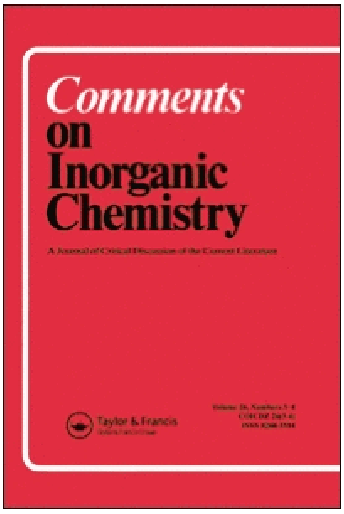

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Molecular Hydrogen Coordination to Transition Metals

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Molecular Hydrogen Coordination to Transition Metals

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The discovery of molecular hydrogen coordination to transition metals and its significance in terms of reactions of σ bonds at metal centers and catalysis is described. The fact that several complexes, known for many years, have only now been shown to contain H_2 ligands after our finding, perhaps best reflects how surprising and well hidden this phenomenon has been. The existence of a tautomeric-like relationship between dihydrogen and dihydride ligands was equally unexpected. Diagnostics for, properties of, and induced cleavage of H_2 ligands are given, along with a bonding model in harmony with these properties.

INTRODUCTION

Transition metal complexes containing reversibly coordinated small molecules such as dioxygen and dinitrogen have now been known for over two decades and are of obvious importance in biological systems as well as coordination chemistry as a whole. In the characterization and subsequent report of the first molecular N_2 complex, $[Ru(NH_3)_5(N_2)]^{2+}$, by Allen and Senoff in 1965,[1] a considerable amount of serendipity, as well as initial disbelief by referees, was involved.[2] Looking back to this landmark finding, we can see

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very similar parallels in our discovery of the first stable molecular hydrogen complexes several years ago (Fig. 1).[3,4] From fundamental bonding concepts, very few chemists, including us, would have believed that an H–H molecule, with only a rudimentary σ bond, could (A) act as a strong enough electron donor (and/or acceptor) to give a stable complex and (B) not be cleaved to hydride ligands on the metal center. Complete breakage of the rather

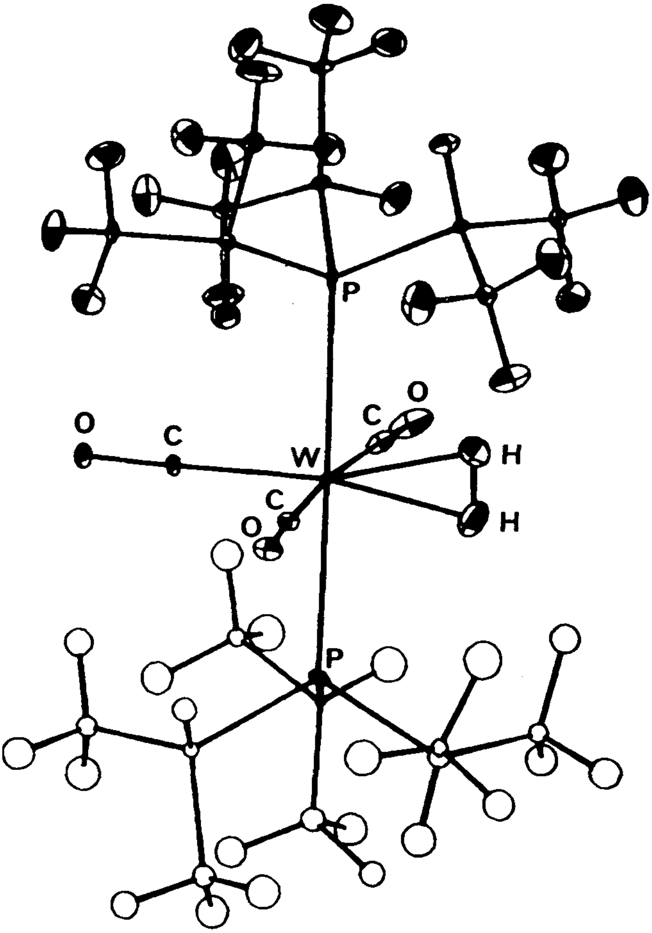
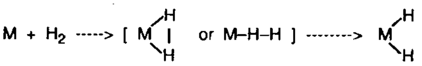


FIGURE 1 Molecular structure of $W(CO)_3[P(i\text{-}Pr)_3]_2(H_2)$ from 30 K neutron data.

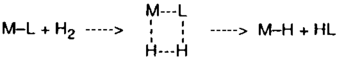
strong H–H bond (103 kcal mol^{-1}) on metal surfaces or metal complexes has long been taught to be dogmatic in the mechanism of catalytic hydrogenation processes (Fig. 2).[5] Depending upon the catalyst system, two types of cleavage had been proposed:

homolytic cleavage:
("oxidative addition")



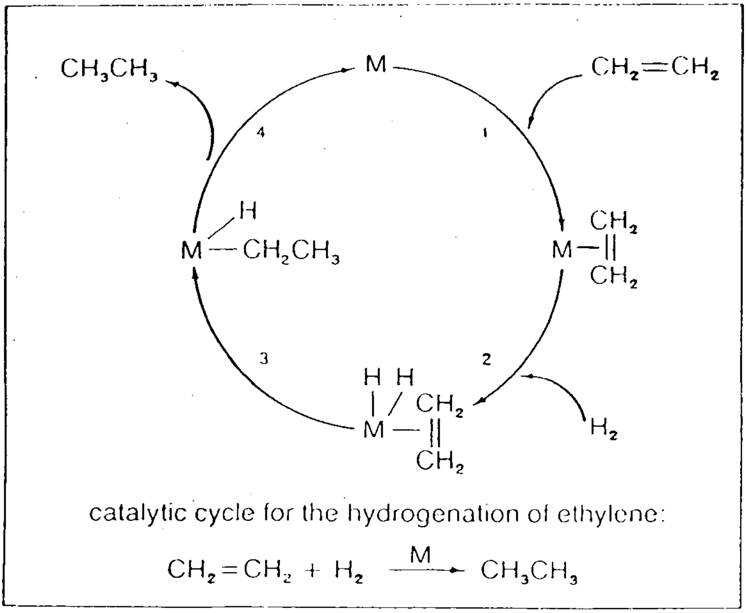
$$M + H_2 \dashrightarrow \left[M\begin{matrix} H \\ | \\ H \end{matrix} \text{ or } M{-}H{-}H \right] \dashrightarrow M\begin{matrix} H \\ H \end{matrix} \qquad (1)$$

heterolytic cleavage:
(L = basic ligand)



$$M{-}L + H_2 \dashrightarrow \begin{matrix} M\text{---}L \\ \vdots \quad \vdots \\ H\text{---}H \end{matrix} \dashrightarrow M{-}H + HL \qquad (2)$$

The initial species (e.g., side-on (η^2) vs. end-on bonded H_2) formed upon approach of H_2 to the metal has been speculated upon for many years[6,7] and was generally regarded to be only a transient. Now that η^2-H_2 complexes are indeed known to be stable, one

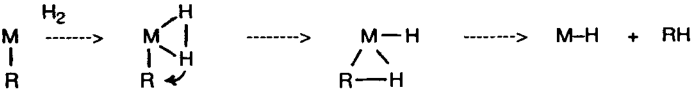


catalytic cycle for the hydrogenation of ethylene:

$$CH_2{=}CH_2 + H_2 \xrightarrow{M} CH_3CH_3$$

FIGURE 2

must re-evaluate past ideas on the activation of H–H and perhaps other σ bonds (e.g., C–H, C–C) and catalytic mechanisms. The real possibility exists that complete scission of H_2 to a dihydride as in (1) is no longer necessary in hydrogenation. The heterolytic cleavage[8] process (2) is in fact closer to what must now be considered as a strong candidate for the mechanism of some or even all hydrogenation processes, namely *direct transfer of a hydrogen from an* η^2-H_2 *ligand to a co-bound substrate*. As in step 3 of the catalytic cycle in Fig. 2, transfer of the H atom to bound $CH_2{=}CH_2$ would give an alkyl hydride complex, $M(H)(CH_2CH_3)$. For the simpler known case of hydrogenation of a metal alkyl, the following can be envisioned:



(3)

The proton can be pictured as merely sliding over from η^2-H_2 to R to give a RH bound ligand, a direct analog of η^2-H_2, which then eliminates as the alkane, RH.[7f] Indeed, hydrogenolysis of d^0 metal alkyl complexes, for which "oxidative" addition of H_2 to hydride ligands is improbable, had been suggested to occur by direct transfer of a proton or H-atom from a transiently-bound H_2 to the alkyl[7f] or by a four-center cyclic transition state[9] as proposed in heterolytic activation[8] (Eq. (2)). In regard to alkane binding, *intra*molecularly bound C–H has been well established ("agostic" interactions[10]) and, like η^2-H_2, is weakly and reversibly held. Such an interaction indeed generally exists in the electronically unsaturated precursors to H_2 complexes, e.g., $W(CO)_3(PCy_3)_2$, which contains a cyclohexyl C–H bond occupying the sixth coordination site (Fig. 3).[11] *Inter*molecularly bound CH_4, coordinated either in η^2-RH fashion as in Eq. (3) or η^1, has been detected at very low temperatures in matrix-isolated $Fe(CO)_4(CH_4)$,[12a] and, although unimaginable prior to the discovery of H_2 binding, may soon prove to be isolatable at room temperature.[12b]

DISCOVERY OF H_2 COMPLEXES

In 1959 Halpern speculated that the activation of hydrogen involved attack of the bonding electrons of H_2 on a vacant metal d

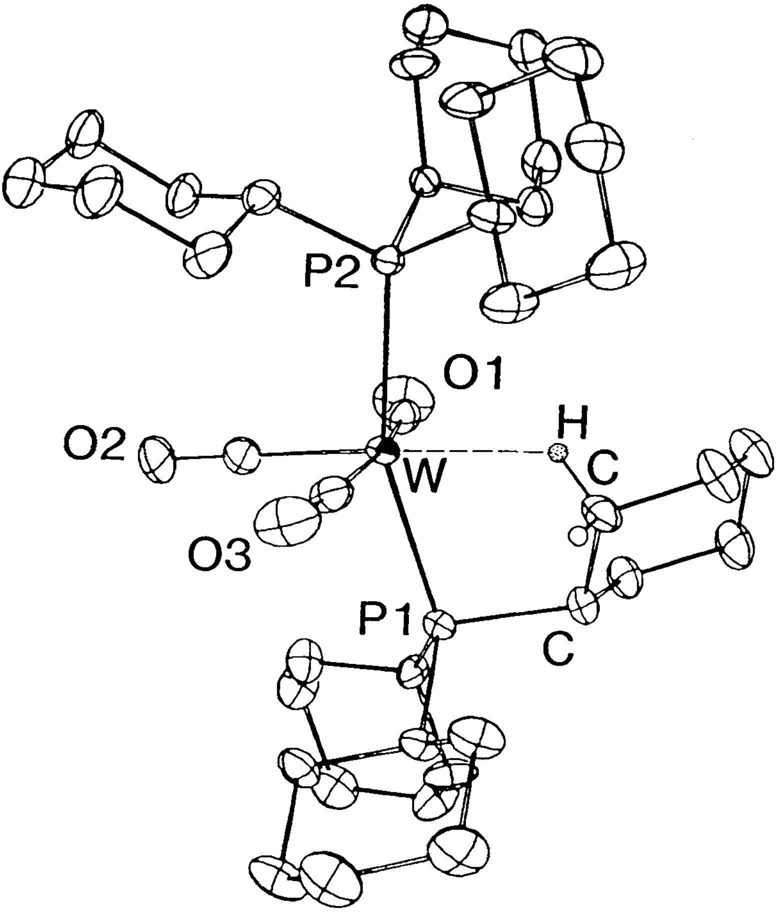
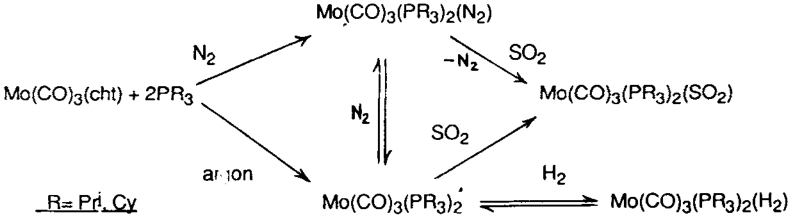


FIGURE 3 Molecular structure of $W(CO)_3(PCy_3)_2$ (Cy = cyclohexyl). Note that the metal is exerting a strong attractive force towards the agostic C–H, as evidenced by the highly distorted geometry about P(1).

orbital.[6a] Other researchers believed the opposite: transfer of electrons from an occupied d orbital to the antibonding (σ^*) orbital of H_2.[6b–d] In a sense both ideas were correct since η^2-H_2 coordination almost certainly involves both σ donation to the metal and backbonding to σ^* as in CO and olefin complexes. This bonding model was apparently first attributable to Orchin and Rupilius[7c] in 1972 and has since been supported by numerous theoretical and experimental studies.[6g,7d–e,13–16] Metal–H_2 interaction was of course generally thought to be only of fleeting existence along the reaction coordinate to dihydride formation. However, occasional reports of possible H_2 binding did appear in the literature before our work,[7b,17] though surprisingly little attention or efforts to confirm them were brought forth. A good example is $RuH_4(PR_3)_3$, which was suggested to contain a neutral H_2 ligand by Ashworth and Singleton[17a] and indeed now appears to be best formulated as $RuH_2(H_2)(PR_3)_3$,[18] a much more reasonable d^6 Ru^{II} configuration. Also, the Fe analogs were noted[19] to give unexplained broad IR bands near 2400 cm^{-1} that now can be presumed to be assignable to the H–H stretching mode. Preliminary neutron diffraction results on $FeH_2(H_2)(PPh_2Et)_3$ indeed show an η^2-H_2 ligand.[18b–c] This complex and many other polyhydrides with suspiciously high formal oxidation states and labile hydrogen have been known for nearly twenty years. Perhaps the real possibility of stable molecular hydrogen coordination seemed too far fetched, but the clues and suggestions were all there.

Our establishment of H_2 coordination, an account of which will now be given, was not completely serendipitous. Although the preparation of $M(CO)_3(PR_3)_2(H_2)$ was unintentional, the possibility of H_2 coordination was recognized early on and efforts to prove it were completely intentional. In 1979 we were examining the remarkable versatility of SO_2 as a bonding probe for transition metal complexes[20] and were unconcerned with hydrogen/hydride chemistry except for seminal ideas relating to SO_2 reduction. Depending upon the metal fragment, SO_2 can behave as a σ base (planar M-SO_2), σ acid (pyramidal M-SO_2), or π acid (η^2-S,O bonded) with distinct structural differences and characteristic ν(SO). A fascinating series of octahedral, zero-valent, d^6 complexes, *cis, trans*-$Mo(CO)_2(PPh_3)_2(SO_2)L$, was synthesized in which the M-SO_2 geometries were highly sensitive to varying just one *cis* ligand, L. If L was a strong π-acceptor such as CO, the SO_2 acted as base (planar S-bound), but if L was an electron donor, the SO_2 switched to its π-acceptor (η^2) mode to accommodate the increased electron density at the metal. When L was alkyl isocyanide, an intermediate case, a near equimixture of S-bound and O,S-bound SO_2 resulted, an unusual example of coexistence of linkage isomers. Thus, the electronic properties of specific sites on metal complexes can be precisely defined by studying the SO_2 coordination geometry at the site and the closely related ν(SO) frequencies. In an effort to explore stereochemical effects, a complex with bulky phosphine ligands, *mer*, *trans*-$Mo(CO)_3(PPr^i_3)_2(SO_2)$, was synthesized and characterized by x-ray crystallography.[20b] The preparative scheme involved stepwise replacement of labile acetonitrile ligands in *fac*-$Mo(CO)_3(NCMe)_3$ by two equivalents of phosphine and SO_2 in benzene. The structure showed that the bulky PPr^i_3 were mutually *trans*, having forced the carbonyls to reorient to the less favored meridional geometry. The SO_2 was η^1-planar, indicating that the metal fragment is relatively electron-deficient. Unlike for most SO_2 complexes, the yield of the reaction was poor, and efforts to overcome this were taken by trying a different starting material, $Mo(CO)_3$(cht) (cht = cycloheptatriene). The phosphines and SO_2 displaced the cht to give the desired complex, although in not much improved yield. However, two key observations were made in the course of carrying out reactions under different conditions. It was noted that gas evolution occurred when SO_2 was added to the reaction mixture generated by addition of PPr^i_3 to the Mo-triene complex under a *nitrogen* atmosphere and that, under *argon* (no SO_2), the latter mixture (normally orange) attained a very dark purple coloration. After further investigation, it became clear that the evolved gas was N_2 from a yellow reversibly-bound N_2 complex and that the deep color was due to a formally coordinatively-unsaturated precursor, $Mo(CO)_3(PR_3)_2$.



The use of nonreactive argon instead of nitrogen was quite fortuitous. A nearly identical reaction had previously been carried out in refluxing benzene under *nitrogen* by Moers and Reuvers,[21] but the deeply colored unsaturated complex was not observed presumably because the yellow N_2 complex formed (only $Mo(CO)_4(PR_3)_2$

from disproportionation was eventually isolated). Similar serendipity involving the reaction atmosphere allowed Yamamoto to prepare $CoH(N_2)(PPh_3)_3$, but here use of N_2 instead of more expensive argon gave the unexpected result.[22] We eventually isolated the electronically-unsaturated $M(CO)_3(PR_3)_2$ species for M = Mo, W and R = Pr^i, Cy (cyclohexyl) as deep purple crystalline solids, stable under argon but quite reactive towards nitrogen and virtually any other weak or strong donor ligand capable of occupying the sixth coordination site.[11,23] Later investigations revealed that the syntheses succeeded only for bulky phosphines and, curiously, only for the Pr^i and Cy derivatives. Since few 5-coordinate Mo (and no W) complexes had been known, it was quite exciting to find new examples that were easy to prepare by simple metathesis and reversibly coordinated nitrogen. However, this discovery was merely a stepping stone to the real breakthrough.

Virtually at the same time that reversible nitrogen binding was observed, it was noted that hydrogen (and ethylene) also reversibly added to the 5-coordinate species to give yellow complexes with properties similar to the N_2 adducts. The reasons for investigating H_2 addition involved our expansion of SO_2 chemistry towards studies of reduction by metal hydrides and H_2.[24] The catalytic activity of $M(CO)_3(PR_3)_2$ towards hydrogenation of ethylene under mild conditions was in fact tested, but no reaction occurred. However, the complexes from H_2 addition to $W(CO)_3(PR_3)_2$ were intriguing because of their anomalous IR frequencies. Instead of the expected ν(WH) at 1700–2300 cm^{-1} and δ(WH) at 700–900 cm^{-1} that would be characteristic of a 7-coordinate dihydride complex, bands near 1570, 950, *and* 465 cm^{-1} were observed for Nujol mull spectra and shifted appropriately on deuterium substitution. The low-frequency mode and the high lability of the hydrogen suggested that "the bonding of the hydrogen to these metal complexes may be novel," as carefully understated in the first communication of the results in 1980.[23] The possibility that *molecular* binding could be present, astounding though it might have been at the time, fortunately was met with an open mind. X-ray diffraction studies were initiated but were frustrated by disorder problems. The hydrogen positions could not be located for the PCy_3 complexes because they and the *trans* carbonyl group were involved in the disorder. Encouragingly, the carbonyl and phosphine ligands were in strictly octahedral configuration, leaving a vacancy in the sixth coordination site presumably containing the hydrogens. Efforts then turned to single crystal neutron diffraction to locate the hydrogens since they have a much larger cross-section towards neutrons than x-rays. Much stimulus was provided by Phillip Vergamini who was setting up a pulsed neutron diffraction instrument at the Los Alamos Neutron Scattering Center. The necessary large single crystals (ca. 10 mm^3) were eventually grown for the $W(CO)_3(PPr^i_3)_2(H_2)$ complex, and data was collected in 1982 using the Laue time-of-flight method on a prototype instrument at room temperature. Although a complete structure could not be obtained, partly because of disorder in one of the phosphines, a difference-Fourier map phased on the non-hydrogen atom coordinates from room temperature x-ray studies demonstrated the presence of an H_2 ligand. Subsequent low-temperature x-ray studies by Harvey Wasserman, a postdoctoral student, confirmed a side-on bonded H_2 (Fig. 1) with H–H = 0.75 (16) Å (x-ray) and 0.84 Å (neutron, ΔF).[3a]

Since the usual uncertainty in x-ray hydrogen locations was destined to create skepticism, further proof was sought. Fortunately a suggestion by Russ Drago, a consultant with us, led to incontrovertible spectroscopic evidence for the presence of a weakened H–H bond. The experiment was elegant in its simplicity: synthesize the HD complex and look for a large HD coupling constant in the proton NMR. The NMR of $W(CO)_3(PPr^i_3)_2(H_2)$ had already been observed to give a broad single resonance (−4.2 ppm) for the η^2-H_2, showing no coupling to phosphorus or ^{183}W. This in itself was unusual compared to classical hydrides, but the HD substitution really proved to be diagnostic: a clear 1:1:1 triplet (deuterium spin = 1) with $J(HD)$ = 33.5 Hz resulted. The value for HD gas had been measured to be 43.2 Hz,[25] and the coupling for hydride–deuteride complexes is less than 2 Hz. Thus, an H–D bond of reduced order was present. The HD complexes also provided a second bonus in the area of vibrational spectroscopy. IR spectra of the HD complexes showed bands at intermediate positions to those for the H_2 and D_2 complexes and not superimpositions of MH and MD modes previously observed for hydride–deuteride species.[26] Finally, to cap it all off, a broad, weak absorption was located in the IR at 2360 cm^{-1} assignable to $\nu(HD)$.

Raman spectra and analysis of vibrational data by Basil Swanson added further evidence for side-on bonded H_2. Bolstered by the new results, we presented the findings at the Spring 1983 American Crystallographic Association and American Chemical Society Meetings, fully 4 years after the H_2 complexes were first synthesized. Ironically, in an inversion of the normal order, spectroscopic rather than crystallographic data provided the convincing evidence. Of course both were ultimately necessary (better low temperature neutron data was obtained later), but perhaps sufficient proof of H_2 coordination could have been obtained sooner if NMR and vibrational methods had been the initial focus. The disorder and other structural problems indeed created considerable initial skepticism in the findings, but the NMR criterion was irrefutable.

NEW EXAMPLES OF DIHYDROGEN COMPLEXES

Two of the first questions to come to mind were: What factors stabilized dihydrogen coordination and would new examples of H_2 complexes be found? Initially it was believed that the extremely bulky P-*i*-Pr_3 and PCy_3 ligands in $M(CO)_3(PR_3)_2(H_2)$ sterically inhibited formation of the 7-coordinate dihydride. However, as will be discussed later, electronic factors now appear to be the primary control over whether the H_2 coordinates as a molecular entity or scissions to hydride ligands. The second question was soon answered in early 1983 when Ray Sweany privately communicated to us spectroscopic evidence for matrix-isolated $Cr(CO)_5(H_2)$ formed by low-temperature photolysis of $Cr(CO)_6$ in the presence of H_2. These results[27] actually predated our neutron work but of course were more tenuous and were admitted to be difficult to publish until our communication establishing $M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ appeared. The matrix work was later published[28] in early 1985 at about the time related papers[29] showed that $Cr(CO)_5(H_2)$ in liquid Xe or cyclohexane is stable for only seconds at 25°C (decomposition products resulted). Several other low temperature stable species such as the Mo and W analogs and Fe $(CO)(NO)_2(H_2)$ have since been identified as products of photolytic displacement of CO ligands.[30-32] Clearly, sterically demanding ligands were not needed for H_2 coordination to occur at low temperatures but possibly were still responsible for imparting thermal stability. There was no sign of a new *stable* complex until, months later, Crabtree reported NMR evidence for $[IrH(H_2)(PPh_3)_2(bq)]^+$, formed by displacement of an H_2O ligand by H_2.[33] Of great significance was his establishment of an alternate NMR criterion for molecular H_2 coordination and its use to provide evidence that many known polyhydride complexes such as $RuH_4(PR_3)_3$ may actually contain H_2 ligands.[18a,34,35] The NMR method utilizes measurement of the relaxation time, T_1, which for bound H_2 has been found to be quite short (4–125 ms, cf. > 300 ms for classical hydrides) because of dipolar interaction between the closely spaced H atoms.

Morris's group then established that *trans*-$[MH(H_2)(dppe)_2]^+$ (M = Fe, Ru), made by protonating $MH_2(dppe)_2$,[36] contained an η^2-H_2 ligand by x-ray and NMR methods. The structure of the Fe complexes[18b,c,36] are so far the only other crystallographic locations of an H_2 ligand. The $[FeH(\eta^2\text{-}H_2)(dppe)_2]^+$cation had actually been prepared many years earlier by several other groups but, as for quite a number of other "hydride" complexes, was unrecognized to contain η^2-H_2.[37] This type of situation wherein the true identity or unique feature of a compound was uncovered (and often made famous) by a second researcher seems to occur often in coordination chemistry. One would expect that such circumstances should become more infrequent considering the rising sophistication of physical characterization techniques. It should be emphasized, however, that our original Mo and W dihydrogen complexes had not been previously prepared and we were completely unaware of any outside efforts concerning H_2 coordination.

The number of proposed[38] and reasonably well-established[18,28–36,39–44] new H_2 complexes have been rapidly increasing every year (Table I). The three major routes to H_2 complexes are (1) addition of H_2 to an unsaturated 16-electron complex normally containing an agostic C–H interaction, (2) photolytic displacement of CO (thermally unstable species generally result), and (3) protonation of metal hydrides. Dihydrogen has also been found to be chemically bound to metals (matrix-isolated "ligand-free" $Pd(H_2)$)[45] and metal surfaces (stepped Ni(100)).[46]

PROPERTIES OF DIHYDROGEN COMPLEXES

The neutron structure[47] of $W(CO)_3(PPr^i_3)_2(H_2)$ and the x-ray structure[36] of $[FeH(H_2)(dppe)_2]^+$ show H–H distances of 0.82 (1)

TABLE I

Molecular hydrogen complexes[a]

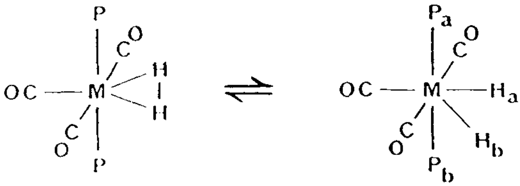
Group 6	Group 7	Group 8	Group 9	Group 10
$\mathbf{Cr(CO)_5(H_2)}^{28-30}$	$ReH_5(H_2)(PPh_3)_2{}^{18a}$	$\mathbf{Fe(CO)(NO)_2(H_2)}^{32a}$	$\mathbf{Co(CO)_2(NO)(H_2)}^{32a}$	$\mathbf{Ni(CO)_3(H_2)}^{44b}$
$\mathbf{Cr(CO)_4(H_2)_2}^{30}$	$ReH_5(H_2)(Ph_2P\text{-}PPh_2)^{18a}$	$\mathrm{FeH_2(H_2)(PEtPh_2)_3}^{18}$	$\mathbf{Co(CH_3)(CO)_3(H_2)}^{44a}$	
$\mathbf{Cr(CO)_4(cyo)(H_2)}^{32b}$		$\mathrm{[FeH(H_2)(R_2P\text{-}PR_2)_2]}^{+\ 36,39}$	$\mathbf{CoH(H_2)(CO)_3}^{44a}$	$\mathbf{Pd(H_2)}^{45}$
$\mathbf{Cr(CO)_3(PCy_3)_2(H_2)}^{c,44c}$				
$\mathbf{Mo(CO)_5(H_2)}^{30}$				
$\mathrm{Mo(CO)_3(PR_3)_2(H_2)}^{3}$		$RuH_2(H_2)(PR_3)_3{}^{18,44d}$	$\mathrm{\{Rh[P(CH_2CH_2PPh_2)_3](H_2)\}}^{+\ b,42}$	
$\mathrm{Mo(CO)(Ph_2P\text{-}PPh_2)_2(H_2)}^{4}$		$RuH_2(H_2)_2(PCy_3)_2{}^{44d}$		
$\mathbf{MoCpH(CO)_2(H_2)}^{31}$		$Ru_2H_4(H_2)(PCy_3)_4{}^{44d}$		
		$\mathrm{[RuH(H_2)(R_2P\text{-}PR_2)_2]}^{+\ 36,39}$		
		$\mathrm{[RuCp(PPh_3)(Bu^tNC)(H_2)]}^{+\ 40a}$		
		$\mathrm{[RuCp(CO)(PMe_3)(H_2)]}^{+\ 41}$	$\mathrm{[IrH(H_2)(PR_3)_2(bq)]}^{+\ 33,35}$	
		$\mathrm{[RuCp(R_2P\text{-}PR_2)(H_2)]}^{+\ 40b,41}$	$\mathrm{[IrH_2(H_2)_2(PCy_3)_2]}^{+\ 34,35}$	
$\mathbf{W(CO)_5(H_2)}^{30}$		$[OsH_3(H_2)(PPh_3)_3]^{+\ 18a}$		
$\mathrm{W(CO)_3(PR_3)_2(H_2)}^{3}$		$\mathrm{OsH(H_2)(Et_2P\text{-}PEt_2)_2]}^{+\ 39}$		
$\mathbf{WCpH(CO)_2(H_2)}^{31}$	Group 5	$\mathrm{[Os(\eta^2\text{-}OAc)(PPh_3)_3(H_2)]}^{+\ 43}$		
$\mathbf{W(CO)_4(cyo)(H_2)}^{32b}$	$NbCp_2H_3{}^{b,38a}$			

[a] Complexes in bold face are thermally unstable and those in italics are likely H_2 complexes. Numeral superscripts correspond to citations in reference section. $R_2P\text{-}PR_2 = R_2PCH_2CH_2PR_2$. cyo = cyclooctene. bq = 7,8-benzoquinolate.

[b] Complexes apparently contain an H_2 ligand in solution but are hydrides in the solid state.

[c] Stable only under high pressures (>300 psi) of H_2.

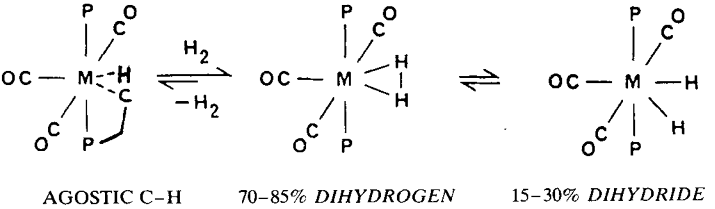
Å and 0.89(11) Å, respectively, compared to 0.74 Å in free H_2. The W–H distances were 1.89(1) Å compared to ~1.7 Å in normal tungsten hydrides. Solid state proton NMR has also been shown to be an effective and precise method for determining the H–H separation (0.890 Å in $W(CO)_3(PCy_3)_2(H_2)$).[48] In regard to other spectroscopic diagnostics for H_2 coordination, solution proton NMR has proven to be invaluable. The majority of H_2 complexes give broad, uncoupled H_2 signals with $T_1 < 125$ ms and $J_{HD} = 22–36$ Hz for the HD isotopomers. However, complexes exhibiting J_{HD} as low as 13 Hz and resolved coupling to phosphorus and metal nuclei have recently been found.[40–43] Whether this is indicative of an elongated H–H bound or rapid equilibrium with a hydride form remains to be seen. The structure and dynamics of H_2 complexes are far more involved than that for any other small molecule, and *solution and solid state structures of dihydrogen complexes can greatly differ*. The $W(CO)_3(PR_3)_2(H_2)$ complexes have indeed been shown by us[3b,4] to exist in solution as an *equilibrium mixture (~5:1) of the octahedral 6-coordinate* η^2*-*H_2 *form and a 7-coordinate dihydride* $WH_2(CO)_3(PR_3)_2$ *derived by H–H bond cleavage*:



The two hydrides (H_a and H_b), as well as the phosphines, are inequivalent at low temperature as shown by NMR experiments. Chinn and Heinekey have also recently demonstrated similar equilibria in cationic complexes of the type $[CpRuLL'(H_2)]^+$ wherein they could actually observe production of the dihydride form on warming a cold solution containing 100% H_2 form.[41] This observation is highly significant in that it demonstrates that dihydrogen and dihydride complexes are interchangeable and can essentially be considered as *tautomers*, a surprising finding. Thus classical polyhydrides may contain in solution varying equilibrium amounts of dihydrogen ligands. This appears to be the case for Cp_2NbH_3, which has been shown by neutron diffraction[49] to be a trihydride in the solid state but which may exist at least partially as $Cp_2NbH(H_2)$ in solution from

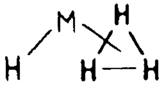
NMR evidence.[38a,50] Similarly, $\{Rh[P(CH_2CH_2PPh_2)_3](H_2)\}^+$ is a classical octahedral dihydride in the solid and in solution below 183 K but in solution above 183 K apparently possesses a trigonal bipyramidal structure with an H_2 ligand.[42] Adding further complexity to the situation, the structure of the hydride tautomer, e.g., $MH_2(CO)_3(PR_3)_2$, can be stereochemically nonrigid, and, in the case of complexes containing both H_2 and normal hydride ligands, rapid exchange between these ligands usually occurs.[33–36,39,41] Thus the NMR spectrum of a dihydrogen complex is highly temperature and field dependent and can show a variety of signals ranging from a single exchange-averaged resonance to several multiplets at the slow exchange limit.

The dihydrogen generally behaves as a labile, weak donor ligand, usually displaceable by N_2 and reversibly dissociating on mild heating or in vacuo. This property further complicates the ligand dynamics by adding the unsaturated complex as a potential third equilibrium species:



(4)

In effect, the H_2 ligand competes with the intramolecular C–H interaction in $W(CO)_3(PR_3)_2$ (Fig. 3). Equation (4) also shows that a ready pathway exists for elimination of H_2 from hydride complexes. Cationic H_2 complexes are generally more robust than the neutral ones, being stable in donor solvents (e.g., acetone) which instantly displace H_2 in the W complexes. As expected, facile exchange of bound H_2 with D_2 occurs in solution, but unexpectedly $W(CO)_3(PR_3)_2(H_2)$ and D_2 were found to give, at a slower rate, statistical amounts of HD, even in the *solid state* (25°, 1 atm, ca. 1–2 week). Thus H–H bond cleavage and scrambling is occurring by an unknown mechanism. Coordination of a second H_2 as a seventh ligand would seem unlikely, as would transient displacement of the phosphine or CO ligands (the scrambling occurs in the solid in the dark). One possibility suggested by Burdett[51] is intermediate formation of polyhydrogen species such as H_3 or H_4, which are known "mass spectrometer molecules."



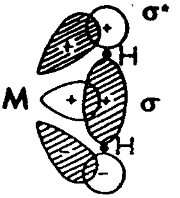
It is possible that such molecules will soon be stabilized on metal complexes. In addition to the probable mechanism for isotopic exchange, two legitimate demonstrations of *direct* reaction of H_2 ligands have been reported. Isotopic labelling experiments pointed to deprotonation by MeLi of the η^2-H_2 rather than the hydride in $IrH(H_2)(bq)L_2^+$.[35] NMR evidence showed that $[CpRu(dmpe)(H_2)]^+$ was deprotonated by Et_3N *in preference to the equilibrium dihydride form.*[41] Although not experimentally confirmed as yet, it would seem reasonable that proton transfer from η^2-H_2 to bound substrates could also take place. Thus H_2 complexes are more than "arrested intermediates" and should be considered to have an identity and a *chemistry* of their own.

Another important dynamical feature of η^2-H_2 is its vibrational modes and rotational motion about the metal–H_2 axis. The H–H stretching frequency has been observed in the IR as a weak, broad absorption in the range 2350–3100 cm^{-1} (cf. 4300 cm^{-1} for free H_2). Two M–H_2 stretches (1570 and 950 cm^{-1}) and a deformation (462 cm^{-1}) have also been located for $W(CO)_3(PR_3)_2(H_2)$ (R = Cy, *i*-Pr) in the IR. The frequencies for the Mo-PCy_3 analog were significantly lower, especially ν(HH) (300 cm^{-1} lower), suggesting weaker coordination of H_2 to Mo than W, in line with thermal stabilities. Curiously, none of these modes have been observed in the cationic complexes and only the stretching modes have been seen in the thermally unstable complexes. Our Group 6 complexes are still the only ones to show a complete set of vibrational frequencies for the M–H_2 coordination and also remain the only neutral, stable H_2 complexes that do not contain other hydride ligands. Perhaps the latter situation favors location of the frequencies.

An important mode to find was that for the torsion (or hindered rotation) of the H_2. Inelastic neutron scattering (INS) proved to be ideally suited for this, and a split band at 330 and 370 cm^{-1} was observed as predicted assuming a potential of the form $1/2V_2\cos2\phi$ and a reduced rotational constant ($B = 50\ cm^{-1}$) because of the elongated H–H bond.[52] The splitting enabled determination of the barrier to rotation to be 762 cm^{-1} (~2 kcal mol^{-1}). The existence of this small but significant energy barrier is experimental evidence for metal d to H_2 σ^* backbonding (see below). To put this in perspective, barriers to olefin rotation of 10–15 kcal mol^{-1} have been commonly found by solution NMR in Rh(I), Ir(I), and Pt(II) olefin complexes, although indications of much lower barriers have been reported.[53,54] Solid state NMR enabled determination of a value of 1.6 kcal mol^{-1} for the axial ethylene ligand in $IrCl(C_2H_4)_4$,[54] which is very similar to that for the H_2 rotation.

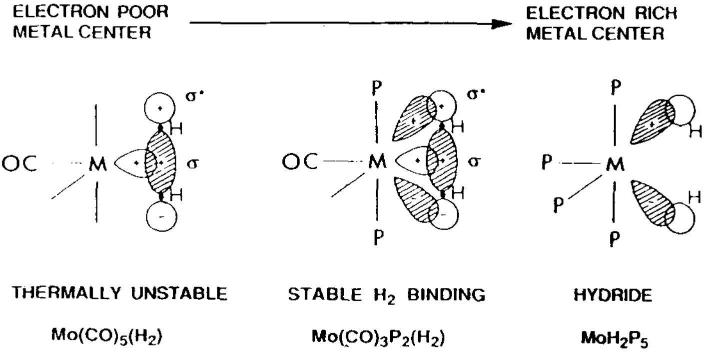
BONDING MODEL AND STEREOCHEMICAL CONTROL OF H_2 COORDINATION

As alluded to previously, theoretical calculations indicate that side-bonded H_2 is both a sigma donor and sigma* acceptor:



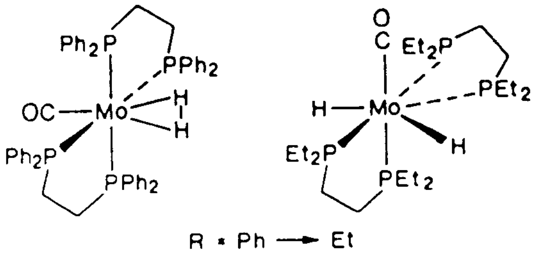
Ab initio calculations by Hay[14] on H_2 addition to a fixed idealized $W(CO)_3(PH_3)_2$ fragment with structural parameters based on $W(CO)_3(PPr^i_3)_2(H_2)$ showed a stable η^2-H_2 complex with 17 kcal mol^{-1} bond energy and H–H = 0.79 Å (vs. 0.82 Å actual). Preference (0.3 kcal mol^{-1}) was found for alignment of the H_2 axis parallel to P–W–P compared to CO–W–CO, as in the actual structure. Orbital population analysis showed that the primary interaction is σ-donation from H_2 into the empty σ orbital on the WL_5 fragment, with a small amount of M → σ* backbonding.

A very important consideration is the electronic and steric influences of ancillary ligands in stabilizing H_2 coordination versus dihydride formation. Assuming the above model, increasing the basicity of the metal center in H_2 complexes would be expected to lead to H–H bond cleavage because of higher $M \rightarrow \sigma^*$ donation. Indeed in the series, $Mo(CO)_xP_{5-x}H_2$(P = phosphine donor), H_2 ligands are present until the strong π-acceptor CO's are completely substituted by basic phosphines ($MoH_2(PMe_3)_5$ is a 7-coordinate dihydride[55]).



Calculations show that mixtures of σ-donor and strong π-acceptor co-ligands favor η^2-H_2 since acceptors, particularly when *trans* to H_2, interact with the d orbital which populates σ* H_2.[16,51] Complexes with *all* acceptors, e.g., $Mo(CO)_5(H_2)$, are thermally unstable to H_2 loss, possibly because $M \rightarrow \sigma^*$ H_2 backbonding is *too* small. Although $[FeH(H_2)(dppe)_2]^+$ contains no stabilizing acceptors, H_2 binds because of the low basicity of Fe,[16b] the *trans*-effect of the hydride, and the positive charge.

In order to define the steric and electronic requirements for H_2 binding versus hydride ligands, we synthesized a series of complexes, $Mo(CO)(R_2PC_2H_4PR_2)_2H_2$, wherein *the coordination mode was found to depend solely upon the nature of R of the chelating phosphine.*[56] For R = Ph, the geometry was octahedral with a labile H_2 ligand *trans* to the CO. However, for more basic ligands (R = Et), NMR measurements were consistent with *hydrides* rather than η^2-H_2. X-ray studies of $MoH_2(CO)(Et_2PC_2H_4PEt_2)_2$ confirmed a *7-coordinate pentagonal bipyramidal* structure similar to that for the dihydride $MoH_2(PMe_3)_5$,[55] with the CO in an axial position *cis* to distal hydrides:



Interestingly, the T_1 value (370 ms) for this dihydride is not as high as that for a typical hydride (~1 s), and in solution in vacuo the hydride ligands slowly eliminate as H_2. Thus a small equilibrium amount of H_2 form may be present. In order to determine if steric effects are important, a complex with a *bulkier* alkyl R = Bu^i (size of $PBu^i_3 \approx PPh_3$) was prepared. Its ^1H NMR signal was identical to that of the Et complex, although the T_1 was now 200 ms, in the "gray area" between H_2 and hydride ligands, and H_2 dissociated *rapidly* in vacuo, possibly indicative of greater solution amounts of H_2 complex. However, IR evidence showed that basically the solid state structure is similar to that for the Et complex. Importantly, this suggests that increasing the basicity of the ancillary ligands is the prime factor in promoting oxidative addition of the dihydrogen, in agreement with theory, and that steric influences are of much less consequence. Whether sterically demanding ligands are important in imparting *thermal* stability of H_2 complexes has not been adequately tested as yet.

As a measure of the electron richness of poorness of binding sites of metal complexes, Morris[58] has studied ν_{NN} of a variety of N_2 complexes and proposed that stable molecular hydrogen complexes should be obtained (on replacement of the N_2) when ν_{NN} is in the range 2060–2160 cm^{-1} versus hydrides for $\nu_{NN} < 2060$ cm^{-1}. The N_2 analogs of all known H_2 complexes have $\nu_{NN} > 2060$ cm^{-1}, in comparison to the more electron rich $Mo(N_2)(PMe_3)_5$ ($\nu_{NN} = 1950$ cm^{-1}) for which the analog $MoH_2(PMe_3)_5$ is known to be a dihydride. Figure 4 shows a correlation of ν_{NN} with the type of complex (dihydrogen or dihydride) resulting when H_2 is placed on Group 6 metal fragments. Note that thermally unstable H_2 com-

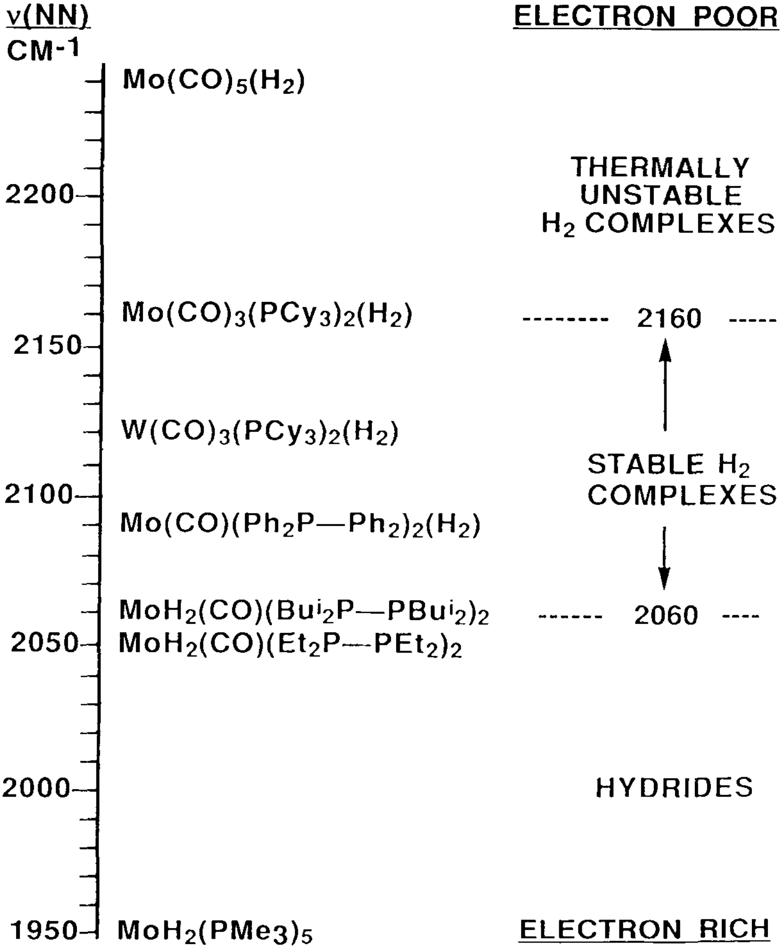


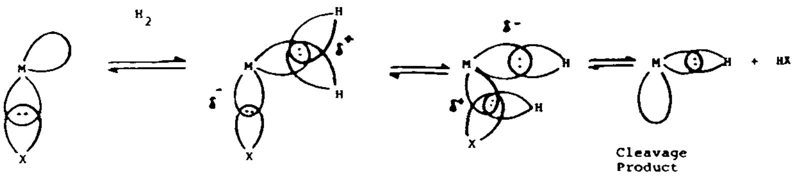
FIGURE 4 Correlation of dihydrogen versus dihydride complex formation with ν(NN) of the analogous dinitrogen complexes.

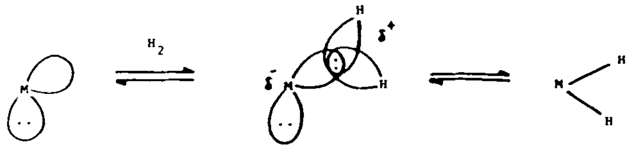
plexes result when ν_{NN} is greater than 2160 cm^{-1} because the binding site is *too* electron poor and very little $d\pi \rightarrow \sigma^*$ backbonding is possible. Interestingly, ν_{NN} for $Mo(CO)(N_2)(Ph_2PC_2H_4PPh_2)_2$, 2090 cm^{-1}, is well within the frequency range for stable H_2 complexes, while that for R = Bu^i (2060 cm^{-1}) is on the dihydrogen/dihydride borderline, and that for R = Et (2050 cm^{-1}) is just inside the hydride range. These data fit remarkably well with the observed structures. We have also made the SO_2 analogs in order to determine if a correlation with M–SO_2 *geometry* (e.g., η^1-planar versus η^2) exists. However, the SO_2 was η^1-planar bound for all of the d^6 Group 6 complexes. A correlation of dihydrogen versus dihydride binding with ν_{SO} was found though. For example ν_{SO} were 1209 and 1052 cm^{-1} for the SO_2 analog of $Mo(\eta^2\text{-}H_2)(CO)(Ph_2PC_2H_4PPh_2)_2$, but the frequencies were significantly lower (1164, 1038 cm^{-1}) when SO_2 replaced the hydrides in $MoH_2(CO)(Et_2PC_2H_4PEt_2)_2$.

Further studies of ligand/metal variations have been carried out by Morris's group on $[MH(H_2)(R_2PC_2H_4PR_2)_2]^+$ within the Fe–Ru–Os triad (R = Ph, Et).[39] In all cases the H_2 ligand remained intact, although the apparent strength of the H–H bonds decreased in the order Ru–Ph > Ru–Et > Fe–Ph > Fe–Et > Os–Et. It is surprising that $[OsH(H_2)(Et_2PC_2H_4PEt_2)_2]^+$ is a dihydrogen complex since a similar complex with less basic monodentate phosphines, $[OsH_3(PPh_3)_4]^+$,[59] has a classical trihydride structure. Geometric constraints imposed by the chelating phosphines may override phosphine basicity arguments here. A chelate ring *size* effect has in fact been found in $[CpRu(Ph_2P(CH_2)_nPPh_2)H_2]^+$, where H_2 coordination is favored in the more constrained system (n = 1).[40b]

CONCLUSIONS AND A GLANCE TO THE FUTURE

The discovery of molecular hydrogen complexes has caused a major shift in the way inorganic chemists must now think concerning bonding and transformations at metal centers. Significantly, coordination of an H–H bond represents the first stable intermolecular interaction of a *sigma bond* with a metal center. Few if any researchers would have believed that H_2 complexes would be stable relative to free H_2 or metal hydrides; now one must ask if there is any limit to the ability of metals to stably bind other sigma bonds, including those in "inert" molecules, e.g., CH_4. The isolation of H_2 complexes and their equilibrium with $M(H)_2$ gives an unprecedented opportunity to study the most fundamental bond breaking/forming process at a metal center. An immediate question is whether the H_2 ligand has an extensive chemistry of its own, i.e., direct transfer of H or H^+ to substrates without initial H–H cleavage. As suggested by Schwartz, "oxidative addition" of H_2 to a metal and its "heterolytic" activation may be but two aspects of the *same* reaction.[7f] In the latter case a bound H_2 ligand transfers a proton to a basic electron pair of the medium or to a bonding electron pair of the complex while in the former the proton is effectively transferred to a lone pair on the metal.





Indeed it is conceivable that H_2 ligands rather than hydride ligands play a major role in catalytic hydrogenation. Even catalysts that are known to form hydrides with H_2 (e.g., $RhH_2Cl(PPh_3)_3$) may operate via direct transfer of H from an η^2-H_2-containing intermediate or equilibrium species. Related to this, the mechanism of H/D scrambling, especially in solid H_2 complexes, remains to be investigated and could provide some valuable information. Another fascinating area for exploration is the range of H–H bond distances and geometries and whether greatly elongated bonds or polyhydrogen ligands (e.g., H_3^+ or H_3^-) will be found. Intermediate values of HD coupling constants (e.g., 13–22 Hz) have been found for certain complexes and the question remains whether these result from H–H bonds greater than 0.9 Å or from other factors. End-on bonded H_2 has been claimed in $Pd(H_2)$ in a Kr matrix at 12 K but still remains to be structurally verified. Lastly, stabilization of H_n ligands ($n > 2$) on metal complexes would prove to be a spectacular experimental confirmation of theoretically predicted molecules.

Acknowledgments

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