $Ta_6X_{12}{}^{n+}$ clusters by McCarley and colleagues[161] and the crystal structure of $H_2[Ta_6Cl_{18}]\cdot 6H_2O$ by Thaxton and Jacobson[162] indicate that Ta is capable of coordination numbers greater than five.

Tebbe and Parshall[163] have reported $(C_5H_5)_2NbH_3$, with $\tau_H = 12.73$ and 13.72 p.p m and $\nu_{Nb-H} = 1710\ cm^{-1}$. In accordance with the work on $(C_5H_5)_2TaH_3$, H_2 is evolved when the Nb trihydride is heated in benzene and H—D exchange with benzene—D_6 occurs. The $(C_5H_5)_2Nb(H)(PEt_3)$ derivative was prepared, with $\tau_H = 17.69$ p.p m. and $\nu_{Nb-H} = 1650\ cm^{-1}$ As with the Ti triad, the d^0 metal hydrides of the V triad become more reactive in going up the group from Ta to V $[(C_5H_5)(C_5H_4)NbH]_2$ with $\tau_H = 12.07$ and $\nu_{Nb-H} = 1680\ cm^{-1}$ was prepared by the thermal decomposition of the trihydride in benzene at 80°C Decomposition of $(C_5H_5)_2TaH_3$ gives $(C_5H_5)(C_5H_4)TaH$ with similar spectral properties. Both dimers are diamagnetic. Treatment of $[(C_5H_5)(C_5H_4)NbH]_2$ with H_2 at 80°C and 800 atm in benzene converts it quantitatively to the trihydride. The following reactions are suggested

$$(C_5H_5)_2NbH_3 \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} (C_5H_5)_2NbH \rightleftharpoons [(C_5H_5)(C_5H_4)NbH]_2 \tag{14}$$

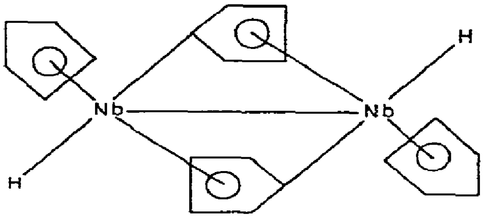
$$(C_5H_5)_2NbH + L \rightarrow (C_5H_5)_2NbHL \qquad L = PR_3, CO, C_2H_4 \tag{15}$$

$$(C_5H_5)_2NbH(C_2H_4) \rightleftharpoons (C_5H_5)_2Nb(C_2H_5) \overset{C_2H_4}{\rightleftharpoons} (C_5H_5)_2Nb(C_2H_4)(C_2H_5) \tag{16}$$

$$(C_5H_5)_2Nb(C_2H_5) \overset{H_2}{\rightleftharpoons} (C_5H_5)_2NbH_2(C_2H_5) \rightarrow C_2H_6 + (C_5H_5)_2NbH \tag{17}$$

The species $(C_5H_5)_2Nb(H)(C_2H_4)$ has been isolated and found to have $\tau_H = 12.95$ p.p m. and $\nu_{Nb-H} = 1735$. Reaction of allene and butadiene with $(C_5H_5)_2NbH_3$ occurs with reduction of the olefins and formation of $(C_5H_5)_2Nb(\pi\text{-}C_3H_5)$; this complex has also been reported by Siegert and De Liefde Meijer[164].

Guggenberger and Tebbe[165] have determined the molecular and crystal structure of $[(C_5H_5)(C_5H_4)NbH]_2$ and found it to be



with the metal in the +4 state.

C LIGAND VARIETY

Several methods for transition metal hydride synthesis were indirectly discussed in the previous section Just about every conceivable type and source of hydrogen has been activated by some transition metal complex in the process of producing a hydrido–metal species Complexes of metals to the right of the transition series add H^+ via oxidative addition, while those to the left add one to nine H^- ligands All the metals and their coordinatively unsaturated complexes (except Cd and Hg) have been found to coordinate molecular hydrogen under one condition or another However, there is overlap in reactivity toward hydrogen species among the transition metal complexes, part of which is caused by variation in ligand effect on the metals Even when considering identical ligands and equivalent degrees of coordinative saturation, there is overlap in the properties of the metals. This is due to two complementary properties which have their greatest effect at opposite ends of the transition metal series They are the greater ease of metal oxidation at the left and top of the series, and the smaller energy separation between highest occupied and lowest empty metal *d* or molecular *s–d–p* hybrid orbitals at the right and top of the transition series

A review of every variation and report of hydride synthesis is not the intent of this paper. However, the interested reader will find Levison and Robinson's[167] discussion of platinum metal hydrides a convenient start for such a review. These authors also describe a clean, one-step homogeneous preparation of Rh, Ru, Ir and Os triphenylphosphine and carbonyl–phosphine hydrides Ibekwe and Taylor[168] also discuss general methods of preparation of hydrides and report the novel reaction

$$trans\text{-}[Ir(CO)(Me_2PCH_2CH_2PMe_2)_2]Cl + 2\,P\phi_3 \xrightarrow[NaB\phi_4]{\text{cold, dry EtOH}}$$

$$trans\text{-}[IrH(CO_2Et)(Me_2PCH_2CH_2PMe_2)_2]B\phi_4 + NaCl$$

Phosphine and carbonyl hydrides have received the greatest amount of attention. This is in part due to the stability of such metal hydride systems, presumably caused by the ability of such ligands to reduce the electron density at the metal in such a way as to increase the covalency of the metal–hydrogen bond However, interest in other ligand systems has developed

(i) Group IV ligands

Recently, Graham and coworkers have extensively investigated hydrides with transition metal–Group IV bonds Jetz and Graham [169] have discussed the photochemical preparation of silyl(transition-metal)hydrides from carbonyl transition metal complexes. The reaction mechanism was reported as

$$ML_m(CO)_n \xrightarrow[<25^\circ C]{h\nu} ML_m(CO)^*_{n-1} + CO$$

$$M(CO)^*_{n-1} + R_3SiH \rightarrow R_3SiMHL_m(CO)_{n-1}$$

$(C_6H_6)CrH(CO)_2(SiCl_3)$ was prepared from $(C_6H_6)Cr(CO)_3$ in oxygen-free hexane or heptane below 25°C yielding the insoluble product. In the crystalline state the hydride is moderately air-stable, but decomposes at room temperature in CH_2Cl_2 with traces of air $(C_5H_5)MnH(CO)_2(SiCl_3)$ and $(C_5H_5)Fe(CO)(SiCl_3)_2$ were prepared and show "striking similarity in their physical properties", presumably because of similar metal *d*-electron configurations. Both complexes are accompanied by substantial decomposition and are moderately air-stable in solid form. $(C_5H_5)CoH(CO)(SiCl_3)$ could not be prepared unless the temperature was kept below 25°C. This complex was the most air-sensitive, and the least thermally stable compound studied, presumably because of relatively low energy separation between occupied and empty molecular orbitals and lack of bulky ligands to prevent geometric isomerization. These authors have also reported [170] the acidity of silyl-(Fe and Mn) hydrides as a function of the ligands, by making use of the reaction

$$M{-}H + (C_2H_5)_3N \rightleftharpoons (C_2H_5)_3NH^+ M^-$$

The acidity of the hydride ligand was found to decrease in the order

$$(Cl_3Si)_2FeH(CO)(C_5H_5) \gg (Cl_3Si)Fe(CO)_4H > [(C_6H_5)_3Si]FeH(CO)_4$$
$$> (Cl_3Si)MnH(CO)_2(C_5H_5) > [(C_6H_5)_3Si]MnH(CO)_2(C_5H_5)$$

Oliver and Graham [171] have prepared $(C_5H_5)RhH(CO)(Si\phi_3)$ and pointed out that the NMR chemical shift τ_H of this compound is close to those of observed hydridic species

	Compound	τ_H (p p m.)
d^6	$(C_5H_5)RhH(CO)(Si\phi_3)$	21 1
d^4	$(C_5H_5)ReH(CO)_2(Si\phi_3)$	19.1
d^4	$(C_5H_5)MnH(CO)_2(Si\phi_3)$	21 7

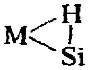
Jetz and Graham[170] reported the τ_H values

	Compound	τ_H (p.p.m.)
d^6	$FeH(CO)_4(SiCl_3)$	19.0
d^4	$CrH(CO)_2(C_6H_6)(SiCl_3)$	20.5
d^4	$MnH(CO)_2(C_5H_5)(SiCl_3)$	19.7
d^4	$FeH(CO)(C_5H_5)(SiCl_3)$	21.6
d^6	$CoH(CO)(C_5H_5)(SiCl_3)$	23.3
d^4	$MnH(CO)_2(C_5H_4CH_3)(Si\phi_3)$	21.5

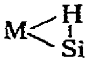
and Knox and Stone[172] reported

	Compound	τ_H (p.p.m.)
d^6	$OsH(CO)_4(SiMe_3)$	19.0
d^6	$OsH(CO)_4(SnMe_3)$	19.6

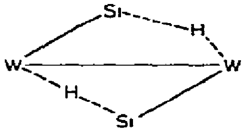
Thus there appears to be an unusual independence of τ_H from the *d*-electron configuration. The reason for this may lie in an unusual structural feature which these complexes exhibit, namely hydrogen bridge bonding between the transition metal and the Group IV metalloid



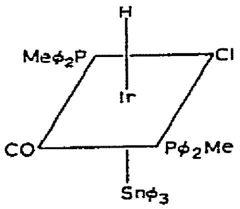
Hart-Davis and Graham[173] have recently reported that the hydride ligand in $(C_5H_5)MnH(CO)_2(Si\phi_3)$ interacts with Si to give a degree of bonding of the type



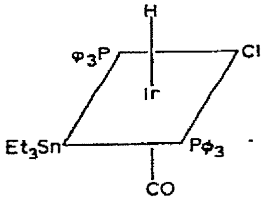
Bennett and Simpson[174] found this interaction to be very significant for systems such as $M_2(CO)_n(H)_m[Si(C_2H_5)_2]_2$ with $W_2(CO)_8H_2(SiR_2)_2$ having the structure



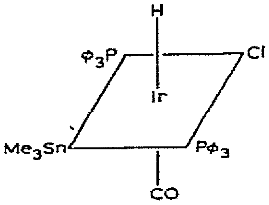
Lappert and Travers[175] have reported the interesting systems



$\tau_H = 15\ 3$ p p m
$\nu(IrH) = 2073\ cm^{-1}$



$\tau_H = 20\ 4$ p p m
$\nu(IrH) = 2067\ cm^{-1}$



$\tau_H = 18\ 8$ p p m
$\nu(IrH) = 2080\ cm^{-1}$

Since H^- *trans* to CO usually resonates at lower NMR fields than H^- *trans* to other ligands in the same stoichiometric compounds, it is unlikely that SnR_3 *trans* to H^- (where bridging is not possible) has lowered τ_H via an inductive effect. Also, the lowering of ν_{IrH} from $SnMe_3$ at 2080 cm^{-1} to $SnEt_3$ at 2067 cm^{-1}, for SnR_3 *cis* to H^-, indicates a direct interaction between hydride ligand and SnR_3. Stobart[176] has reported a related observation for $(GeH_3)_2Fe(CO)_4$ where the Raman spectrum of Ge–Fe stretching is unusual. Usually a symmetric metal–metal stretch is at lower energy than an asymmetric vibration, however, for this compound the opposite is true. This could be explained by hydrogen bonding between Fe and Ge in addition to the direct Fe–Ge bond. Caution must be used, however, in correlating IR and NMR spectra with structure. In this regard, Hagen et al.[177] have reported $\tau_H = 5–6$ p.p m. for $(SiH_3)M(CO)_3(C_5H_5)$ where M = W, Mo or Cr.

Glockling and Wilbey[178] have studied germyl–transition metal hydrides and found the stability and reactivity of these hydrides depends on the steric and electronic character of the groups attached to Ge. Even though the Ge–H bond is stronger in Cl_3GeH, this germane is more reactive toward forming transition metal hydride complexes than R_3GeH The Cl_3Ge–transition metal hydride is also more stable toward heat and O_2. If R is non-bulky, complexes such as $M(H)_2(GeR_3)L_3$ are formed while for R = φ, five-coordinate complexes are formed. NMR indicates that the H^- ligands are *cis* to GeR_3.

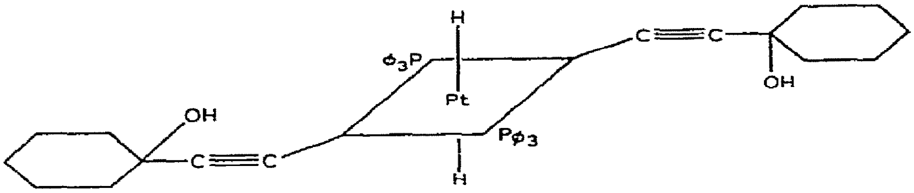
Finally, Highsmith et al.[179] reported the reaction

$$Me_3Si–NMe_2 + HCo(PF_3)_4 \rightarrow [Me_3SiN(H)Me_2^+]\,Co(PF_3)_4^-$$

which is the first case of a silicon amine adding H^+ without breaking the Si–N bond. The IR and NMR data were consistent with the above product formulation, but this is surprising in light of the stabilizing effect of PF_3 on metal hydrides and the tendency for SiR_3 to be associated with H^-.

Transition metal hydrides with carbon bonded ligands are well known and most have been reviewed in Sect. B. However, a few comments on other carbon–metal systems are required

Pi-bonded Pt–acetylene complexes have been known for some time and were briefly discussed (see p. 285) More recently σ-bonded Pt–acetylene complexes were isolated by Roundhill and Jonassen[180]. The octahedral Pt^{IV} complex



was isolated. The complex is air-stable in dry solid form, but decomposes when heated in solution or on addition of alcohol. The NMR spectrum shows $\tau_H = 32.88$ p.p.m. Nelson et al.[181] observed that the steric nature of the acetylene determines whether σ- or π-bonded acetylene–Pt complexes form. Small unhindered acetylenes form the usual π-bonded complexes with reduction of C≡C to C=C, while sterically hindered acetylenes form Pt^{IV}–acetylide hydrides A reaction mechanism for formation of the σ-bonded acetylenes is given. Furlani et al.[182] have also discussed these σ-bonded Pt–acetylides.

There have been many reports of $(C_5H_5)^-$ and C_6H_6 coordination to metal hydrides and some of these systems have been discussed by King and Efraty[183] with the report of $MoH(CO)(C_5H_5)(C_4\phi_4)$ This cyclobutadiene complex of Mo shows $\tau_H = 16.83$ p.p m and $\nu_{MoH} = 1818\ cm^{-1}$, and comparison is made with $(C_5H_5)MoH(CO)_3$, $\tau_H = 15.52$ and $\nu_{MoH} = 1790\ cm^{-1}$.

Hydrides of transition metal cyanides have also received attention Krogmann and Binder[184] have reported the preparation of $K_3RhH(CN)_5$ from an anhydrous methanol and KCN solution of $[Rh(CO)_2Cl]_2$. Jewsbury and Maher[185] have investigated the mechanism for this reaction and suggest that small amounts of HCN in the reaction solution give rise to the hydride species. The NMR spectrum shows $\tau_H = 21\ 33$ p p m Christian and Roper[186] have prepared

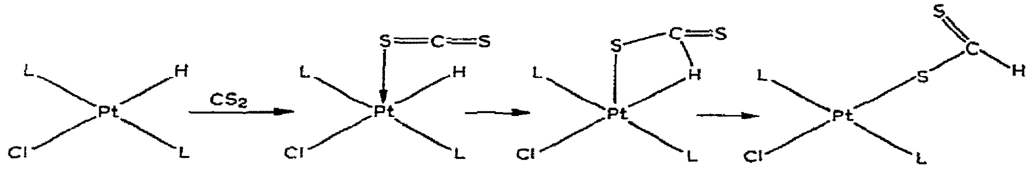
Compound	τ_H (p.p m)
$RuHCl(CO)(CNR)(P\phi_3)_2$	15 5
$RuH(OClO_3)(CO)(CNR)(P\phi_3)_2$	15.4
cis-$RuH(CO)_2(CNR)(PO_3)_2^+$	16 0
trans-$RuH(CO)_2(CNR)(P\phi_3)_2^+$	17.3
$RuH(CO)(CNR)(PO_3)_2^+$	18 3

Coordination of CS_2 by transition metal hydrides was reported by Commereuc et al.[187]. The following reaction was observed.

$$\mathrm{IrH(CO)(P\phi_3)_3 + CS_2 \rightarrow IrH(CO)(CS_2)(P\phi_3)_2 + P\phi_3}$$

$$\tau_H = 20.51\ \mathrm{p.p.m.} \qquad \tau_H = 32.3\ \mathrm{p.p.m.}$$

The carbon disulfide complex contrasts with the carbon monosulfide complex [188] $IrH(CS)(P\phi_3)_3$, with $\tau_H = 23.0$ p.p.m. Palazzi et al. [189] reported that CS_2 inserts into the M–H bond for M = Ni, Rh, Ir, Pt, Re and Mn, giving, for the case of Ir above, $Ir(CO)(S_2CH)(P\phi_3)_2$. Kinetic studies on $PtHClL_2$ suggested the mechanism

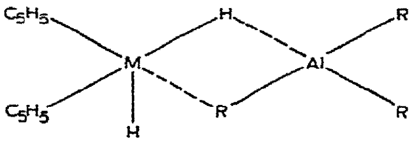


(ii) Group III ligands

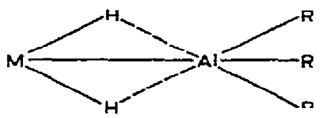
Transition metal hydrides with Group III ligands have been investigated by Storr and Thomas [190], who reported the reactivity of $(C_5H_5)_2WH_2$ and $(C_5H_5)_2MoH_2$ toward AlR_3 in terms of the Lewis acid–base concept. The following complexes were prepared.

Compound	τ_H (p.p.m.)
$(C_5H_5)_2WH_2$	22.28
$(C_5H_5)_2WH_2-AlMe_3$	23.29
$(C_5H_5)_2WH_2-AlMe_2H$	22.47
$(C_5H_5)_2WH_2-AlEt_3$	22.43
$(C_5H_5)_2WH_2-Al\phi_3$	22.57
$(C_5H_5)_2MoH_2$	18.77
$(C_5H_5)_2MoH_2-AlMe_3$	18.77
$(C_5H_5)_2MoH_2-AlEt_3$	18.84
$(C_5H_5)_2MoH_2-Al\phi_3$	18.50

The IR spectra of these complexes show no indication of bridge structures such as



and therefore M–Al bonds are postulated. From the NMR data it appears that structures of the type

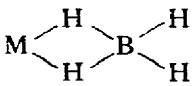


are ruled out. However, the singularly large change in going from $(C_5H_5)_2WH_2$ to $(C_5H_5)_2WH_2$—$AlMe_3$ is interesting. These complexes decompose via H_2 or RH elimination with formation of polymeric R_2Al—ML_2 systems. Kroll and McVicker[191] have reported the reaction as

$$R_2AlR' + H\text{—}Mo(C_5H_5)(CO)_2L \rightarrow R_2Al\text{—}Mo(C_5H_5)(CO)_2L + R'H$$

This protolysis of R′ proceeds readily at room temperature with the order of reactivity being $Bu_2AlH > AlEt_3 > AlMe_3$ When AlR_2H is used, H_2 exclusively is evolved The Mo—Al bond is considered covalent and is broken by weak organic acids to give $HMo(C_5H_5)(CO)_3$ and R_2AlOR'. The NMR of the methyl protons in Me_2Al—$Mo(C_5H_5)(CO)_2(PR_3)$ indicates an exchange process is taking place, with the broad room temperature peak sharpening to a singlet at 60°C. This is attributed to conformational equilibrium.

Hydrogen bridge bonding between transition metals and Group III metalloids is achieved by adding BH_4^- to the metal complex, and in this regard the Group III metalloids are similar to Group IV. The difference between the groups is the oxidative addition—elimination of C—H, Si—H, etc. to $M(CO)_n$ to give $MH(CO)_{n-1}(QR_3)$ (where Q = C, Si, Ge or Sn), while BH_4^- adds via substitution on MX_n to give $MX_{n-1}(BH_4)$ and structures similar to

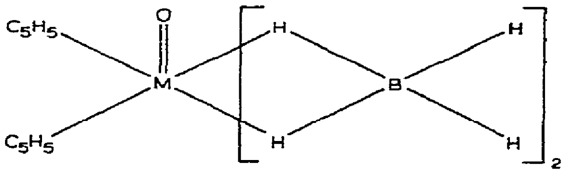


before reduction by BH_4^- Apparently the coordinatively unsaturated Group III metalloids are stronger Lewis acids than the coordinatively unsaturated Group IV metalloids with respect to H^-.

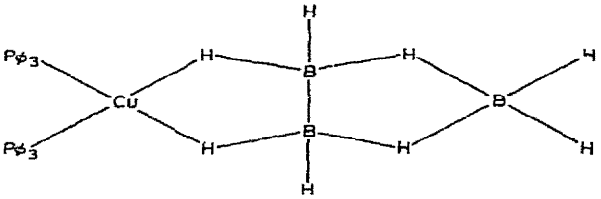
Anand et al.[192] have discussed transition metal borohydrides and reported the reaction

$$(C_5H_5)_2MCl_2O + 2\,NaBH_4 \rightarrow (C_5H_5)_2MCl_2O(BH_4)_2 + 2\,NaCl$$

where M = Mo or W. The product is assumed to have the structure



Lippard and Melmed[193] have found the structure of $Cu(P\phi_3)_2(B_3H_8)$ to be



by X-ray crystal analysis. Bushweller et al.[194] found that the NMR of this compound at −97°C is consistent with the above structure. Beall et al.[195] studied the rate of intramolecular hydrogen exchange as a function of the ligands on Cu. By following the variation in averaging of the NMR signal for the four different hydride sites on boron as a function of temperature they found $P(O\phi)_3$ ligands slowed intramolecular hydride exchange more than $P\phi_3$; this was attributed to the greater π-bonding ability of the $P(O\phi)_3$ ligands

$Zr(BH_4)_4$ was discussed earlier (p. 299), but a further word on the bonding is of interest. The structure of the complex has been determined as a tetrahedral arrangement of B around Zr with triple hydrogen bridges between Zr and each B. Smith and James[196] have discussed these structural features in terms of the IR and Raman spectra of the complex.

(iii) Polymetallic systems

Other polymetallic systems of interest which have been studied are the homogeneous and heterogeneous transition metal cluster hydrides. Johnson, Lewis and coworkers have investigated homogeneous, heterogeneous and ionic polymetallic hydrides Johnson et al.[197] reported the preparation of

Compound	τ_H (p p m)	
$H_2Ru_4(CO)_{13}$	19 1	singlet
β-$H_4Ru_4(CO)_{12}$	18.6	singlet
α-$H_4Ru_4(CO)_{12}$	27 6	singlet

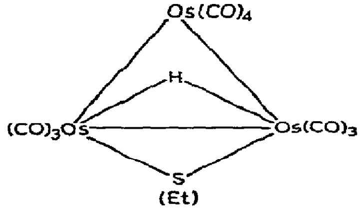
by treating $Ru_3(CO)_{12}$ with base followed by acid, or by treating with $NaBH_4$. The NMR and deuterio-solvent experiments indicate rapid intramolecular hydride exchange or geometric equivalency of the hydride ligands. It was pointed out that for the same metal, τ_H in mono-nuclear metal carbonyl hydrides is at lower field (~16 p.p.m.) than for the bridging hydride in polymetallic hydrides (up to 35 p.p.m.). On the basis of this observation the Ru complexes above were assigned terminal or bridging hydride structures. Kaesz et al.[198] reported the preparation of $H_3Re_3(CO)_{12}$, $H_4Re_4(CO)_{12}$, $H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$ in high yield and purity by treatment of the corresponding metal carbonyls at 90–170°C in hydrocarbon solvent with H_2 at one atm. $H_4FeRu(CO)_{12}$ was also formed, but was unstable These authors prepared the α form of $H_4Ru_4(CO)_{12}$

(τ_H = 28 p.p.m.) but found the β-form could not be isolated by either their method or that of Johnson, Lewis et al. The products from the Johnson–Lewis procedure were found to be contaminated by $Ru_3(CO)_{12}$. Piacenti et al.[199] also studied the reactivity of $Ru_3(CO)_{12}$ in the presence of H_2 and CO, and found the products to be active catalysts in hydroformylation of alkenes. Johnson et al.[200] reported hydrogen abstraction by $Ru_3(CO)_{12}$ from hydrocarbons, alcohols, and other sources yielding hydrido–carbonyl species, and further evidence is given in support of an α and β form of the hydrido–carbonyls.

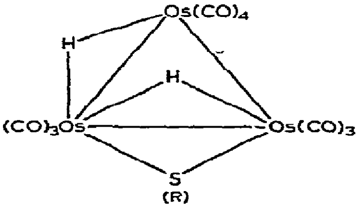
Deeming et al.[201] reported the reaction

$$Os(CO)_{12}Cl_2 \xrightarrow{NaBH_4} HOs_3(CO)_{10}Cl$$

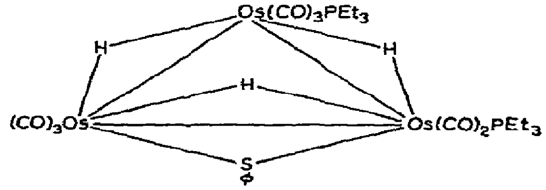
and discussed the product in terms of known systems such as



They also reported[202] that $HOs_3(CO)_{10}(S\phi)$ dissolves in concentrated sulfuric acid to produce the cationic hydride $H_2Os_3(CO)_{10}(S\phi)^+$ with bridging hydride ligands. The product does not undergo hydrogen exchange with the solvent The mono-hydride shows τ_H = 26.5 p.p.m. while the di-hydride shows two τ_H, one at 27 p.p.m. and the other at 29 p.p.m These τ_H are believed due to a structure such as

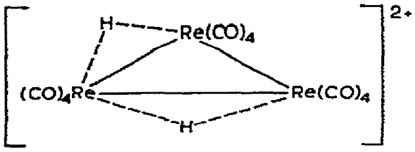


where the 2 p.p.m. difference in τ_H is attributed to the difference in SR position relative to H. If carbonyl is replaced by PR_3 in $HOs_3(CO)_{10}(S\phi)$ the cationic species $H_3Os(CO)_{10-n}(PR_3)_n(S\phi)^{2+}$ are formed in sulfuric acid. for which three high-field τ_H are observed. In the case of $H_3Os(CO)_8(PEt_3)_2(S\phi)^{2+}$, τ_H = 24.97, 29 44 and 30.73 p.p.m. and the structure is believed to be

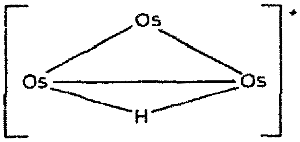


Deeming et al [203] also reported that polymetallic carbonyl complexes such as $Os_3(CO)_{12}$ act as a source of electron density for H^+ and form cationic hydride species in sulfuric acid. As mentioned in their earlier reports for $HM_3(CO)_{12}$, they found the ease and degree of protonation to increase as carbonyl ligands are replaced by PR_3. This was attributed to the increased Lewis basicity of the PR_3 complexes, in keeping with the stronger σ-donor and weaker π-acceptor properties of phosphine as compared with CO. Thus electron-withdrawing ligands stabilize neutral or anionic transition metal hydrides while electron-donating ligands stabilize cationic and protonated transition metal hydrides. τ_H values for the di-hydride complexes were in the 29 5 and 30 0 p p m region for both hydrogens. Increased protonation results in cleavage of metal–metal bonds and the formation of $HOs(CO)_5^+$.

Churchill et al. [204] have prepared $[H_2Re_3(CO)_{12}]^-As\phi_4^+$ with a hydride NMR singlet at 27.2 p p m. and ReH Raman stretch at 1100 cm^{-1}. The X-ray data and low-frequency ν_{ReH} are consistent with the structure



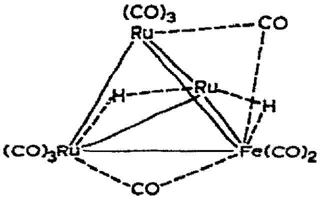
Knight and Mays [205] have isolated $[HRu_3(CO)_{12}]PF_6$ and $[HOs_3(CO)_{12}]PF_6$ from sulfuric acid solutions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. Comparison of X-ray data for isoelectronic $H_2Re_3(CO)_{12}^-$ and $HRe_3(CO)_{12}^{2-}$ support the structure



for $HOs_3(CO)_{12}^+$. An unusually large kinetic isotope effect was found for the protonation. The rate of protonation by H_3O^+ was 17 times greater than for D_3O^+.

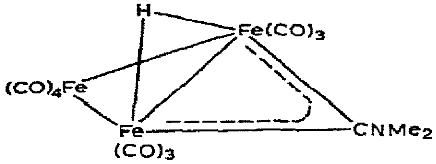
Kaesz et al [206] have isolated $[H_6Re_4(CO)_{12}^{2-}][As\phi_4]_2^+$ with τ_H = 27.4 p p.m. (singlet) and ν_{Raman}(ReH) = 1165 cm^{-1}. Yawney and Stone [207] prepared $H_2FeRu_3(CO)_{13}$ with a singlet NMR at 28.5 p.p.m. in CH_2Cl_2 and 28 7 p.p.m. in deuterobenzene and $H_2Ru_4(CO)_{13}$ with an NMR singlet at 28.6 p.p.m. in CH_2Cl_2.

Gilmore and Woodward [208] have assigned the structure of $FeRu_3(CO)_{10}H_2$, τ_H = 28.7 p.p.m. (singlet), as



Knight and Mays[209] have described the recent interest in mixed-metal polynuclear carbonyl hydrides and reported preparation of $HMOs_2(CO)_{12}$, $HMOs_3(CO)_{16}$, $HReOs(CO)_{15}$ and $H_3MOs_3(CO)_{13}$, where M = Mn or Re. They also discussed the mechanism for stepwise CO elimination by stepwise increase in metal–metal bonding.

Flynn and Pope[210] have discussed $V_2W_4O_{19}{}^{4-}$ and its conversion to $HV_2W_4O_{19}{}^{3-}$ by protonation. Rhee et al.[211] reported $HFe_3(CO)_{11}NMe_2$ with $\tau_H = 27.8$ (singlet) and $\nu_{FeH} = 770\ cm^{-1}$, but Greatrex and Greenwood[212] reported that the product is actually



(iv) Cationic hydrides

A number of papers on cationic mononuclear transition metal hydrides has appeared. Deeming and Shaw[213] have discussed oxidative addition reactions of cationic Ir complexes, while Church et al.[214] have discussed the preparation and reductive elimination of hydrogen from cationic Ir phosphines and arsines. The protonation of $(C_6H_6)Mo(PR_3)_3$ to give the di-hydride was reported by Green et al.[215]. Green and Munakata[216] prepared cationic square-planar Pd hydrides which are catalysts for butadiene oligomerization, and Mukhedkar et al.[217] prepared five-coordinate cationic Pt hydrides

(v) Group V ligands

Group V complexes of transition metal hydrides are well known. However, some less frequently studied Group V ligands are discussed here. The nature of N_2-coordinated transition metal hydrides has been discussed (pp. 289 and 290). Such complexes have stimulated interest in other nitrogen ligand systems for the metal hydrides. Eliades et al.[218] have reported the substitution reaction of NOCl for hydrogen in $RuH_2(P\phi_3)_3$ to give $RuCl_3NO(P\phi_3)_2$. Also reported was the reaction

$$RuH_2(P\phi_3)_3 + 2\,SO_2 \rightarrow Ru(SO_2)_2(P\phi_3)_2 + H_2 + P\phi_3$$

Reed and Roper[219] have reported that $Ir(NO)L_3$ acts like a d^{10} metal system and adds HCl to form $IrHCl(NO)L_2$ as an intermediate to the final product $IrCl_2(NO)L_2$. The hydride was isolated from reaction of $[IrH(NO)L_3]ClO_4$ with LiCl in ethanol, $[IrH(NO)L_3]ClO_4$ being prepared from $Ir(NO)L_3$ and perchloric acid. Reed and Roper[220] have also prepared $IrH(NO)(P\phi_3)_3{}^+$, $IrHX(NO)(P\phi_3)_2$ and $IrX_2(NO)(P\phi_3)_2$. The NO^+ ligand behaves peculiarly in that the ν_{NO} frequency decreases from $1600\ cm^{-1}$ for $Ir(NO)(P\phi_3)_3$ to $1560\ cm^{-1}$ for $IrX_2(NO)(P\phi_3)_2$, where X is Cl^-, Br^- or I^-. Normally ν_{NO} should increase as the metal is oxidized and less able to back-bond electron density to the N–O antibonding molecular orbitals. This anomaly is dependent only on X being a halogen anion, while for H^- the ν_{NO} increases as expected. For the analogous Rh complexes the anomaly does not exist. This has been explained as a change in bonding from Ir–N–O to $Ir{<}\substack{N\\ O}$ on oxidation of Ir by halogens. It is interesting to note that for the more easily oxidized Rh a linear Rh–N–O arrangement is retained on oxidation by halogens.

Cash and Harris[221] reported the reaction

$$\mathrm{Ir(CO)(P\phi_3)_2(NCO)(NO_3)_2} \xrightarrow[\text{air and light}\ \text{for several days}]{\mathrm{CHCl_3+EtOH}} \mathrm{Ir(P\phi_3)_2(NO_3)_2H}$$

where Ir is in the +3 oxidation state The hydride has $\nu_{\mathrm{IrH}} = 2274$ and 2259 cm^{-1} compared with $\mathrm{IrH(Br)_2(P\phi_3)_2}$ $\nu_{\mathrm{IrH}} = 2250\ \mathrm{cm}^{-1}$, and $\mathrm{IrH(Cl)_2(P\phi_3)_2}$. $\nu_{\mathrm{IrH}} = 2242$. Insolubility did not allow NMR studies.

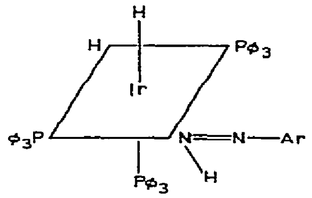
1,3-Diaryltriazenides, $\mathrm{R{-}N{=}\bar{N}{=}N{-}R}$, have been investigated by Robinson and Uttley[222]. Monomeric metal complexes with either chelating or monodentate triazenido ligands occur in contrast to the usual bridging triazenido structure because of the bulky aryl groups on the ligands. The following hydrido species were prepared.

Compound	τ_H (p p m)
$\mathrm{RhH_2(dtt)(P\phi_3)_2}$	27 35
$\mathrm{IrHCl(dpt)(P\phi_3)_2}$	33 53
$\mathrm{IrH_2(dpt)(P\phi_3)_2}$	31 89
$\mathrm{RuH(dpt)(CO)(P\phi_3)_2}$	22 33
$\mathrm{OsH(dtt)(CO)(P\phi_3)_2}$	22 85
$\mathrm{OsH_3(dpt)(P\phi_3)_2}$	19 35

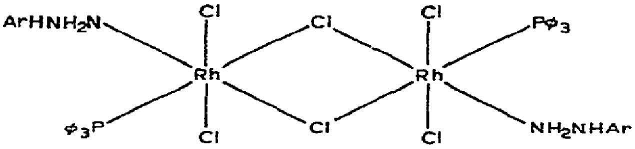
The Os trihydride is apparently a seven-coordinate species. Under suitable conditions 1,3-diaryltriazenes will react with metal halides and $\mathrm{P\phi_3}$ to give arylazo derivatives $\mathrm{ArN_2}$.

McCleverty and Whiteley[223] have reported that addition of aryldiazonium salts to transition metal hydrides proceeds either with formation of an arylazo complex and elimination of the hydrido ligand or with reduction of the diazonium group and formation of a metal–di-imide, M(NH=NAr).

Toniolo and Eisenberg[224] have reported that $\mathrm{IrH_3(P\phi_3)_3}$ adds aryldiazonium cations to form



while $\mathrm{RhH_2Cl(P\phi_3)_2(solvent)}$ adds the diazonium cation to form

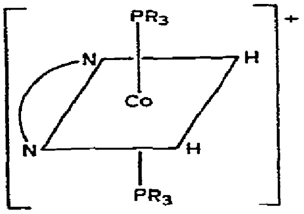


which is in agreement with Parshall's model for nitrogen reductase [297].

Misono et al.[225] have reported preparation of organonitrile cobalt hydrides, $CoH(N{\equiv}CR)(P\phi_3)_3$. The acetonitrile complex is prepared by addition of acetonitrile to a toluene solution of $CoHN_2(P\phi_3)_3$ at room temperature in absence of air. No ν_{CoH} was observed and no τ_H reported. The hydrido structure was assigned on the basis of chemistry.

Cetinkaya et al.[227a] have reported the preparation of amido, $R_2C{=}N^-$, complex metal hydrides from $LiN{=}C(CF_3)_2$ and $PtHClL_2$. *Trans*-$PtH(N{=}C(CF_3)_2)(P\phi_3)_2$ with $\tau_H = 22.8$ p.p m., $\nu_{PtH} = 2146$ cm^{-1} and $J_{PtH} = 748$ Hz; and *trans*-$PtH(N{=}C(CF_3)_2(POMe_2)_2$ with $\tau_H = 24.3$ p p.m. and $\nu_{PtH} = 2115$ cm^{-1} were prepared.

Bipyridine and phenanthroline cobalt hydrides have been isolated by Mestroni et al.[228]. The structures for the complexes are



with τ_H in the 32 p.p m. region. The complexes are useful hydrogenation catalysts because dienes will replace the hydrogens in a facile and reversible reaction with excess diene or H_2

Benfield and Green [229] have reported that treatment of $(C_5H_5)_2Mo(SMe_2)Br^+$ with amines, $RR'CHNH_2$, in water gives amine metal hydrides The following species were reported, all of which are air-sensitive.

	ν_{MoH} (cm^{-1})	τ_H (p p m)
$(C_5H_5)_2Mo(NH_2Me)H^+$	1890	18.9
$(C_5H_5)_2Mo(NH_2Et)H^+$	1830	19.0
$(C_5H_5)_2Mo(NH_2Pr^i)H^+$	1830	19.0
$(C_5H_5)_2Mo(NH_2Bu^n)H^+$	1830	19.0
$(C_5H_5)_2Mo(NH_2\text{-}2\text{-}Bu)H^+$	1830	19.0

The following ethylenediamine complexes were reported by Thomas and Wilkinson [226].

Complex	τ_H (p.p m.)	J_{RhH} (Hz)	ν_{RhH} (cm^{-1})
trans-$[Rh(en)_2(NH_3)H ClO_4]_2$	27.8	22	2056
cis-$[Rh(en)_2(NH_3)H ClO_4]_2$	26.3	19	2025
trans-$[Rh(en)_2(H_2O)H]^{2+}$	32.2	30	
$\{$*cis*-$[Rh(en)_2(H_2O)H]ClO_4\}_2$	32.6	30	2135
$\{$*trans*-$[Rh(pn)_2(NH_3)H]ClO_4\}_2$	27.4	24	2060
cis-$[Rh(pn)_2(NH_3)H]^{2+}$	26.3	21	
cis-$[Rh(pn)_2(H_2O)H]^{2+}$	32.3	30	
trans-$[Rh(pn)_2(H_2O)H]^{2+}$	31.7	32	
$[Rh(NH_3)_5H]SO_4$	27.1	14.5	2079
$[Rh(NH_3)_4(H_2O)H]SO_4$	32.0	25	2146

The direct correlation between the three spectroscopic parameters for these complexes will be discussed later. Gillard et al [227] reported

Complex	τ_H (p p m)	J_{RhH} (Hz)	ν_{RhH} (cm^{-1})
$Rh(en)_2H(OH)^+$	30.6	30	2058
$Rh(NH_3)_4H(H_2O)^{2+}$	32.0	24	2146

It is interesting to note that τ_H is smaller for the stronger base NH_3 than for H_2O.

Malin and Taube [230] have reported the reaction

$$OsO_2(en)_2{}^{2+} \xrightarrow[H^+]{\text{Zn amalgam}} [OsH_2(en)_2]ZnCl_4$$

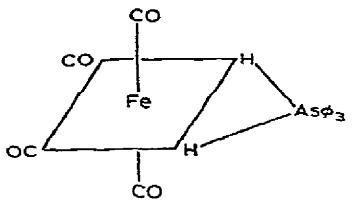
The hydrido ligands in this compound are hydridic and exchange rapidly with D_2O, but are resistant to deprotonation in NaOH. In strong base τ_H shifts from 14.2 p.p.m. to 11.9 p p.m , which is attributed to deprotonation of ethylenediamine nitrogens

Moers [231] has reported the reaction

$$OsHCl(CO)(P\phi_3)_2 + Py \rightarrow OsHCl(CO)(P\phi_3)_2(Py)$$

where Py = pyridine.

An interesting observation for hydrido–iron–$As\phi_3$ was reported by Farmery and Kilner [232]. The Mössbauer spectrum of the complex supports the stoichiometry $FeH_2(CO)_4As\phi_3$ but no ν_{FeH} or τ_H were observed. This was attributed by the author to the structure

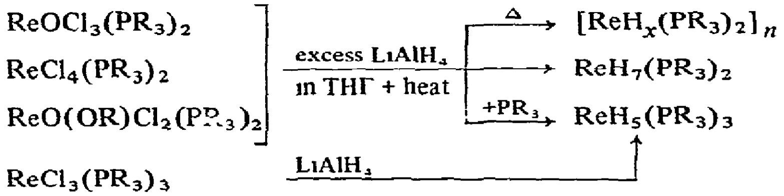


(vi) Group VI ligands

Transition metal hydrides with Group VI ligands have received little attention, except for oxygen complexes. Stiddard and Townsend[233], however, have reported the preparation of benzenethiolato derivatives of Ir. The Ir—H stretching vibration for these complexes is quite high, in the region of 2200 cm^{-1}. Roundhill et al.[234] have reported the oxidative addition of thioacetic acids to $Pt(PR_3)_4$. In a study of oxidative addition of acids to Pt^0 phosphine complexes it was found that the strength of the acid is important but is frequently subjugated to the ability of the conjugate base to coordinate with the metal. In this regard, it was found that sulfur is a strong coordinating ligand *trans* to H, as is nitrogen in CN^-, but oxygen is a poor ligand in organic acids. H_2S was found to be a weaker ligand than the thioacetic acids It is also pointed out that τ_H and ν_{PtH} increase in the order $COOCF_3 > NCS > Br \simeq Cl > (CH_2)_2(CO)_2N > SCOCH_3 > CN$, following the decreasing order of the kinetic *trans* effect with the exception of NCS No explanation is offered for this "anomaly".

(vii) Multi-hydrido complexes

Multi-hydrido complexes are another type of ligand system which have received attention for a number of years, Ginsberg et al.[235] prepared K_2ReH_9 from $KReO_4$ and $LiAlH_4$ more than ten years ago, while Chatt and Coffey[236] reported the reactions



The NMR spectra show equivalency of all hydrido ligands, and catalytic studies show exchange with deuterium. Thus intramolecular hydride exchange occurs at room temperature The τ_H values for these d^0 systems are in the region of 15 p p.m., slightly greater than the Ta—d^0 systems at 13 p p m These authors have pointed out that τ_H increases as the electron density of the metal increases, with τ_H = 15.10 p p.m. for $ReH_7(PEt\phi_2)_2$ and 16.00 p.p.m. for $ReH_5(PEt\phi_2)_3$. Also, τ_H increases in going from $P(aryl)_3$ to $P(alkyl)_3$, in keeping with the weaker σ-bonding and stronger π-bonding ability of the aryl phosphines τ_H values for AsR_3 are 0.5—1.0 p p.m higher than for PR_3 complexes. The UV and visible spectra of ReH_7L_2 show no $d \rightarrow d$ transition, in keeping with a d^0 metal electron configuration. The authors point out that the reaction of Re^{IV} and Re^V with $LiAlH_4$

appears to be oxidative addition of the metal to Re^{VII}, while for Ir^{III}, treatment with $LiAlH_4$ gives rise to ligand substitution and not oxidative addition. All of the multi-hydrido Re complexes are thermally stable and many have melting points or decomposition points above 100°C.

Moss and Shaw[237] reported the preparation of $WH_6(PMe_2\phi)_3$ with $\tau_H = 11.93$ p.p.m., and Douglas and Shaw[238] prepared OsH_4L_3 and $OsH_5L_3^+$ by the reaction

$$OsCl_3L_3 \xrightarrow[\text{or } LiAlH_4 \text{ in THF}]{NaBH_4 \text{ in EtOH}} OsH_4L_3$$

Thus there appears to be an increasing resistance to metal oxidation in going from W to Ir. The tetra-hydrido Os complexes display τ_H values in the 19 to 20 p.p.m. region, and are air- and heat-stable. All these Os hydrides show equivalent H^- in the NMR, indicating rapid intramolecular rearrangement. $OsH_6(PMe_2\phi)_2$ was also isolated, while the protonated species $OsH_5L_3^+$ is formed in acid solutions and is a catalyst toward H–D exchange

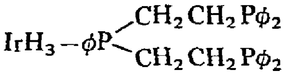
Pennella[239] prepared $MoH_4(PE\phi_2)_4$ and $MoH_4(\phi_2PCH_2CH_2P\phi_2)$ from $Mo(PR_3)_2Cl_4$ and excess ligand in ethanolic $NaBH_4$. An equivalent chemical shift of 12.20 p.p.m. was observed for all hydrido ligands in $(Et\phi_2P)_4MoH_4$ and a J_{PH} splitting pattern of four. These hydrides are diamagnetic and appear to undergo rapid intramolecular H^- exchange

Mann et al.[240] studied the reaction

$$IrH_5(PEt_2\phi)_2 + L \rightarrow IrH_3(PEt_2\phi)_2L + H_2$$

The product distribution indicated a preference for H^- *cis* to PR_3 rather than *trans*, and τ_H for H^- *trans* to L varied in the same order as Horrocks and Taylor's[284] list of metal electron withdrawing ligands. The highest *trans* τ_H values occur for L with the least ability to withdraw electrons from the metal. τ_H for H^-*cis* to L did not follow the order for *trans* τ_H; the *cis* τ_H values were constant with a maximum spread of 1 p p m , while *trans* τ_H varied with a spread of 7 p.p.m.

King et al.[241] have prepared



$$IrH_3-\phi P\begin{matrix} \nearrow CH_2CH_2P\phi_2 \\ \searrow CH_2CH_2P\phi_2 \end{matrix}$$

and Green and Silverthorn[242] prepared $C_6H_6Mo(P\phi_3)_2H_2$.

D PHYSICAL PROPERTIES

(i) The metal–hydrogen bond

The nature of the transition metal–hydrogen bond has been a subject of great interest and controversy for many years. At first, attempts were made to explain the high-field NMR shifts of hydride ligands in terms of a hydride proton "buried" in the metal electron cloud. However, with the discovery by X-ray structural analysis that the hydride ligand must occupy specific sites around the metal in order to rationalize the molecular symmetry and to deal with geometrically significant "holes" in the molecular electron density, the model was changed to that of a geometrically well behaved ligand with an unusually short M–H bond length (i.e. M–H distance less than the sum of covalent radii). Besides explaining τ_H in terms of simple through-space electrostatic interactions, this short-bond model was thought to explain the unusually strong *trans*-directing ability of the hydride ligand. Several reports were published supporting the theory that the M–H bond length was less than the sum of covalent radii. Farrar et al.[243] calculated the Mn–H distance for $HMn(CO)_5$ from broad-line proton NMR. By application of Van Vleck's second moment nuclear quadrupole model, values of 1.281 and 1.950 Å were obtained for the Mn–H bond length from the two real roots of the Van Vleck equation. The 1.950 Å value was considered unlikely because it required the intermolecular H–H distance to be 1.57 Å in contradiction to the normal van der Waals contact of 2.2 Å. Thus the value of 1.281 Å was selected for the Mn–H distance, which is 0 3 Å less than the sum of the covalent radii at 1.57 Å. Farrar et al.[244] also reported a similar study for $HCo(CO)_4$ where the Co–H distance was assigned a value of 1.2 Å in comparison with 1.46 Å for the sum of the covalent radii. Later, however, these bond lengths were re-evaluated and found to be longer For example, Sheldrick[245] reported the Mn–H distance in $HMn(CO)_5$ to be 1.44 Å from broad-line NMR, and Robiette et al.[246] reported the distance to be 1.425 Å from gas-phase electron diffraction

Simultaneously, other groups felt that the reliability of these methods was of the same order as the differences to be detected, and that the hydride ligand was well behaved in bond length as well as geometry. In 1963 La Placa and Ibers[247] reported the bond length of Rh–H in $HRh(CO)(P\phi_3)_3$ to be 1.72 Å from low-angle X-ray structural analysis. In comparison with the sum of covalent radii, 1.542 Å, this was 0.2 Å too long Not until La Placa et al.[248] determined the Mn–H distance in $HMn(CO)_5$ by neutron diffraction was a M–H bond length determined by reliable and meaningful procedures. This distance was found to be 1.601 Å and the diffraction angle was 105°. Gregory et al [249] also reported ~1.7 Å distances from X-ray data for $RuH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2$ and its Os counterpart. Thus it is clear that the covalent and terminally bonded hydride distance from the metal is normal. Therefore, we need only be concerned with models which start with a topologically well behaved hydride ligand and which explain the characteristic spectral and chemical properties of the M–H system. It is unfortunate, nonetheless, that more neutron diffraction studies have not been made on the transition metal hydrides, especially since additional stable complexes have been synthesized since the time of earlier work.

Before going on to discuss models of the M–H bond based on NMR calculations, some final characteristics of these systems need to be discussed

The large high-field shift of τ_H for transition metal hydrides has been referred to throughout this paper. It has been observed that τ_H is at a low value of 10 p.p.m. for d^0 transition metal systems and that the values increase for the d^0 systems in going from left to right or in going from top to bottom in the metal series. The largest τ_H value for a diamagnetic complex was reported by Masters et al.[250] for $IrHCl_2(PBu^t{}_2Me)_2$ at 60.5 p p.m. This Ir^{III} complex is believed to have square-pyramidal geometry, and is found to have low-frequency electron transitions ($\lambda < 600$ nm). When a sixth ligand is supplied for coordination *trans* to hydrogen, τ_H decreases to 20–25 p.p m.

Several reports have been discussed which note that τ_H decreases as the ligand *trans* to H^- increases in ability to reduce electron density at the metal and that the correlation does not hold if the ligand is *cis* to H$^-$. However, Birnbaum[251] has noted that for octahedral Ir and Rh hydrides τ_H increases in the order Cl > Br > I when the halogen is *trans* to H$^-$ and in the reverse order when it is *cis* to H$^-$. This order also holds for square-planar Pt and Pd hydrides

Although Atkins et al.[252] have observed a correlation of increasing J_{Pt-H} with increasing τ_H it is not rigorous and Church and Mays[253] have found the irregularities to vary as in Table 5. Mann et al[254] have found that J_{Os-H} increases as the electron-donating ability of the *trans* ligand increases, and that the reduced indirect coupling constant, $K_{M-H} = J_{M-H}/\hbar(\gamma_M \gamma_H)$, increases, but not linearly, from WH_6L_3 to OsH_6L_2 to $PtHXL_2$

TABLE 5

NMR data for $[PtHL(AsEt_3)_2]ClO_4$

L	τ_H	J_{Pt-H}
trans		
$P(OMe)_3$	15.28	699
$P(O\phi)_3$	15.92	716
Me_3CNC	18.27	721
$P\phi_3$	17.34	739
CO	15.65	768
$AsEt_3$	19.73	846
cis		
$P\phi_3$	18.51	881
$P(O\phi)_3$	18.13	886
$P(OMe)_3$	17.81	936
PEt_3	19.05	945

We have also noted that many of the multi-hydrido complexes are either fluxional or rapidly exchange hydrides intramolecularly. Since the effects of this are drastic with respect to a M–H bonding scheme used in any calculation, and because mono-hydrides have shown similar activity, this property needs further discussion before examining models and calculations for the M–H systems

Meakin et al.[255] observed similar NMR properties for $H_2Fe[P(OC_2H_5)_3]_4$ to those discussed for multi-hydrido complexes, and established that the room-temperature equivalency of the hydrido or phosphite ligands is due to stereochemical nonrigidity (concluded from the result that the temperature-dependent hydride spectra are invariant to concentration changes or addition of free phosphite) τ_H for the complex is 23.86 p.p m. at 30°C and is temperature-dependent Tebbe et al[256] pointed out that for this Fe hydride, observations argue against bimolecular or solvent-assisted hydride exchange. In examining the NMR line-shape of the complex by permutational methods it was found that the stereochemical nonrigidity is probably due to movement of the hydrogen nucleus from one C_3 axis, in the tetrahedral skeleton of the four $P(OC_2H_5)_3$, across the edge of the tetrahedron to another C_3 axis. However, a distorted tetrahedral intermediate could not be ruled out. The consequences of this are the mixing of nonbonding Fe orbital electron density with that of the Fe—H bond (first mechanism), or mixing of the Fe—H molecular orbital with the orbital bonding scheme for the tetrahedrally coordinated phosphite ligands (second mechanism).

The process of hydrogen exchange (within the coordination sphere) across the edge of the tetrahedron is also suggested by Knox and Kaesz[257] for $H_4M_4(CO)_{12}$ complexes, and Wilson and Osborn's[258] observations on $MH(NO)L_3$, where M = Ru or Os, indicate that the stereochemical nonrigidity in these molecules is not like that in H_2FeL_4 in that the temperature behavior of the proton NMR is different and suggests that the process is a total bond skeleton fluxing.

Finally, Dewhirst et al [259] have reported two interesting observations. They propose that if stereochemical nonrigidity in mono-hydrides is due to the exchange of hydrogen ligands (either inter- or intramolecular) then all hydride line-widths in the NMR spectrum should broaden with increase in temperature, but if it is the L ligand which is exchanging then only some of the hydride lines will broaden with increase in temperature (assuming only one L exchanges at a time) They also found that τ_H changed by only 1.7 p.p m. from $HRhL_4$ to $HRhL_3$, where $HRhL_3$ was assumed to be tetrahedral and $HRhL_4$ to be trigonal bipyramidal, $L = P\phi_3$.

The M—H bond has been closely examined in an attempt to understand, in terms of physical models, the NMR behavior of the hydride ligand as a function of chemical (i.e. electronic) changes in the complexes. The simple quantum mechanical nature of the hydrogen species and the relatively simple classical and quantum mechanical NMR operators have generated early and active interest in arriving at a physical model from quantum mechanical calculations.

In 1950 Ramsey[260] wrote an expression for the absolute chemical shift of a nucleus under the influence of electron current densities, to the second-order perturbation approximation. This expression for chemical shift is considered rigorous within the limits of perturbation theory, but was difficult to apply except for the simplest electronic systems, because excited-state wavefunctions were required. The operator, however, was separable into a first-order diamagnetic + paramagnetic term and a second-order paramagnetic term, which proved useful, since the excited state terms were restricted to paramagnetic contributions. Thus it was possible to ignore for some systems the second-order paramagnetic term, which varied as $1/r^3$ (where r = distance from the resonating nucleus to the paramagnetic center), and use only the "diamagnetic term", which is dominated by $1/r$.

(ii) PMR chemical shift

The more interesting systems could not be treated by such simple approximations, and so various variational and variational—perturbational methods for evaluating the second-order term were developed.

In 1962, Stevens et al [261] demonstrated that it was not necessary to postulate unusually short M—H bond lengths in order to obtain agreement between calculated and observed τ_H values for $HCo(CO)_4$. Rather than using Ramsey's more rigorous Hamiltonian equation, a choice of gauge (a scalar function was added to the vector potential of the magnetic field under which the electron of interest was being subjected) was made which eliminated the second-order paramagnetic term Such a gauge was proportional to the second-order matrix elements and thus transferred the excited-state wave function dependency from the paramagnetic term to the new "diamagnetic term". The net result of this mathematical process was to subtract a scalar function from the Ramsey equation equal to the scalar, second-order, paramagnetic, observable of Ramsey's paramagnetic term

Values of the total calculated shift from the bare proton for the hydride ligand were obtained for four different wavefunctions and were compared with the experimental value of 45.3 ± 2.5 p.p.m. (upfield). Even in light of errors resulting from assignment of bonding and non-bonding Co metal orbitals and in the form of the Hamiltonian equation, a value of 42.158 p.p.m. was obtained from a covalent, valence bond, groundstate wavefunction. The M—H distance was assumed to be 1.534 Å and the basis set on Co was selected such that sp^3 hybridization was used for an assumed tetrahedral bonding of the four carbonyl ligands, while the hydrogen was bonded through its $1s$ orbital to a Co $3d_{z^2}$ orbital. All Co orbitals were orthogonal and no orthogonality assumption was placed on H_{1s}. The contributions to the total shift from each orbital in the basis set were displayed It was found that 79% of the resultant shift was a diamagnetic shielding by one electron in the H_{1s} orbital, in comparison to H_2O protons this shift contribution was 3 p.p m above that for H_2O This is in quantitative agreement with shielding in systems such as CH_4 and TMS. Also in agreement with this, Sebastian and Grunwell [262] examined the effect of the charge on carbon in R—H systems with respect to τ_H and reported that large differences in the chemical shift are dominated by changes in the hydrogen electron densities. They also found, in agreement with Ramsey and experimental observations for the H atom, that a change of 26.6 p.p.m /electron was observed for various charged C—H systems, with a similar effect of 34.4 p.p m./electron observed in the calculations of Stevens et al. However, experiment shows this contribution to be limited to $\tau_H \simeq 5$ p p.m (H^-). According to Stevens et al. the next largest contribution is 19% diamagnetic shielding from the bonding sp^3 orbitals to which the four CO are bonded. This is in qualitative agreement with the observations for multi-hydride d^0 complexes that as the number of bonded anions increases (preserving d^0 metal configuration) τ_H increases. Only a 2% contribution is observed for the Co—d_{x^2} orbital and a negligible contribution from the electron-occupied Co nonbonding orbitals. These results are in obvious contradiction to increase in τ_H with decrease in *trans* ligand ability to lower metal electron density, or with decrease in metal oxidation state, and with increase in number of nonbonding metal electrons. Some of these problems arise from the choice of sp^3 bonding of Co to CO ligands and d_{z^2} for Co to H. Several X-ray structural analyses have shown that for HML_4 systems the barrier between tetrahedral ML_4 symmetry and trigonal-bipyramidal symmetry is not always very large. Baker et al. [263] have reported the phosphine and arsine ligands in $RhH(P\phi_3)_3(As\phi_3$ occupy essentially Td symmetry about the Rh with H^- not interfering, while Titus et al [264] reported that the phosphite ligands in $CoH[P(EtO)_3]_4$ take an approximate trigonal-bipyramidal configuration with H^- along the C_3 axis. Since these two geometries are closely related by addition of H along a C_3 axis of the tetrahedron followed by flattening of the plane perpendicular to it, this variation and sometimes ambiguity in structure is understandable. The selection of tetrahedral symmetry for CO bonded to Co through sp^3 hybrides and H bonded to Co d_{z^2} underestimates quantum interactions between the M—H and M—L bonds, and overestimates the energy separation between nonbonding Co orbitals and the M—H orbital

Buckingham and Stephens[265] performed a more rigorous calculation by keeping the second-order term of Ramsey's equation. By operator algebra manipulation of Ramsey's equation they definitively established that the result of the gauge function choice of Stevens et al.[261] was to ignore the excited state paramagnetic contribution to the shielding This term was evaluated using Slater functions, and its contribution was followed as the M—H distance varied from 1 to 1.5 Å, as the Slater radial exponent of the *d* orbitals varied, and as the energy separation of excited and ground state varied. When the M—H distance is ~1 Å the second-order paramagnetic term overwhelms the first-order "diamagnetic term", and on the assumption that this distance is in reality between 1 and 1 5 Å it was concluded that the paramagnetic contribution is the most important factor in determining chemical shifts above τ_H = 5 p p.m. Several authors, including Atkins et al.[252] and Masters et al [250] have followed this line of reasoning in correlating τ_H values with chemical variation However, in light of what has been said above about the M—H distance it is more reasonable to judge the second-order paramagnetic contribution on the basis of an M—H distance in the range of 1.5 to 2 Å. Such an evaluation was made for 1.5 Å, and it is obvious that this term *does not* contribute strongly unless there is a considerable population of excited states or an M—H distance less than 1.5 Å Further, because this shielding term was functionally and relatively insensitive to changes in ΔE it was assumed that variation and uncertainty of ΔE was not significant with respect to variation of the M—H distance. This appears to be an incorrect assumption, but more neutron diffraction studies are necessary to establish the allowable degree of variation in the M—H distance In all the discussions of the relative contributions of the "diamagnetic term" and paramagnetic term two facts appear to have been overlooked. First, the diamagnetic contribution for a system assumed to have "normal" M—H distance does give rise to a $\tau_H \geqslant 40$ p p m (well capable of covering most observed τ_H for transition metal complexes), and secondly, the "diamagnetic term" varies as $1/r$ while the paramagnetic term varies as $1/r^3$. Thus contributions from the second-order term certainly are observed but are not generally the overwhelming contribution unless there are low-lying excited states or an M—H distance less than 1.5 Å. The most surprising and indisputable result of the Buckingham and Stephens calculation which was not recognized beforehand was that paramagnetism in the populated wavestates can and does give rise to shielding rather than anti-shielding at the hydride nucleus. In simple physical terms this is visualized as the paramagnetic character of one orbital reinforcing the external polarizing magnetic field at the bonding electron density of a different orbital, giving rise to diamagnetic shielding of nuclei in the bonding orbital. Which term, paramagnetic or diamagnetic, will overpower the other is determined by the distance of the nucleus of interest from the paramagnetic center. Since a measure of this distance is the radial extent of the paramagnetic orbital, the sign and magnitude of the second-order term is expected to vary dramatically with change in the Slater radial exponent for these orbitals. Such was observed in Buckingham and Stephens' calculation, where it was found that the shielding effect, of the paramagnetism in an orbital orthogonal to the M–H orbital, overwhelms the direct through-space anti-shielding effect at the hydrogen nucleus.

Thus it is clear that without better wavefunctions and evaluations of ΔE little can be said definitively about the M–H distance from NMR quantum mechanical calculations, while without further neutron diffraction studies on M–H distances little can be said definitively about the entire spectrum of variation in τ_H with chemical environment.

At this point the effects of theory and observations on τ_H variation can be summarized in diagram form (Fig 2).

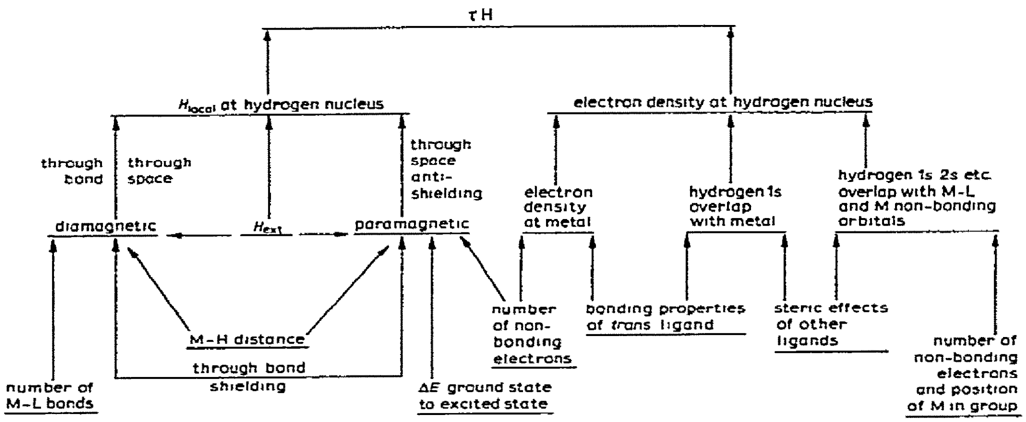


Fig. 2 Origin of hydride chemical shift

(iii) Bridged hydrogen hydrides

Models, calculations and neutron diffraction studies of the M–H system relate primarily or only to terminal hydrides Little is known about the bridged hydrogen complexes with hetero- or homogeneous metals in these regards. In 1966 Hayter[266] discussed some of the theoretical, physical and experimental problems surrounding such hydrogen-bridged species, while in 1971 a simplistic review of bridged hydrogen complexes and their spectral properties was given by James[267]. Handy et al.[268] have shown for $Cr_2(CO)_{10}H^-$ that the Cr–Cr distance increases by 0.44 Å in going from the nonprotonated species $Cr_2(CO)_{10}{}^{2-}$, in keeping with the self-consistent covalent radii set for M–H bond lengths It was also observed that the M–H–M angle varied depending on the metals and ligands and that the M–M distance varied conversely. The bonding in such systems was described as a three-center, two-electron bond, and their earlier reports were corrected with regard to the nature of the three resulting molecular orbitals It was pointed out that there are two bonding and only one antibonding molecular orbital, with no nonbonding molecular orbital resulting from the three atomic orbitals involved. The results of such bonding schemes with respect to Buckingham and Stephens' calculation are not clear, but even more perplexing in this respect are the observations by Churchill and Wormald[269] of triply bridging hydride ligands in $H_2Ru_6(CO)_{18}$.

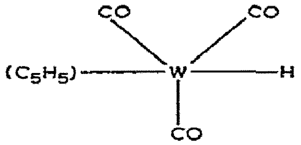
(iv) Infrared activity

Besides the problems with NMR, it has been observed on occasion that the ν_{M-H} is inactive in the IR, while the Raman and NMR are active, without any apparent symmetry explanation. Levison and Robinson[270] have reported this for $[CoHP(OR)_3]_4$ and attributed it to interactions between the hydride and aryl ligands

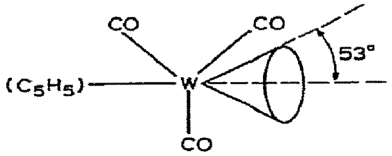
Several other physical and spectroscopic studies of the transition metal hydrides have recently been reported.

(v) Structural determinations by NMR in ordered solvents

McIvor[271] has reported a structural determination of $(C_5H_5)W(CO)_3H$ in a nematic solvent using NMR The method is one developed by Saupe[272], and Meiboom and Snyder[273] for structural studies on organic molecules in "liquid crystals". Judging from the results obtained for organic molecules, this method appears to be more accurate than other NMR methods (e g. Van Vleck's equation) for bond length determinations The method is limited, however, by the fact that there is no inherent gauge with respect to which distances can be measured. Thus it is necessary to introduce at least one bond length from X-ray data into the calculation in order to solve the resulting simultaneous equations Nonetheless it has proven to be a unique complement to X-ray analysis in that it gives dynamic structural information. McIvor's application of the method is the first reported use for inorganic complexes This is primarily the result of the reactive nature of liquid crystalline solvents and instability of inorganic hydrides. However, the greatest difficulty with the method is that few inorganic complexes of interest can be dissolved in anisotropic solvents Starting with the assumed geometry



it was found that the NMR data and X-ray data could agree only if the dynamic structure is



However, this result may come about from the original symmetry assumption and may disappear if a Td arrangement for C_5H_5 and CO around W is assumed; the effect of such changes can only be determined by complete calculation. The possibility of application of this method has increased in the past two years with the synthesis of many new, stable hydrides. Particularly favorable conditions are found for complexes with PF_3 and $P(CF_3)_2$ or $P(CF_3)_3$ ligands. Bennett and Patmore[274] have found the PF_3 complexes of

Co–hydrides to be considerably more stable with respect to heat and oxidation than their CO analogues, while Dobbie and Whittaker[275] have found $P(CF_3)_2$ complexes of Fe–hydrides to be remarkably stable, and of course such systems have an abundance of NMR-active nuclei which split the hydrogen resonance in characteristic ways.

Wei and Fung[276] have recently discussed the use of NMR deuterium quadrupole coupling constants as a supplement to NMR chemical shift data for obtaining structural information on transition metal hydrides These authors supply the most convincing argument for substantial paramagnetic contributions to transition metal hydride chemical shifts in noting that unlike the anomalous high-field shifts the deuterium quadrupole coupling constants depend only on ground state contributions and show no anomalous behavior However, caution must be used in interpreting such sensitive parameters.

(vi) Mossbauer effect and metal charge

A problem which has existed for some time is the determination of actual oxidation state of the metal in hydride complexes. Wickman and Silverthorn[277] have discussed the use of the Mössbauer effect in studies of the oxidation states of the Ir center in complexes with small gaseous molecules such as H_2, O_2, etc. The Mossbauer center shift and quadrupole splitting has also been discussed by Bancroft et al.[278], who found that H^- is a stronger donor ligand than CN^-. On the basis of these Mossbauer parameters and their relationship to ligand bonding properties the spectrochemical series of ligands was re-evaluated.

(vii) Mass spectra

An interesting application of mass spectroscopy has been proposed by Johnson et al.[279] for differentiation between terminal and bridging hydrogen complexes. It was found that hydrogen is not lost from the bridging hydride species in the mass spectrum, while terminal hydrides lose hydrogen (as well as other small gaseous ligands). Thus the mass spectra become more powerful than NMR or IR spectra for deciding between these two structures.

(viii) Other items

The polarographic behavior of $(C_5H_5)FeH(CO)(SiCl_3)_2$ was reported by Breckenridge et al[280] using acetonitrile as solvent The data support the reaction

$$(C_5H_5)FeH(CO)(SiCl_3)_2 \rightarrow H^+ + (C_5H_5)Fe^-(CO)(SiCl_3)_2$$

Finally, one of the most active controversies in the last four years has been over the existence of *cis*-$PtHCl(PR_3)_2$. Although it is now known that what was thought to be the *cis* isomer is in fact only a different crystal form of *trans*-$PtHCl(PR_3)_2$, much disagreement did occur. Collamati et al[281] have discussed this problem and the evidence supporting the non-existence of the *cis* isomer. In an attempt to observe a transient *cis* isomer in the NMR spectrum, De Roos and McCue[282] isolated two pre-charge transfer bands in the UV spectrum of *trans*-$PtHCl(P\phi_3)_2$ by means of matched filter technique and irradiated an NMR sample (quartz tube) of *trans*-$PtHCl(P\phi_3)_2$ at these frequencies in a Varian HR-60 spectrometer. No *cis* isomer was observed under steady-state conditions.

Dumler and Roundhill[283] have also found $PtH_2Cl_2(PR_3)_2$ to be a crystalline modification of *trans*-$PtHCl(PR_3)_2$.

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