Fundamentals of H_2 Binding and Reactivity on Transition Metals Underlying Hydrogenase Function and H_2 Production and Storage

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1. Introduction and Historical Perspective

Dihydrogen (H_2) is not only considered to be the fuel of the future but is also vital in chemical processes such as hydrogenation of organic compounds. Catalytic hydrogenations are the largest-volume human-made chemical reactions in the world, and all crude oil is treated with H_2 to remove sulfur and nitrogen by hydrodesulfurization and hydrodenitrogenation. Hundreds of million tons of ammonia fertilizer are produced annually from H_2 and N_2 by the Haber process which supports much of the world's population. The H_2 molecule is held together by a very strong two-electron H−H bond but is only useful chemically when the two H's are split apart in controlled fashion. To obtain proper perspective, one needs to be aware of how activation (the bond cleavage process) of H_2 occurs on metal complexes (e.g., industrial catalysts) and on enzymes in nature such as hydrogenases, which is one of the main focal points of this article. Remarkably, the detailed mechanism at the molecular level by which the H−H union splits to form for example a metal dihydride complex was not clearly established until only relatively recently in the history of H_2 activation. One of

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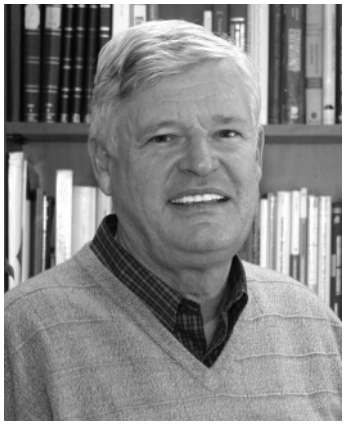
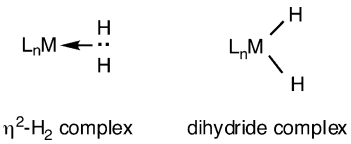


Gregory Kubas received his B.S. from Case Institute of Technology in 1966 and his Ph.D. from Northwestern University with Duward Shriver in 1970. He performed postdoctoral studies at Princeton with Tom Spiro and moved on to Los Alamos initially as a postdoc and then as a staff member. He became a Laboratory Fellow in 1987 and more recently a Fellow of the American Association for the Advancement of Science. His discovery of metal complexes that bind dihydrogen molecules led to the 1993 American Chemical Society Award in Inorganic Chemistry and the 1994 E. O. Lawrence Award in Chemistry from the Department of Energy. His research on dihydrogen complexes led to new views of chemical bonding and hydrogen activation and opened new fields of chemical research on metal σ-bond complexes. Greg is author of the 2001 book considered to be the bible of this field, *Metal–Dihydrogen and σ-Bond Complexes*.

the reasons is that H_2 contains only a strongly bonded electron pair that was always assumed to be inert to further chemical interaction, except perhaps in a weak sense, e.g., physisorption. Thus, H_2 had never been caught in the act of chemically binding to a metal center or main group atom, usually the first step in breaking up a strong bond. The discovery by Kubas and co-workers in 1984 of coordination of a nearly intact H_2 molecule to a metal complex (L_nM; L = ligand) caught this in close detail and led to a new paradigm in chemistry.[1−7]



η^2-H_2 complex dihydride complex

The H_2 binds side-on to the metal center primarily via donation of its two σ electrons to a vacant d orbital and forms a *stable* dihydrogen complex. It is remarkable that these already strongly bonded electrons can donate to a metal center (empty d orbital) to form a nonclassical 2-electron, 3-center bond, as in other "electron-deficient" molecules such as diborane (B_2H_6) as well as the bonding in hydride-bridged[8] M−H−M topologies. Such a complex can encompass interaction of any σ bond (C−H, Si−H, etc.) with a metal center and was termed a "σ complex" by Crabtree.[9]

Our discovery of metal−H_2 complexes was totally unexpected. Metal dihydrides formed by oxidative addition of the H−H bond to a metal center had early on been known to be a part of well-established catalytic cycles,[10] and a retrospective account of homogeneous hydrogenation was published in 1980 by a pioneer in the field, Jack Halpern.[11] Although some type of metal−H_2 interaction was assumed to be an intermediate in dihydride formation, it was not thought to be observable and certainly not isolable under ambient conditions. We were not seeking a dihydrogen

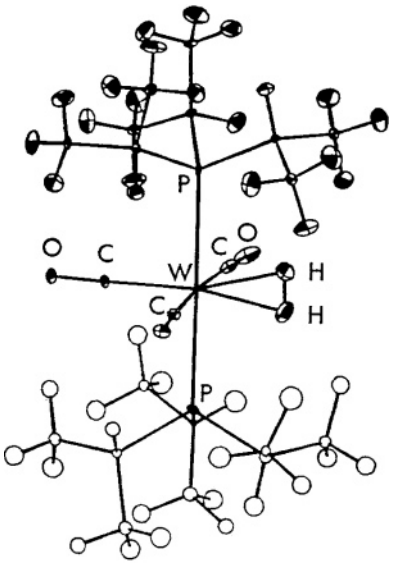
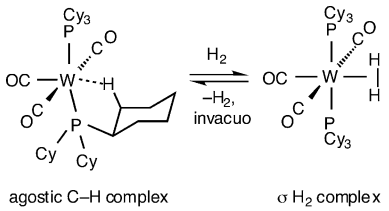


Figure 1. ORTEP drawing of the neutron structure of $W(CO)_3(P^iPr_3)_2(H_2)$ at 30 K, showing the intact H−H bond elongated to 0.82(1) Å. The lower phosphine is disordered.

complex, and the first such complex, $W(CO)_3(PR_3)_2(H_2)$ (Figure 1), was found serendipitously, an edifying saga detailed by this author.[3,6] This stable crystalline complex was also notable in that it represented the first chemical compound isolable under ambient conditions containing a nearly intact H_2 molecule other than elemental hydrogen itself. The H−H bond length in $W(CO)_3(P^iPr_3)_2(H_2)$ (0.89 Å) is stretched about 20% over that in free H_2 (0.74 Å), showing that the H_2 is not physisorbed but rather chemisorbed, where the bond is "activated" toward breaking. This initially enigmatic interaction lies at the heart of all interactions of σ bonds X−Y with metals.[5,6,9]

The serendipitous synthesis of an "unsaturated" 16-electron precursor, $M(CO)_3(PCy_3)_2$ (M = Mo, W; Cy = cyclohexyl), in 1979 led to the discovery of the H_2 complex.[12] This deep purple complex was a "5-coordinate" zerovalent group 6 complex, the first of its type. Importantly, the color changed instantly and reversibly to yellow on exposure to N_2 and H_2 both in solution and in the solid state, signifying adduct formation with the small molecules (eq 1). It was not until



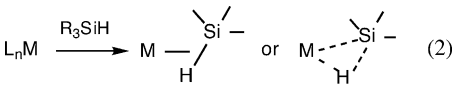
agostic C–H complex σ H_2 complex (1)

much later (1986) that a crystal structure of a tungsten analogue revealed a phosphine C−H bond weakly occupying the sixth binding site.[13] This type of intramolecular interaction of a C−H bond had been known and has been popularly termed "agostic".[14] As here, it often serves to relieve electronic unsaturation in coordinatively unsaturated complexes that otherwise might not be stable and is entropically stabilized, i.e., a type of "chelate effect". Importantly, H_2 was found to displace this C−H interaction in $M(CO)_3(PCy_3)_2$ and could then be removed *reversibly* many times simply by exposure to vacuum or inert gas at ambient temperature to re-form the agostic complex. This property

was novel and is relevant to new materials for hydrogen *storage*, another subject of this article that will be discussed after the main subject, which is the relevance of H_2 complexes to hydrogen production and the function of hydrogenases.

Part of the reason that H_2 complexes were so well hidden was the stubborn notion that such complexes could not be stable versus classical dihydrides. At about the time of our finding, evidence for *unstable* $M-H_2$ interactions had been obtained spectroscopically by Turner, Sweany, and others via photolysis of $Cr(CO)_6$ in the presence of H_2 at low temperatures.[17−20] $Cr(CO)_5(H_2)$ was postulated based on IR CO stretching frequencies, but its molecular structure could not be determined and only recently has its proton NMR spectrum been observed, again at low temperature.[21,22] Remarkably, even the theoretical basis for interaction of H_2 and σ bonds with a metal was still in its infancy this late in the history of inorganic chemistry. Theoretical analysis of the bonding of H_2 and CH_4 to metal fragments such as $Cr(CO)_5$ was published by Saillard and Hoffmann[23] in 1984, shortly after our publication of the $W-H_2$ complex, without mutual knowledge of our work. The interplay between theory and experiment has continued hand-in-hand to this day as one of the most valuable synergistic relations in all of chemistry.[24,25] The apparent simplicity of H_2 was attractive, but the structure, bonding, and dynamics of complexes containing H_2 ligands proved to be unimaginably complex, resulting in abundant opportunities for study (>300 purely computational publications and dozens of others combining experiment with theory).

Initially, H_2 binding seemed unique to our $M(CO)_3(PR_3)_2(H_2)$ complexes because the bulky phosphines (R = cyclohexyl or isopropyl) seemed to sterically inhibit formation of a classical 7-coordinate dihydride via oxidative addition. Kaesz viewed this as "arrested oxidative addition", a term he used to describe the bonding in a silane complex, $CpMn(CO)_2(\eta^2\text{-}HSiPh_3)$.[26] Silane complexes[27−29] were some of the first examples of σ-bond complexes but were initially unrecognized as such because the asymmetrically bound silane ligand lacked the superb clarity of the H_2 ligand, which has electrons only in the H−H bond. The hundreds of H_2



(2)

complexes that would be synthesized after our discovery were unimaginable to us, and it was difficult to even know where to search for new examples. It would take over a year before they were found by other researchers, most notably Morris, Crabtree, Chaudret, and Heinekey. This quartet has since performed elegant NMR and reactivity studies on H_2 and silane complexes[9,30−35] and was later joined by well over a hundred other investigators worldwide. Remarkably, several complexes initially thought to be classical hydrides were revealed to be H_2 complexes by Crabtree beginning in 1989,[9,36] using as criteria his finding that the H_2 ligand has very short proton NMR relaxation times (T_1 < 100 ms). The most interesting was $RuH_2(H_2)(PPh_3)_3$, originally reported in 1968 by Knoth,[37] which possessed unusual properties that elicited comments by Singleton in 1976 about the "dihydrogen-like nature" of the binding.[38] Ironically, attempts to obtain definitive proof for H_2 binding in this complex were difficult, even long after H_2 binding was established.[39]

The variety and abundance of H_2 complexes is remarkable: about 500 H_2 complexes are known (most are stable) for nearly every transition metal and type of coligand. They are the focus of nearly 1500 publications, dozens of reviews, and three monographs.[3,6,9,24,25,30−35,40−55] It is now clear that $M-H_2$ serves as the prototype for other metal σ-bond complexes[6,9] that can be important in catalytic systems and perhaps other applied research as well. Two of the most frequently asked questions after the discovery of H_2 complexes were (1) are they relevant in catalysis, i.e., direct transfer of hydrogen from an H_2 ligand to a substrate, and (2) can methane bind to metal complexes? The answer to both is yes, although, so far, a *stable* methane complex has yet to be isolated (complexes containing higher alkanes have been reported). As will be shown, for all their apparent simplicity, $M-H_2$ (and other σ-bond interactions with metal centers) are arguably the most dynamic, complex, and enigmatic chemical topologies known from a structure/bonding/dynamics viewpoint. Only recently has the viewpoint on dihydrogen complexes shifted from its significance in basic science toward more practical aspects, most importantly hydrogen production and storage and the presumed intermediacy of metal−H_2 binding in biological systems such as hydrogenases. These will be the primary focal points of this article.

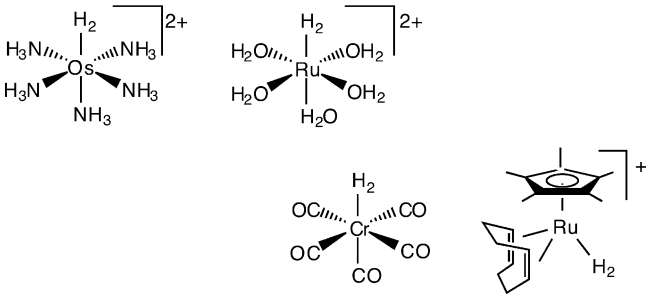
2. Types and Synthesis of H_2 Complexes

2.1. Stable H_2 Complexes

Hundreds of stable H_2 complexes have now been synthesized and characterized spectroscopically or structurally, and many others either are thermally unstable, are transient species, or are proposed to contain H_2 ligands. Almost every transition metal from V to Pt is represented (V, Ni, and Pd form only low-temperature stable species), and one lanthanide complex[56] is known. Only the very early transition metals and actinides have thus far not been observed to form stable H_2 complexes. As will be detailed below, the coupling constant J_{HD} in isotopomeric HD complexes is the best diagnostic for molecular hydrogen binding, i.e., the presence of a stretched H−H bond, and can be as high as 35 Hz versus <2 Hz for classical hydride complexes. The great majority of complexes contain octahedrally coordinated d^6 metals that are relatively low-valent (divalent or lower), primarily because of the favorable electronic situation for side-on coordination of σ bonds to such metal centers. Virtually all H_2 complexes are coordinatively saturated, and the few that are not normally contain π-donating halide or pseodohalide ligands, e.g., $RuHX(H_2)(PR_3)_2$ (X = Cl, I, SR).[57,58] Paramagnetic σ complexes are extremely rare, but apparent high-spin Fe and Mo H_2 complexes have recently been reported.[59]

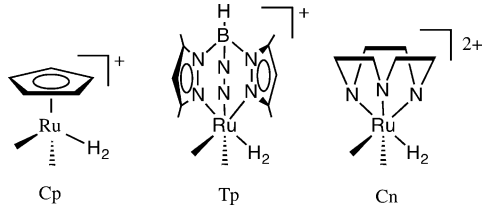
Most H_2 complexes are cationic because the increased electrophilicity of the metal reduces $M \rightarrow H_2$ backdonation (BD) that leads to oxidative addition (OA) of H_2. Neutral complexes normally contain a mixture of donor ligands, usually phosphines, with at least one π-acceptor ligand such as CO or strong trans-effect ligands such as hydride to moderate BD, as will be discussed further below. H_2 complexes can be stabilized by classical nitrogen-donor ancillary ligands such as ammine, e.g., $[Os(NH_3)_5(H_2)]^{2+}$, and its ethylenediamine analogues, which have very long H−H distances (d_{HH} = 1.34 Å) more characteristic of dihydrides.[60] These complexes indeed were initially believed to be dihydrides. As shown below, complexes containing

only aqua,[61] CO,[21,22] or carbon[62] coligands are known but in some cases are only marginally stable. The highly acidic



pentacarbonyl Cr−H_2 complexes (and monophosphine and W derivatives) were recently observed by low-temperature NMR.[21,22] The first example of an H_2 complex with carbene coligands, $[Cp^*Ir(bis\text{-}carbene)(H_2)]^{2+}$, exhibits a much shorter H−H distance (1.04 Å) than its bis-phosphine analogues that contain highly elongated H_2 (1.45 Å).[63]

The group 8 triad contains the overwhelming majority of dihydrogen complexes, with Ru and Os displaying the greatest variety of fragment types, especially "half-sandwich" complexes with cyclopentadienyl-type ligands (Cp, Tp, and Cn).[42] As will be discussed in section 8.2.3, the H_2 ligands



in these and related cationic complexes can be quite acidic, especially in highly electrophilic *di*cationic species. The most common fragment in the group 8 triad is $[MH(H_2)P_4]^+$, where there are >45 different variants, almost half of which are for Ru (P = phosphorus donor, primarily in a planar array). Such series are ideal for correlating structural, electronic, and physical properties, e.g., H−H distance with J_{HD}, as will be discussed below.[64] This is particularly the case for the series $[Os(H_2)(L)N_4]^{+/2+}$ ($N_4 = 4NH_3$ or 2 ethylenediamine), which contains over two dozen members.[60,64a,b]

Several isoelectronic series exist across the periodic table, e.g., $Mo(CO)(H_2)(PP)$, $[Mn(CO)(H_2)(PP)]^+$, and $[Fe(CO)(H_2)(PP)]^{+2}$ (PP = diphosphine) and $W(H_2)(CO)_3(PR_3)_2$, $[Re(H_2)(CO)_3(PR_3)_2]^+$, and $[Os(H_2)(MeCN)_3(PR_3)_2]^{+2}$.[5,6] The dicationic complexes of iron, the metal most relevant to biological enzymes such as hydrogenases, often can bind H_2 more tightly than the cationic or neutral analogues because increased electron donation from H_2 offsets decreased backdonation (BD) from the metal. Note that the Os complex does not contain π-acceptor CO ligands that generally stabilize H_2 coordination against oxidative addition to hydride ligands. Instead, the dipositive charge on the metal reduces backdonation that otherwise might promote oxidative addition. Highly electrophilic cationic metals are thus excellent targets for design of σ complexes because increased σ donation to M stabilizes the interaction but can never cause the σ bond to rupture.

Isolable *bis*-H_2 complexes are rare, e.g., $RuH_2(H_2)_2(PR_3)_2$ (R = cyclohexyl (Cy) and cyclopentyl (Cyp)),[35,65] $[RhH_2(H_2)_2(PCy_3)_2]^+$,[66] and $Tp^*RuH(H_2)_2$.[67] The first neutron diffraction structure of a bis-H_2 complex was determined on

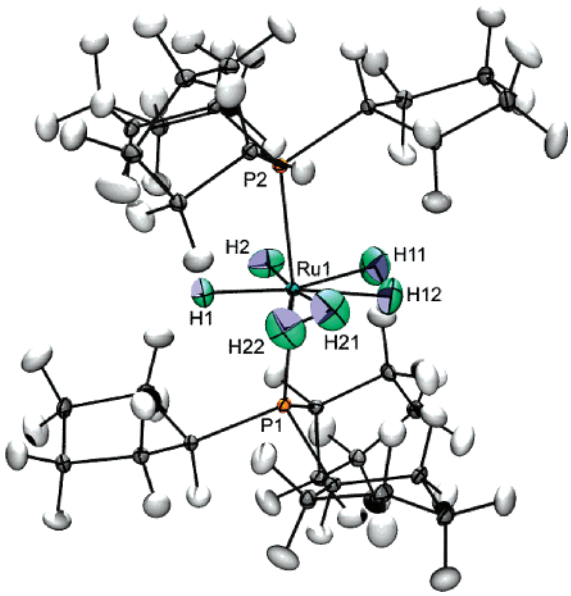
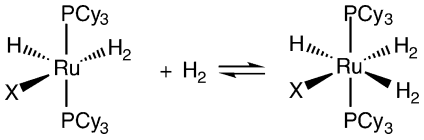


Figure 2. Structure of $RuH_2(H_2)_2(PCyp_3)_2$ from a neutron diffraction study.

$RuH_2(H_2)_2(PCyp_3)_2$ and showed cis-H_2 ligands with very short d_{HH} = 0.825(8) Å (Figure 2).[65] The novel, X-ray characterized 16e species $RuHX(H_2)(PCy_3)_2$ (X = Cl, I) add a second H_2 ligand in equilibrium fashion (eq 3, observable only in solution).[57,58]



(3)

Only about a dozen polynuclear dihydrogen complexes are known, and these are primarily dinuclear hydride- and/or halide-bridged Ru, Os, and Ir complexes containing H_2 bound to only one of the metals.[6] Bridging H_2 ligands have not been definitively proven by diffraction methods, and indeed, it can be extremely difficult to determine conclusively whether or not even mononuclear complexes contain classical hydride ligands versus a nonclassical H_2 ligand (or how many of each). This is especially a problem in polyhydride complexes that contain both classical hydrides and η^2-H_2 that undergo dynamic exchange even at the lowest temperature accessible by solution NMR. The classic example is $RuH_2(H_2)(PPh_3)_3$, which, as mentioned above, had long been speculated to contain molecular H_2 binding but had defied attempts to definitively prove it by diffraction methods.[39] Not surprisingly, as shown by Heinekey,[68] there have been cases where misassignments have been made, even for complexes containing only two hydrogens on a metal. About a dozen complexes exist that possibly may contain coordinated H_2 and/or have d_{HH} in the "gray zone" (1.4−1.6 Å) between formulation as H_2 or dihydride complexes. Such complexes have been referred to as "compressed hydrides" with NMR features differing from elongated H_2 complexes; for example, J_{HD} increases with temperature for the former and decreases for the latter.[34,69] These are relative terms, since the H−H bond is always stretched on binding, and indeed, as will be shown below, a near *continuum* of d_{HH} exists.[6,35,69,70]

Dihydrogen complexes may also exist in solutions of organometallic complexes as equilibrium or transient species

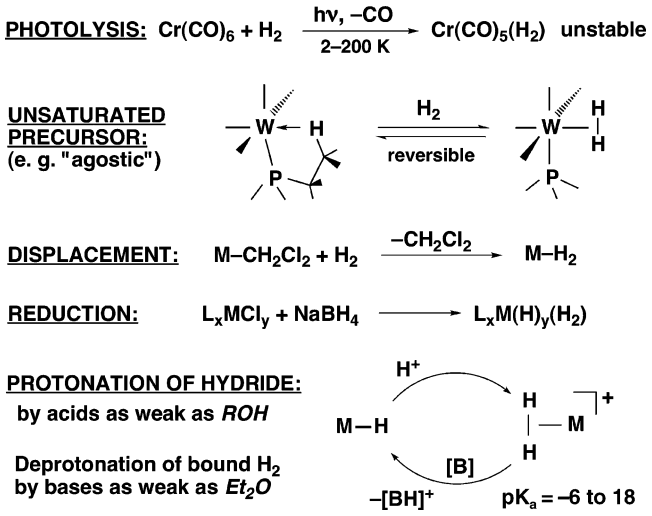
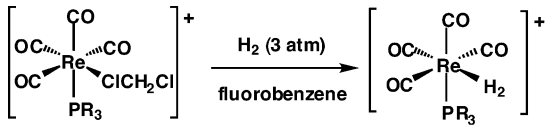


Figure 3. Synthetic methods for H_2 complexes.

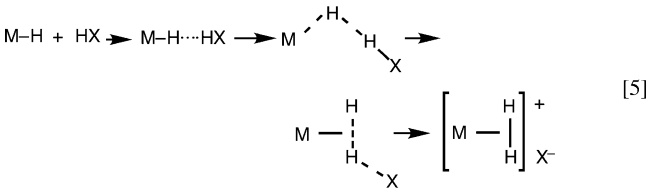
that cannot be observed spectroscopically. Weak interactions of H_2 with surface species, bare metal ions, and main group Lewis acids/bases are known and will be discussed in sections 2.2.2 and 11.3. Short d_{HH} as low as 1.5 Å ("hydrogen pairing") are proposed to be present in certain intermetallic rare-earth hydrides, as evidenced by solid state ^{1}H NMR[71,72] and theoretical calculations.[73] The observation, for example, of a characteristic splitting pattern (Pake doublet) at 140 K gives a d_{HH} of 1.48 ± 0.02 Å in $CeNiInH_{1.0}$, suggesting that the hydrogens may occupy nearest-neighbor tetrahedral sites separated by about 1.5 Å (2.1 Å had generally been believed to be the closest possible spacing in metal hydrides).[71]

Several synthetic routes to H_2 complexes are available (Figure 3) and will be discussed in detail below. The simplest method is reaction of H_2 gas with a coordinatively unsaturated complex or one that is effectively unsaturated, such as $W(CO)_3(PR_3)_2$, which contains an agostic interaction of a C−H bond weakly occupying the sixth site (eq 1). Displacement of a weakly bound "solvento" ligand such as dichloromethane or a coordinated anion can be utilized, although a less coordinating solvent such as fluorobenzene may need to be employed.[74] By far the most common method of



[4]

preparation is protonation of metal hydride complexes (eq 5).[33,44,55,75] Reaction proceeds via observable hydrogen bond-



[5]

ing of the acid (which can be as weak as alcohols) to the basic hydride.[55,75] This method has been widely applicable because it does not require an unsaturated precursor that often either does not exist or is difficult to synthesize. Neutral polyhydride complexes L_nMH_x are often easy targets for protonation to cationic hydrido-H_2 complexes, $[L_nM(H_2)H_{x-1}]^+$, which frequently are more robust than complexes prepared from H_2 gas.

2.1.1. Complexes Synthesized by Addition of H_2 Gas to an Unsaturated Precursor

A common method of preparation is the reaction of H_2 gas at about 1 atm pressure with a coordinatively unsaturated precursor complex, ML_n **(**eq 6**)**:

$$L_nM + H_2 \rightleftarrows L_nM(H_2) \qquad (6)$$

The precursor complex can be a formally 16e species possessing an agostic C−H interaction that is in effect displaced by the incoming H_2 ligand, as was shown above in eq 1. The agostic interaction can readily displace the η^2-H_2 if excess H_2 is not present, facilitating the reversibility of the binding. This is the case for the original series of H_2 complexes, $M(H_2)(CO)_3(PR_3)_2$ (M = Cr, Mo, W; R = Cy, *i*-Pr) and certain others formed directly by *reversible* addition of H_2 gas to an isolated, formally unsaturated, precursor complex (Table 1). Virtually all of the precursors are "operationally unsaturated", i.e. formally 16e species stabilized by agostic interactions, π-donation from halide ligands, or hydride ligands. In a few cases, the precursor has an anion such as triflate or solvent (e.g. CH_2Cl_2) occupying the coordination site that can reversibly be displaced by H_2, as in eq 4 above and further discussed below. The percentage of H_2 complexes synthesized by H_2 addition to precursors is actually surprisingly small (∼10−15%). The reactions are generally carried out in noncoordinating or weakly coordinating organic solvents such as toluene or CH_2Cl_2, although solid−gas reactions can also be used.[76−79] Low-coordinating anions such as $B[3,5\text{-}C_6H_3(CF_3)_2]_4^-$, abbreviated as BAr_f, are often needed to stabilize cationic M and prevent anion binding to M, especially for M = Mn, Re in Table 1. For example, the complex $[Re(H_2)(CO)_3(PCy_3)_2]^+$ with BF_4 anion loses H_2 at low temperature, but the complex with less coordinating BAr_f can be isolated as a solid at room temperature.[80]

2.1.2. Complexes with the Most Weak, Reversible H_2 Binding and the Shortest H–H Distances

The $Cr(H_2)(CO)_3(PR_3)_2$ complexes are among the most unstable H_2 complexes isolable as solids at 25 °C.[82] The deep-blue precursor, $Cr(CO)_3(PCy_3)_2$, was prepared initially by Hoff.[83] In solution, the latter binds H_2 (or N_2) only at high pressures (>10 atm). The H_2 complex is stable under H_2 but, immediately on dissolving in toluene, loses all bound H_2 as H_2 gas, which vigorously effervesces from solution to give a deep-blue solution of $Cr(CO)_3(PCy_3)_2$. Such a large difference in stability between solution and solid states is rare in chemistry. It appears that coordinated H_2 can effectively be "trapped" in the less flexible solid state, possibly as a result of product solubility differences. This is reasonable in that the H_2 is not merely leaving the coordination site in these complexes; the whole molecule must rearrange to give back the agostic interaction with more acute P−Cr−P, Cr−P−C, and P−C−C bond angles. Also, in toluene, transient solvent binding might induce rapid H_2 loss kinetically by mass action effects, although hydrocarbon binding could never actually be observed by NMR for any of these group 6 systems, even at low temperature. Evidence for H_2 substitution by hydrocarbon solvents (toluene or even hexane) is seen for the series of iridium(III) complexes,

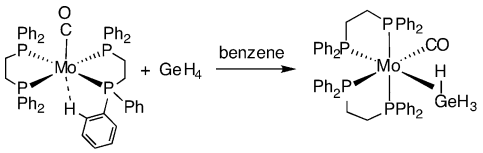
Table 1. Complexes Prepared by Reversible Addition of H_2 to a Known Precursor Complex

complex[a]	precursor structure	H_2 lability	ref
$M(H_2)(CO)_3(PR_3)_2$ (M = Cr, Mo, W)	agostic	v high to med	2, 82[b]
trans-$Mo(H_2)(CO)(PP)_2$	agostic	med	88c, 89
$[Mn(H_2)(CO)_3(P)_2]^+$	agostic,[c] solvento[d]	high	99
trans-$[Mn(H_2)(CO)(PP)_2]^+$	agostic	high	97, 98, 100
trans-$[Mn(H_2)(CO)\{P(OR)_3\}_4]^+$	agostic?	high	*e*
$Tc(H_2)Cl(dppe)_2$	trig bipy	med	*f*
$[Re(H_2)(CO)_3(PR_3)_2]^+$	agostic	med	80, 204c, 360[g]
$[Re(H_2)(CO)_4(PR_3)]^+$	solvento	high	74, 277
$[Re(H_2)(CO)_2(triphos)_2]^+$	agostic	med	*h*
$[CpRu(tmeda)(H_2)]^+$	2-leg piano stool	low	76, 77
$[Ru(H_2)H(PP)_2]^+$		med to high	202[i–k]
$[M(H_2)(CN)(PP)_2]^+$ (M = Fe, Ru)	anion-coord	med	274, 275
$[M(H_2)(L)(PP)_2]^{2+}$ (M = group 8; L = CO, CNH)	anion-coord	med	266, 274, 275[l]
$Ru(H_2)H_2(CO)(P^tBu_2Me)_2$	sq pyr	high	*m, n*
$[Ru(H_2)Cl(PP)_2]^+$	trig bipy	v high to med	105–109[l]
$Ru(H_2)Cl_2(P\text{-}N)(PR_3)$	sq pyr	high	*o*
$M(H_2)Cl(H)(CO)(PPr_3)_2$ (M = Ru, Os)		med	*p, q*
$(H_2)(dppb)Ru(m\text{-}Cl)_3\text{-}RuCl(dppb)$	dimer	high	*r, s*
$[Os(H_2)Cl(PP)_2]^+$	trig bipy	low	225[c,l]
$OsH_3Cl(H_2)(P^iPr_3)_2$	distorted oct	low	*t, u*
$OsH_2(X)(Y)(H_2)(P^iPr_3)_2$ (X, Y = Cl, Br, I)	distorted oct	med	*t, u*
$Ir(H_2)H_2Cl(PR_3)_2$	trig bipy	v high	78, 79
trans-$Ir(H_2)HX_2(PR_3)_2$ (X = Cl, Br)	sq pyr?	v high	166[v,w]
$Ir(H_2)(H)(diphpyH)(PR_3)_2$	agostic	med	*x*
$[PtH(H_2)(PR_3)_2]^+$	anion/ solvento	v high	101[y,z]

[a] Abbreviations: P-N = *o*-diphenylphosphino-*N,N*-dimethylaniline; diphpyH = 2,6-diarylpyridine. [b] Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855. [c] P = PCy_3. [d] P = $P\{(OCH_2)_3CMe\}_2$. [e] Albertin, G.; Antoniutti, S.; Bettiol, M.; Bordignon, E.; Busatto, F. *Organometallics* **1997**, *16*, 4959. [f] Burrell, A. K.; Bryan, J. C.; Kubas, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 1575. [g] Albertin, G.; Antoniutti, S.; Garcia-Fontan, S.; Carballo, R.; Padoan, F. *J. Chem. Soc., Dalton Trans.* **1998**, 2071. [h] Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203. [i] Saburi, M.; Aoyagi, K.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1990**, 601. [j] Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1993**, *115*, 9794. [k] Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1997**, *16*, 1253. [l] Rocchini, E.; Mezzetti, A.; Ruegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711. [m] Poulton, J. T.; Sigala, M. P.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 5490. [n] Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Esenstein, O.; Caulton, K. G. *Inorg. Chim. Acta* **1997**, *259*, 5. [o] Mudalige, D. C.; Rettig, S. J.; James, B. R.; Cullen, W. R. *J. Chem. Soc., Chem. Commun.* **1993**, 830. [p] Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1. [q] Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563. [r] Joshi, A. M.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1785. [s] Chau, D. E. K.-Y.; James, B. R. *Inorg. Chim. Acta* **1995**, *240*, 419. [t] Gusev, D. G.; Kuznetsov, V. F.; Eremenko, I. L.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 5831. [u] Kuhlman, R. L.; Gusev, D. G.; Eremenko, I. L.; Berke, H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1997**, *536–537*, 139. [v] Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Volpin, M. E. *Inorg. Chim. Acta* **1990**, *177*, 115. [w] Bakhmutov, V. I.; Vymenits, A. B.; Grushin, V. V. *Inorg. Chem.* **1994**, *33*, 4413. [x] Albeniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 242. [y] Gusev, D. G.; Notheis, J. U.; Rambo, J. R.; Hauger, B. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 7409. [z] Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1998**, *37*, 2422.

$IrXH_2(H_2)(P^iPr_3)_2$ (X = Cl, Br, I), which, like the Cr(0) complex, readily liberates H_2 on dissolution in hydrocarbons.[84] The Cr and Ir complexes contain the most weakly, reversibly bound H_2 ligands in an isolable species. They have very short d_{HH} (0.85 Å, solid-state NMR for Cr[82] and neutron diffraction for Ir[85]), and the Cr complex has one of the highest J_{HD} measured, 35 Hz, for all H_2 complexes. $Cr(CO)_5(H_2)$, which is stable only at low temperature, has J_{HD} = 35.8 Hz, which would correspond to d_{HH} = 0.84 Å from a known correlation (eqs 18 and 19 below).[21,22] The highest value for an isolated complex, 37 Hz, has been reported for $[RuH(H_2)(BINAP)(dpen)]^+$, although no structural details are available.[86]

In addition to mass action effects, *entropy* effects are also often critical in determining the relative stabilities of these weak complexes because enthalpies of ligand binding can be as low as 15 kcal/mol for M–H_2 or even lower for alkane complexes. This is particularly true when σ ligands are competing for binding sites against external ligands such as H_2O and N_2 and at the same time against intramolecular agostic interactions. The latter are favored because addition of an external ligand ("two particles to form one") has an *entropic* cost, $T\Delta S$, of ≈10 kcal/mol at room temperature.[87] Other complexes prepared according to eq 6 are listed in Table 1 along with the structure of the precursor complex if known. Several 16e precursors have true 5-coordinate geometries without agostic interactions, and H_2 binds highly reversibly to them. The 16e complex, $Mo(CO)(Ph_2PC_2H_4\text{-}PPh_2)_2$, was the first to show coordination of H–H, Si–H (silane coordination), and agostic C–H bonds to the same metal fragment and also coordinates germanes, $HGeR_3$, via Mo(η^2-Ge–H) bonding, including GeH_4.[88–91]



(7)

2.1.3. Complexes Prepared from H_2 Gas by Ligand Displacement or Reduction

A related method of synthesis from H_2 gas involves displacement of a labile ligand (eq 8)

$$L_nML' + H_2 \rightleftarrows L_nM(H_2) + L' \qquad (8)$$

Neutral ligands L′ which have been displaced include H_2O,[61,92,93] N_2,[94,95] NH_3,[96] CH_2Cl_2,[74,97–101] and PMe_2Ph.[102] One of the simplest conceivable H_2 complexes, $[Ru(H_2O)_5(H_2)]^{2+}$, is formed by displacement of an aqua ligand from the hexaqua complex by pressurized H_2 in aqueous solution.[61] Although it cannot be isolated, NMR indicates it has d_{HH} of 0.90 Å on the basis of the observed J_{HD} of 31.2 Hz. Displacement of a charged ligand, X^-, by H_2 has occasionally been employed for synthesis (eq 9).

$$L_nMX + H_2 \rightleftarrows [L_nM(H_2)]^+ + X^- \qquad (9)$$

Complexes prepared as in eq 9 are $[M(H_2)H(depe)_2]^+$, M = Fe, Ru, Os,[104] $[M(H_2)Cl(depe)_2]^+$, M = Ru, Os,[105–108] $[Ru(H_2)H(dcype)_2]^+$,[109] and $[Os(H_2)H(CO)(P\text{-}i\text{-}Pr_3)_2]^+$, where X = BH_4^-.[110] Often, a group 1 metal cation such as Na^+ or alternatively Tl^+ is present to precipitate with the anion. Remarkably, H_2 directly displaces a normally strongly bound chloride ligand in $Re(CN\text{-}t\text{-}Bu)_3(PCy_3)_2Cl$ in CH_2Cl_2, without such help to give $[Re(CN\text{-}t\text{-}Bu)_3(PCy_3)_2(H_2)]Cl$ where the Cl becomes the counteranion.[111]

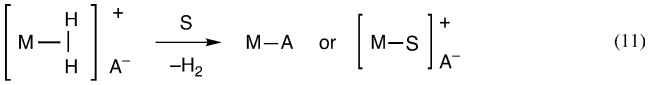
The syntheses of polyhydride complexes containing η^2-H_2, such as $RuH_2(H_2)(PPh_3)_3$, can be accomplished by hydride reduction according to eq 10.[112]

$$L_nMX_m + mH^- + H_2 \rightarrow L_nM(H_2)H_m + mX^- \quad (10)$$

Common sources of hydride in eq 10 are NaH, $NaBH_4$, and $LiAlH_4$, and the anion, X^-, is usually chloride or bromide. Complexes include $ReH_7(PR_3)_2$,[113] $[FeH(H_2)(pp_3)]^+$,[114] $M(H_2)H_2(PR_3)_3$ (M = Fe, Ru),[36,38,115] $Ru(H_2)H_2(cyttp)$,[116,117] and $Rh(H_2)H_2(HB(3,5\text{-}Me_2pz)_3)$.[118]

2.1.4. Protonation of a Hydride Complex

A very common and convenient method of preparation of H_2 complexes is the addition of H^+ to a hydride or polyhydride complex, as shown in eq 5 above. In most cases, the resulting complex is cationic, and the proton source can range from strong acids such as $HBF_4 \cdot Et_2O$ or triflic acid to very weak acids, even alcohols. The reactions are usually carried out below room temperature (ca. −60 °C), especially with strong acids, which often need to have low-interacting anions such as BF_4 or BAr_f. This method was first employed by Crabtree in 1985 by reaction of $IrH_2(PPh_3)_2(bq)$ (bq = benzoquinolinate) with $PhCH(SO_2CF_3)_2$,[92,93] and a variety of H_2 complexes too numerous to list in detail have been prepared by protonation. The large class of half-sandwich complexes, $[Cp'M(H_2)(L)(L')]^+$ (M = Fe, Ru, Os; Cp′ = cyclopentadienyl derivative), have all been prepared by protonation, for example. Normally, the low-temperature protonation initially gives a $[M-H_2]^+$ complex, but on warming, rearrangement to a dihydride or equilibrium mixture sometimes results. Occasionally the product is unstable toward loss of H_2 and coordination of anion or solvent (S) if the electronics and thermodynamics of the system do not favor H_2 binding. The stability of H_2

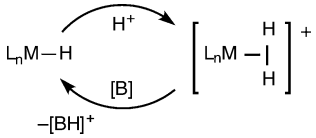


(11)

complexes prepared by protonation thus varies greatly: some are stable only below room temperature and cannot be isolated as solids, and others are among the most robust H_2 complexes known. Generally, the lability of an H_2/hydride system increases upon protonation or multiple protonation. Thus, $M(dppe)_2$ (M = Ni, Pd, Pt) had been reported in 1966 to give a dicationic complex on double protonation (eq 12), which in light of current knowledge can be speculated to occur via a monohydride and an unstable H_2 complex, which readily loses H_2:[119]

$$M(dppe)_2 \xrightarrow{HClO_4} [MH(dppe)_2][ClO_4] \xrightarrow{HClO_4}$$
$$[M(H_2)(dppe)_2][ClO_4]_2 \xrightarrow{-H_2} [M(dppe)_2][ClO_4] \quad (12)$$

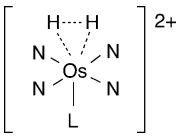
Needless to say, complexes formed by protonation, especially where HA is a strong acid, are readily *deprotonated*, even by bases [B] as weak as diethyl ether, and are highly sensitive to solvent media and trace water. Much of these properties



relate to the high acidity of certain H_2 complexes, which can have pK_a as low as −6, e.g., when generated from triflic acid, as will be discussed below in section 8.2.3.

2.1.5. Other Methods of Preparation

Some less common preparations have been reported. The reduction of complexes of Re^V or Os^{III} in the presence of a source of protons and electrons (H^+ and Mg or Na) gives the complexes $ReCl(H_2)(PMePh_2)_4$[120] and $[Os(H_2)(NH_3)_5]^{2+}$, respectively. The latter and its ethylenediamine (en) congeners are unique in containing pure σ-donor ligands, and a large series of such complexes have been prepared with a variety of ligands (L) trans to the H_2.[60,121−126] The dipositive



charge is rare among H_2 complexes and undoubtedly is responsible for arresting oxidative addition. However, the d_{HH} is very long, ca. 1.35 Å, in these species, indicating they are closer to being dihydrides. The reaction of Ru(cod)(cot) with PCy_3 and H_2 gives $RuH_2(H_2)_2(PCy_3)_2$,[35] and protonation[127] of $[RuH_5(P^iPr_3)_2]^-$ gives $RuH_2(H_2)_2(P^iPr_3)_2$. These are among only a handful of well-characterized complexes that contain more than one η^2-H_2 and have received extensive study by Chaudret and co-workers.[35]

Decomposition of $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ in alcohols produced $OsH_2(H_2)(CO)(P^iPr_3)_2$,[128] which, despite its facile loss of H_2 and wide use as a hydrogen transfer catalyst, was initially belived to be a tetrahydride and was not shown[129] to have an η^2-H_2 ligand until 10 years after its original synthesis. This is yet another dramatic example of how difficult it can be to prove the presence of H_2 ligands. Another unusual synthesis involves hydrogenation of an ethylene complex either in solution or even in the solid state at 60 °C (eq 13).[130,131]

$$[IrH_2(triphos)(C_2H_4)]^+ + 2H_2 \rightarrow$$
$$[IrH_2(triphos)(H_2)]^+ + C_2H_6 \quad (13)$$

2.2. H_2 Complexes Unstable at Room Temperature

Many H_2 complexes are unstable at room temperature, in some cases those formed by protonation (eq 5). However, they often can still be studied by low-temperature NMR methodologies and determined to have η^2-H_2 by measurement of J_{HD} and T_1. Virtually any metal system that eliminates H_2 gas via any route (protonation, photolysis, heating, etc.) must do so by a transient H_2 complex as demanded by the principle of microscopic reversibility. Obviously, the transient will have widely varying degrees of stability, roughly corresponding to the various points along the reaction coordinate toward OA along which H_2 complexes can be arrested. The sections below describe identification of H_2 complexes by non-NMR methods.

2.2.1. Organometallic Complexes Observed at Low Temperature in Rare Gas or Other Media

The first spectroscopic evidence for H_2 coordination was obtained in matrix-isolated $Cr(CO)_5(H_2)$ by Sweany virtually at the same time as that for $W(CO)_3(PR_3)_2(H_2)$. The investigations of low-T stable H_2 complexes (Table 2) in solid

Table 2. Low-Temperature-Stable H_2 Complexes and Surface-Bound H_2

complex	conditions	ν(H−H), cm^{-1}	ref
$ScH_x(H_2)_n$ ($x = 2, 3$)	Ar matrix		*a*
$YH_2(H_2)_n$	Ar matrix		*a*
$V(CO)_5(H_2)$	heptane, Xe soln		*b*
$CpV(CO)_3(H_2)$	heptane, Xe soln	2642	*c*−*e*
$CpNb(CO)_3(H_2)$	heptane, Xe soln	2600 (equil)	*c*−*f*
(indenyl)$Nb(CO)_3(H_2)$	heptane, Xe soln, PE		*e*, *f*
$CrH(H_2)_2$ (X = 1, 2; $n = 1, 2$)	Ar, Ne matrix		*g*, *h*
$CrO_2(H_2)$	laser ablation, IR, theory	$[3950]_{calc}$	*i*
$CrO_2(H_2)_2$	laser ablation, IR, theory	2728, 2640	*i*
$Cr(CO)_5(H_2)$	matrix, Xe soln, PE	3030	18−20, 22[j]
	heptane, photoacoustic		134[k]
$Cr(CO)_4(H_2)_2$	matrix, Xe soln		18, 19b
$Cr(CO)_n(L)(H_2)$ ($n = 3, 4$; L = olefin or diolefin)	Xe soln		*l*−*n*
(arene)$Cr(CO)_2(H_2)$	Xe soln		*o*
$Mo(CO)_5(H_2)$	Xe soln, PE	3080	19b, 134
	heptane, photoacoustic		*j*
$CpMoH(CO)_2(H_2)$	matrix		*p*, *q*
$Mo(CO)_n(L)(H_2)$ ($n = 3, 4$; L = olefin or diolefin)	Ar matrix, Xe soln, PE		*m*, *n*, *r*
(arene)$Mo(CO)_3(H_2)$	matrix	3200	*s*
$Mo(H_2)_n$ ($n = ?$)	Kr, Xe matrix, laser ablated		*t*
$W(CO)_5(H_2)$	matrix, soln, and gas phases, PE	2711	19b, 22,[o,u] 134
$W(CO)_n(L)(H_2)$ ($n = 3, 4$; L = olefin or diolefin)	Xe soln		*l*−*n*
$CpWH(CO)_2(H_2)$	matrix		*p*, *q*
$CpMn(CO)_x(H_2)$ ($x = 1, 2$)	gas phase, $scCO_2$		*x*
$Cp^*Mn(CO)_2(H_2)$	Xe soln		*o*
$(C_5Et_5)Mn(CO)_2(H_2)$	heptane		*y*
$MnX(CO)_4(H_2)$ (X = Cl, Br)	matrix		*z*
$Fe(CO)(NO)_2(H_2)$	Xe soln	2973	*aa*
$Fe(C_4H_4)(CO)_2(H_2)$	Xe soln		*o*
$Fe(CO)_3(H_2)(DF)$	PE		*r*
$Co(CO)_2(NO)(H_2)$	Xe soln	{2976, 3100}	*aa*
$CoH(H_2)(CO)_3$	matrix		*bb*
$Co(CH_3)(H_2)(CO)_3$	matrix		*bb*
$CpIr(CO)(H_2)$	matrix		*cc*
$Ru(H_2)_x(CO)_n$ ($x = 1, 2$; $n = 1, 2$)	Ar matrix, laser ablated		*dd*
$RuO_2(110)(H_2)$	surface, HREELS	2960	471, 472
$RhH_x(H_2)$ ($x = 0-3$)	Ar, Ne matrix, theory		*g*
$[RhH_2(H_2)]^-$	Ar, Ne matrix, theory		*g*
$Ni(CO)_3(H_2)$	Ar matrix		96
$NiCp_2'(H_2)$	matrix	3250	*s*
$Ni(510)(H_2)$	surface, EELS	3205	195
$Ni(111)(H_2)$	surface, HREELS		*ee*
$Pd(H_2)_x$ ($x = 1-3$)	Kr, Xe matrix, laser ablated	2971 ($x = 1$)	152
$Pd_2(H_2)$	laser ablated		152b
$Pd(210)(H_2)$	surface, HREELS		*ff*
$Cu_2H_2(H_2)_x$ ($x = 1, 2$)	Ar matrix		457
$Cu_3(H_2)$	Ar matrix		457
$CuCl(H_2)$	Ar matrix		*gg*
[Cu^+-zeolite-H_2]	theory, IR		*hh*
$[Cu_2\text{-}(H_2)_n]^+$	mass spec, surface ionization		*ii*
$CuH(H_2)$	theory, matrix		*jj*, *kk*
$AgH(H_2)$	theory, matrix		*jj*, *kk*
$AuH_x(H_2)$ ($x = 1, 3$)	Ar, Ne matrix, theory		*jj*−*oo*
$MH_2(H_2)$ (M = La, Ce, Pr)	Ar matrix, theory		*a*, *pp*

[a] Wang, X.; Chertihin, G. V.; Andrews, L. *J. Phys. Chem. A* **2002**, *106*, 9213. [b] George, M. W.; Haward, M. T.; Hamley, P. A.; Hughes, C.; Johnson, F. P. A.; Popov, V. K.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 2286. [c] Haward, M. T.; George, M. W.; Howdle, S. M.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1990**, 913. [d] Haward, M. T.; George, M. W.; Hamley, P.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1101. [e] Childs, G. I.; Gallagher, S.; Bitterwolf, T. E.; George, M. W. *J. Chem. Soc., Dalton Trans.* **2000**, 4534. [f] Childs, G. I.; Grills, D. C.; Gallagher, S.; Bitterwolf, T. E.; George, M. W. *J. Chem. Soc., Dalton Trans.* **2001**, 1711. [g] Wang, X.; Andrews, L. *J. Phys. Chem. A* **2002**, *106*, 3706. [h] Wang, X.; Andrews, L. *J. Phys. Chem. A* **2003**, *107*, 570. [i] Zhou, M.; Zhang, L.; Shao, L.; Wang, W.; Fan, K.; Qin, Q. *J. Phys. Chem. A* **2001**, *105*, 10747. [j] Walsh, E. F.; Popov, V. K.; George, M. W.; Poliakoff, M. *J. Phys. Chem.* **1995**, *99*, 12016. [k] Poliakoff, M.; Howdle, S. M.; George, M. W. *Process Technol. Proc.* **1996**, *12*, 67. [l] Jackson, S. A.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J.; Burdett, J. K.; Grevels, F.-W. *J. Chem. Soc., Chem. Commun.* **1987**, 678. [m] Jackson, S. A.; Hodges, P. M.; Poliakoff, M.; Turner, J. J.; Grevels, F.-W. *J. Am. Chem. Soc.* **1990**, *112*, 1221. [n] Jia, G.; Lin, Z.; Lau, C. P. *Eur. J. Inorg. Chem.* **2003**, 2551. [o] Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804. [p] Sweany, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 6986. [q] Sweany, R. L. *Organometallics* **1986**, *5*, 387. [r] Childs, G. I.; Cooper, A. I.; Nolan, T. F.; Carrott, M. J.; George, M. W.; Poliakoff, M. *J. Am. Chem. Soc.* **2001**, *123*, 6857. [s] Grinval'd, I. I.; Lokshin, B. V.; Rudnevskii, N. K.; Mar'in, V. P. *Dokl. Acad. Nauk SSSR* **1988**, *298*, 1142. [t] Wang, X.; Andrews, L. *J. Phys. Chem. A* **2005**, *109*, 9021. [u] Andrea, R. R.; Vuurman, M. A.; Stufkens, D. J.; Oskam, A. *Recl. Trav. Chim. Pays Bas* **1986**, *105*, 372. [v] Ishikawa, Y.; Weersink, R. A.; Hackett, P. A.; Rayner, D. M. *Chem. Phys. Lett.* **1987**, *142*, 271. [w] Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Phys. Chem.* **1989**, *93*, 652. [x] Zheng, Y.; Wang, W.; Lin, J.; She, Y.; Fu, K.-J. *J. Phys. Chem.* **1992**, *96*, 9821. [y] Johnson, F. P. A.; George, M. W.; Bagratashvili, V. N.; Vereshchagina, L. N.; Poliakoff, M. *Mendeleev Commun.* **1991**, 26. [z] Sweany, R. L.; Watzke, D. *Organometallics* **1997**, *16*, 1037. [aa] Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547. [bb] Sweany, R. L.; Russell, F. N. *Organometallics* **1988**, *7*, 719. [cc] Bloyce, P. E.; Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1988**, 846. [dd] Wang, X.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 9892. [ee] Kresse, G. *Phys. Rev. B* **2000**, *62*, 8295. [ff] Schmidt, P. K.; Christman, K.; Kresse, G.; Hafner, J.; Lischka, M.; Gross, A. *Phys. Rev. Lett.* **2001**, *87*, 096103. [gg] Plitt, H. S.; Bar, M. R.; Ahlrichs, R.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 832. [hh] Solans-Monfort, X.; Branchadell, V.; Sodupe, M.; Zicovich-Wilson, C. M.; Gribov, E.; Spoto, G.; Busco, C.; Ugliengo, P. *J. Phys. Chem. B* **2004**, *108*, 8278. [ii] Manard, M. J.; Bushnell, J.; Bernstein, S. L.; Bowers, M. T. *J. Phys. Chem. A* **2002**, *106*, 10027. [jj] Balabanov, N. B.; Boggs, J. E. *J. Phys. Chem. A* **2001**, *105*, 5906. [kk] Andrews, L.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 11751. [ll] Bayse, C. A.; Hall, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 1348. [mm] Bayse, C. A. *J. Phys. Chem. A* **2001**, *105*, 5902. [nn] Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2001**, *123*, 12899. [oo] Wang, X.; Andrews, L. *J. Phys. Chem. A* **2002**, *106*, 3744. [pp] Wilson, S. P.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 1640.

or liquid rare gas media have continued to be a subdiscipline that has gone hand-in-hand with studies of stable complexes, as shown in reviews by Sweany[132] and Poliakoff.[133] In most cases, the preparations involve photochemical displacement of CO either in a rare gas matrix or in liquid Xe.

$$L_xM(CO)_n + H_2 \xrightarrow[2-200\ K]{h\nu,\ -CO} L_xM(CO)_{n-1}(H_2) \qquad (14)$$

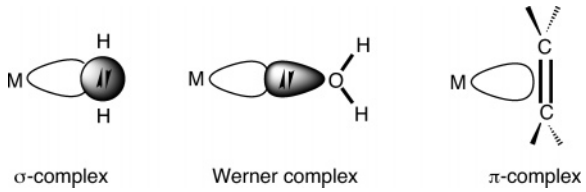
The most intensely studied species are the group 6 pentacarbonyls, $M(CO)_5(H_2)$, which have been observed in rare gas matrices, in liquid Xe solutions at −70 °C (a very useful medium), in alkane solvents, and even in the gas phase. As shown in Table 2, these and other complexes have relatively high H−H stretching frequencies in the 3000−3500 cm^{-1} range, indicative of weakly bound H_2. As will be discussed in section 5, most stable H_2 complexes have ν(HH) lower than this. Perhaps the most novel preparation is photolysis of the hexacarbonyls impregnated in polyethylene (PE) disks under H_2 or N_2 pressures to give $M(CO)_{6-n}(L)_n$, where n = 1−2 for L = H_2 and 1−4 for L = N_2.[134] Reactivity follows the order Mo > Cr > W, and H_2 can displace coordinated N_2 in the PE systems. In all media, vibrational spectroscopy provides evidence for H_2 rather than dihydride binding, and the H−H, H−D, and D−D stretching modes are often observed because of the clear spectroscopic window in rare gas media.

In nearly all cases, these complexes decompose rapidly and irreversibly at or near room temperature because of the weak H_2 binding on such CO-rich metals, where less backdonation is present. Their instability is exacerbated because the 16e product of H_2 dissociation is extremely reactive, since it is not stabilized by internal agostic C−H interactions or solvent binding (hydrocarbon solvents are even more weakly bound than H_2). The rate of dissociation of H_2 from $Cr(CO)_5(H_2)$ in hexane at 25 °C is actually slower than that for many stable species. Thus, this complex and others like it might otherwise be stable under H_2. One such complex initially presumed to be unstable, $CpMn(H_2)(CO)_2$, has in fact been isolated as a relatively stable solid from supercritical CO_2 ($scCO_2$) at 25 °C in a flow reactor by photolysis of $CpMn(CO)_3$ in the presence of H_2 and rapid expansion of the $scCO_2$.[135] $CpMn(H_2)(CO)_2$ is one of the simplest stable H_2 complexes and has by far the lowest molecular weight (178) and highest percentage of H_2 by weight (1.1%) of an isolable transition metal H_2 complex, an important factor in materials for hydrogen storage. Analogues with Cp* and N_2, C_2H_4, and η^2-$SiHEt_3$ ligands have also been prepared, and interchange of these labile ligands can be promoted.[135]

2.2.2. Binding of H_2 to Bare Metal Atoms, Ions, and Surfaces

H_2 has also been found to molecularly bind to metal surfaces such as Ni(510), metal atoms or cations, and small metal atom clusters (e.g. $Cu_2(H_2)_2$, $Cu_2(H_2)_3$, $Cu_3(H_2)$, and $Fe_x(H_2)$ (x = 3 or 4) at low temperature (Table 2). Monometallic species such as $Pd(H_2)$ were first studied by Ozin (see section 3.1) and then later by Andrews[53] for many metals, including gold. The evidence again is entirely spectroscopic, primarily vibrational and mass spectroscopy. H_2 is believed to be bound in η^2-fashion on the stepped edges of the Ni(510) surface, which are coordinatively unsaturated. Electron energy loss spectroscopy (EELS) at 100 K shows several bands comparable to those for organometallic H_2 complexes. No such chemisorption is observed on the flat Ni(100) surface, which lacks the residual unfilled d states at the step sites that bind the H_2. Undoubtedly, side-on molecular H_2 coordination is the first step in the dissociation of H_2 on metal surfaces to form hydrides and is followed by rapid splitting of H−H analogous to OA in homogeneous solution activation.

Scheme 1

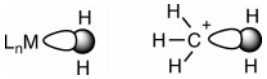


Diatomic and triatomic Cu and Pd clusters formed by vaporization react with up to three H_2 to form complexes in argon matrices at 7−15 K. Analogous reaction of H_2 with iron clusters forms only Fe_3 or Fe_4 hydrides (Fe_2 is unreactive). Main group species such as alkali halides, boron hydrides, and Lewis bases interact very weakly with H_2 at low temperature (ν_{HH} is perturbed only slightly, see section 5 below).

3. Structure and Bonding of H_2 Complexes

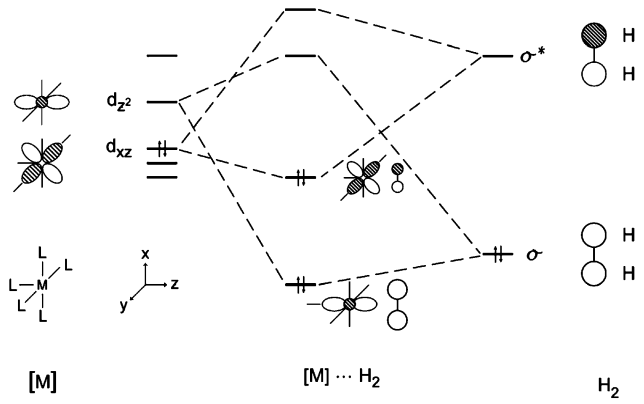
3.1. Theoretical Analysis of Nonclassical Bonding of H_2

Knowledge of the structure and bonding aspects of dihydrogen complexes is critical in understanding their properties, reactions, and dynamics. Several review articles and book chapters focus at least in part on the theoretical aspects of H−H bond coordination and activation,[5,6,24,48a,136−138] including five in a special volume of *Chemical Reviews* devoted to computational transition metal chemistry.[25,139−141] The nonclassical 3-center interaction of H_2 with the metal perfectly complements classical Werner-type compounds where a ligand donates electron density through its *nonbonding* electron pair(s) and π-complexes such as olefin complexes in which electrons are donated from bonding π-electrons (Scheme 1). It is remarkable that the *bonding* electron pair in H_2 can further interact with a metal center almost as strongly as a nonbonding pair. The resulting side-on (η^2) bonding in M−η^2-H_2 and other σ-complexes (and bridging hydrides/alkyls[7]) is *nonclassical*, by analogy to the 3c-2e bonding in carbocations and boranes. The M center may be considered to be a "superelectrophile" isolobal with H^+ and CH_3^+, mimicking carbocation chemistry; that is, a σ complex such as M^+-CH_4 is equivalent to CH_5^+, which in turn is now viewed as a highly dynamic H_2 complex of CH_3^+.[143] H_2 is thus a weak Lewis base that can bind to strong



electrophiles, but transition metals are unique in stabilizing H_2 and other σ-bond complexes by *backdonation* (*BD*) of electrons from a filled metal d orbital to the antibonding orbital of H_2 (σ^*), a critical interaction unavailable to main group atoms (Schemes 2 and 3).[5] Although it may seem paradoxical that an antibonding orbital such as H_2 (σ^*) can form a chemical bond, this orbital is only antibonding with respect to the H atoms and can still be bonding with respect

Scheme 2



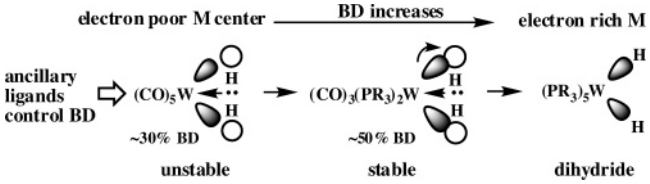
to M and H. Backdonation is a synergistic effect and can relieve the metal center of some of its excess electron density, which in turn can stabilize binding of π acceptor ligands such as CO, olefins, and even H_2. The backbonding interaction was found to present calculationally by Hay[144] in our original tungsten−H_2 complex and is analogous[5] to that in the Dewar−Chatt−Duncanson model[145,146] for π-complexes, e.g., M-ethylene. Seminal theoretical and experimental studies of Pd(H_2) laid the groundwork for understanding the side-on bonding of H_2, including the presence of BD.[147−152]

The electronic features of bonding in a metal complex truly are complex. Pauling's electroneutrality principle is important here and states that molecules arrange themselves so that their net charges fall within fairly narrow limits, about +1 to −1 overall, usually less.[153] Nonmetals such as C, N, or O prefer a charge closer to −1 while metals tend to be closer to +1. An isolated Co^{3+} ion is not an electroneutral species, since it has excessively high positive charge. It will tend to seek to form compounds with good donor ligands such as O^{2-} to form an oxide Cr_2O_3 or, in the case of coordination complexes discussed here, with NH_3 to form ammine complexes. On the other hand, an isolated M(0) atom is relatively too negatively charged ("electron-rich"), so it will prefer to attract and bind to net electron-withdrawing ligands such as CO. Complexes containing only CO ligands such as $W(CO)_6$ are known and now actually become electron-poor, relatively speaking. Electron balance is important in coordination complexes, and in formation of a ligand field around a metal, electrons tend to redistribute as evenly as possible over all the M−L bonds. Electron-rich complexes are better backbonders, and as we go from left to right in the transition series or down a group to third row metals, backdonation ability increases.

3.2. M → H_2 Backdonation and Influence of CO Ligands on Activation of H_2

Backdonation of electrons from M to H_2 is crucial not only in stabilizing σ bonding but also in activating H−H toward homolytic cleavage to a dihydride. If BD becomes too strong, e.g., by increasing the electron-donor strength of coligands on M, the σ bond cleaves to form a dihydride because of overpopulation of H_2 σ*. Replacing electron-withdrawing CO ligands by strongly donating phosphines ruptures the H−H bond in the tungsten system (Scheme 3). More quantitative measures of BD are provided by charge decomposition analysis (CDA) and extended transition state (ETS) analysis.[154−160] Frenking's CDA calculations break down the bonding into donation and backdonation terms to compare binding of H_2 to that of conventional ligands.[155−157]

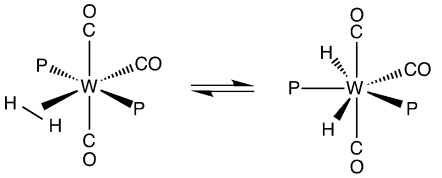
Scheme 3. Backdonation (BD) Is Critical to the Stability of H_2 Complexes and H−H Cleavage



For example, CO is found to be both a good σ donor and a strong π acceptor, consistent with its ability to bind to most metal fragments. Cyanide is a powerful donor but a weak acceptor while N_2 is the opposite: a very poor donor and moderate acceptor. By comparison, H_2 is a slightly better acceptor than N_2 but, unlike N_2, H_2 is a good donor. This is beautifully corroborated experimentally by small molecule interactions with the strongly electrophilic complex $[Mn(CO)_3(PCy_3)_2]^+$, which binds H_2 reversibly but not N_2, even at low temperature.[99] This binding difference may be important in hydrogenases where atmospheric dinitrogen could potentially bind and inhibit H_2 activation at the enzyme's dimetallic core. For $W(CO)_5(H_2)$, donation from H_2 (0.349 e) is greater than BD (0.129 e), as expected for this related electron-poor system.

For very electrophilic centers, *loss in BD is almost completely offset by increased electron donation from H_2 to the electron-poor center*. The M−H_2 energy for electron-poor $Mo(CO)_5(H_2)$ is surprisingly similar to that for the more electron-rich, isolable, phosphine complexes. *H_2 is the perfect ligand because it is effectively amphoteric like CO and is perhaps the most adaptable "weak" ligand*, reacting with virtually every unsaturated M fragment. As pointed out by Hoffmann,[161] the reason CO is an excellent, ubiquitous ligand is the balance between its good donor/acceptor capabilities and its innate stability. The H_2 ligand offers the same advantages, albeit on a lesser energy scale. These and other electronic factors are important in understanding both activation of H_2 in metalloenzymes and reversible binding of H_2 for purposes of hydrogen storage that will be discussed below.

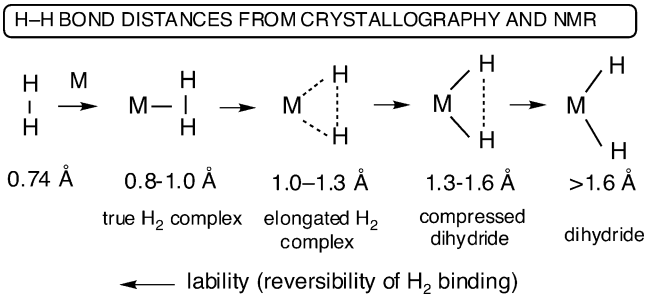
Because of the above electronic considerations, particularly BD, there is a fine line between H_2 and dihydride coordination, and in some cases, *equilibria* exist between the two forms in solution for $W(CO)_3(PR_3)_2(H_2)$ (R = *i*-Pr; K = 0.25) (eq 15).[2,3,6] Our seminal studies thus clearly demonstrated



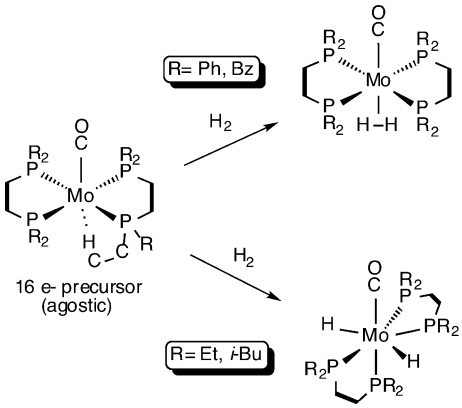
(15)

that side-on coordination of H_2 is the first step in H−H cleavage to dihydride. Equally important is that even though a complex may ostensibly be observed to contain only hydride ligands, a low-energy pathway to a coordinated H_2 ligand may exist (e.g., via the reverse of eq 15) that can result in dissociative loss of H_2 as in eq 1. Both processes can be completely reversible, providing the complex is stabilized in the absence of H_2 by either steric protection and/or agostic interaction (eq 1). Although the electronic factors for oxidative addition of H_2 in eq 15 were well-established calculationally, the role of steric factors was not. The phosphines are bulky (R = cyclohexyl or isopropyl) and at first were believed to inhibit H_2 splitting to form a 7-coordinate complex.[162] This later was shown to be true to

Scheme 4



some extent: for less bulky R = Me, the equilibrium lies completely to the right, i.e., the complex is a *dihydride*,[163] and increasing phosphine size in $[Cp^*OsH_2(H_2)(PR_3)]^+$ led to elongation of d_{HH} in the H_2 ligand.[70] Another dramatic demonstration of the fine effects of changing electronics and sterics is H_2 addition to the agostic complex $Mo(CO)(R_2PC_2H_4PR_2)_2$, whereby merely changing R controlled whether a H_2 or dihydride complex was stable (eq 16).[88] The more

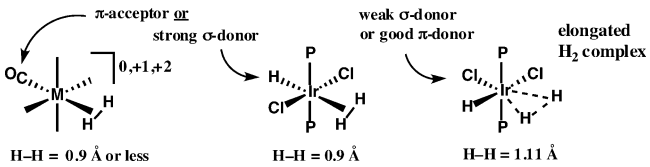


(16)

electron-donating alkyl diphosphines such as depe (R = Et) lead to increased BD, ultimately favoring H−H rupture to form a dihydride. It would appear that electronic rather than steric factors are more crucial in stabilizing H_2 versus dihydride coordination, since the phosphines with R = *i*-Bu and phenyl (dppe) are similar in size. Changing M in $Mo(CO)(dppe)_2$ to W also leads to dihydride formation[164] because W is a better backbonder than Mo (third-row metals have more diffuse d orbitals).

Another indication that electronic effects predominate in stabilizing molecular H_2 versus dihydride binding is that H_2 binding was eventually found in complexes containing only very small coligands such NH_3 (section 2.1.5);[60,121−126] that is, bulky phosphine ligands are not needed to sterically favor 6-coordinate H_2 complexes over 7-coordinate dihydrides. Second, the H−H distances were found to vary greatly completely independent of ligand size and in some of these complexes were well over 1 Å. Both of these observations represented further paradigm shifts. This led to extensive efforts by many researchers to vary the metal, ancillary ligands, and other factors to study the stretching of the H−H bond. Within the large regime of hundreds of L_nM-H_2 complexes, it was possible to map out the entire reaction coordinate for the activation of H_2 on a metal as a function of the degree of backdonation. Complexes with d_{HH} varying enormously from 0.82 to 1.5 Å were found (Scheme 4). This arresting of bond rupture along its entire reaction coordinate is unprecedented in chemistry. Although the d_{HH} ranges shown are arbitrary, each category of complexes has distinct

Scheme 5. σ Complex Favored by Strong trans Ligand and Positive Charge



properties. The d_{HH} is relatively short (0.8−1.0 Å) and reversibly bound in "true" H_2 complexes best exemplified by $W(CO)_3(PR_3)_2(H_2)$, much as in physisorbed H_2, where d_{HH} is <0.8 Å. Elongated H_2 complexes,[30,34] where d_{HH} = 1−1.5 Å, were first clearly identified in 1991 in $ReH_5(H_2)(PR_3)_2$, where neutron diffraction showed a d_{HH} of 1.357(7) Å between two hydrides.[165] Complexes with such very long d_{HH} over 1.3 Å are now viewed as "compressed hydrides", with NMR features differing from those of elongated H_2 complexes; for example, J_{HD} increases with temperature for the former and decreases for the latter.[30,69] These are relative terms, since the H−H bond is always stretched on binding, and indeed, a near *continuum* of d_{HH} exists. The activation of H_2 is very sensitive to the nature of M, L, and charge. Strongly donating L, third-row M, and neutral charge favor elongation and splitting of H−H to hydride, while first-row M, electron-withdrawing L, and positive charge shorten d_{HH} and favor molecular H_2 binding.

The ligand trans to H_2 has a powerful influence: strong π-acceptors such as CO (and also strong σ-donors such as H) greatly reduce BD and normally keep d_{HH} < 0.9 Å, as in the Mo complexes. Thus, a σ complex can be designed by placing the potential σ ligand trans to CO or another strong π acceptor (charge is not critical), or also a very strong trans donor ligand such as a hydride. Conversely, mild σ-donors such as H_2O or π-donors such as Cl trans to H_2 elongate d_{HH} (0.96−1.34 Å), as dramatically demonstrated by the isomers of $IrCl_2H(H_2)(PR_3)_2$ (Scheme 5).[166] The cis-Cl complex is actually a "compressed trihydride" (d_{HH} ∼ 1.5 Å) in solution but in the solid state is an elongated H_2 complex (d_{HH} = 1.11 Å) due to Ir−Cl···H−Ir hydrogen bonding, illustrating the hypersensitivity of d_{HH} to both intra- and intermolecular effects.[167] Intermolecular interactions (e.g., crystal packing forces) can substantially affect bond lengths, so solution and solid-state d_{HH} may differ. The isomer with hydride trans to H_2 shows d_{HH} to be 0.9 Å, i.e., a true H_2 complex. The reason here is that if the trans ligand is a strong σ-donor such as hydride, there is a powerful trans influence that reduces σ electron donation from H_2 to keep the orbital electron population in balance because the orbitals are shared.[168] This in turn weakens the $M-H_2$ bonding and contracts d_{HH} even though the complex as a whole is relatively electron-rich and neutral. On the other hand, a *weak* σ-donor ligand trans to H_2 elongates the H_2 as shown in the dicationic complex, $[Ru(H_2)(PP)_2]^{2+}$ ($PP = Bz_2PC_2H_4PBz_2$), where an agostic aryl C−H interaction is trans to the H_2 ligand.[169] This has the longest d_{HH} (1.05 Å) observed for a *dicationic* $Ru-H_2$ complex, which would be expected to have a short d_{HH} because of the double positive charge.

The influence of cis ligands is less consequencial because the orbitals are independent of each other. Exceptions to the above effects exist to make life interesting: the isomers of $Cr(CO)_4(PMe_3)(H_2)$ have similar J_{HD} (∼34 Hz, hence d_{HH} ∼ 0.86 Å) whether H_2 is trans to a CO or the good donor PMe_3.[22] The strongly electron-withdrawing CO ligands may affect the electronics differently here than in an electron-

rich complex such as the Ir complex above. An even more glaring exception to the principles discussed above is $FeH_2(CO)_4$, which was prepared in 1931 and was the first organometallic hydride complex.[153] However, because of its electron-poor nature as in the above Cr complex and in $W(CO)_5(H_2)$ in Scheme 3, it would be expected to be an H_2 complex.[6] Nonetheless, relatively recent experimental and computational studies confirm that the complex is a dihydride.[170] The nature of the electronic state of the complex plays a large role, as will be discussed below for H_2 addition to iron atoms (section 11.2). As previously emphasized, the dichotomy between H_2 and dihydride coordination is much more complex than could have been imagined.

There is little H−H bonding interaction remaining for $d_{HH} > 1.1$ Å,[34] so at what point is the bond "broken"? Theoretical analyses suggest 1.48 Å, i.e. twice the normal length.[64b] In certain "elongated" H_2 complexes, e.g., $[OsCl(H_2)(dppe)_2]^+$, the energy barrier for stretching the H−H bond from 0.85 Å all the way to 1.6 Å is calculated[34,69] to be astonishingly low (on the order of 1 kcal/mol!). The H_2 molecule is extremely delocalized: the H atoms undergo large amplitude vibrational motion along the reaction coordinate for H−H breaking (section 6). Remarkably, d_{HH} is both temperature and isotope dependent in $[CpM(diphosphine)(H_2)]^{n+}$ (M = Ru, Ir; n = 1, 2).[172] These phenomena illustrate the prodigious dynamic properties of coordinated H_2 (section 6), which can even exhibit quantum mechanical behavior such as rotational tunneling in inelastic neutron scattering spectroscopy (section 11.4).[173]

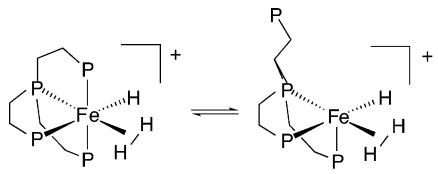
4. Properties and Spectroscopic Diagnostics for H_2 Complexes

4.1. Properties of H_2 Complexes

The properties of H_2 complexes vary tremendously, depending on the degree of activation of the H_2 ligand toward the dihydride form, i.e., the value of d_{HH}, which in turn depends on a multitude of factors as shown in section 3.2.[6] In some instances, polyhydrides are known that adopt more than one structure in solution or that adopt different structures in solution versus the solid state, e.g., dihydrogen−dihydride and classical tetrahydride forms.[174] True H_2 complexes with short $d_{HH} < 0.9$ Å typically have labile H_2 ligands that readily exchange with D_2 and in some cases give isotopic scrambling to HD. Atmospheric N_2 can even displace the H_2 ligand in these complexes (section 8.2.7). Most H_2 complexes are air-sensitive, reacting with oxygen to give decomposition, or very rarely, O_2 binding. The exceptions tend to be cationic species of later metals such as $[IrH(H_2)(PPh_3)_2(bq)]^+$, $[RuCl(H_2)(PP)_2]^+$, and $[PtH(H_2)(P^iPr_3)_2]^+$. The latter is air-stable even in solution (although it is thermally unstable above −30 °C).[101] Thus, H_2 complexes are best prepared, handled, and stored under atmospheres of rare gases such as argon or helium containing some hydrogen. Occasionally, the solid complexes can be handled under N_2 or even briefly in air, though it is often necessary to use an argon-flushed glove bag ultimately filled with an argon−H_2 (or D_2) mixture, e.g., when preparing Nujol-mull IR samples of H_2 or D_2 complexes. Air-stability increases toward the later transition elements, down the group, and for complexes that are more hydridic in character (longer d_{HH}). A trace amount of water in the atmosphere or solvent is usually not a problem if excess H_2 is present, since, as will be shown in section 8.2.7, binding of H_2 competes favorably with H_2O binding (an important feature in biological systems).

Another key feature is lability of the H_2 ligand, which has two important connotations, namely *reversibility* and *ease of displacement* by other ligands. Reversibility in the strictest sense means that the H_2 can be removed *in vacuo*, by passage of an inert gas over the complex, or by heating, either in solution or solid states, to regenerate a stable precursor that re-adds H_2 for at least several cycles. Degradation or loss/gain of other ligands must not occur in the process. This property was found for the original W complex and is obviously more common for the complexes prepared from H_2 gas, which are shown in Table 1 (though not all such complexes show facile reversibility). Often the solid will have a measurable H_2 dissociation pressure (~10 Torr for $W(H_2)(CO)_3(P^iPr_3)_2$), necessitating a H_2-enriched atmosphere over the complex at all times. Reversible color changes, e.g., yellow to deep purple for the Kubas complexes, can occur on H_2 loss in vacuo and re-addition of H_2 and are usually rapid, even in the solid. This is often an easy (and visually impressive) test of reversibility. It is important to note that such *reversibility does not prove the existence of H_2 ligands*, although it may suggest it. Many examples of multimetallic hydrides or even complexes with −SH ligands (section 8.2.5) are known to dissociate and re-add H_2 reversibly.[45c] Morris has tabulated the stability of a wide variety of H_2 complexes to H_2 loss in both solution and solid states.[30] Dissociation of H_2 to generate a vacant coordination site for substrate binding is a critical step in many catalytic hydrogenation and related processes; that is, dihydrogen complexes can function as excellent catalyst precursors.[40,43,175]

Facile displacement of η^2-H_2 by more strongly bound ligands can occur both for the above cases and also for systems that do not bind H_2 reversibly.[30] For group 6 and certain other complexes, this includes coordinating solvents such as THF and acetonitrile, although some complexes are stable to H_2 loss even on heating in such solvents. In a tetraphosphine Fe complex, the H_2 is so strongly bound that when it is used as a hydrogenation catalyst for alkynes to alkenes, a free coordination site for the incoming alkyne is provided by detachment of a phosphine arm instead of H_2 loss.[176] However, catalysis by the Ru analogue occurs via



usual H_2 loss,[177] illustrating the difficulty in predicting stability, particularly for the iron group metals.[30,178]

The photochemical stability of H_2 complexes has not been well-studied, but H_2 dissociation on exposure to visible light has been commonly observed in matrix-isolated species (section 2.2.1). The electrochemistry of H_2 complexes has also not been widely studied and is limited to cyclic voltammetric determinations. Oxidation of H_2 complexes is much more common than reduction because the majority are low valent complexes. Reversible redox systems are quite rare and include $ReCl(H_2)(PMePh_2)_4$[179] and $[Os(H_2)(NH_3)_5]^+$,[121] which show respective $E_{1/2}$ values of −0.07 and 0.58 V in organic solvents. In the latter case, oxidation is irreversible in acetone because the resulting Os(III)−H_2 complex reduces acetone to isopropanol, an unusual case where oxidation transforms a complex into a better reducing agent. Irrevers-

ible systems that primarily show anodic peaks are summarized by Jessop and Morris.[30] One of the few complexes to be reduced electrochemically is $[FeH(H_2)(pp_3)]^+$, which irreversibly goes to $FeH_2(pp_3)$.[180] $W(CO)_3(PCy_3)_2(H_2)$ can be electrochemically oxidized to $[W(CO)_3(PCy_3)_2(H_2)]^+$, whereupon the H_2 ligand becomes highly acidic (protonates weakly basic THF solvent). [181] As will be shown, overall positive charge and electron-withdrawing coligands such as CO positioned trans to the H_2 ligand greatly increase its acidity, another critical feature in dihydrogen coordination chemistry relevant to biological activation.

4.2. Spectroscopic and Other Diagnostics for H_2 Complexes

Characterization of and evidence for dihydrogen ligands encompass several spectroscopic and crystallographic techniques, and in some cases more than one may be needed to prove the existence of H_2 binding. X-ray and neutron diffraction and NMR spectroscopy are the major techniques for determination of the structure of H_2 complexes, particularly H−H separation, by far the parameter of most interest yet the most difficult to pinpoint accurately. All stable complexes studied to date feature symmetrically side-on (η^2-) bound H_2 as in olefin binding in order to maximize backdonation (BD) from M. However, the H−H distances (d_{HH}) span a huge range (Scheme 4), and certain polyhydride complexes studied by neutron diffraction show weak bonding interactions between two hydride ligands with $d_{HH} = 1.6$ Å in $OsH_6(P^iPr_3)_2$,[182] 1.49(4) Å in $[OsH_5(PPhMe_2)_3]^+$,[183] and 1.36(1) Å in $ReH_7(P(p\text{-tolyl})_3)_2$.[165] A useful empirical correlation devised by Morris enables one to predict whether or not a certain ML_n fragment will bind H_2 or form a dihydride by determining ν_{NN} for its corresponding dinitrogen complex, $M(N_2)L_n$.[184]

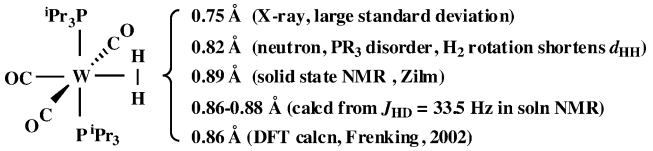
The determination of d_{HH} and d_{MH} both accurately and precisely is nearly always a challenge. In certain cases, especially polyhydride complexes, there is ambiguity as to whether H_2 ligands are really present, even in neutron diffraction structures. For example, $[OsH_5(PPhMe_2)_3]^+$ was originally formulated as an H_2 complex[113,185] and then calculationally as a pentahydride, and finally, a neutron diffraction study at 11 K showed that it is indeed closer to a pentahydride with widely varying d_{HH} (1.49, 1.75, and 1.98 Å).[183] It took eight experimental and theoretical papers from six different research groups over a 25-year period to resolve the structure and bonding in a single complex. Thus, it is not surprising that σ H_2 coordination was not found until the1980s. Locating hydrogen bound to heavy atoms by X-ray methods is a well-known problem, and even determination of d_{HH} by neutron diffraction is complicated by rapid rotation of η^2-H_2 that shortens the observed d_{HH}.[88c] Solid-state proton NMR can be used to accurately determine d_{HH} with good precision (±0.01 Å).[186,187] The first complex studied, $W(CO)_3(PCy_3)_2(H_2)$, showed a d_{HH} of 0.890 ± 0.006 Å.[187] These values are nearly always significantly longer (roughly 0.07 Å on average) than neutron values that are uncorrected for the effects of H_2 rotation. Solid-state NMR directly measures the H−H internuclear separation (rotational and other dynamics are *not* factors) and can be a better gauge than neutron diffraction.

Solution ^{1}H NMR spectra of η^2-H_2 ligands normally give broad uncoupled signals throughout a large range of chemical shifts (2.5 to −31 ppm) that can overlap with those for classical hydrides. NMR can be used to determine d_{HH} in solution by two different techniques involving measurement of either J_{HD} or relaxation time, T_1. J_{HD} for the HD isotopomer of an H_2 complex is the premier diagnostic for H_2 versus hydride coordination. The signal for an HD complex becomes a 1:1:1 triplet (D has $I = 1$) with a much narrower line width and is direct proof of the existence of an H_2 ligand, since classical hydrides do not show significant $^1J_{HD}$ because no residual H−D bond is present. J_{HD} for HD gas is 43 Hz, the maximum value ($d_{HD} = 0.74$ Å), and lower values represent proportionately shorter d_{HD}. J_{HD} determined in solution correlates well with d_{HH} in the solid state,[64] and both Morris[64c] and Heinekey[64d] developed empirical relationships, shown in eqs 18 and 19:

$$d_{HH} = 1.42 - 0.0167J_{HD}\ \text{Å} \quad \text{[Morris]} \qquad (18)$$

$$d_{HH} = 1.44 - 0.0168J_{HD}\ \text{Å} \quad \text{[Heinekey]} \qquad (19)$$

Input data include d_{HH} from X-ray and neutron diffraction methods plus solid-state NMR[186,187] measurements. For $W(CO)_3(P^iPr_3)_2(H_2)$, J_{HD} is 34 Hz, giving $d_{HH} = 0.86-0.88$ Å versus 0.89 Å from solid-state NMR and 0.82(1) Å from neutron diffraction (uncorrected for the effects of H_2 libration). The value calculated by DFT methods is quite close

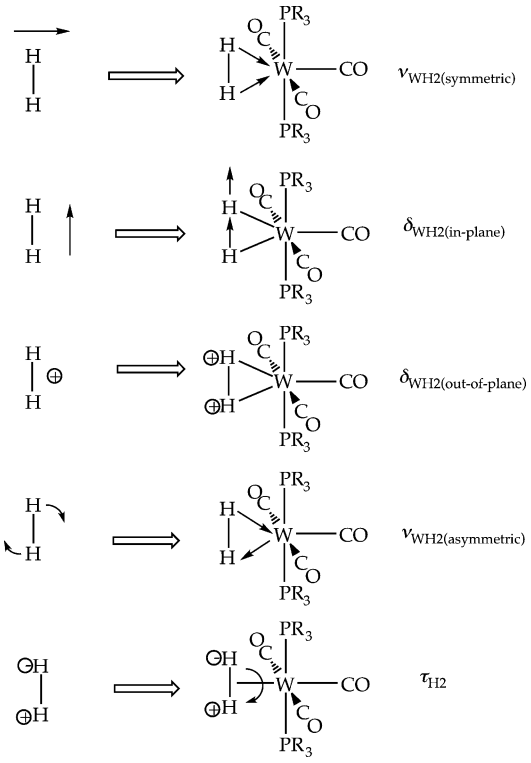


to this, 0.86 Å,[188] and in general, there is remarkably good agreement between experiment and theory in metal−H_2 complexes. Short T_1 values for the H_2 ligand were originally found by Crabtree to be also diagnostic of H_2 coordination (e.g., 4 ms for the W complex here versus >100 ms in hydrides).[9,36] T_1 values are temperature dependent and go through a minimum, and the value of T_1^{min} is the important diagnostic parameter here. Because T_1 depends on d_{HH}, it is extremely sensitive to the presence of H's that are close together as in an H_2 complex. However, care must be exercised in interpretation because several factors influence T_1 values.[120,129,189,190] Observed J_{HD} values can also exhibit temperature and even solvent dependence in certain situations, e.g., equilibria between two different structures such as a solvated dihydride of Ir(III) and an H_2 complex of Ir(I).[191]

5. Vibrational Spectroscopy of H_2 Complexes

Another valuable though underutilized characterization tool is infrared spectroscopy. The vibrational modes for M(η^2-H_2) are distinct from those for hydrides, which have only two fundamental modes: ν(MH) at 1700−2300 cm^{-1} and a M−H bending mode at 700−900 cm^{-1}. However, the initial routine IR spectrum of solid $W(CO)_3(PR_3)_2(H_2)$ showed two bands that were outside these ranges and additionally displayed an unusual low-energy band near 460 cm^{-1} that was the first substantial clue to the novel dihydrogen structure here.[1−4,6] When diatomic H_2 combines with a M−L fragment to form a η^2-H_2 complex, five "new" vibrational modes in addition to ν_{HH} are created which are related to the "lost" translational and rotational degrees of freedom for H_2 (Scheme 6). ν_{HH} is still present, but it is shifted to much lower frequency and becomes highly coupled with a MH_2

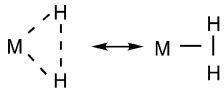
Scheme 6



mode, $\nu_{as}(MH_2)$.[4] Thus, six fundamental vibrational modes are expected to be formally isotope sensitive: three stretches, ν(HH), $\nu_{as}(MH_2)$, $\nu_s(MH_2)$; two deformations, $\delta(MH_2)_{in-plane}$ and $\delta(MH_2)_{out-of-plane}$; and a torsion ($H_2$ rotation), $\tau(H_2)$. The bands shift hundreds of wavenumbers on isotopic substitution with D_2 or HD, which greatly facilitates their assignment. Importantly, the frequencies of the bands for the η^2-HD complexes lie between those for the η^2-HH and η^2-DD isotopomers and are not a superimposition of MH_2 and MD_2 bands as seen for classical hydrides. This is another valuable diagnostic for distinguishing H_2 versus dihydride coordination, although these vibrational modes are often difficult to observe. All six bands have in fact been observed and assigned only in the first H_2 complex, $W(CO)_3(PR_3)_2(H_2)$ (R = Cy, ^{i}Pr), but this may only be due to lack of a concerted effort for other complexes. All but $\nu_s(MH_2)$, observed in both the IR and Raman spectra, are weak, and many of the bands tend to be obscured by other ligand modes, except for certain complexes such as $Cr(CO)_5(H_2)$ that are normally stable only at low temperature.[18−20,132−135] Table 3 lists the modes observed for selected complexes.

In the Nujol-mull IR spectrum of $W(CO)_3(PCy_3)_2(H_2)$, four bands, ν(HH) at 2690 cm^{-1}, $\nu_{as}(MH_2)$ at 1575 cm^{-1}, $\nu_s(MH_2)$ at 953 cm^{-1}, and $\delta(MH_2)_{in-plane}$ at 462 cm^{-1}, can be observed to shift to lower frequency for the D_2 analogue. The band at 442 cm^{-1} in the D_2 complex is assigned to $\delta(WD_2)_{out-of-plane}$. The modes for H_2 rotation about the M−H_2 axis, $\tau(H_2)$, and also $\delta(MH_2)_{out-of-plane}$ near 640 cm^{-1} are observable only by inelastic neutron scattering (INS) methods, a powerful technique to locate such large amplitude vibrations involving hydrogen.[4,6,173] These lower frequency deformations and torsions have been the least observed modes in H_2 complexes.

The frequency of most interest, ν_{HH}, varies tremendously and is often near the ν_{CH} region, where it can be obscured because most ancillary ligands such as phosphines have strong ν_{CH} bands. Use of perdeuterated phosphine ligands to eliminate such interference enabled location of ν_{HH} in $W(CO)_3[P(C_6D_{11})_3]_2(H_2)$ as a broad, weak band at 2690 cm^{-1}.[4,6] About 30 other compounds, including surface and cluster species, exhibit ν_{HH} in a range, 2080−3200 cm^{-1}, that is considerably lower than that for free H_2 gas (4300 cm^{-1}).[4] As expected, there is a large dependence of ν_{HH} and MH_2 modes on both metal and ligand sets. One might anticipate a correlation of ν_{HH} with d_{HH} and the electron-backdonating ability (electron-richness) of the metal, as found for ν_{NN} and ν_{CO} in similar π-acceptor N_2 and CO ligands. However, as can be seen from Table 3, this is not the case because of the complexity of the bonding and extensive mixing of ν(HH) and $\nu(MH_2)$ modes as shown by the normal coordinate analysis of $W(H_2)(CO)_3(PCy_3)_2$.[4] The latter, in fact, treats the W−H_2 interaction as a triangulo system, i.e., where direct BD electronic interactions exist between W and H atoms (below, left), rather than as the strictly 3-center bonding representation (below right).



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Modes other than ν_{HH} have been less often observed in room-temperature stable complexes, partly because of interference from coligands or difficulty in assignment, especially if hydride ligands are also present. Low-energy modes have been identified mainly by INS methods, e.g., the torsional mode at 200 cm^{-1} for $TpRhH_2(H_2)$.[192] Four modes were seen in the Raman spectrum of $[CpRu(dppm)(H_2)]BF_4$, which has an elongated H−H bond (1.10 Å) and one of the lowest reported values for ν_{HH}, 2082 cm^{-1}.[193] The H_2 in elongated H_2 complexes can also be highly delocalized, and new vibrational modes must be defined (see Scheme 8 and section 6 below).[69,172b,194] Modes for surface-bound H_2 such as on the stepped edges of a Ni(510) surface can be observed, and electron energy loss spectroscopy (EELS) at 100 K shows several bands comparable to those for H_2 complexes such as $W(CO)_3(PCy_3)_2(H_2)$.[195]

6. Dynamics of H_2 and Hydride Complexes

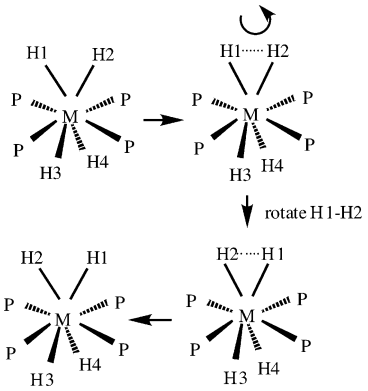
Long before the "nonclassical" dihydrogen complexes were discovered, classical polyhydride complexes had been known to be stereochemically nonrigid (fluxional) in solution, which was viewed as isolated H-atoms moving over the surface of the metal center.[196−198] However, their association as H_2 ligands as intermediate steps is now much more attractive. For example, for hydride site exchange in polyhydrides such as ML_4H_4 (M = Mo, W; L = P-atom donor), transient intermediates with a geometry very much like $MH_2(H_2)L_4$ or *trans*-$M(H_2)_2L_4$ with elongated d_{HH} were considered possible even in 1973, long before H_2 complexes were actually discovered (Scheme 7). Since the dihydrogen ligand nearly freely rotates, that is, has a relatively low barrier to rotation (1−10 kcal/mol), hydride ligand rearrangement could easily take place by rotating the intermediate H1−H2 ligand as shown. Many new examples of hydride fluxionality and facile intramolecular and intermolecular hydrogen transfer reactions were later discovered, and the principle mechanistic aspects have been reviewed to include systems containing η^2-H_2 ligands.[30,50,140b,199] For example, fast exchange between terminal and bridging hydrides in dinuclear rhenium complexes has been shown calculationally to be facilitated by formation of dihydrogen-containing intermediates,[200] which may be an important feature in H_2ases. As will be shown

Table 3. IR Frequencies (cm^{-1}) for ν_{HH} and MH_2 Modes in H_2 Complexes Compared to d_{HH} (Å)

complex	ν(HH)	$\nu_{as}(MH_2)$	$\nu_s(MH_2)$	$\delta(MH_2)$	d_{HH}	ref
$CpV(CO)_3(H_2)$	2642					*a*
$CpNb(CO)_3(H_2)$	2600					*a*
$Cr(CO)_5(H_2)$	3030	1380	869, 878			19b
$Cr(CO)_3(PCy_3)_2(H_2)$		1540	950	563[b]	0.85	82
$Mo(CO)_5(H_2)$	3080					19b
$Mo(CO)_3(PCy_3)_2(H_2)$	~2950[c]	~1420[c]	885	471	0.87	2
$Mo(CO)(dppe)_2(H_2)$	2650		875		0.88	88c
$W(CO)_5(H_2)$	2711		919			19b
$W(CO)_3(P^iPr_3)_2(H_2)$	2695	1567	953	465	0.89	2, 4
$W(CO)_3(PCy_3)_2(H_2)$	2690	1575	953	462	0.89	2, 4
$W(CO)_3(PCyp_3)_2(H_2)$[d]		1565	938			*k*
$Fe(CO)(NO)_2(H_2)$	2973	1374	~870			*l*
$Co(CO)_2(NO)(H_2)$	{3100, 2976}[e]	1345	868			*l*
$FeH_2(H_2)(PEtPh_2)_3$	2380		850	500, 405[f]	0.82	115
$RuH_2(H_2)_2(P^iPr_3)_2$	2568	1673	822[b]		0.92	127
$Tp^*RuH(H_2)_2$	2361				0.90	224
$Tp^*RuH(H_2)(THT)$	2250				0.89	224
$[Os(NH_3)_5(H_2)]^{2+}$	2231[b]				[1.34][g]	121
$[CpRu(dppm)(H_2)]^+$	2082[b]	1358[b]	679[b]	486, 397[b]	[1.10][h]	193
$Tp^*RhH_2(H_2)$	2238				0.94[i]	67
$Pd(H_2)$ (matrix)	2971	1507	950		0.85[i]	152[a,b]
$Ni(510)-(H_2)$[j]	3205	1185	670			195

[a] George, M. W.; Haward, M. T.; Hamley, P. A.; Hughes, C.; Johnson, F. P. A.; Popov, V. K.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 2286. [b] Assignments unclear; in the case of the elongated Ru andOs complexes, these are highly mixed modes that could involve M−H modes (if present). [c] Estimated from observed D_2 isotopomer bands. [d] Cyp = cyclopentyl. [e] Split possibly by Fermi resonance. [f] Assignment unclear (data from INS). [g] For $[Os(ethylenediamine)_2(H_2)(acetate)]^+$ (ref 60). [h] For the Cp* analogue (ref 225a). [i] Calculated from inelastic neutron scattering data or DFT. [j] Data from EELS spectroscopy. [k] Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855. [l] Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547.

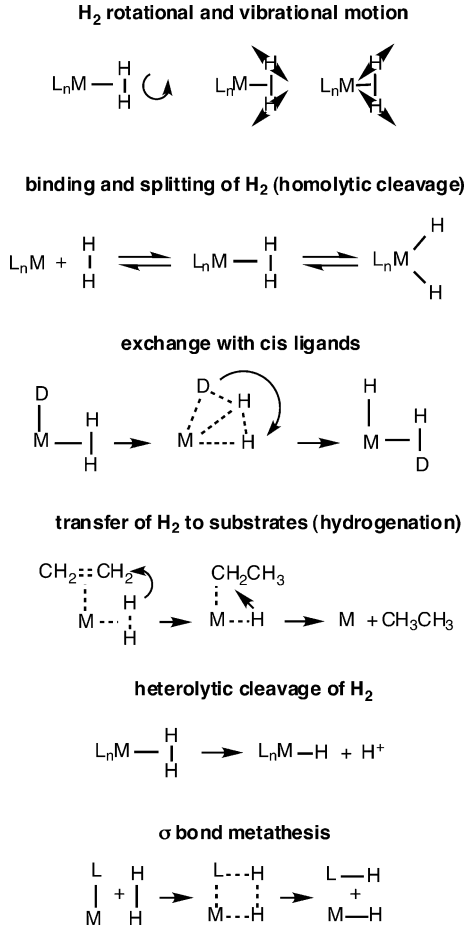
Scheme 7



below, remarkably facile hydrogen site exchange between cis hydride and H_2 ligands can occur even in the *solid state* at temperatures below 77 K with activation barriers as low as 1.5 kcal/mol.

For the H_2 ligand, the structure and dynamics are much more extensive and richer than those for hydride ligands. These can include rotational/vibrational motion of η^2-H_2, binding and splitting of H_2 (including equilibria between η^2-H_2/dihydride tautomers), transfer of hydrogen to substrates, heterolytic cleavage of H_2, and σ bond metathesis processes (Scheme 8). Several of these processes can occur simultaneously on a metal center, and all will be discussed in more detail below. Often, these dynamics cannot be frozen out on the NMR time scale even at the lowest attainable temperatures for the system. The H_2 ligand by itself is remarkably dynamic. As discussed above, the first set of equilibria essentially represents the reaction coordinate for H−H bond cleavage/formation, which in several systems takes place in solution at room temperature. In addition to or instead of this process, virtually all complexes with H_2 ligands cis to hydride undergo extremely facile ligand exchange with very low barriers of ~5 kcal/mol or less, as

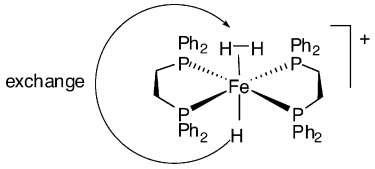
Scheme 8



will be discussed below. Finally, in most cases, η^2-H_2 rapidly rotates (librational motion is more accurate) even in the solid state, further delocalizing the H atom positions over virtually

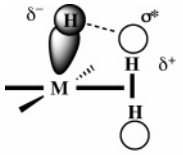
the entire coordination sphere of a metal complex. One of the key diagnostics for coordination of *molecular* H_2 is in fact the observation by inelastic neutron scattering (section 11.4) of rotational transitions for η^2-H_2, which cannot exist for classical *atomic* hydrides. Hydrogen reorientation among either chemically equivalent or inequivalent sites is extremely complex and can even involve *quantum mechanical* phenomena such as tunneling and exchange coupling between hydride ligands.[201]

Facile intramolecular site exchange of H atoms between H_2 and hydride ligands is common.[6,92,202−206] The ^{1}H NMR signals of the cis H_2 and hydride ligands in $[Ir(H_2)H(bq)(PPh_3)_2]^+$ coalesce at 240 K because of exchange,[92] and even the hydride trans to H_2 in $[Fe(H_2)H(dppe)_2]^+$ exchanges positions with the H atoms of η^2-H_2.[202] Ab initio calculations



(21)

show that a variety of mechanisms are possible for the site exchange.[203,207] Both experimentally and calculationally, complexes that contain a hydride cis to a H_2 ligand often show structural and dynamic features indicative of mutual interaction.[57,115,166,178,203,208−212] For example, the barrier to H_2 rotation (section 11.4) can be perturbed by the presence of a hydride cis to H_2. Calculations by Eisenstein show that this results from a "cis-interaction", a hydrogen-bonding like interaction between the hydride ligand and σ^* H_2.[115,209] This

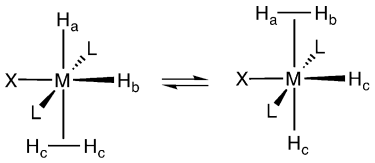


(22)

cis-interaction

interaction is significant because of its apparent role as the nascent interaction in facile intramolecular hydrogen exchange processes, many of which can be viewed as a type of σ-bond metathesis process (Scheme 8), a term for a more general form of the above hydrogen exchange analogous to olefin metathesis.[140b,213−216] The H_2 ligand can also interact with other atoms bound to the metal center such as B, Si, and C and undergo interconversions via σ-complex-assisted metathesis (σ-CAM), which is distinct from σ-bond metathesis and oxidative−reductive elimination mechanisms.[215] Such processes can be considered to be related to the heterolytic cleavage processes discussed below that are relevant to H_2 activation in hydrogenases.

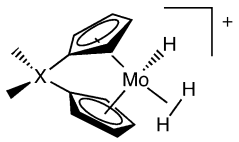
A well-studied extremely fluxional complex is $IrClH_2(H_2)(P^iPr_3)_2$, where INS studies showed the lowest barrier to H_2 rotation (0.51(2) kcal/mol) ever measured for a metal complex.[85,217] Solid-state ^{1}H NMR studies on a single crystal provided key initial information on the fluxional behavior.[218] A transition state with C_{2v} symmetry is attained in this and related systems by stretching the H−H bond followed by concerted migration of metal-bound hydrogens. This transient structure inverts with H_a and H_b forming a new H_2 ligand, all of which occurs in the equatorial plane of the molecule (eq 23). This is a remarkably low barrier for a solid-state process at 77 K involving considerable ligand rearrangement.



(23)

$MH_2(H_2)L_3$ (M = Fe, Ru)
$MH_2(H_2)(CO)L_2$ (M = Ru, Os)
$IrH_2(H_2)XL_2$ (X = Cl, Br, I)

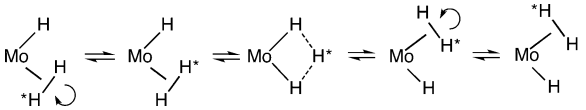
Recent studies have been carried out on bis(cyclopentadienyl)Mo type complexes, the first complexes with d^2 electronic configurations to have cis hydride−dihydrogen ligands. In contrast to $[Cp_2MoH_3]^+$, which is a thermally stable *trihydride* complex, the *ansa*-bridged analogues $[Me_2X(C_5R_4)_2MoH(H_2)]^+$ (X = C, R = H; X = Si, R = Me) have been independently determined by both Heinekey[220] and Parkin[221] to be thermally labile *dihydrogen/hydride* complexes. Rapid dynamic processes interchange the



(24)

X = C (**1**), Si (**2**)

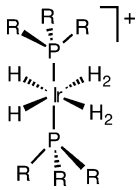
hydride and dihydrogen moieties in these complexes. The bound H_2 ligand in **1** exhibits hindered rotation with $\Delta G^{\ddagger}_{150}$ = 7.4 kcal/mol, comparable to previously reported observations in d^2 Ta and Nb dihydrogen complexes.[222] However, H-atom exchange is still rapid at temperatures down to 130 K, and eq 25 depicts the dynamic process envisaged, with the central Mo−trihydrogen structure representing a transition state for atom transfer from one side of the molecule to the other. Complex **2** has an X = Si linker and methyl



(25)

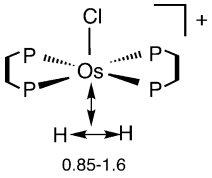
substituents on the ring carbons.[221] "Side-to-side" motion of the central hydrogen or deuterium atom as in eq 25 remains rapid on the NMR time scale at all temperatures studied. The barrier to rotation of the H_2 ligand is 9.0 kcal mol^{-1} at 25 °C.

There are only a handful of *bis-H_2 complexes*, which typically additionally have classical hydride ligands and present another example of the very low barriers for exchange of H_2 and hydride ligands situated cis to each other around the equatorial plane of a complex. The complex $[IrH_2(H_2)_2(PCy_3)_2]^+$ is a good example, and separate ^{1}H NMR resonances for the hydride and H_2 ligands could be observed on cooling of the complex to 188 K.[223] These peaks coalesce



at 200 K, and Morris[30] calculates the $\Delta G^{\ddagger}$ at this temperature to be 8.4 kcal mol^{-1}. Chaudret's bis-H_2 complexes, RuH_2-

Scheme 9



$(H_2)_2(PR_3)_2$, are also highly fluxional,[35] as is his Tp*RuH-$(H_2)_2$ complex, with the hydride and two η^2-H_2 residing on the same side of the complex.[224] Although crystallographic evidence is unavailable, NMR data is compatible with averaging of the H positions in solution, and cis-interactions between the hydrogen/hydride ligands appear likely here.

Last, the hydrogens in elongated H_2 complexes undergo rapid motion in a flat potential energy surface. Certain complexes such as $[Cp^*Ru(H\cdots D)(dppm)]^+$ and *trans*-$[OsX(H\cdots D)(dppe)_2]^+$ (X = H, Cl) showed unusual behavior in the temperature dependence of J_{HD}, indicative of highly delocalized bonding.[64c,g,172,225] In the OsCl complex (Scheme 9, d_{HH} = 1.22 Å, neutron diffraction), for example, J_{HD} unexpectedly varied from 13.6 to 14.5 Hz depending on both temperature (253−308 K) and solvent.[64c] Several different explanations evolved, including rapid temperature-dependent interconversion of H_2−dihydride tautomers, but these were discarded in favor of rapid motion of two hydrogen atoms in a flat potential energy surface with a shallow minimum at the neutron-diffraction determined position of 1.2 Å.[34]

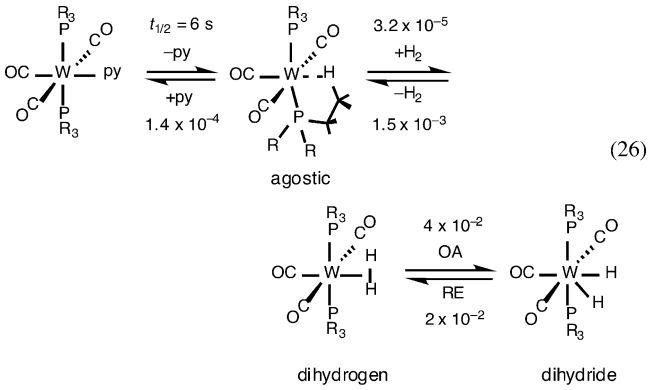
This study led to theoretical investigations that revealed the extraordinarily delocalized nature of the bonding here: d_{HH} can vary from 0.85 to 1.6 Å (with concomitant variation in d_{MH}) at a cost of only 1 kcal/mol! Subsequent NMR studies by Heinekey[172] of the HD, HT, and DT isotopomers of $[Cp^*Ru(H_2)(dppm)]^+$ show remarkably high isotope and temperature dependence of the bond distance (ranging from 1.037 Å for d_{DT} at 220 K to 1.092 Å for d_{HD} at 286 K) as determined by the various NMR *J* couplings. This is attributed to the extremely flat PES which defines the H−H and M−H interactions in this complex, which allows the zero-point energy differences among the various isotopomers to be directly reflected in d_{HH}. The striking change of d_{HH} with small changes in temperature is due to thermal population of vibrational excited states that are only slightly higher in energy than the ground state, an unprecedented situation in a readily isolable molecule. In certain cases, new vibrational modes needed to be defined involving a low-energy mode along the reaction coordinate for H_2 splitting and a high-energy mode orthogonal to this (Scheme 8, uppermost line).[69,172b,194] The very strong temperature dependence of J_{HD} for $[Ir(dmpm)Cp^*H_2]_2^+$ (dmpm = bis-(dimethylphosphino)methane) was modeled simply by the Boltzmann average of the zero-point vibrationally averaged J_{HD} of two isomers.[64g] For this complex and four others, the vibrational corrections to J_{HD} were shown to be highly significant and led to improved agreement between theory and experiment. The zero-point vibrational correction is important for all complexes. Depending on the shape of the potential energy and *J*-coupling surfaces, for some of the complexes, higher vibrationally excited states can also contribute to the vibrational corrections at temperatures above 0 K and lead to a temperature dependence.

7. Thermodynamics, Kinetics, and Isotope Effects for H_2 Binding

Solution calorimetric measurements on reactions of H_2 complexes and their precursor complexes were first carried out by Hoff and co-workers on $W(CO)_3(PCy_3)_2$ and $W(CO)_3(PCy_3)_2(H_2)$.[226] Pyridine was reacted with both of these complexes to form $W(CO)_3(PCy_3)_2(py)$. The enthalpy term for reaction with $W(CO)_3(PCy_3)_2$, $\Delta H°$, was −18.9 ± 0.4 kcal/mol in toluene, and that for reaction with the H_2 complex was −9.5 ± 0.5 kcal/mol under an H_2 atmosphere. The difference in enthalpies corresponds to the enthalpy of H_2 addition to $W(CO)_3(PCy_3)_2$, which is exothermic by 9.4 ± 0.9 kcal/mol. Note that these enthalpies are not the true binding energies because an agostic interaction is being displaced in $W(CO)_3(PCy_3)_2$ (see eq 1). Thus, the energy of the agostic interaction should be added to the measured enthalpies to obtain the true binding energies but could only be estimated to be about 10 kcal/mol.

Calculations indicate that 5 kcal mol^{-1} of the interaction is assigned to the net agostic interaction associated with moving from a nonagostic local minimum configuration of the PCy_3 ligands to the agostically bonded global minimum.[227] Therefore, the binding energy of H_2 in $W(CO)_3(PCy_3)_2(H_2)$ can best be approximated to be 20 ± 7 kcal/mol. This agrees well with the values from theoretical calculations, 17−20 kcal/mol. H_2 is often a stronger ligand than one might have imagined, much like N_2, with which it is electronically similar in terms of π-acceptor strength. However, as will be shown below, H_2 is a much better σ donor than N_2 and is *a more versatile ligand than any other weak ligand (and many strong ligands) in terms of the variety of L_nM fragments to which it binds*. H_2 can coordinate or oxidatively add to both highly electrophilic and electron-rich L_nM. Thus, H_2 can be competitive with weak to moderately strong pure σ donors such as THF, water, and dichloromethane, and mass action effects are critical, as will be discussed below. Bonding strength is highly dependent on degree of H_2 activation, and much like hydrides, elongated η^2-H_2 ligands cannot easily be displaced even by moderate donors such as acetonitrile.

The thermodynamic and kinetic reaction profile for H_2 addition to $W(CO)_3(PR_3)_2$ and equilibrium H−H cleavage has been determined for R = Cy, ^{i}Pr.[226] The results of stop-flow kinetic studies of displacement of H_2 by pyridine (py) are given in eq 26, which shows reaction rates in terms of $t_{1/2}$ (in seconds; pseudo-first-order conditions; [py] = $[H_2]$ = 0.01 M; [W] = 5 × 10^{-4} M). In the first step of the



(26)

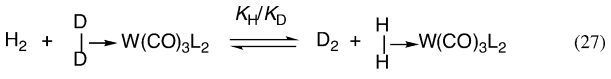
reaction sequence shown in reverse, pyridine dissociates to generate a vacant site at M on the slow time scale of seconds.

The agostic species $W(CO)_3(PCy_3)_2$ can then react with either pyridine or H_2 with $t_{1/2}$ of 140 and 32 ms, respectively, where the rate constant $k = 2.2 \times 10^6\ M^{-1}\ s^{-1}$ for H_2 reaction. If the H_2 complex is formed, it may dissociate H_2 and regenerate $W(CO)_3(PCy_3)_2$ within 1.5 ms ($k = 469\ s^{-1}$) or undergo reversible oxidative addition (OA), where $K = \sim 0.25$ (298 K), to form the dihydride tautomer with $t_{1/2} =$ 40 ms. Under these conditions, the ratio of the rate of binding of H_2 to the rate of H_2 dissociation to the rate of OA is roughly 1200:25:1. The most surprising feature here is *the rate of dissociation of H_2 is faster than the rate of OA* by at least 1 order of magnitude. Thus, H_2 binds and dissociates many times prior to OA, which has vital importance in understanding σ bond activation processes and attendant homogeneous catalytic reactions in general. The barrier to breaking the σ bond in σ complexes is the dominant (and variable) factor in reaction rates rather than the binding of the σ ligand. The complete reaction profile for H_2 addition to $W(CO)_3(PR_3)_2$ has been determined. The enthalpy of activation, $\Delta H^{\ddagger}$, for loss of coordinated H_2 is 16.9 ± 2.2 kcal/mol, which implies a barrier of 6.9 ± 3.2 kcal/mol for the forward reaction between $W(CO)_3(PCy_3)_2$ and H_2, based on $\Delta H°$ measured for the latter reaction, 10.1 kcal/mol.

Direct measurements of the rate constants and activation volumes for the binding of H_2, D_2, N_2, C_2H_4, and CH_3CN to the agostic complex $W(CO)_3(PCy_3)_2$ have recently been carried out, including both theoretical and experimental studies with time-resolved step-scan FTIR and UV−vis spectroscopy.[228] The second-order rate constant for H_2 addition ($k = 2.0 \times 10^6\ M^{-1}\ s^{-1}$) was similar to that found by Hoff above. This rate is faster than that for N_2 addition but slower than acetonitrile binding.

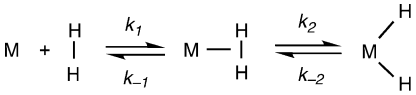
Isotope effects can be very informative in understanding chemical reactions. Both kinetic and equilibrium (or thermodynamic) effects can provide crucial information about reaction mechanisms that is unavailable from other methods. However, isotope effects often are poorly understood or may even seem paradoxical. Unlike the situation in organic chemistry, the ability of metal sites (enzymes included) to reversibly coordinate substrates prior to rate determining steps complicates the original isotope effect "rules" formulated by organic chemists. For example, the nature of equilibrium isotope effects for H_2 versus D_2 addition to metal complexes has been understood only recently. The situation can become even more complex for σ ligands that can undergo homolytic or heterolytic cleavage, either of which can also be reversible. A "normal" isotope effect occurs when the rate of reaction of an unlabeled compound is faster than that for the corresponding labeled species, i.e., $k_H/k_D > 1$. It is "inverse" for $k_H/k_D < 1$, and this terminology also applies to equilibrium isotope effects (EIEs), K_H/K_D.

The vibrational complexity of $M-H_2$ coordination (six modes) as shown in section 5 gives rise to an *inverse equilibrium isotope effect*; that is, D_2 binds slightly more strongly than H_2.[4] For example, $K_H/K_D = 0.70$ for $W(CO)_3(PCy_3)_2(H_2)$. This may be of consequence in isotopic studies of H_2 reactions, e.g., deuterium exchange reactions. Related to this is the tendency for D to concentrate in the hydride site in certain (but not all) hydride(H_2) complexes versus in η^2-H_2.[206]



(27)

There is very limited data on kinetic isotope effects (KIEs) for H_2 coordination/dissociation or cleavage equilibria as shown in eq 28. For H_2 loss from the $W(CO)_3(PCy_3)_2$



(28)

fragment, $k_{-1} = 469\ s^{-1}$ for H_2 and $267\ s^{-1}$ for D_2, giving $k^H_{-1}/k^D_{-1} = 1.7$.[226d] Applying the EIE data above and the following expressions, this gives $k^H_1/k^D_1 = 1.2$ for H_2-binding.

$$K_H/K_D = k^H_1/k^H_{-1} \times k^D_{-1}/k^D_1 \quad (29)$$

$$k^H_1/k^D_1 = K_H/K_D \times k^H_{-1}/k^D_{-1} = 0.7 \times 1.7 = 1.2 \quad (30)$$

In comparison, the reaction in eq 31 occurs 1.9 times faster for H_2 than D_2 ($10^4\ s^{-1}$).[20]

$$Cr(CO)_5(C_6H_{12}) + H_2 \rightarrow Cr(CO)_5(H_2) + C_6H_{12} \quad (31)$$

The subsequent rate of loss of H_2 ($2.5\ s^{-1}$) is five times faster than that for D_2, consistent with stronger binding of D_2 over H_2.

The directly measured kinetic isotope effects for the forward and reverse reactions for the formation of W−L (L = H_2 and D_2) from $W(CO)_3(PCy_3)_2$, obtained by the photoinduced method of Grills et al., are 1.3 ± 0.2 and 1.4 ± 0.3, respectively, in toluene at 25 °C.[228] These are slightly smaller than Hoff's value of 1.7 but probably within the respective experimental errors.

8. Biological Activation of H_2 in Hydrogenase Enzymes

8.1. Introduction and Structure and Function of Hydrogenases

The biological activation of H_2 in hydrogenase metalloenzymes is a main focus of this article and others in this Thematic Issue. They are redox enzymes that evolved billions of years ago in micro-organisms and catalyze *completely reversible* interconversion of H_2 and protons/electrons to either utilize H_2 as an energy source or dispose of excess electrons as H_2 (eq 32) at very high rates (10^4 turnovers/s).[229−245]

$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad (32)$$

This is a rare true equilibrium process much like that in the hydrogen electrode; for example, there is a fine dependence on H_2 pressure whether H_2 is produced or consumed by the micro-organism. From isotope exchange evidence such as the catalytic reaction shown in eq 33 (wherein the HD/H_2 ratio is pH-dependent), it is inferred that the H_2 molecule is split *heterolytically* on the metal center rather than homolytically.

$$H_2 + D_2O \rightleftarrows HD + HDO \quad (33)$$

Heterolysis of H_2 on transition metal complexes is a well-known process in inorganic chemistry, and catalysis and will be discussed in detail below along with other aspects of H_2 coordination on metals that form a marvelously close

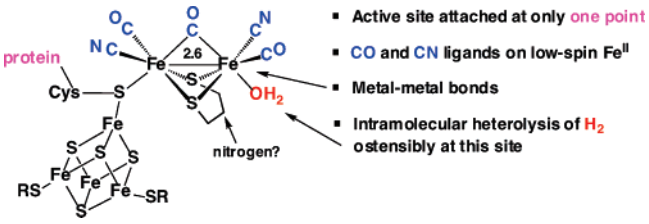
relationship to H_2 activation in Nature. Importantly, the microscopic reverse of heterolysis is formation of H_2 via, for example, protonation of a hydride ligand to form metal-coordinated H_2 that can dissociate to provide fuel for a hydrogen economy. This would be a step in the reverse of eq 32 where the electrons could come from solar photocatalytic water splitting. There is also hope that replacement of platinum in fuel cells for H_2 oxidation could be achieved using base metal catalysts (iron, nickel, etc.) modeled on the active sites in H_2ases. Since the literature on hydrogenases and modeling studies of their active sites is vast and will be addressed by other authors in this volume, only a brief introduction will be given.

Three basic types of H_2ase active sites have been identified. The most prevalent contain Ni in combination with Fe, but a select few contain only Fe and are classified as iron-only [FeFe] H_2ases. A third class was originally thought to be metal free but has recently been identified to contain iron. Although the active site is deeply buried (e.g. ~30 Å from the protein surface), channels generally exist for both proton and H_2 diffusion away from it. Amino acid residues carry protons away, and studies of xenon binding identify hydrophobic channels for H_2 gas ingress to or egress from the active site.[246] The [NiFe] systems generally function to consume H_2 and are less active, but more resistant to oxidation, than the anaerobic [Fe] enzymes, which usually produce H_2. X-ray crystallography of the [FeFe] system indicates that there is an accessible site on Fe for H_2 binding and cleavage, but the activation site on the [NiFe] systems is not clearly established. Hydride ligands, both bridging and terminally bound, are likely to be transiently involved at some stage in the activation processes on both types of enzymes. The utilization of a bimetallic site in H_2ases is intriguing because H_2 is easily activated on a large array of mononuclear organometallic complexes without need for a second M. The M−M bonds (Ni−Fe and Fe−Fe) present in the H_2ases would then be expected to serve a useful function in Nature, perhaps as the initial site of metal protonation. Electron transfer to an attached Fe−S cubane redox-active cluster could also be facilitated. All these aspects that relate to organometallic chemistry will be covered below.

Nature has evolved extremely efficient ways to use the more abundant first-row metals such as Fe and Ni in metalloenzymes rather than the precious metals widely used as industrial catalysts. Most notably, the active sites of H_2ases *feature the first biological systems with CO and cyanide ligands as intrinsic constituents*, which are coordinated to dinuclear Fe−Fe bonded centers, such as shown in Scheme 10 for an iron-only H_2ase.

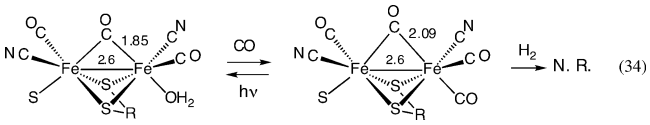
Although infrared spectroscopy provided the first evidence that CO and CN are present in H_2ases (see below), the structure of the active site determined by protein crystallography of *C. Pasteurianum* (1.8 Å resolution)[233] by Peters in 1998 captured the attention of organometallic chemists in startling fashion. This structure and the related structure of *Desulfovibrio desulfuricans* (1.6 Å)[247] pointed to a remarkable similarity between H_2 activation on organometallic centers and biological systems. Five CO and/or CN ligands are identified to be bound to a dinuclear iron center in *C. Pasteurianum*, including one in a *bridging* position. The bridging diatomic ligand is undoubtedly CO and not CN, which is not known to bridge through carbon only. Bridging CO ligands are common in organometallic chemistry and are often found in polynuclear clusters. An electron-

Scheme 10



transfer Fe_4S_4 "cubane" cluster is directly attached to Fe via a cysteine thiol bridge as shown in Scheme 10, which represents the most probable structure of the active site with one CN and CO on each Fe. An Fe−Fe bond (2.6 Å) is present in both *C. Pasteurianum* and *D. desulfuricans* that is typical of dithio-bridged organometallic Fe−Fe systems. It is important to note here that the dinuclear Fe core contains mostly *exogenous* ligands with the only attachment to the protein being through the cysteinyl sulfur bridging to the Fe_4S_4 cluster, i.e., a nearly independent organometallic complex within a protein pocket. The cyanide ligands probably engage in hydrogen bonding to the protein, which may be an important function for this biologically unprecedented moiety. Also noteworthy is the dithiolate ligand linked by a three-atom bridge, which was later speculated (and supported calculationally) to contain a nitrogen as the middle atom (as an amine group) to aid in the heterolysis of H_2.[248] Such a precisely positioned pendant base would serve as a highly efficient proton relay to shuttle protons from the active site to exit channels in the protein, minimizing reorganization energies associated with, e.g., the approach of an external base for proton transfer. DuBois has extensively studied inorganic model systems with such pendant amines that heterolyze H_2, as will be shown below (e.g., see Scheme 13).

Mossbauer spectroscopy indicated that the Fe oxidation state is 2+ in the reduced form but $Fe^{II}Fe^{III}$ in the oxidized form, but the states are not well established and $Fe^{I}Fe^{II}$ is equally probable.[249] Although, as will be shown, CO ligands are crucial in the active site, additional CO is a known inhibitor of H_2 activation by the enzyme and irreversibly binds to the site occupied by the water molecule (eq 34**)**, as shown crystallographically.[250] This mimics the behavior in

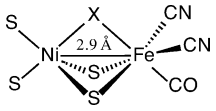


(34)

organometallic systems where CO is well established to be a much stronger ligand than either H_2O or H_2. Furthermore, X-ray diffraction studies of a single crystal of the CO adduct after photolysis show dissociation of the CO and replacement by H_2O. The Fe−C distance to the μ-CO is significantly elongated when CO is bound trans to it, reflecting the strong competition for obtaining M→CO backdonation engendered between mutually trans π-accepting CO ligands. The terminal CO trans to the μ-CO is thus more labile than the other CO ligands, which are trans to electron-donating sulfur donors that enhance π-electron acceptance by CO. This leads to stronger Fe−CO bonding, again a characteristic feature in organometallic chemical bonding. The electronic influence of a ligand on the ligand trans to it is normally quite powerful ("trans influence") and is a major tenet in all of metal coordination chemistry (see section 3.2). These and other

important inorganic chemistry principles will be discussed below in relation to the structure and function of H_2ases.

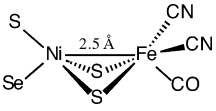
The [NiFe] H_2ases contain at least one NiFe-containing cluster considered as the probable H_2 activation site.[251] The enzyme's metal center has several states in the activation process and has received extensive theoretical analysis. The crystal structure[251a] of the "unready" state of *Desulfovibrio gigas* shows a metal−metal bond (2.9 Å) as in the Fe−Fe H_2ase in Scheme 10 and two unlinked bridging thiolates.



The Ni center contains only thiolate ligands, and the cubane cluster is missing. Rather than a bridging CO as in Scheme 10, a bridging X (H_2O, OH^-, or O^{2-}) is present. Upon further hydrogen activation or reductive titration, the catalytically active Ni−C form binds H_2 as either H_2 or hydride ligands. CO is a competitive inhibitor of H_2 binding, forming a bound Ni−CO complex in *D. Vulgaris* that was observed crystallographically,[251e] which supports the role of Ni as the initial site of H_2 activation.

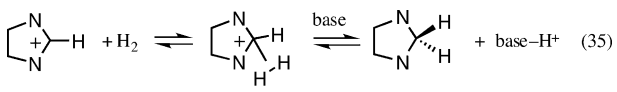
The early crystallographic data for the active site of *D. gigas* in 1995 and 1996 had revealed only the presence of three exogenous diatomic ligands bound to Fe, and the low resolution (2.54 Å) was incapable of identification as CO and CN. The first evidence for these ligands occurring as prosthetic groups in H_2ases (and indeed any biological molecule) was provided by Bagley, Albracht, and Woodruff in IR studies of *Chromatium vinosum* that showed three high-frequency IR bands at 1944, 2081, and 2093 cm^{-1}. The lower frequency band was assigned to CO, and the higher bands were suspected to be due to another multiple-bonded diatomic such as CN.[252,253] Later, Happe et al. identified the ligands as two CN and one CO after elegant investigation of band shifts and intensities in ^{13}C- and ^{15}N-enriched samples of *C. vinosum*.[254] When Woodruff, a colleague of mine at Los Alamos National Laboratory, queried me about the possibility that the bands could be due to CO, it made perfect sense because such strong acceptor ligands were present in $W(CO)_3(PR_3)_2(H_2)$ and would be expected to favor reversible molecular H_2 coordination versus hydride binding. Irreversible formation of a dihydride complex would shut down a catalytic process here.

The oxidation/spin states of Ni are controversial, but almost all forms of H_2ases contain low-spin Fe^{II}, which is in the d^6 electronic state nearly always favored for H_2 binding in organometallic systems. Biologically rare Fe^{I} is also possible in some of the redox states of these dinuclear M−M bonded systems. The CO and CN ligands favor both low oxidation and low spin states, which will be shown to be crucial in these systems. The crystal structure (2.15 Å resolution) of a *reduced* [NiFeSe] H_2ase from *D. Baculatum* provides insight into the actual catalytically active Ni−C state.[255] The overall architecture of the active site is very similar to that in *D. gigas* but with Se replacing one S.



Significantly, however, the putative oxo ligand X present in the unready oxidized form is absent, and the Fe−Ni distance is 0.4 Å shorter than that in the above oxidized *D. gigas* enzyme. The structure suggests that the closely spaced metals may now be bridged by a hydride, which cannot be seen by X-ray but is supported by theoretical calculations and ENDOR spectroscopy.[251c] As will be discussed below, metal−metal bonds in organometallic complexes are quite basic and can readily be protonated to form a bridging hydride complex. This could be the first step in the formation of H_2 in H_2ases and may rationalize why two metal atoms are utilized when one would seem to suffice.

Remarkably, a H_2ase (Hmd) found in methanogenic archaea, *Methanobacterium Thermoautotrophicum*, was initially thought to contain no transition metals at all.[243] It catalyzes the reduction of a pterin compound, methenyl−H_4MPT^+, by H_2 and also produces a proton, as a step in methane formation from CO_2 and H_2. An electrophilic site



(35)

where positive charge is delocalized among conjugated N−C−N atoms as modeled by the formamidinium ion in eq 35 appeared to be critical to H_2 activation, as shown by ab initio studies.[256,257] This mechanism is analogous to the reverse of that for the reversible formation of carbocations and H_2 from alkanes in superacid media, e.g., the isobutane conversion studied by Olah.[258] However, recent X-ray absorption spectroscopy and single crystal diffraction studies revealed that a mononuclear iron site is present in the enzyme and octahedrally ligated by two *cis*-CO molecules, a cysteic sulfur atom, a pyridone nitrogen atom originating from the organic skeleton of the Hmd cofactor, an unknown ligand trans to a CO, and a hydrogen-bonded water trans to the pyridone.[259] The mechanism for conversion of the pterin, methenyl−H_4MPT^+, to methylene−H_4MPT, is now believed to involve a ternary complex catalytic mechanism requiring the presence of all three components (pterin, H_2, and Hmd) for enzymatic activity to occur. Thus, the iron center must be involved in the conversion, which, as for other H_2ases, undoubtedly involves heterolysis of H_2 (eq 36).

$$\mathrm{Fe(SCys)(CO)_2(pyridone)-H_2-methenyl-H_4MPT^+ \rightarrow methylene-H_4MPT + H^+} \quad (36)$$

It is important to note that Hmd is phylogenetically unrelated to the other H_2ases, and the activity of this enzyme is not reversible and does not function to produce H_2. Although it now appears that a metal center is involved in the above activation of H_2, H_2 was recently reported to split by nucleophilic activation at a single carbon center in a carbene, R_2C, although, in this case, the hydrogens become irreversibly bound to the carbon to form R_2CH_2.[260]

8.2. Dihydrogen Coordination and Organometallic Chemistry Relevant to H_2ases

8.2.1. Introduction

Formation of stable iron hydrides on more nucleophilic (electron-rich) metal centers than those found in hydrogenases with CO ligands would inhibit or at least slow down function. Nature has thus been opportunistic in designing an electronically finely tuned organometallic site for elec-

trophilic H_2 activation, beating organometallic chemists to the punch 2−4 billion years ago, when microorganisms with these metalloenzymes first appeared. However, the active sites are deceptively complex: synthesis of a complete structural mimic identical to that in Scheme 10 has eluded the intense efforts of inorganic chemists over the past 8 years since the structure was reported. Organometallic models with most of the pieces have been assembled and have been valuable in understanding the structure and functions of H_2-ases. Well-established principles of inorganic, organometallic, and, more specifically, dihydrogen coordination chemistry all apply here, as will be discussed in detail in this section.

Recent developments in metalloenzyme and organometallic chemistry point to a growing link between these seemingly incongruent fields. The chemistry of organometallic compounds (standardly defined as containing one or more metal−carbon bonds[153]) is almost always carried out in nonaqueous media in the absence of oxygen because organometallic compounds often rapidly decompose in the presence of air and/or water. The latter is an alien concept in most life systems, although the active sites in some H_2-ases that are present in anaerobic organisms may indeed be sensitive to oxygen but are protected in some way. Organometallic transition metal complexes typically contain abiological and often highly toxic ligands such as organophosphines and carbon monoxide that would appear to be abhorred by Nature. These notions of incompatibility were thoroughly dispelled by the relatively recent spectacular discovery of not only CO but also cyanide ligands bound to dinuclear Fe−Ni and Fe−Fe sites in H_2ases discussed above. In these often anaerobic life processes it is now abundantly clear that Nature has carried out sophisticated organometallic chemistry at the transition metal cores of hydrogenases. It is indeed humbling to consider that Nature evolved structures and methodologies eons ago that have taken the world's premier inorganic chemists over a century to independently discover and understand in their own field. This may also be said about other life sustaining biological molecules such as DNA and hemoglobin, but the organometallic features found in the dimetallo core of H_2ases had always been relegated to the domain of practiced transition metal chemists and were quite unexpected to see in Nature.

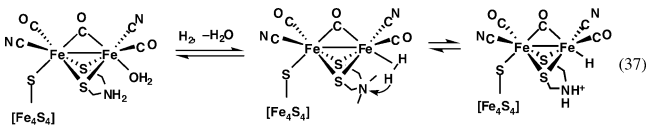
This section will then also discuss the organometallic chemistry performed by the active site of H_2ases, both from a historical perspective as well as highlighting current attempts to understand their structure and function via synthetic models and theory. Questions will be addressed such as why are normally poisonous CO and CN molecules used by H_2ases, the first example of such ligands in naturally occurring biological molecules. Does molecular binding of H_2 to iron occur (at least transiently) as in known transition metal dihydrogen complexes, and can such coordination be observed? The answers will clearly be important in the future design of biomimetic catalysts for hydrogen production. Much is known about the activation of the strong H−H bond toward cleavage on organometallic complexes. Both *homolytic* cleavage of H_2 to metal dihydrides (oxidative addition) and *heterolytic* cleavage of the H−H bond to a metal hydride plus a proton have long been known. Inorganic chemists have established key tenets here, e.g., molecular binding and heterolysis of H_2 are favored by ancillary ligands such as CO. However, it is now clear that Nature has utilized the same strategies in hydrogen activation by H_2ases far longer!

Importantly, the lessons learned from H_2ases and related biological systems may be technologically critical to our future energy security because these utilize base metals (principally iron) to catalyze hydrogen production at extraordinarily high rates. One of the key challenges in improving chemical processing is the use of nonprecious metal catalysts in aqueous media, i.e., production of fuels, plastics, and consumer products by employing low cost abundant materials in environmentally benign "green chemistry." Biomimetic production of hydrogen from splitting of water[261] is of particularly high interest in this regard, especially if it can be fueled by natural resources, e.g., solar energy using direct chemical coupling, as in biological photosystems.[235,262−264] Nature solved the problem of efficient capture, transport, and storage billions of years ago, through the development of photosynthetic systems. Photosynthesis converts solar energy into high-energy chemical bonds by splitting water to form ATP, NADPH (equivalent to hydrogen), and O_2. Water oxidation is catalyzed by the oxygen-evolving complex of photosystem II. Hydrogenases from various microorganisms catalyze the production of hydrogen from protons and electrons at extraordinarily high rates using nonprecious metals, principally iron. Despite decades of effort, scientists have not yet come close to mimicking these natural systems. Two major scientific barriers persist: developing efficient (molecular) catalysts for water oxidation and H_2 production, and coupling these reactions to a photochemical energy source. Knowledge about hydrogen activation on transition metals, e.g., splitting of the H−H bond both homolytically and heterolytically, will be crucial in these pursuits, since the *microscopic reverse* is H−H bond *formation* and elimination as hydrogen gas, i.e., production of hydrogen fuel.

Knowledge about the key bonding concepts in organometallic chemistry also aids in understanding the structure and function of H_2ases. The Chatt−Dewar−Duncanson model originally developed for the bonding of the carbon−carbon double bond in olefins to metals is one of the cornerstones of organometallic chemistry.[145,146,153] The olefin donates π electrons to vacant metal d orbitals and in turn receives "backdonation" (also termed backbonding) from filled metal orbitals into antibonding π^* orbitals of the multiple bond (section 3.1). Backdonation explained the relatively high metal−ligand (M−L) bond strength of ethylene and later on the even higher M−L bonding strengths of multiply bonded molecules such as CO and CN now found in the active sites of H_2ases. Although the latter are end-on bonded through carbon rather than side-on bonded as in ethylene coordination, M$\rightarrow\pi^*$ backbonding to these powerful π acceptors is very strong. Indeed, CO has been characterized to be a "universal ligand" to lower-valent metal centers,[161] and metal carbonyl complexes such as $Fe(CO)_5$ and $Ni(CO)_4$ were among the earliest discovered organometallic compounds. As discussed in section 3.2, backdonation also greatly enhances the bonding energy of molecular H_2 to metals, where, in this case, the metal donates electrons into the H−H σ^* orbital.

Organometallic linkages were first recognized in biology in the metal−alkyl groups in cobalamins in the early 1960s, giving birth to bioorganometallic chemistry.[153] However, there have not been many examples of M−C bonds in Nature and certainly none as sophisticated as those in H_2ases. Biological activation and production of small molecules containing very strong "inert" σ-bonds such as H_2 by H_2-ases and CH_4 by methane mono-oxygenases have been known for many decades, but the structure and mechanisms had remained mysteries. Remarkably, the unexpected ability of dihydrogen (H_2) molecules to bind to metals to form stable

molecular hydrogen complexes (adducts analogous to hemoglobin−O_2) was not recognized until the early 1980s. As described above, the discovery of the first H_2 complex $W(CO)_3(PR_3)_2(H_2)$ led to a new field of chemistry involving nonclassical three-center two-electron interaction of the H−H bond with a metal center with some similarity to olefin π coordination. As originally noted by Crabtree,[265] several properties of the H_2 ligand, such as its greatly enhanced acidity compared to elemental H_2 (see below) and its ability to compete with N_2 ligands, clearly must be considered in relation to the structure and function of enzymes such as H_2ases and N_2ases. For example, these enzymes catalyze H/D exchange between H_2O and D_2 (eq 33), which an acidic H_2 ligand can easily promote via heterolytic cleavage of the coordinated H−H bond (eq 37), the key step in biological H_2 activation, as will be discussed below. It is believed that

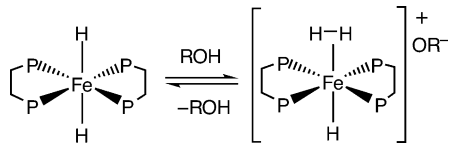


(37)

a proton may initially transfer within the active site to either a thiolate sulfur or a basic group on the thiolate bridge in the Fe−Fe H_2ases. In order for this to occur, H_2 must ligate competitively with water as well as atmospheric N_2, and this is the case in organometallic systems, as will be shown below. The electronics at the metal center M must also be just right: H_2 is a better ligand[98] than N_2 on electrophilic M, but if M is too electrophilic, water may bind more strongly than H_2. An organometallic biological active site with a mix of strong acceptor and donor ligands such as CO and CN is advantageous here and also for heterolytic splitting of H_2.

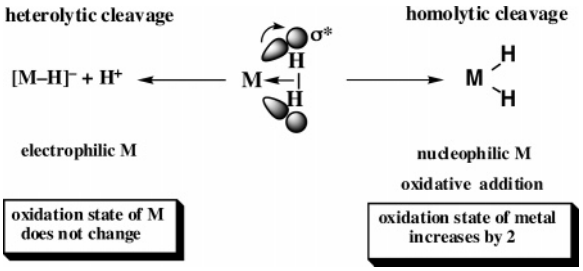
8.2.2. Formation of H_2 Ligands by Protonation and Factors That Control H_2 Binding and Activation in H_2ases

As discussed in section 2.1.4, a common method to form H_2 ligands is protonation of a metal hydride complex. Importantly, double protonation of a neutral complex can lead to formation of H_2 gas via an unstable H_2 complex that releases H_2 as in eq 12. As will be discussed below in section 8.2.11, this is a likely mechanism for formation of H_2 in H_2ases, although here this would occur at a dinuclear metal center. Iron hydride complexes are well-known to be protonated by acids to form dihydrogen complexes.[202] In one case, even very weakly acidic alcohols were found to be capable of reversibly protonating a hydride.[202b] This demonstrates that protons in biological systems should be quite capable of protonating the metallo site of H_2ases to form H_2 ligands that can dissociate H_2 and in a reverse process bind and split H_2.



Transition metals are unique in stabilizing H_2 complexes by M(dπ)→H_2(σ*) backdonation (section 3.2), and the degree of backdonation is critical to the activation of H_2 toward homolytic cleavage. Increasing the electronic population of H_2(σ*) via backdonation causes the H−H bond to elongate and eventually rupture, and examples of complexes with H−H distance (d_{HH}) varying from 0.82 to 1.6 Å have been isolated and characterized by crystallography, NMR, and other means (Scheme 4). Several factors can stabilize molecular H_2 binding versus oxidative addition to a stable dihydride complex that would be undesirable in the function of H_2ases. These are (1) electron-withdrawing ancillary ligands such as CO, particularly trans to the σ ligand, (2) positively charged metal centers, i.e., cationic rather than neutral complexes, (3) less electron-rich first row metals such as iron (versus, e.g., Ru), and (4) orbital hybridization, i.e., octahedral coordination and a d^6 electronic configuration. It is thus significant that the active sites of H_2ases have most all of these attributes (factor 2 may or may not be relevant or necessary here). *The nature of the ligand trans to H_2 is most often an important factor in determining whether H_2 binds molecularly and is heterolytically cleaved (versus homolytically cleaved to a dihydride or an elongated H_2 complex that is essentially a dihydride).*[5,6,362] The *trans influence*, i.e. the electronic influence of the ligand trans to the ligand of interest (section 3.2), is crucial here, as it is in all of coordination chemistry. Complexes such as $W(CO)_3(PR_3)_2(H_2)$ and $[FeH(H_2)(dppe)_2]^+$ have either the strong acceptor CO or the high trans-effect hydride ligand positioned trans to H_2. Their H−H distances are <0.9 Å, indicative of true H_2 complexes that characteristically have labile, reversibly bound H_2, properties that are crucial to the rapid binding and loss of H_2 in enzymatic catalysis. The CO ligands, when either trans or cis to H_2, greatly reduce backbonding and stabilize molecular H_2 binding. This clearly must be their function in H_2ases, since there would seem to be no other reason for Nature to employ this toxic molecule. Importantly, d_{HH} is normally <0.9 Å (thus, H_2 is quite labile) in complexes with CO trans to H_2, regardless of ligand set or overall charge. Conversely, complexes with mild σ-donor ligands such as H_2O trans to H_2 or *π-donors* such as Cl have elongated H−H bonds (0.96−1.34 Å) because of increased backbonding. If the trans ligand is a strong σ-donor such as hydride, there is a powerful trans labilizing effect that reduces donation from H_2, which once again weakens M−H_2 binding and contracts d_{HH} as shown in Scheme 5. The important concept is that *the influence of the trans ligand on H_2 activation is generally greater than that of the cis ligands*. This large dependence on fragment stereochemistry can be critical in understanding how hydrogen is activated in both inorganic and biological systems. In H_2ases, the unusual CN ligand is not a strong acceptor and is an excellent electron donor that serves to preserve a low-spin state for the active site. Thus, it must be concluded that CO is the crucial ligand in controlling the electronics of the system regarding increasing the electrophilicity of the binding site to enhance both reversible molecular binding and heterolytic cleavage of H_2 (see below). Remarkably, highly electrophilic dicationic fragments such as $[Fe(CO)(Ph_2PC_2H_4PPh_2)_2]^{2+}$ can still bind H_2 trans to CO in a stable fashion via the enhanced σ donation from H_2, offsetting the greatly reduced backdonation.[266] This must be the case in the [Fe] H_2ases in which both irons are surrounded by CO, including in one case a bridging CO. This would disfavor OA of H_2 to give nonlabile metal hydrides and increase the acidity of iron-bound H_2 toward heterolysis. The IR value of 1945 cm^{-1} believed to be due to Fe-bound CO in the Ni−Fe H_2ase *C. vinosum* is quite high and characteristic of a fairly electrophilic metal center. An important experimental finding is that IR spectral changes occur when the H_2 atmosphere over the fully activated enzyme is replaced by CO gas. The ν_{CO} for the CO ligand that binds to the Ni, which is the apparent site of H_2 activation, is even higher, 2060 cm^{-1},[251e,253] and this

Scheme 11. Dual Pathways for σ Bond Cleavage



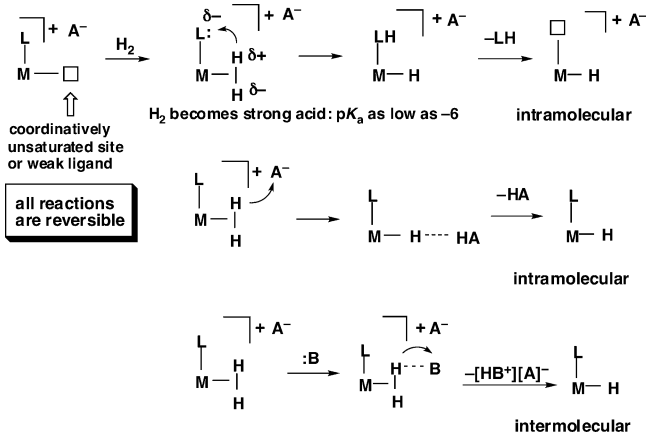
indicates a very electrophilic site. This site is possibly more electron-poor than those in organometallic carbonyl complexes such as $Fe(CO)_5$ (ν_{CO} = 2013 cm^{-1}), and as will be discussed below, the acidity of H_2 bound to it could far exceed normal physiological pH values.

8.2.3. Heterolytic Cleavage and Acidity of H_2 Coordinated to Metal Complexes

The very unusual (for biology) ligand set around Fe in H_2ases bears resemblance to many organometallic octahedral fragments that bind and activate hydrogen toward cleavage. The anionic cyanide complex, $Co(CN)_5^{3-}$, was one of the first organometallic complexes found to homolytically cleave H_2, forming the monohydride $CoH(CN)_5^{3-}$, a rare example of the hydrogens transferring to two metals. Such metal centers are very electron-rich because of the strongly donating CN ligands, which favors oxidative addition of H_2 to form hydride complexes, most often dihydrides, as in Scheme 11. The latter are very common in inorganic chemistry, especially as industrial catalysts for homogeneous hydrogenation reactions.

Significantly, the oxidation state of the metal increases by two here (one in the less common case of the Co complex), and the stereochemistry around the metal changes because of the increase in the number of ligands. An H_2 ligand occupies only one coordination site in, e.g., a 6-coordinate complex but cleaves to form two hydrides, giving a 7-coordinate complex with a different arrangement of ligands where hydrides may even be distal to each other, as in eqs 15 and 16. Large oxidation state changes and drastic stereochemical rearrangements might be expected to diminish the extremely rapid rates of H_2 splitting/formation in hydrogenases. Even more importantly, in hydride complexes the hydride ligands are tightly bound and difficult to release as H_2, clearly not an advantageous property for reversible uptake and release of hydrogen in either organometallic chemistry or biology. A second pathway involving *heterolytic cleavage*, wherein the H−H bond is effectively broken into H^+ and H^- fragments, would be expected to enhance facile H_2 catalytic activation (Scheme 11).[30,31,46,267,268] This is one of the oldest, most significant, and widespread reactions of coordinated H_2, and importantly, here *neither the metal oxidation state nor the coordination number changes*. The earliest homogeneous (solution-phase) catalytic hydrogenation processes go back to 1938 and indeed involved heterolysis of H_2 as the key step.[267,269] In such systems, the metal center is generally electron-poor (electrophilic), which can be accomplished by ligating π-acceptor groups such as CO to the metal and/or placing a positive charge on the complex (cationic complex). There are two pathways for heterolytic cleavage on H_2 complexes, which are most often generated either by addition of H_2 gas to unsaturated precursors (section 2.1.1) or by protonation of a M−H bond (section 2.1.4). A

Scheme 12



proton can split off from the H_2 ligand and either migrate to an external Lewis base (intermolecular) or directly transfer to a coligand or anion (intramolecular) as in Scheme 12. On electron-poor cationic complexes, the H_2 ligand is highly acidic, i.e., polarized toward $H^{\delta+}-H^{\delta-}$, where the highly mobile H^+ readily transfers. Free H_2 is an extremely weak acid with a pK_a estimated to be 49 in THF, but when H_2 is bound to a highly electrophilic cationic M, *the acidity of H_2 gas can be increased spectacularly, up to 55 orders of magnitude*.[30,31,42,46,268] The pK_a of H_2 can become as low as −6, and the acidity of η^2-H_2 is as strong as that of sulfuric or triflic acid. *Intramolecular* heterolysis involves proton transfer to a cis ligand L (e.g., H or Cl) or to the counteranion (A^-) of a cationic complex. This reaction is especially facilitated if the cis ligand is Lewis basic, e.g., an amine or thiolate ligand. The basic group does not have to attached directly to the metal but can be a component of a ligand positioned near to the metal, as will be shown in section 8.2.5. This is the process most relevant to the heterolytic cleavage of H_2 on H_2ases. *Intermolecular* heterolysis involves protonation of an external base B to give a metal hydride (H^- fragment) and the conjugate acid of the base, HB^+, i.e. the reverse of the protonation reaction (eq 5) used to synthesize H_2 complexes. It is critical to note that all reactions in Scheme 12 can be reversible, which is an important feature in designing molecular catalysts for hydrogen production by, for example, mimicking biological H_2 activation. As pointed out by DuBois, the heterolytic cleavage of H_2 should be at or near equilibrium to avoid high-energy intermediates.[270] This implies the hydride (H^-) acceptor ability of the metal and the proton (H^+) acceptor ability of the base (either external or internal) must be energetically matched to provide enough energy to drive the heterolysis of H_2, but this reaction should not be strongly exergonic.

Positive charge and electron-withdrawing coligands such as CO, particularly when trans to H_2, greatly increase the acidity. Electron deficient cationic and dicationic H_2 complexes with strong short H−H bonds (<0.9 Å) and weakly bound H_2, such as $[Cp^*Re(H_2)(CO)(NO)]^+$ and $[Re(H_2)(CO)_4(PR_3)]^+$, are among the most acidic complexes, with pK_a values determined to be as low as −2 (Table 4). Note that the value for the *neutral* Ru complex is very much higher, 36 (as measured in THF). The highly acidic complexes typically have relatively high values of J_{HD} for their η^2-HD isotopomers, although pK_a values do not correlate well with J_{HD} except within specific complex types such as $[FeH(H_2)(depe)_2]^+$ versus $[FeH(H_2)(dppe)_2]^+$. A good example of the effect of positive charge is $W(CO)_3(PCy_3)_2$-

Table 4. Reported pK_a Values (Pseudo-aqueous Scale) and Corresponding J_{HD} of Selected H_2 Complexes, Emphasizing Highly Acidic Species

complex[a]	pK_a	J_{HD}, Hz	ref
$[Cp^*Re(H_2)(CO)(NO)]^+$	−2	27	103
$[Re(H_2)(CO)_4(PPh_3)]^+$	−2 to 1	33.9	74, 272
$[FeH(H_2)(depe)_2]^+$	∼16	28	364
$[FeH(H_2)(dppe)_2]^+$	12.1	30	364
$[FeH(H_2)(dtfpe)_2]^+$	7.8	32	364
$RuH_2(H_2)(PPh_3)_3$	36		268b[b]
$[CpRu(H_2)(dmpe)]^+$	10.1	22.1	271
$[CpRu(H)_2(dppe)]^+$	7.5	dihydride tautomer	*c*
$[CpRu(H_2)(dppe)]^+$	7.0	24.9	*c*
$[CpRu(H_2)(dfepe)]^+$	−5	29.1	276
$[OsCl(H_2)(dppe)_2]^+$	7.4	13.9	64c
$[Os(CH_3CN)(H_2)(dppe)_2]^{2+}$	−2	21.4	31
$[Os(CO)(H_2)(dppp)_2]^{2+}$	−5.7	32.0	*d*

[a] depe = 1,2-bis(diethylphosphino)ethane; dppe = 1,2-bis(diphenylphosphino)ethane; 1,2-bis(diphenylphosphino)ethane; dfepe = $(C_2F_5)_2PC_2H_4P(C_2F_5)_2$; dtfpe = 1,2-bis[di-(*p*-trifluoromethylphenyl)-phosphino]ethane; dppp = 1,2-bis(diphenylphosphino)propane; dmpe= 1,2-bis(dimethylphosphino)ethane. [b] Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471. [c] Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. [d] Rocchini, E.; Mezzetti, A.; Ruegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711.

(H_2), which can be deprotonated only by strong bases such as alkoxides and KH but can be electrochemically oxidized to $[W(CO)_3(PCy_3)_2(H_2)]^+$ that now is acidic enough to protonate weakly basic THF solvent.[181] Crabtree first demonstrated heterolysis of η^2-H_2 as in Scheme 12 by isotopic labeling studies to show that H_2 in $[IrH(H_2)(benzoquinolinate)(PPh_3)_2]^+$ is deprotonated by LiR in preference to the hydride.[92] A milder base, NEt_3, was shown by Chinn and Heinekey[271] to specifically deprotonate the η^2-H_2 tautomer in the equilibrium mixture (84:16 ratio of η^2-H_2 to dihydride form) in eq 38:

$$[CpRuH_2(dmpe)]^+ \rightleftharpoons [CpRu(H_2)(dmpe)]^+ \overset{NEt_3}{\rightleftharpoons} CpRuH(dmpe) + [NEt_3H]^+ \quad (38)$$

This indicated a pK_a of 17.6 in CH_3CN, and, more importantly, NMR evidence showed that the H_2 tautomer is deprotonated more rapidly than the dihydride form, which showed a *greater kinetic acidity of the H_2 ligand* (the dihydride is actually a slightly stronger acid with a pK_a of 16.8). The main reason H_2 complexes have greater kinetic acidity than classical hydrides of similar structure is that deprotonation of an H_2 complex involves *no change in coordination number*. Also, the η^2-H_2 can become polarized toward $H^{\delta-}-H^{\delta+}$, and H^+ is exceedingly mobile, especially for cationic complexes.

8.2.4. Intermolecular Heterolytic Cleavage of Coordinated H_2

One of the best examples of *intermolecular* heterolytic cleavage of η^2-H_2 is the protonation of ethers by extremely electrophilic cationic H_2 complexes containing electron-withdrawing ligands such as CO (eqs 39 and 40).[74,103,272]

$$M-H + H^+ \rightarrow [M-H_2]^+ \overset{Et_2O}{\longrightarrow} [M_2(\mu\text{-}H)]^+ + Et_2OH^+ + H_2 \quad (39)$$

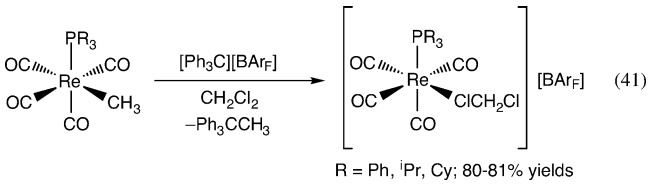
$$M = Cp^*Ru(CO)_2, Cp^*Re(CO)(NO)$$

$$[M'-CH_2Cl_2]^+ + H_2 \rightarrow [M'-H_2]^+ \overset{Pr_2O}{\longrightarrow} [M'_2(\mu\text{-}H)]^+ + Pr_2OH^+ + H_2 \quad (40)$$

$$M' = cis\text{-}Re(CO)_4(PR_3)$$

In all cases, a hydride-bridged complex is the product even though the mononuclear hydride M−H is known in eq 39 and is used to generate the thermally unstable H_2 complex by protonation with HBF_4. A mononuclear hydride complex is not observed by NMR in eq 40, indicating a strong thermodynamic preference for the μ-H dimer. Interestingly, hydrogenase enzymes heterolytically activate H_2 and have dinuclear active sites that are capable of forming bridging hydrides by reversible protonation of M−M bonds. The pK_a of bound H_2 in eqs 39 and 40 can be estimated to be near −2 (the pK_a of Et_2OH^+ is −2.4 in sulfuric acid[273]), although the irreversible formation of the μ-H product provides a driving force for deprotonation that could raise the effective pK_a of the H_2 complex a few units. A notable difference between eqs 39 and 40 is that $[Re(H_2)(CO)_4(PR_3)]^+$ is *synthesized directly from reaction of H_2* with an isolable precursor,[74] while the Cp complexes are formed by protonation of a hydride with a strong acid.[103] Only a few other examples of highly acidic η^2-H_2 directly generated from H_2 gas are known.[130,274−277]

A crucial initial step in heterolysis of σ bonds is generation of a complex with either a coordinatively unsaturated site or more commonly a site occupied by a weak, easily displaceable ligand such as a solvent molecule. Dichloromethane is very convenient here because it is an excellent solvent for cationic complexes and forms isolable complexes despite the high lability of the CH_2Cl_2 ligand. A good synthetic route to CH_2Cl_2 complexes is abstraction of a methyl ligand using a trityl salt with a low coordinating anion such as BAr_f ($B[3,5\text{-}C_6H_3(CF_3)_2]_4^-$). For example, treatment of [*cis*-Re(Me)(CO)$_4$(PR$_3$)] (R = Ph, Cy) with $[Ph_3C][BAr_f]$ in CH_2Cl_2 solution produced $[cis\text{-}Re(CO)_4(PR_3)(CH_2Cl_2)][BAr_f]$, where the CH_2Cl_2 is bound via a lone electron pair on Cl.[74] The fact that CH_2Cl_2 (as well as Et_2O) complexes

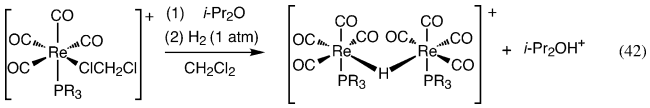


R = Ph, ^{i}Pr, Cy; 80-81% yields (41)

are isolable is attributed to the strong electrophilicity of the 16e $[Re(CO)_4(PR_3)]^+$ fragment. The importance of a non-interacting counterion for weak ligand binding, such as dichloromethane in this and other highly electrophilic systems, is reflected by the isolation of species such as *cis*-Re(CO)$_4$(PPh$_3$)(FBF$_3$) and *cis*-Re(CO)$_4$(PPh$_3$)(OTeF$_5$) where the *anion* is coordinated rather than, for example, CH_2Cl_2.[278−280] Although dichloromethane has been traditionally thought of as a noncoordinating solvent, the isolation of stable CH_2Cl_2 complexes has been a recurring theme in recent literature,[101,281−286] particularly for extremely electron deficient cationic metal centers with low-interacting anions such as BAr_f. Another strategy for generating unsaturated sites for H_2 addition is abstraction of a chloride ligand by silyl cations.[64f,201] Reaction of $[Cp^*Ir(P-P)Cl][B(C_6F_5)_4]$ (P−P = diphosphine) with $[Et_3Si][B(C_6F_5)_4]$ in methylene chloride

under 1 atm of hydrogen gas afforded the dicationic compressed dihydride complex $[Cp^*Ir(P-P)H_2][B(C_6F_5)_4]_2$.[64f]

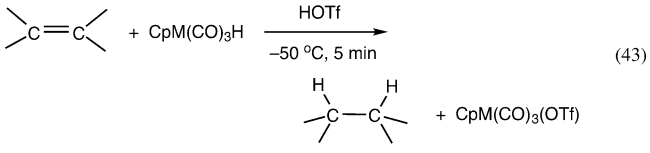
Regarding displacement of the very labile CH_2Cl_2 ligand by H_2 in $[Re(CO)_4(PR_3)(CH_2Cl_2)]^+$, no peaks attributable to the expected η^2-H_2 complexes were observed in ^1H NMR spectra taken at −80 to 20 °C under H_2 atmosphere in CD_2Cl_2 solution.[74,277] However, when solutions in noncoordinating C_6D_5F were placed under 3 atm of H_2, broad resonances for η^2-H_2 were observed at −4.69 ppm for $[cis\text{-}Re(CO)_4(PPh_3)(H_2)][BAr_f]$. The addition of H_2 was completely reversible, but the H_2 complexes could not be isolated due to loss of H_2 and decomposition in C_6H_5F solutions. The HD complexes were prepared, and the J_{HD} coupling constants were measured to be 33.9 and 33.8 Hz for the PPh_3 and PCy_3 complexes, respectively. The high J_{HD} observed for these complexes is consistent with those observed in other electrophilic cationic $M(H_2)$ systems and suggested a short H−H distance of ∼0.87 Å and a bonding picture in which the metal−H_2 σ interaction is greatly enhanced relative to the backbonding interaction. Although the ^1H NMR signals for coordinated H_2 were not observed in CD_2Cl_2 solutions of $[Re(CO)_4(PR_3)(H_2)]^+$, heterolytic activation of H_2 was evident in CH_2Cl_2 by protonation of free diisopropyl ether. When $^iPr_2O$ (4−10 equiv) was added to CD_2Cl_2 solutions of the CH_2Cl_2 complexes followed by placement under H_2 atmosphere, complete conversion to the hydride-bridged dimers $\{[cis\text{-}Re(CO)_4(PR_3)]_2(\mu\text{-}H)\}\{BAr_f\}$ was observed.



(42)

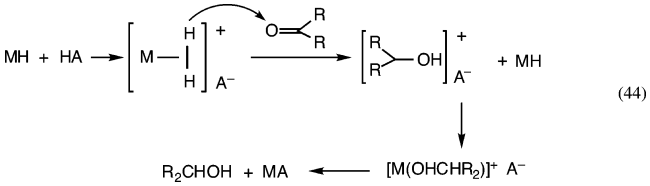
Evidently, CH_2Cl_2 and H_2 complexes existed in equilibrium in CH_2Cl_2 solution, but the exchange was too fast on the NMR time scale to observe the intermediate $[Re(CO)_4(PR_3)(H_2)]^+$ complex that protonated the ether. The pK_a of the H_2 complex was estimated to be approximately 1 to −2. Heinekey observed similar deprotonation of $[Cp^*Re(CO)(NO)(H_2)][BF_4]$ with Et_2O to give a hydride-bridged dimer.[103] Surprisingly, the nature of the anion was found to be important in the deprotonation of *trans*-$[FeH(H_2)(dppe)_2]^+$ by Et_3N.[287] The reaction rate was accelerated by BF_4^- and PF_6^- and decelerated in the presence of bulkier BPh_4^-, which hinders the approach of base via intermediate structures containing Fe−H_2···N and Fe−H···H···N dihydrogen bonds (see eq 5, which shows the reverse reaction, the protonation of a hydride).

The heterolytic activation of H_2 in the above system is particularly interesting in that it may be applicable to reactions in which ionic hydrogenation of hindered substrates from a metal catalyst and H_2 is desired. In 1989 Bullock reported the first examples of ionic hydrogenation wherein a mixture of an organometallic hydride such as $CpMoH(CO)_3$ and a strong acid such as HO_3SCF_3 reduces sterically hindered olefins to alkanes via protonation to carbocations followed by hydride transfer from the metal hydride (eq 43).[288] Several other examples have since been reported,



(43)

including hydrogenation of alkynes and ketones.[289−291] It is likely that an acidic H_2 (or dihydride) complex is involved in the proton-transfer step of some of these reactions (eq 44). This system is significant in that it indicates that H_2



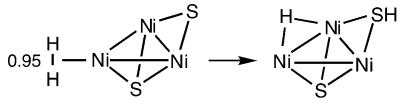
(44)

ligands can be *directly* reactive in catalysis via proton transfer and not just as an intermediate to formation of catalytically active dihydride ligands.

Although the primary focus of this article is on heterolysis of established dihydrogen and σ bond complexes, considerable research has been carried out on heterolytic activation of hydrogen involving classical hydride systems or unidentified transient species. Important data on the thermodynamics of H_2 splitting and the hydride donor abilities of $[MH(PP)_2]^+$ (M = Ni, Pd, Pt; PP = diphosphine) have been reported by DuBois and Curtis.[270c,292] The dicationic complexes $[M(PP)_2]^{2+}$ heterolytically cleave H_2 in equilibrium fashion in the presence of bases such as amines to give protonated amine and $[MH(PP)_2]^+$. The involvement of a dihydrogen (and/or dihydride) complex could not be directly identified, illustrating the frequent problem encountered in activation of σ bonds, namely whether the mechanism involves a σ complex, i.e., $M(\eta^2\text{-}H_2)$ (or generically $M(\eta^2\text{-}X{-}H)$), or oxidative addition to M(X)(H).

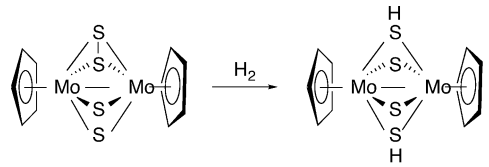
8.2.5. Intramolecular Heterolytic Cleavage of H_2

*Intra*molecular heterolytic cleavage of H_2 is one of the oldest reactions of H_2 and is among the first homogeneous catalytic conversions. η^2-H_2 can protonate a counteranion or a basic ancillary ligand, either at the M−L bond or at a ligand lone pair. Intramolecular heterolysis of H−H is most likely an essential step in many diverse systems ranging from industrial processes to the function of metalloenzymes such as hydrogenases. These include heterogeneous catalysis such as in the world's largest man-made chemical reaction, hydrodesulfurization (HDS) of crude oil on metal sulfides, typically MoS_2 and RuS_2. Heterolysis of H_2 on these and other sulfides to form M−H and M−SH groups is well-known[293,294] and has been modeled calculationally on NiS and a Ni_3S_2 cluster.[293b,294] A transient Ni−H_2 species is calculated to be stable by ∼16 kcal/mol and energetically capable of transferring one H to S (eq 45).[293b] H_2 also readily



(45)

reacts with a select few organometallic sulfides to give SH complexes (eq 46) which can show exchange behavior (eq 48).[295−298] Although the mechanism of eq 46 is unknown,[295,298] a four-center S_2H_2 transition state can be envisioned, since there are no vacant coordination sites available on the metal. $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)]^{2+}$ reversibly forms $[(triphos)Rh(\mu\text{-}SH)_2Rh(triphos)]^{2+}$ under H_2.[297] Equation 47 represents the first example of H_2 addition to a nonbridging disulfide complex.[296] An undetected H_2 complex may explain NMR evidence for H-atom exchange in eq 48, including the protons in dissolved H_2 gas.[296] A



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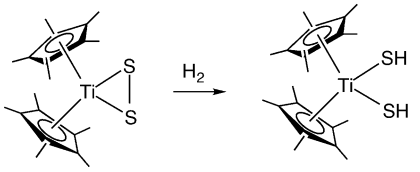
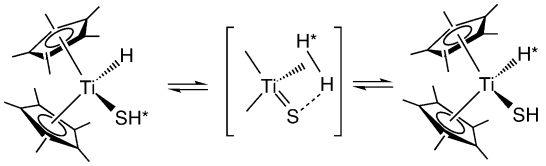
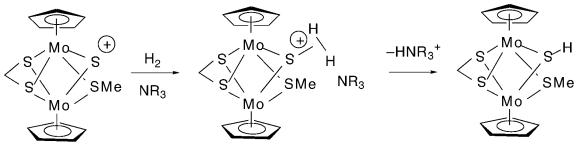


(47)



(48)

related Mo−S system shows reaction of H_2 with saturated cationic sulfide-bridged complexes in the presence of a base (NR_3), which may be explainable by direct attack of H_2 on sulfur to form a 3c2e S−H_2 interaction, followed by intermolecular heterolytic cleavage of H_2.[295,298] Although this



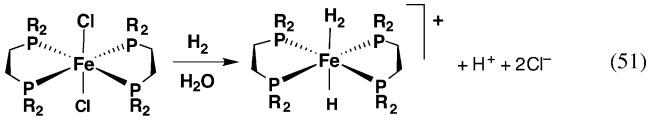
(49)

type of reaction is quite rare, it is possible that activation of H_2 could be entirely *sulfide ligand-based* in these reactions as well as in certain biological and industrial catalyst systems. Unlike the active sites in H_2ases, there is no open (or displaceable) site on the metal for H_2 coordination and heterolysis. The richness and versatility of *Mo-based* clusters in undergoing such unique reactions that can involve internal Mo−S redox processes could relate to their presence in nitrogenase enzymes and in HDS catalysts (W analogues do not display the reactivity in eqs 46 and 49).[299,300] The Mo−SH groups formed in the above reactions can act as reducing agents toward, for example, SO_2, where hydrogenation to elemental sulfur and H_2O was found to occur.[7,301]

Intramolecular heterolysis of H_2 with elimination of HX (X = Cl) is commonly observed under homogeneous reaction conditions.[44,106,302−304]

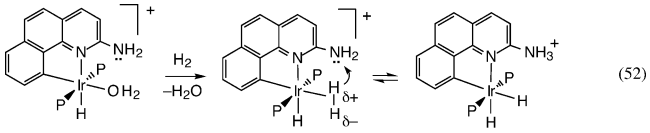
$$L_nMX + H_2 \rightarrow L_nMX(H_2) \rightarrow L_nMH\ [\text{or } L_nMH(H_2)] + HX \quad (50)$$

The mechanism in most cases follows that in Scheme 12 where the proton transfers to a cis ligand X. This reaction is useful for preparative and catalytic chemistry; for example, a metal halide (including bridging X) can be converted to a metal hydride in the presence of base or under phase-transfer or high-pressure conditions. In some cases, a dihydrogen-(hydride) complex can be directly prepared via heterolytic cleavage of H_2 and subsequent displacement of chloride by H_2.[106,303] This can even be done in aqueous solution for water-soluble phosphines (R = methoxypropyl).[303] In the Ru analogue, the H_2 ligand is found to participate in intermolecular hydrogen bonding in solution.[303b]



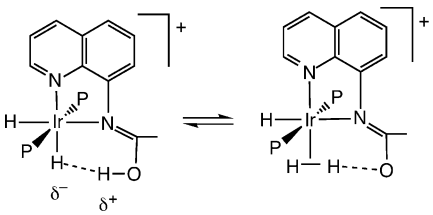
(51)

Another important type of heterolytic cleavage of H_2 highly relevant to that presumed to take place at the active site of H_2ases is shown in eq 52.[305,306] The conversion is



(52)

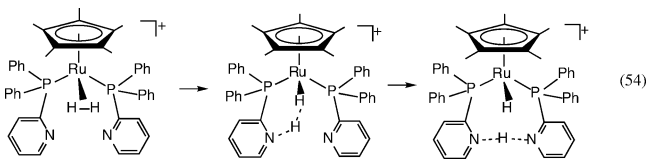
completely reversible by removing the H_2 gas from solution and is remarkably sensitive to phosphine size and ion-pairing effects. A similar proton transfer occurs to a Ru-bound NH_2 (amido) ligand on heterolysis of H_2 on (PCP)Ru(CO)(NH_2) (PCP = 2,6-$(CH_2PBu_2)_2C_6H_3$).[307] An ammonia ligand is formed which then dissociates to give (PCP)RuH(CO). Such "ligand-assisted heterolysis" of the type M(amide) + H_2 → MH(amine) had earlier been found by Fryzuk at about the time M−H_2 complexes were first discovered, and thus, intermediate H_2 coordination was not initially speculated to be a part of the mechanism of such processes.[308] These reactions are possibly facilitated by intramolecular hydrogen bonding interactions, e.g., eq 53, where the OH and IrH hydrogens scramble via rotation of the H_2 ligand. The



(53)

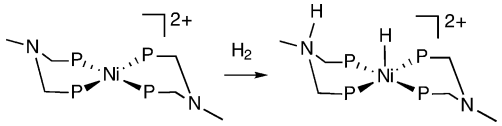
H···H interactions (1.75−1.9 Å) here and related systems are referred to as "proton-hydride bonding" by Morris[127,309] and "dihydrogen bonding" by Crabtree,[310−312] who, along with others,[313−315] have studied or reviewed such *unconventional hydrogen bonds* that include M−H···H−M′, M−H···H−X, and X−H···σ interactions in general (X = C, N, P, O, etc). Remarkably, the H_2 ligand in water-soluble Ru diphosphine dihydrogen complexes has recently been found to hydrogen bond to bulk solvent.[303b] These complexes can represent intermediates in the heterolytic splitting of H_2 and illustrate both the basicity of the M−H bond and the acidity of η^2-H_2. The interactions can be comparable in strength to classical X−H···(lone pair) hydrogen bonds (3−7 kcal/mol). The discovery of the dihydrogen bond and new findings in this area have given significant rebirth of interest in hydrogen bonding in transition metal chemistry[316,317] that can parallel well-known hydrogen-bonding effects in biological systems.

Related H_2 heterolysis also occurs via intramolecular proton transfer between nitrogens on Ru complexes containing phosphinopyridine ligands (eq 54).[318] Reversible heterolysis of H_2 occurs via dihydrogen bonding involving a protonated pyridine group similar to that in eq 53. An

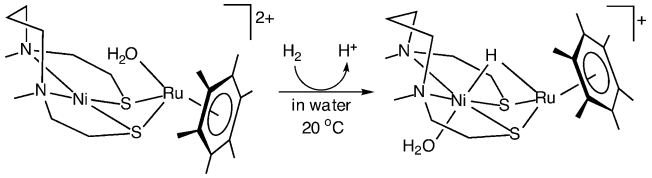


(54)

Scheme 13



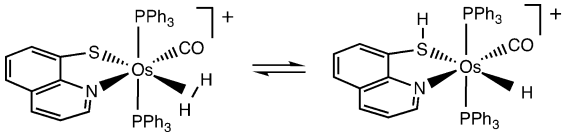
Scheme 14



additional intramolecular proton-transfer process is proposed to occur between the nitrogens of the pyridine rings on adjacent phosphine ligands; that is, DFT calculations show that a proton can be "handed off" from one ring to another via a symmetrical proton-bridged transition state. The complex catalyzes deuterium exchange with methanol-d_4, where initially 50% of the Ru-bound H_2 is labeled after 7 min. DuBois found that a Ni(II) complex heterolyzes H_2 to form a Ni hydride bond and a protonated pendant amine.[270c] Although an intermediate H_2 complex was not observed, DFT calculations on a closely related model complex indicated one exists with an energy 2.1 kcal/mol above that of the reactants.[270a]

A heterolysis of H_2 on a Ni−Ru complex to form a *bridging* hydride complex directly relevant to the function of NiFe H_2ases was recently reported by Ogo and co-workers (Scheme 14).[319] This system is unique in that it undergoes the crucial reaction with H_2 under ambient conditions in water to give the Ni(μ-H)Ru structure analogous to that proposed to occur in the active form of the enzyme, albeit with Ru instead of Fe and different coligands (see Figure 4).

The first direct observation of equilibrium between an acidic H_2 complex and a corresponding hydride complex with a protonated ancillary ligand is shown in eq 55.[320] Here a



(55)

proton migrates from H_2 to a thiolate ligand trans to it, possibly via base-assisted heterolysis (initial intermolecular proton transfer to solvent) or initial intramolecular transfer to a phosphine ligand. Several other cases of η^2-H_2 ligands reacting intramolecularly with thiolate and sulfide ligands are known or believed to be intermediate steps in, for example, SH ligand formation from reaction of sulfides with H_2[297,298,321−333] and are relevant to biological systems such as H_2ases. Particularly related to modeling the heterolysis of H_2 in H_2ases is the work of Rauchfuss, who showed how the hydrido(hydrosulfide) complex $[Ir_2H_2(\mu\text{-H})(\mu\text{-SH})(\mu\text{-S})(PPh_3)_4]$ is obtained from a double hydrogenation of the dinuclear iridium(II) complex $[Ir_2(\mu\text{-S})_2(PPh_3)_4]$. In the stepwise process, the first added H_2 molecule undergoes *homolytic cleavage* while the second process is purely *heterolytic*.[324] The related dicationic complex [(triphos)Rh-(μ -S)$_2$Rh(triphos)]$^{2+}$ [triphos = $CH_3C(CH_2PPh_2)_3$] is known to reversibly activate two dihydrogen molecules and produce the bis(μ-hydrosulfido) product [(triphos)(H)Rh(μ-SH)$_2$Rh-

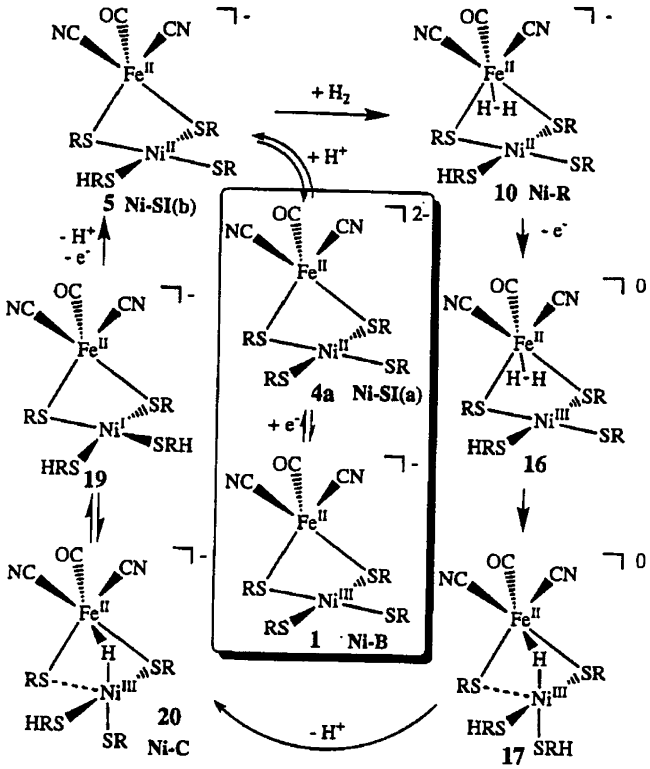
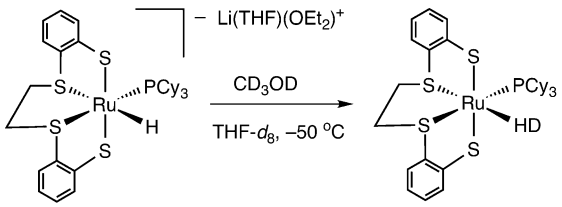


Figure 4. Possible mechanism for hydrogenase function as suggested by the calculations of Niu et al.[383]

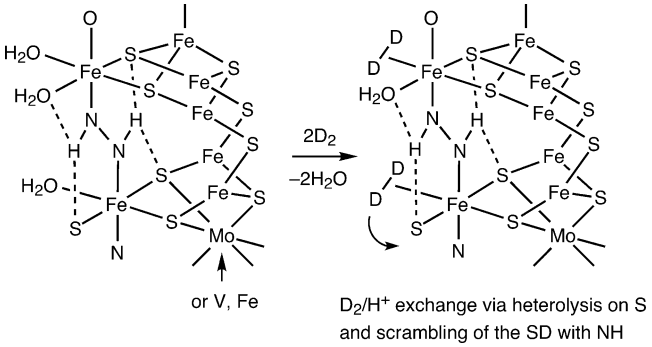
(H)(triphos)]$^{2+}$.[297,321] DFT calculations show that each d^6 metal ion in a model complex, with local square pyramidal geometry, is able to anchor one H_2 molecule in the side-on coordination.[321] This is followed by heterolysis of the H−H bond over one adjacent and polarized Rh−S linkage and is repeated for addition of the second H_2 molecule. NMR experiments, including para-hydrogen techniques, identified that double heterolysis occurs in stepwise fashion, although there was no experimental evidence for a Rh-(H_2) adduct, probably due to its very short lifetime. The computational results support the energetic feasibility of the whole process, including its reversibility, which is favored by the unique proximity of electrophilic metal centers and nucleophilic sulfur atoms. In this case, the process compares (but is not exactly equal) to σ-bond metathesis, since the newly formed Rh−H and S−H bonds stem from H−H and Rh═S bonds. The mechanism differs from that for the above neutral Ir_2S_2 core, perhaps because the Rh complex is dicationic and more electrophilic, favoring double heterolysis.

In order for proton transfer from a η^2-H_2 ligand to a coordinated base to occur, the pK_a of the H_2 ligand and the protonated base must be similar (for a reversible process). Morris has estimated that coordinated alkanethiol ligands have pK_a values between 5 and 10, which matches well with the acidity of many H_2 ligands.[331] Protonation of an anionic Ru hydride using CD_3OD gives an unstable HD complex (eq 56).[328] This reaction can be reversed by displacing the

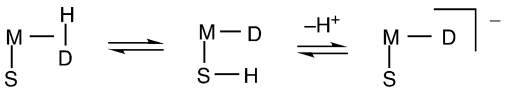


(56)

Scheme 15



H_2 by DMSO to give Ru(DMSO)(PCy_3)(S_4), which yields $Na^+[RuH(PCy_3)(S_4)]^-$ and MeOH when treated with H_2 in the presence of NaOMe. This demonstrates that H_2 can be heterolytically cleaved at M−S sites, and a mechanism had been elucidated for an analogous neutral Rh−hydride system.[326,327] In this case, the electrophilic metal and the basic thiolate donors attack the η^2-H_2 in concerted fashion to give an identifiable thiol hydride species, $[RhH(PCy_3)(^{bu}S_4-H)]^+$. The similarity between the Ru and Rh systems suggests that the HD (or a D_2) ligand in eq 56 can be intramolecularly cleaved (eq 57), which is essential to rationalize the D_2/H^+ exchange between D_2 and EtOH that these complexes catalyze. For the Ru system, the thiol hydride could not be



(57)

detected, while, for the Rh system and also $[IrH_2(HS(CH_2)_3SH)(PCy_3)_2]^+$ (which similarly catalyzes D_2/H^+ exchange),[330] the H_2 complex could not be seen but is a transient. A related system, Ni(NHP^nPr_3)(S_3) clearly shows that heterolysis of D_2 can also occur at nickel sites, which may be relevant to H_2 activation in [FeNi] hydrogenases.[329]

Regarding the structure and function of nitrogenases in producing ammonia from N_2, Sellmann has studied several model systems wherein heterolytic activation of H_2 occurs on sulfur ligands.[334] A core geometry based on a hybrid of the FeMoco active site structure with a dinuclear diazene complex, $[Fe(“N_HS_4”)]_2(\mu\text{-}N_2H_2)$, is a proposed model (Scheme 15). In nitrogenase (section 9), H_2 reduction is proven by the formation of HD from D_2 gas and protons derived from H_2O, which occurs only in the presence of N_2 (eq 58).

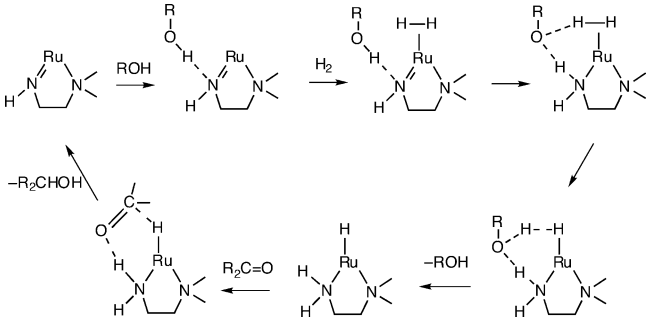
$$2H^+ + D_2 + 2e^- \rightarrow 2HD \quad (58)$$

Sellmann's model is claimed to be consistent with the severe constraints imposed on this "N_2-dependent HD formation" from D_2 and protons. Other modeling studies have shown that protons can be transferred from acidic H_2 ligands in cationic Ru−H_2 complexes to N_2 ligands in $W(N_2)_2(P)_4$ complexes (P = phosphine donor), in some cases even forming ammonia (eq 59).[335,336]

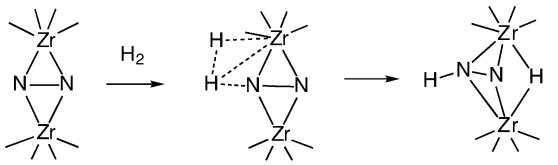
$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] + trans\text{-}[RuCl(H_2)(dppe)_2]^+ \xrightarrow[55\ ^\circ C,\ 24\ h]{H_2} NH_3 \quad (59)$$

Detailed studies with several Ru(H_2) complexes showed that the yield of NH_3 critically depended upon the pK_a value of the Ru(H_2) complexes.[336] When the W−N_2 complex was

Scheme 16



treated with 10 equiv of $[RuCl(H_2)(dppe)_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) with pK_a = 6.0 under 1 atm of H_2, NH_3 was formed in up to 79% total yield (free NH_3 plus NH_3 released on base distillation). If the pK_a of the Ru(H_2) complex was increased to ∼10, the yield of ammonia decreased remarkably. Heterolytic cleavage of H_2 was proposed to occur at the Ru center via nucleophilic attack of the coordinated N_2 on the coordinated H_2, where the coordinated N_2 is protonated and a hydride remains at the Ru atom. Only a very limited number of reactions of bound N_2 with H_2 are known, e.g., eq 60, which slowly occurs in toluene over 1−2 weeks for a dinuclear Zr complex capped by macrocyclic ligands with N and P donor atoms.[337,338]



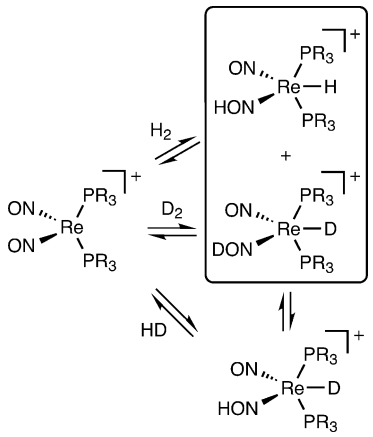
(60)

However, here the reaction stopped at the stage of N_2H, and no NH_3 was formed. Chirik recently found NH_3 is produced on reaction of H_2 with a similar μ-N_2 complex containing two methyl-substituted Cp ligands on each Zr.[339] Remarkably, side-on N_2 bonding and NH_3 production occurred only upon a seemingly insignificant change from pentamethylated to tetramethylated Cp ligands. A related hafnocene system hydrogenated the N_2 ligand but did not produce NH_3.[340] Heterolysis of H_2 also occurs on a Fe(μ-N)Fe species to form Fe(μ-NH)(μ-H)Fe species, but NH_3 was not seen.[341] Ammonia and hydrazine have been seen to form in bis(diphosphine)iron systems that are proposed to heterolyze H_2 to form protons. Here, H_2 becomes the actual source of electrons for N_2 reduction.[342]

The catalytic system discovered by the recent Nobel laureate, Ryoji Noyori, for asymmetric hydrogenation of simple ketones to alcohols is an elegant example of the importance of heterolytic activation of H_2 in a commercially valuable industrial process. This conversion is catalyzed by *trans*-$RuCl_2$[(*S*)-binap][(*S*,*S*)-dpen] (binap = [1,1′-binaphthalene-2,2′-diylbis(diphenylphosphane)]; dpen = diphenylethylenediamine) and is remarkable in several respects.[343−345] The reaction is quantitative within hours, gives enantiomeric excesses (ee) up to 99%, and shows high chemoselectivity for carbonyl over olefin reduction, and the substrate-to-catalyst ratio is >100,000. The nonclassical metal−ligand bifunctional catalytic cycle is mechanistically novel compared to that of the structurally similar classical ruthenium hydrogenation catalysts (Scheme 16).

The process involves heterolytic splitting of H_2 assisted by coligands (see eqs 47 and 48 and ref 308) and possibly

Scheme 17



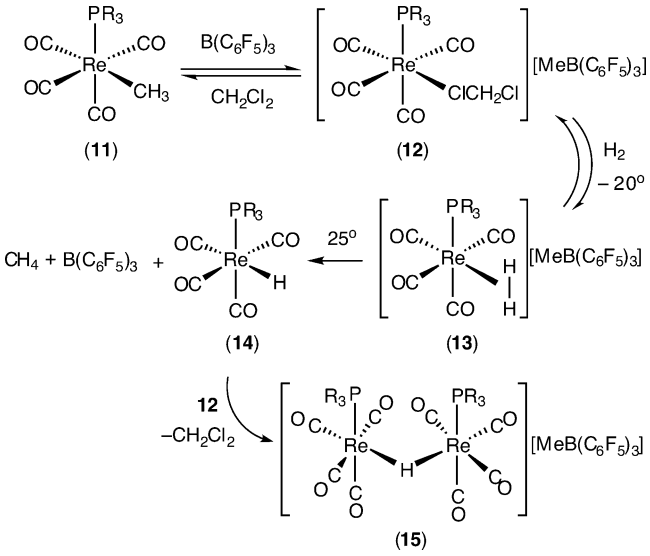
solvent to form a catalytically active Ru(hydride)(diamine) complex as a key step. Computational and experimental modeling studies involving similar heterolysis of H_2 in dihydrogen complexes have been shown by Morris and others to be the critical step in the mechanism of reaction processes related to the Noyori systems.[86,346−348] Bergens reported the first direct observation of a cationic $[RuH(H_2)(diphosphine)(diamine)]^+$ complex as a putative intermediate, where the H_2 ligand was very labile and had the highest observed J_{HD} (37 Hz) to date.[86] Evidence suggests that H_2 heterolysis is the key step in Scheme 16 and can be facilitated by alcohols, underscoring the importance of alcohol-containing solvents in promoting heterolysis of H_2 here and in other metal bifunctional catalysis.[348a,b] Base-assisted heterolysis of coordinated H_2 has been analyzed computationally for a $Rh(H_2)(PH_3)(HCO_2)\cdots NH_3$ model system.[349] Both the kinetics and thermodynamics of the metathesis process for transfer of H to the oxygen of HCO_2 were favored by the presence of external amine. In Scheme 16, after the amide nitrogen cleaves H_2, the resulting NH_2 functionality in the diamine ligand along with the hydride ligand deliver hydrogen to the ketone via a six-membered, pericyclic transition state, giving the alcohol product. Thus, the 18-electron Ru center and the ligands directly cooperate in the bond-breaking and bond-forming processes. The hydride on Ru possesses sufficient nucleophilicity, while the NH moiety exhibits a hydrogen-bonding ability to activate the carbonyl function.

Catalytic H/D scrambling of mixtures of H_2 and D_2 often takes place via intramolecular heterolysis of H_2, as will be discussed further below. A recent example was proposed to involve cleavage of H_2/D_2 and proton transfer to NO ligands (Scheme 17).[350] Although the protonated NO ligands were not actually observed, analogous heterolysis of a Si−H bond in a silane did give a complex with a silylated nitrosyl ligand, Et_3SiON. Reactivity directly analogous to that in Scheme 17, e.g., protonation of similarly π-accepting CO ligands, would not be expected in H_2ases, since more basic sites are available, but nothing can be ruled out.

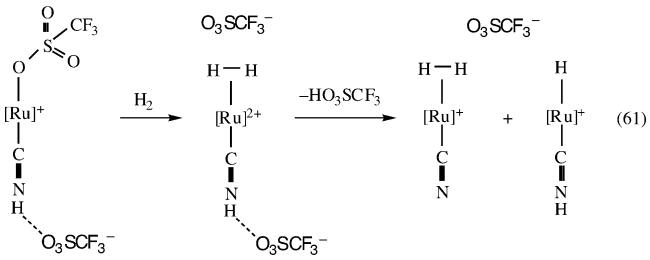
8.2.6. Proton Transfer to Anions

Strong acids such as HCl can be eliminated by proton transfer from η^2-H_2 ligands to the counteranions of highly electrophilic $[L_nM]^+$ complexes. One of the strongest acids known, *triflic acid*, CF_3SO_3H, can even be eliminated from a dicationic H_2 complex formed from reaction of H_2 gas with $[Ru(CNH)(PP)_2][OTf]_2$ (PP = diphosphine), which contained

Scheme 18



a coordinated triflate anion and a protonated cyanide ligand (eq 61).[274] Another "superelectrophilic" 16e Ru complex,



$\{Ru[P(OH)_3](PP)_2\}[OTf]_2$, heterolytically cleaves not only H_2 but other σ H−X bonds in silanes ($HSiR_3$) and boranes ($BH_3{\cdot}PR_3$) to give $\{RuH[P(OH)_3](PP)_2\}[OTf]$ plus XOTf (X = H, SiR_3, $BH_2{\cdot}PR_3$).

A further interesting case involves protonation of borane anions where the d^6 rhenium(I) complex, **11**, is in nearly 1:1 equilibrium with **12**, formed by methyl abstraction by $B(C_6F_5)_3$ to give the $MeB(C_6F_5)_3^-$ counterion (Scheme 18).[277] This indicates that the electrophilicity of the $[Re(CO)_4(PR_3)]^+$ fragment is similar to that of $B(C_6F_5)_3$. **12** reacts under H_2 atmosphere below room temperature to form equilibrium amounts (~5%) of the H_2 complex (**13**). On warming the solution, methane, $B(C_6F_5)_3$, and *cis*-$Re(CO)_4(PR_3)H$ (**14**) form, apparently by protonation of the anion $MeB(C_6F_5)_3$ by the acidic H_2 in **13**. **14** is not observed by NMR but presumably quickly reacts with unreacted **12** (or **13**) to form the hydride-bridged dimer **15**, which is a "thermodynamic sink" in these systems (see eq 42). Another possible scenario in Scheme 18 is *intermolecular* heterolysis of H_2, e.g. protonation of the Me group in equilibrium quantities of **11** by the acidic H_2 in **13** to give CH_4,**12**, and **14**. Regardless of mechanism, this system demonstrates the stability of *hydride-bridged complexes* that have been proposed in the mechanism of H_2 cleavage/formation at the dinuclear active sites in hydrogenases.

8.2.7. Strength of Binding of H_2 Compared to Water and N_2. Importance of Entropy Effects

An important question is how can a seemingly weak ligand such as H_2 compete with stronger ligands such as water or even atmospheric dinitrogen that are present in the environ-

ment of life forms. It is illuminating to compare the binding energy of H_2 to that for the aqua ligand, H_2O, the archetypal lone-pair donor in classical coordination chemistry. Addition of excess H_2O to a concentrated tetrahydrofuran (THF) solution of $W(CO)_3(P^iPr_3)_2(H_2)$ gives instant vigorous effervescence of H_2, even under an H_2 atmosphere.[226c] X-ray diffraction of the product obtained on crystallization showed it to be $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot$THF, containing an H_2O ligand replacing the H_2 and lattice solvent (THF). The structure is novel in that the H-atoms on the aqua ligand hydrogen bond to the lattice THF oxygen atom and a CO oxygen on an adjacent molecule. Such hydrogen bonding in organometallic systems is becoming an increasingly recognized phenomenon,[316] and it is conceivable that hydrogen bonding of protein residues to CO ligands may be present in hydrogenase active sites (although weaker and less consequential than hydrogen bonding to the cyanide ligands). Interestingly, the aqua complex does not precipitate if addition of H_2O to $W(CO)_3(P^iPr_3)_2(H_2)$ is done in the nonpolar solvent *hexane* under an H_2 atmosphere with a large excess of water present as an immiscible phase.

$$W(CO)_3(P^iPr_3)_2(H_2) + H_2O \xrightarrow[\text{hexane}]{H_2} \text{N. R.} \quad (62)$$

$$W(CO)_3(P^iPr_3)_2(H_2) + H_2O \xrightarrow[\text{hexane}]{\text{argon}} W(CO)_3(P^iPr_3)_2(H_2O) \xrightarrow[-H_2O]{\text{vacuum}} W(CO)_3(P^iPr_3)_2 \quad (63)$$

As soon as the H_2 atmosphere is replaced by argon (eq 63), the less soluble H_2O complex precipitates. Subsequent exposure to vacuum rapidly leads to dissociation of H_2O and precipitation of insoluble $W(CO)_3(P^iPr_3)_2$. This demonstrates the extremely delicate reversible nature of the H_2O and H_2 binding and indicates that *H_2 can compete both thermodynamically and kinetically with H_2O as a ligand*. A major factor is mass action, i.e., concentration of unbound ligand in solution. In hexane the low solubility of H_2O limits its maximum concentration to the same order as that of dissolved H_2 (ca. 0.005 M), as opposed to the situation in THF, where the high concentration of miscible H_2O overwhelms that of H_2. Other complexes demonstrating this effect are $[Ru\{HB(pz)_3\}(PPh_3)_2(H_2O)]^+$ [352] and $[Ru(H_2O)_6]^{2+}$, where an H_2O ligand can be displaced by H_2 under pressurized H_2 even in H_2O solution.[61] One of the first H_2 complexes, $[IrH(H_2)(PPh_3)_2(bq)]^+$, was prepared by displacement of H_2O under 1 atm of H_2 in organic solvents.[92,93]

The fact that H_2 and water can closely compete for the same binding site is clearly relevant to biological activation of H_2 by hydrogenases. The thermodynamic data below show that binding of H_2 should easily occur on large hydrophobic metalloenzyme sites where the effective H_2O concentration is low. The equilibrium constants for displacement of H_2 by H_2O in THF can be determined by IR data at several atm H_2 pressures at 25 to −70 °C.[226b] The thermodynamic parameters for eq 64 are readily obtained from van't Hoff plots:

$$W(CO)_3(P^iPr_3)_2(H_2) + H_2O + \text{THF} \rightleftarrows W(CO)_3(P^iPr_3)_2(H_2O)\cdot\text{THF} + H_2 \quad (64)$$

$$\Delta H = -4.5 \pm 0.2 \text{ kcal/mol}; \qquad \Delta S = -18.8 \pm 2.0 \text{ cal/(mol deg)}$$

Displacement of H_2 by water is exothermic by 3−4 kcal/mol, but hydrogen bonding between coordinated H_2O and solvent appears to play a role in the thermodynamics. Also, bound H_2 has been shown to hydrogen bond to bulk H_2O solvent in a water-soluble Ru-diphosphine complex.[353] In this case, the coordinated H_2 is surprisingly inert to substitution by water. Such species are proposed to be key intermediates in numerous important reactions such as the proton-transfer pathway of H_2 production by hydrogenase enzymes.

The surprisingly high negative entropy change in eq 64 no doubt reflects free THF becoming bound (three particles converting to two). The unfavorable entropy of binding of H_2O is largely the reason why the equilibrium favors H_2 binding at room temperature and H_2O binding at low temperature. ΔG_{298} can be calculated to be 1.1 kcal/mol, i.e., favoring the left side of eq 64. *Entropic factors can thus be critical in competition between weak ligands for binding sites*, as will be seen below for N_2 versus H_2 binding.

The enthalpies of binding of H_2O in eq 64 are relative to H_2, so it is of interest to determine the enthalpy of binding of H_2 to $W(CO)_3(P^iPr_3)_2$, which is directly measured to be -11.2 ± 0.5 kcal/mol in toluene at 20 °C (eq 65).

$$W(CO)_3(P\text{-}i\text{-}Pr_3)_2 + H_2 \rightarrow W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2) \quad (65)$$

The affinity of H_2 versus other ligands such as N_2 for L_nM varies and can be entropy-dependent. In some cases, N_2 is a better ligand than H_2, and sometimes the opposite is true, or N_2 does not bind at all. Binding a gaseous ligand increases the total entropy of $ML_n(H_2)$ relative to ML_n but does so by a relatively minor amount compared to the entropy lost by the ligand.[87] On this basis, the total entropy of exchange for eq 66 should depend primarily on the differences in absolute entropies for $N_2(g)$ and $H_2(g)$.

$$ML_n(N_2)(\text{soln}) + H_2(g) \rightarrow ML_n(H_2)(\text{soln}) + N_2(g) \quad (66)$$

The third-law entropies, $S°$, of the two gases can be calculated by using standard formulas of statistical thermodynamics.[87] At room temperature, the entropy is due exclusively to the translational and rotational components. Due to its lower mass and moment of inertia, the absolute entropy of H_2 (31.2 cal/(mol deg)) is 14.6 cal/(mol deg) lower than that for N_2. If eq 66 is re-examined, it is clear that if the total entropies of the complexes in solution exactly canceled, the predicted entropy change would be 14.6 cal/(mol deg). This then favors the right side of eq 66, i.e., H_2 binding, since $\Delta G = \Delta H - T\Delta S$. Thus, because H_2 has the smallest absolute entropy ($S°$) of any diatomic gas, H_2 will be more competitive in binding relative to N_2 or other small molecules, which may be important in biological activation of H_2. Other factors include the electron-richness of the metal center, which is particularly dependent on overall charge. As the electrophilicity of M increases and M → L backdonation decreases, H_2 becomes an increasingly better ligand than N_2. The disparity here apparently stems from N_2 being a poor σ-donor,[354−358] weaker than even H_2, although a good π-acceptor like H_2.[155,355] Summarizing, nonclassically bound H_2 is a more versatile ligand than many classically coordinated ligands such as N_2 in the ability of H_2 to adjust to a larger range of electronic situations. It can also have steric (small size) and entropic advantages over other ligands.

8.2.8. Isotopic Exchange and Other Intramolecular Hydrogen Exchange Reactions

Hydrogen-containing systems readily lend themselves to isotopic substitution or labeling by deuterium and tritium.

This is most useful in IR and NMR spectroscopic studies, particularly for determining J_{HD}, which is often critical to the proof of molecular H_2 coordination. Importantly, in the context of this article, transition metal-catalyzed H_2/D^+ and D_2/H^+ exchange reactions, where the H^+ and D^+ originate from water or alcohols, are of significant relevance to the study of H_2ase enzymes.[327,359,360] For example, the D_2/H_2O exchange catalyzed by H_2ases has been instrumental in monitoring the activity and studying the mechanism of this important class of enzymes.[359a−d] Consequently, this exchange process has often been a primary screening tool for functional models of H_2ases.[359e−l,360] Such functional models usually invoke heterolytic cleavage of H_2 through the intermediacy of a transition metal dihydrogen complex, as discussed above. Recent interest in performing hydrogenations in aqueous solution has also spurred an interest in synthesis of water-soluble transition metal H_2 complexes and hydrogenation catalysts to catalyze this type of H/D exchange.[61,303,342,359m,n]

Before isotopic exchange with water is discussed, it should be realized that H_2, D_2, and HD ligands can exchange and scramble with each other, with hydride ligands, or with H_2 (or D_2 or HD) gas. Usually, HD or D_2 ligands can be directly coordinated to metal centers by direct addition to unsaturated precursors such as agostic complexes. In some cases, however, a convenient precursor does not exist, and labeling can be done only by facile exchange of the H_2 ligand with HD or D_2 gas, possibly combined with intramolecular isotopic scrambling (eqs 67−71), or by adding a source of D^+ to a hydride complex (eq 72).[30]

$$M(H_2)(H)L_n \overset{D_2}{\rightleftharpoons} M(D_2)(H)L_n \quad (67)$$

$$M(D_2)(H)L_n \overset{H_2}{\rightleftharpoons} M(HD)(D)L_n \quad (68)$$

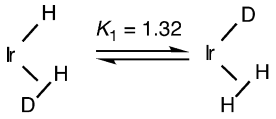
$$M(HD)(D)L_n \overset{D_2}{\rightleftharpoons} M(DD)(D)L_n \quad (69)$$

$$M(H_2)(H)L_n \overset{HD}{\rightleftharpoons} M(HD)(H)L_n \quad (70)$$

$$M(HD)(H)L_n \overset{H_2}{\rightleftharpoons} M(H_2)(D)L_n \quad (71)$$

$$MHL_n \overset{D^+}{\rightleftharpoons} [M(HD)L_n]^+ \quad (72)$$

Intramolecular H/D exchange gives essentially a statistical mixture of isotopomers, but not always exactly statistical because deuterium usually prefers to be in the (HD) or (DD) site. Isotopomers can be detected by solution NMR or by IR in low-temperature matrices. Separate resonances for H_2 and hydride site isotopes are observed in the spectra of complexes when no intramolecular exchange occurs, but in cases where eq 68 is fast, only averaged chemical shifts and J_{HD} are observed. In the fast exchange ^1H NMR spectra of isotopomers of nonclassical polyhydrides, a phenomenon called isotopic perturbation of resonance (IPR) occurs.[94,204a,206] For example, in a partially deuterated $MH(H_2)$ complex, each isotopomer (H_3, DH_2, and HD_2) shows a separate hydride resonance for the species provided the M−H and $M(H_2)$ sites have significantly different chemical shifts and sizable deuterium fractionation exists between the sites. There is a nonstatistical site preference for the deuterium isotope that varies with the degree of deuteration in $[TpIrH(H_2)(PR_3)]^+$ (eqs 73 and 74).[206] The equilibrium constants shown are



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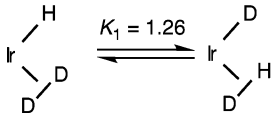


(74)

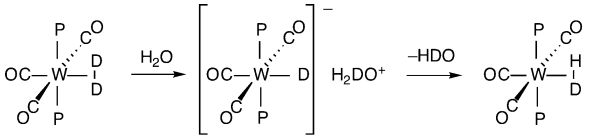
actually Boltzmann factors (statistics not included), but they indicate that the heavier isotope prefers to occupy the hydride site.

H_2 complexes containing hydride ligands, $M(H_2)H_xL_n$, are usually effective catalysts for $H_2/HD/D_2$ scrambling, but several coordinatively saturated H_2 complexes with no hydrides also catalyze exchange. While the former exchange has several reasonable pathways, scrambling of D_2 with $W(CO)_3(PR_3)_2(H_2)$ and a few other 18e complexes as in eq 75 is more enigmatic.[2,88b,361−363]

$$D_2 + W(H_2)(CO)_3L_2 \rightleftharpoons HD + W(HD)(CO)_3L_2 \rightleftharpoons H_2 + W(D_2)(CO)_3L_2 \quad (75)$$

Equimolar amounts of D_2 gas (1 atm) and the H_2 complexes give complete isotope equilibration *even in the solid state* within days for group 6 species or 12 h for $[Re(CO)_3(PR_3)_2(H_2)]^+$ in solution. Prior loss of CO or phosphine to allow D_2 into the coordination sphere followed by isotopic exchange as in eq 69 seems unlikely because ligand loss would be a high-energy process, especially in the solid. Possible mechanisms could involve seven- or eight-coordinate 20e intermediates such as a $(H_2)(D_2)$ complex or a dihydride−dideuterium complex, $WH_2(D_2)(CO)_3(PR_3)_2$. However, no evidence exists for either the dihydride form in the solid state or seven- or eight-coordinate complexes of the type discussed here.

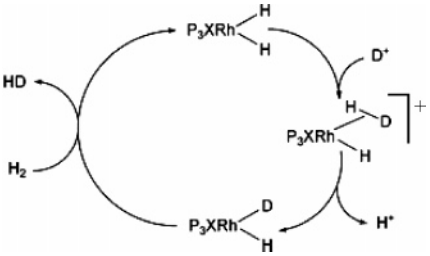
Trace quantities of adventitious water may lead to exchange, since isotopic scrambling of the D_2 ligand in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ with H_2O occurs in solution within days[226c] or less for other metal-D_2 complexes.[94,326,353,359m,n,360,364−366] A reasonable mechanism for exchange for complexes with one open coordination site is deprotonation of η^2-H_2 by the weak base water followed by reprotonation with H_2DO^+. Such a mechanism may be



(76)

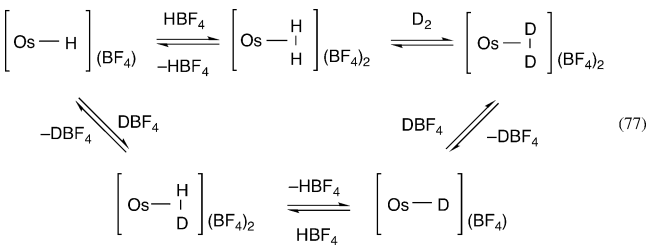
important in isotopic exchange processes in enzymatic systems such as H_2ases and N_2ases. As discussed above, η^2-H_2 can be quite acidic and is known to hydrogen bond to water.[353] Kovacs proposed a mechanism for $Rh(TPPMS)_3Cl$ catalyzed H_2/D_2O exchange (TPPMS = water soluble phosphine) where the catalyst first undergoes oxidative addition of H_2 to make the dihydride (Scheme 19).[359n] A hydride ligand can than react with D^+ to form an HD ligand, which can lose H^+ to create isotopic exchange. A similar mechanism was proposed for $TpRuH(PPh_3)(CH_3CN)$ where D_2O initially hydrogen bonds to the hydride ligand, followed by transfer of D^+ to give a cationic HD complex

Scheme 19



with an OD^- anion. [359o] This may also be a possibility in exchanges such as in eq 76, and $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ is known to exist in solution equilibrium with its dideuteride isomer, $WD_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$.

For cationic complexes such as $[Os(H_2)(CH_3CN)(dppe)_2][BF_4]_2$ formed by protonation of $[OsH(CH_3CN)(dppe)_2][BF_4]$ by $[H(OEt_2)BF_4]$, isotopic exchange with D_2 gas occurs (eq 77).[362] Reversible deprotonation of the D_2 ligand by ether present in CD_2Cl_2 solvent is proposed to occur, forming equilibrium amounts of "free" acids, HBF_4/DBF_4 (these are actually present in eq 77 as ether solvates $H[OEt_2]BF_4/D[OEt_2]BF_4$). This facilitates complete exchange to give the HD complex. The isotopic exchange in CD_2Cl_2 is slow



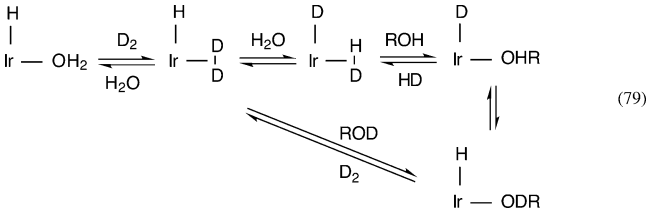
(77)

(days), as for the $W(CO)_3(PR_3)_2$ system, and the deutero solvent does not become involved (see below). However, in eq 76, much stronger bases than H_2O, such as alkoxides,[367] are required to deprotonate the W complex. Also, the rate of H_2/D_2 exchange is much faster than H_2O/D_2 exchange, which is unlikely to occur as above in the solid state and is not seen for solid $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ plus H_2O. This pathway could operate in solution for systems with more acidic η^2-H_2, but another explanation is needed for scrambling in group 6 complexes.

In solution, isotopic incorporation of deuterium from deuterated solvents into metal-bound hydrogen is common; for example, reaction of acetone-d_6 and $[RuCl(dppe)_2(H_2)]^+$ or $[OsH(H_2)(PP_3)]^+$ gives the HD isotopomer in 20 min and the fully deuterated complexes in a few hours.[94,106] Complexes with both hydride and H_2 ligands such as $[Ir(H_2)H(bq)(PPh_3)_2]^+$ and $Ir_2H_3(\mu\text{-}H)(H_2)(\mu\text{-}Pz)_2(P^iPr_3)_2$ or unsaturated hydrides such as $IrClH_2(P^iPr_3)_2$ are advantageous for such isotopic exchange. This is because ligand exchange involving H_2, D_2, and substrates with exchangeable protons is facile, and barriers to intramolecular exchange with cis hydride ligands are low. The latter two complexes undergo H/D scrambling with toluene-d_8 solvent, which could bind to Ir by adding as a sixth ligand or displacing H_2.[78a,368] The cationic Ir complex is an excellent catalyst for deuterium incorporation into alcohols for example (eq 78).[360]

$$ROH + D_2 \xrightleftharpoons[R = Me,\ Et,\ ^tBu]{[Ir(H_2)H(bq)(PPh_3)_2]^+} ROD + HD \qquad (78)$$

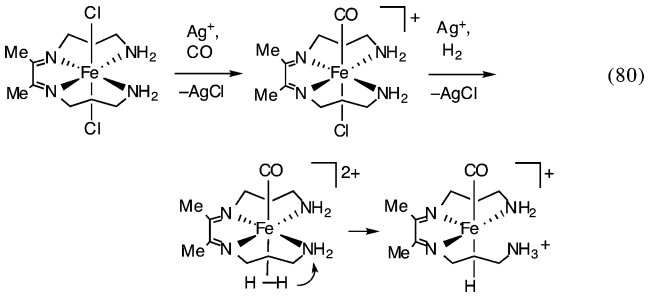
In addition to a possible deprotonation mechanism as in eq 76, a mechanism involving exchange with the cis-hydride is likely here (eq 79).



(79)

8.2.9. The Need for a Low-Spin State in H_2ases and the Possible Role of Cyanide Ligands

Another important question is why does Nature utilize toxic cyanide ligands in hydrogenases? CN ligands could be involved in proton transfer or important hydrogen-bonding interactions with protein components. The cyanide complex, $[Fe(H_2)(CN)(R_2PC_2H_4PR_2)_2]^+$, is known and can indeed exist as an FeH(CNH) tautomer depending on R.[107] A more likely role for the cyanide ligands relates to the spin state of hydrogenases, which are known to be *low spin* in all redox states. Why then is a low-spin state crucial? The answer comes from fundamental inorganic and organometallic coordination chemistry. In accord with the general principles of transition metal chemistry,[369,370] the overall ligand field strength strongly influences the spin state of the dimetallic active sites, which generally feature Fe(CO)(CN) moeities linked by thiolate bridges. As will be shown below, this must be taken into account in efforts to model any facet of hydrogenase chemistry. If one assumes that carbonyl (CO) ligands are critical in hydrogenases (section 3.2), their binding to iron must be very strong to both maintain the integrity of the active site and prevent poisoning of the host organism by release of CO. CO is a very powerful ligand and has been characterized to be a "universal ligand" to lower-valent metal centers.[161] Strong CO binding to iron in hemoglobin is particularly notorious in regard to the toxicity of CO. Of particular relevance in Fe−heme systems is the spin-state change (spin crossover) from high-spin Fe^{II} ($S = 2$) to low-spin Fe^{II} ($S = 0$) on CO binding,[369,371−374] which is much less facile in inorganic and organometallic complexes than may generally be appreciated. Anomalously weak CO binding in $Cp_2VI(CO)$ and $Cp_2Cr(CO)$ was noted decades ago independently by Calderazzo[375] and Brintzinger,[376] both of whom rationalized that spin pairing has to take place upon carbonylation of the high-spin fragments. In his review article on such effects of the spin state, Poli[370] notes that "in spite of this early work, the importance of electron pairing in organometallic stability and reactivity has remained essentially unappreciated." This was encountered in attempts by Kubas to bind CO to iron(II) complexes with nitrogen-donor ligands to model heterolytic cleavage of H_2 as in hydrogenases.[377] The intent was to synthesize Fe^{II} complexes with CO trans to H_2 in order to observe *intramolecular* heterolysis of H_2 where a proton transfers to a basic cis N-donor ligand, e.g., via eq 80, similar to that in eq 52.



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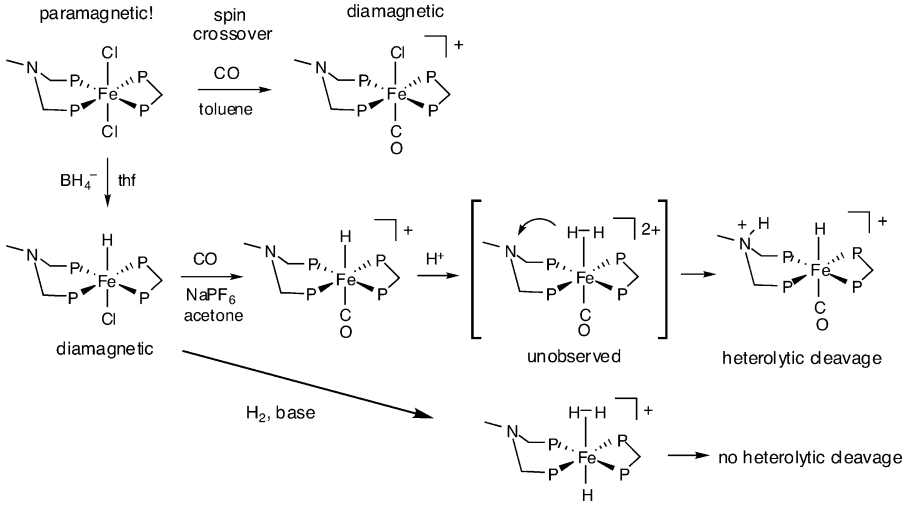
Similarity to the structure of hydrogenases was not of concern, and the multidentate α-diimine ligands had been previously studied on Pd^{II} and Pt^{II} centers.[378] The important feature is that the diimines contain basic pendant side arms (the amine groups in eq 80) that could accept a proton from H_2 heterolysis. Intramolecular heterolysis of η^2-H_2 on Fe^{II} centers as in eq 80 had not been previously directly observed, although while this work was in progress, DuBois[379] independently found such heterolysis in a related phosphine system, *trans*-[Fe(X)(Y)(PNP)(dmpm)]$^+$ (dmpm = dimethylphospinomethane), also containing a proximal basic amine group in the chelating PNP ligand (Scheme 20). Although the precursor dichloro complex was high spin, spin crossover to low-spin complexes occurred on CO addition or replacement of Cl by H. Protonation of [FeH(CO)(PNP)(dmpm)]$^+$ was observed to give a final product with the proton on the basic N atom of the PNP ligand, implying that an incipient unobserved H_2 ligand, if formed, would heterolytically cleave. However, when a hydride is positioned trans instead of CO, H_2 binds but does not heterolyze to protonate the amine. Thus, heterolysis of η^2-H_2 is much more effective when CO is trans to it, in keeping with the principles in sections 3.2 and 8.2.2 outlining how it appears that Nature was opportunistic in employing CO ligands for this purpose.

In eq 80, stepwise removal of chloride ligands from a dichloro precursor using Ag^+ would have been expected to produce a complex with H_2 trans to CO, and the acidic H_2 ligand might then protonate the cis pendant amine. However, the very first step unexpectedly proved to be a major barrier: the metal−diimine system *rejected* binding of CO. The apparent rationale here is that the iron is in a high-spin state in the Fe(diimine)Cl_2 precursor and [Fe(diimine)Cl]$^+$ fragments formed on Cl abstraction and does not undergo spin crossover to a low-spin state that would appear to be necessary for stable CO binding. However, DuBois had found that *trans*-$FeCl_2$(PNP)(dmpm) *is also paramagnetic but does directly react with CO* to displace chloride to form *diamagnetic* [*trans*-Fe(PNP)(dmpm)Cl(CO)]$^+$, a rare example of spin crossover. So why the difference? The inability of the diimine and most Fe^{II} high-spin systems to undergo carbonylation was initially considered to possibly be symptomatic of a "spin-blocked" reaction, where a barrier may exist due to the crossing between reactant quintet and product singlet surfaces. Whether spin-state changes inhibit organometallic reactions has been a decades-old debate and has recently been shown computationally by Harvey and Poli to be highly dependent on the system.[380] However, this and other current literature indicate that the term "spin-block" (or "spin-forbidden") should be reserved for *kinetic* effects, and theoretical calculations on CO interaction with model Fe^{II}−diimine centers demonstrated that the lack of CO binding is *thermodynamic* in origin. Addition of CO to a high-spin Fe−diimine model complex was essentially thermoneutral. Thus, in the failed nitrogen donor system (eq 80) versus the successful phosphine donor system (Scheme 20), the *ligand field strength* of the N-donor versus P-donor ligands is of critical importance. The diimine complexes do not bind CO even weakly, but as expected, analogues containing diphosphines with strong ligand fields (strong electron donors) bind CO tightly, even in cationic species.

It thus may seem ironic that binding of CO to hemoglobin is one of the few facile "spin-forbidden" reactions of this toxic molecule with high-spin Fe^{II} centers. On the other hand, Nature has designed hydrogenases to possess low-spin Fe centers that powerfully and purposefully bind CO. Hydrogenases must possess enough electron density at iron to strongly bind CO while maintaining a fine balance of electrophilic character to reversibly bind and heterolytically cleave H_2. The peculiar presence in these enzymes of *cyanide* ligands could then be related to their high ligand-field strength. This would assist in maintaining a low-spin configuration for Fe throughout the large known array of redox state and ligation changes[381−383,229,232] that occur during the function of the enzyme. Dissociation of either the CO or CN ligands would be destructive to the active site here. Weaker-field ligand sets than CO/CN such as those typically found in enzymes (histidine, cysteine, etc.) would not fulfill this function, since nitrogen-donor ligand sets such as imine/

Scheme 20

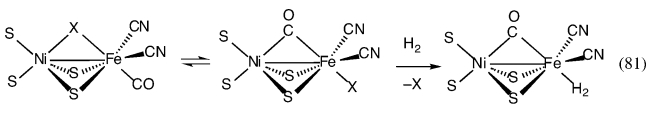


amine in eq 80 give *high-spin* complexes incapable of even weak CO binding. It is significant that CN can be formed biologically along with CO,[384,385] unlike organophosphines or most other strong field ligands in inorganic and organometallic complexes. In the above context, Rauchfuss had previously also demonstrated the positive influence of cyanide on binding of CO to Fe^{II} and on facilitating carbonylation of Fe^{II} thiolate complexes.[386] Darensbourg had speculated that an anionic cyanide would help stabilize a bridging CO ligand.[248b] Another possible role for a strongly electron-donating cyanide ligand is its influence on the redox potentials, e.g., lowering the electrochemical potential for H_2 production.

8.2.10. Why Do Enzymes Such as H_2ases Have Polymetallic Active Sites with Metal–Metal Bonds?

An obvious question is why are two metals employed by most H_2ases when one would seem to work for H_2 splitting/formation as in organometallic chemistry? The active sites of nitrogenases, oxygenases, and certain other non-heme enzymes also contain two or more transition metals (most often Fe, Mn, Ni, Cu, Mo) in close proximity.[242,387] Bonding between the metals can involve two electrons or less, as in organometallic dithiolate-bridged Fe dimers where Fe−Fe separations are ~2.6 Å for a normal two-electron bond, ~3.0 Å for a one-electron[388] ("half") bond, and >3.4 Å for no bond.[389] These interactions allow complexes to exist in multiple oxidation states interconvertible by reversible one-electron-transfer steps if necessary. Multifunctional Fe_2S_2, Fe_3S_4, and Fe_4S_4 clusters containing Fe−Fe bonds are as common as heme groups in biology and facilitate electron transfer, influence protein structure, and can act as catalysts and sensors.[390] Antiferromagnetic coupling via oxo-bridges in methane monooxygenase compounds reduces the Fe−Fe separation to as low as 2.46 Å for O_2 activation.[391] In nitrogenase, changes in Fe−Fe bonding by electron addition to the $MoFe_7S_9$ cofactor and/or P-cluster may be crucial to the binding and activation of N_2.[392−394] Other functions of polymetallic sites include molecular recognition and stabilization of transition states by charge delocalization over multiple atoms.[242,387]

An obvious question remains though: why are two metals employed by H_2ases? As will be discussed below, the electron-transfer process could be facilitated in some way, e.g., via M−M bonds, but also the active site is much more flexible in terms of stereochemistry and reactivity. The dinuclear site has three types of bridging ligands that can easily shift positions between bridging and terminal sites while the dinuclear configuration is retained: CO, hydride, and even SR (though less likely). These shifts are well-known in organometallic chemistry and could position the critical CO ligand trans to H_2 (e.g., in a bridging location) to favor its heterolysis. This could be especially important in the Ni−Fe H_2ases where the CO is trans to X in the crystal structure but could shift to a bridging position to become trans to the site of H_2 binding and subsequent heterolysis. An H_2 ligand



(81)

has yet to be definitively observed to bridge two or more metals in inorganic complexes, so this is unlikely to happen in the enzyme. Bridging *hydride* on the other hand is well-known and has been proposed in the H_2ase mechanisms. As will be discussed below, M−M bonds can be quite basic and can be protonated,[395] perhaps the first step in the H_2 production mode of the enzymes.

8.2.11. Mechanism of Hydrogen Activation in Hydrogenases

Much effort has been carried out in modeling the active site of H_2ases both experimentally and calculationally in an effort to understand the mechanism of H_2 activation and is the subject of many publications both in this thematic issue and elsewhere. Therefore, the discussion here will be restricted to application of well-established principles of organometallic chemistry and dihydrogen activation (as detailed above) that could aid understanding the mechanism of biological H_2 activation. Theoretical calculations using data from the X-ray structures provide guidance for the mechanism of H_2 activation and are addressed in the article by Siegbahn in this thematic issue and other publications.[396] Some computational aspects will be discussed here in conjunction with the organometallic principles. There are many mechanistic possibilities at the multifaceted dinuclear active sites of H_2ases, and some aspects of H_2ase chemistry are still poorly understood or controversial. However, it is generally agreed that the critical step of the mechanism in H_2 conversion to protons and electrons involves heterolysis of an H_2 ligand initially (and perhaps only transiently) bound to a metal center in the active site. In regard to computational analysis, Siegbahn stated that energies are in general more critical tests of a model than are structures, and it is important that they match the experimental energetics of the H_2 reaction.[396b,c] The activation of H_2 should have a barrier of ~10 kcal/mol, be slightly exothermic, and most likely include an H_2 complex along the reaction coordinate. His early calculations on modeling the Ni−Fe H_2ases established that the only site to which H_2 binds significantly (binding energy computed to be 3.1 kcal/mol) is the electrophilic Fe (where $d_{HH} = 0.78$ Å). This was later supported by Niu and Hall[397] and is consistent with organometallic systems where nickel is not known to form stable H_2 complexes and indeed very few Ni hydrides are known. The estimated barrier height for H−H cleavage is 8.7 kcal/mol, a reasonably low energy in accord with an enzymatic process.

Calculations by other researchers indicate that the Ni site, possibly as high-spin Ni(II), could be involved in the activation, so this is still a controversial area.[398] It is likely that a complex with a hydride ligand bridging both metals is an intermediate in the mechanism, as will be discussed below. This was inspired by ENDOR studies that indicate that two types of exchangeable H nuclei are present in the vicinity of the Ni ligands in the Ni−C active form of a [NiFe] enzyme, consistent with μ-H.[399] More recently, Lubitz directly detected by ENDOR a hydride ligand (presumably formed by heterolysis of H_2) occupying a bridging position at the Ni−Fe center of *Ralstonia Eutropha* in its reduced state.[251c] Thus, it appears that either the nickel or iron center could be involved in forming an incipient Ni−H_2 complex that undergoes intramolecular heterolysis to form the bridging hydride. Since a bridging *dihydrogen* ligand has yet to be observed in the vast array of inorganic H_2 complexes, it is unlikely that both metals initially cooperate in binding H_2 in a bridging position. DFT calculations by Hall postulate iron as the site of initial H_2 binding/heterolysis and incorporate monoanions as some of the key intermediates (Figure 4**)**.[382]

These computations do not take into account the protein backbone or hydrogen bonding of the CN to the protein known[400] to be present, potentially important considerations. Optimized geometries reveal that H_2 prefers to bind to Fe rather than Ni, and d_{HH} is again 0.77 Å, although the H_2 is trans to CO rather than CN here. The Fe^{II} center is perfectly configured for capture of H_2 as it diffuses to the active site. The H_2 coordination leads to an increase in d_{NiFe} with respect to that in Ni−SI. The proposed mechanism for H_2 activation again features hydride-bridged frameworks for the key intermediates that would be expected to be present on such dinuclear sites, as suggested by Fontecilla-Camps.[251a] It is notable that heterolysis of H_2 on organometallic complexes can lead to hydride-bridged complexes (Scheme 18 above), although the mechanism is different. The calculated d_{NiFe} values vary greatly in these species as shown, and this flexibility would be expected to facilitate both the electron- and proton-transfer processes (the M−M bond is a possible site for protonation). Although the proposed mechanisms may not be completely correct, the structure/bonding principles mirror those of H_2 activation on organometallic complexes.

The Fe−Fe H_2ases are even more organometallic in character and have been the focus of more modeling studies than the Ni−Fe enzymes. The bridging CO in Fe H_2ases is crucial because it places CO trans to the aqua ligand located crystallographically on Fe (Scheme 10), as in $W(CO)_3(PR_3)_2(H_2O)$, wherein H_2 is known to displace H_2O, and H_2 binding is favored by 1−2 kcal/mol in terms of ΔG (section 8.2.7). In *C. Pasteurianum*, the probable site for H_2 binding/elimination is thus trans to μ-CO, which would stabilize σ H_2 coordination, favor reversible binding and elimination of H_2, and promote heterolytic cleavage. As discussed above, the CO ligands in H_2ases would appear to be designed by Nature to increase the electrophilicity of the active site, thereby enhancing intramolecular heterolysis of H_2 as in carbonyl-rich $[Re(CO)_4(PR_3)(\eta^2\text{-}H_2)][MeB(C_6F_5)_3]$ (Scheme 18). As discussed in section 8.2.7, such electrophilic metal sites as also in $[Mn(CO)_3(PCy_3)_2]^+$ greatly favor binding of H_2 over N_2, which is well-known to bind to low-valent organometallic complexes with more electron-rich nucleophilic metal centers. Atmospheric dinitrogen is a potential competing ligand in enzymes with low-valent metallo sites such as H_2ases (Fe(I) and/or Fe(II) oxidation states) that could inhibit their function. This is thus another reason that H_2ases possess some electrophilic character and employ CO ligands for this purpose. The inorganic models for the active sites based on $(CO)_2(CN)Fe(\mu\text{-}SR)_2Fe(CO)_2(CN)$ type cores also do not bind N_2. It is notable that nitrogenases that *do* bind and activate atmospheric N_2 as their primary function have more nucleophilic metallo centers without electron-withdrawing CO ligands.

The highly electrophilic $[Re(CO)_4(PR_3)]^+$ center with *four* CO ligands also coordinates H_2O trans to CO,[277] although the aqua ligand is less labile than in the neutral $W(CO)_3(PR_3)_2(H_2O)$ and appears to be more strongly bound than H_2. Thus, the active site in H_2ases cannot be overly electrophilic or aqua ligands would bind tightly and inhibit H_2 binding. Again, H_2ases have a proper balance of electrophilic and nucleophilic character, with the Fe center in Ni−Fe H_2ases and Fe(2) in Fe−Fe H_2ases being the more electrophilic sites for H_2 Fe−H_2O binding and heterolysis. Binding energies up to 23 kcal/mol have been calculated in a model $Fe^{II}-Fe^{II}(H_2O)$ species for *D. Vulgaris*, but reduction to $Fe^{I}-Fe^{II}$ can release H_2O to make the site available for H_2 binding,[381,401] which may be key to activation of the oxidized inactive form. Addition of H_2 to a $Fe^{I}-Fe^{II}$ species with an empty coordination site is computed to be exothermic by 6.1 kcal/mol (d_{HH} = 0.824 Å in the resulting η^2-H_2), and this EPR-active species is postulated to convert to an EPR silent $Fe^{II}-Fe^{II}(H_2)$ form via electron (or proton) transfer.[401]

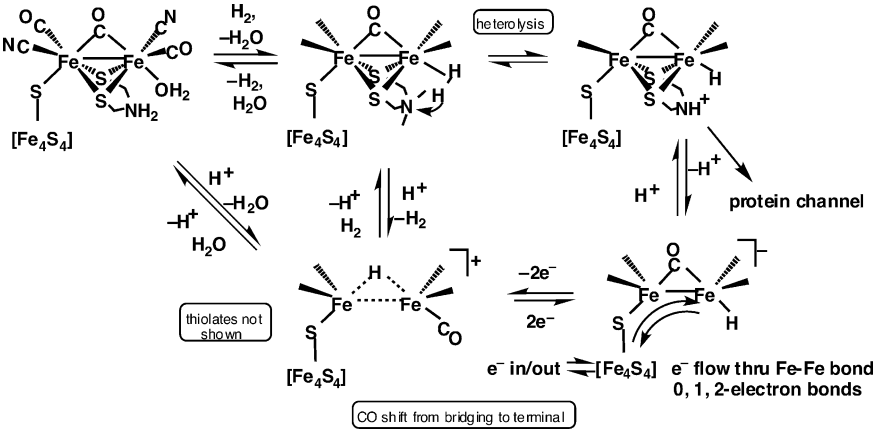
Another of the many variables is the overall *charge* on the metals in the active site. In organometallic complexes, positively charged (i.e., cationic) metals greatly increase heterolytic cleavage of H_2. Thus, $[W(CO)_3(PR_3)_2(H_2)]^+$ is much more easily deprotonated (by ethers) than the neutral complex, which requires a strong base (section 8.2.3).[181] In H_2ases, it is likely that the Fe active site is somewhere midway in electrophilicity but could be tuned by oxidation of a neutral active site to a cationic one (or vice versa). Thus, for conversion of H_2 to protons and electrons, heterolysis of H_2 could be "switched on" by initial removal of an electron from the dimetallo core.

$$[Fe-Fe] \xrightarrow{-e^-} [Fe-Fe]^+ \xrightarrow{H_2} [Fe{-}Fe{-}H_2]^+ \rightarrow [Fe{-}Fe{-}H] + H^+ \quad (82)$$

The proton would initially be expected to transfer intramolecularly to a basic site and then intermolecularly away from the active site. This process could then be repeated to remove the hydride as a proton. The metal−hydride bond is an interesting paradox in inorganic chemistry in that it can vary from being hydridic (acting as H^-) to protonic (acting as H^+) to anywhere in between.[49,270c,292] Thus, the "hydride" in a metal hydride complex can be fairly acidic (protonic) and removable as a proton, especially if the coligands are CO, e.g., $FeH_2(CO)_4$. The "hydricity" of hydride complexes has been intensively studied by DuBois and Curtis.[270c,292]

The active site of *D. desulfuricans* is similar to that of *C. Pasteurianum*, but in lieu of μ-CO, a monatomic oxygen species such as H_2O or OH apparently bridges the irons (it could also be terminal) and Fe(2) is proposed to be coordinatively unsaturated.[247] A 1,3-propanedithiolate type ligand bridges the Fe, where R could also be $-CH_2NHCH_2-$ with a basic nitrogen site to accept protons from H_2 heterolysis. Assuming accurate crystallography, one explanation of the structural differences is that the two structures represent different oxidation states and that the open coordination site in *D. desulfuricans* is the potential site for H_2 binding (it may actually be occupied by H_2, since crystallization was done under H_2). Also, shifts of CO between terminal and bridging positions and similar ligand rearrangements are extremely facile in organometallic systems, so in the enzyme mechanism, H_2 and hydride ligands could be positioned trans to a variety of ligands in either bridging or terminal sites. Calculations (below) show that such transformations are nearly barrierless processes on models for the active site. Because of the many easily accessible ligand arrangements and strong trans-ligand influences, the active site is tremendously flexible for either consuming or releasing H_2, adjusting the acidity of η^2-H_2 for heterolysis, and attaining the relatively low redox potentials typical of these active sites. As stated by Pardo et al. regarding DFT studies on Ni−Fe H_2ases, the channel for H_2 cleavage/formation is very wide, and the enzyme may be a good catalyst because there are many low-energy productive reaction coordinates.[398] With this in mind, Scheme 21 presents one (of many) reasonable mechanism for

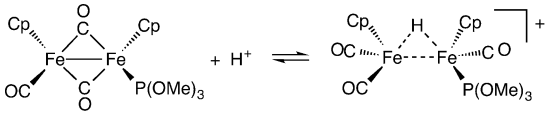
Scheme 21. Possible Mechanism for Hydrogenase $H_2 \rightleftharpoons 2H^+ + 2e^-$



reversible H_2 consumption/production on the Fe−Fe enzyme *C. Pasteurianum* that has been proposed by this author.[6,277]

This mechanism is intended primarily to illustrate the basic principles of organometallic systems that can be applied to the function of the Fe−Fe active site here and possibly other H_2ases as well. Scheme 21 assumes that, as generally believed, one CN and one CO is coordinated to each Fe^{II} and a low spin d^6 Fe^{II} octahedral configuration is present, which is well-known to favor H_2 binding. The transformations shown may involve participation of intermediate species not shown. Although there is yet no observable evidence for H_2 coordination in any form of the H_2ase enzymes, an H_2 complex of a rudimentary model for a H_2ase active site, $[Ru_2(\mu\text{-}H)(\mu\text{-}S_2C_3H_6)_2(H_2)(CO)_3(PCy_3)_2]^+$, has been synthesized, albeit with Ru instead of Fe and with phosphine ligands that do not occur in enzymes.[402] The J(HD) value for the HD complex is 31 Hz, indicative of $d_{HH} = 0.90$ Å, i.e. a true H_2 complex. Solutions catalyze H_2/D_2 exchange, which is characteristic of H_2ases. In the mechanism for H_2 consumption in Scheme 21 (conversion to electrons and protons), an intermediate Fe−H_2 complex is produced by displacement of the H_2O ligand in the enzyme's "precursor" form observed crystallographically. The bound H_2 then heterolytically cleaves and transfers a proton to, for example, the basic amine functionality proposed to be present on the thiolate bridge in close proximity to the H_2.[381] Both Crabtree and Morris have demonstrated that such intramolecular heterolytic cleavage (and its microscopic reverse reaction) readily occurs in organometallic complexes, as exemplified by the equilibrium proton transfers shown in eqs 52 and 55. Transfer of a proton from η^2-H_2 to the μ-thiolates in H_2ases is also possible as in eq 55. Calculations support such heterolysis, although it is endothermic by 15 kcal/mol.[401] Transfer of a proton to CN is nearly isoenergetic, but a high barrier is computed (38 kcal/mol, compared to 17 kcal/mol for transfer to sulfide). Oxidation to a cationic center could precede heterolysis and favor it, as in eq 82. The next steps for H_2 consumption involve movement of protons away from the active site to protein channels and synchronous or asynchronous electron transfer to the cubane cluster and away from the site via other Fe−S clusters. The electrons in the H−H bond could essentially flow through the Fe−Fe bond and, depending on whether one- or two-electron-transfer processes take place, one-electron Fe···Fe bonds (2.9−3.1 Å)[388] may be present in the intermediates (a two-electron-transfer step is shown in Scheme 21). The high flexibility of the M−M separation (2.6−3.2 Å, corresponding to 0, 1, or 2e M−M bonds) could facilitate electron/proton transfer here and in the [NiFe] H_2ases. As will be discussed below, the M−M bond can easily be protonated to form a bridging hydride (and deprotonated) as part of the mechanism. Also, ligand shifts between bridging and terminal positions involving CO as well as hydride ligands are extremely facile in dinuclear organometallic complexes and are likely to occur here as well. Once the H_2 is converted to electrons and protons, or in the reverse reaction is eliminated, recoordination of an aqua ligand is unnecessary and would only slow the reaction rate. It is likely that the intermediate with the bridging hydride transfers the H away from the active site (as a proton) and another H_2 molecule immediately recoordinates to start another catalytic cycle.

The reverse reaction, formation of H_2 from $2H^+$ and $2e^-$, involves protonation of the 2Fe center to form a metal hydride. The most basic site for initial protonation in the enzyme active sites may be the electrons in the M−M bonds, which can readily be reversibly protonated to form hydride-bridged species.[395] The Fe−Fe bonds in $[CpFe(CO)(PR_3)(\mu\text{-}CO)]_2$ are as basic as weak amines (pK_b around 6), and concomitant shift of μ-CO to terminal positions occurs on protonation (eq 83).[403] Protonation of the Fe−Fe bond in $[Fe(CO)_2(PR_3)(\mu\text{-}SR')]_2$ occurs in preference to protonation of the sulfur ligands (eq 84).[404] These are Fe^I centers, and



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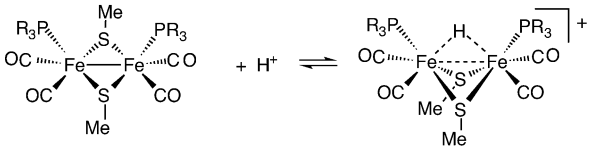
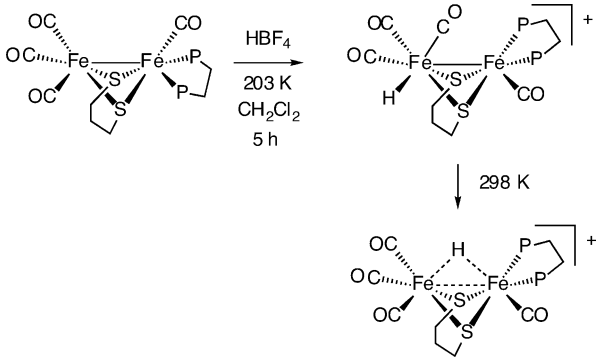


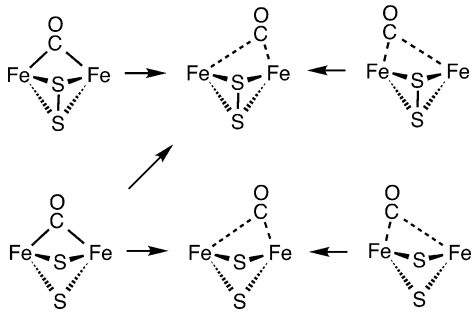
(84)

the Fe^I oxidation state has been proposed to occur in some forms of H_2ase metal cores. The basicities of M−M bonds such as in $[CpRu(CO)_2]_2$ are substantially higher than that of the metal sites in related 18e mononuclear complexes and are highly sensitive to the nature of the ancillary ligands.[395] As discussed above, theoretical studies of [NiFe] hydrogenase mechanisms indicate that Fe(μ-H)Ni intermediates are energetically favorable and might also be expected to play a role in the [FeFe] H_2ases. Formation of a terminal hydride species is a possible intermediate in these M−M bond protonation processes. As shown in Scheme 21, hydride ligands could reversibly shift between bridging and terminal positions and be protonated to a readily dissociable H_2 ligand,

Scheme 22

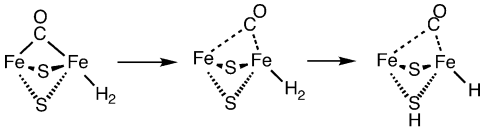


Scheme 23



leading to a cyclic process for either H_2 consumption or production. Indeed, the first examples of protonation of asymmetric iron hydrogenase active site mimics to form bridging hydride complexes via intermediacy of terminal hydrides and related studies were recently reported (Scheme 22).[405] NMR evidence showed that protonation of the carbonyl−diphosphine complex at 203 K gave slow formation of a terminal hydride complex that isomerized to the μ-H complex on warming.[405a] In the process, the diphosphine ($Ph_2PC_2H_4PPh_2$) shifted to a basal−basal position. Protonation at 233 K gave evidence for a species with hydride bound to the phosphine-containing iron as well. Protonation of a bis-carbene analogue also showed spectroscopic evidence for the initial presence of terminal hydrides.[405b] A symmetric analogue of the complex in Scheme 22 with 2CO and PMe_3 on each Fe and containing an NR group in the middle of the bridge linking the sulfides instead of CH_2 showed that protonation at the metal bond to form a bridging hydride was thermodynamically more favorable than at the nitrogen (kinetically favored).[405d] The synthesis of the diferrous terminal hydride complex $[Fe(H)(PMe_3)_2(\mu\text{-}CO)\{\mu\text{-}S(CH_2)_2S\}Fe(CO)(PMe_3)_2](PF_6)$ has been recently reported; its proton NMR spectrum exhibits a signal at −4.6 ppm, which has been assigned to the terminal hydrido ligand.[405c] The corresponding μ-hydride compound $[Fe_2\{\mu\text{-}S(CH_2)_2S\}(\mu\text{-}H)(CO)_2(PMe_3)_4](PF_6)$ displays a signal at −20.6 ppm, which has been attributed to the bridging hydride. The structures of both of these compounds were determined crystallographically.[405c]

Such bridging/terminal shifts involving CO as well as H would be especially likely to occur in the [Fe] H_2ase sites, which are attached to the protein only via the 4Fe-4S cluster, versus the [NiFe] sites, which are more tightly attached via cysteine groups that also bridge the metals. DFT calculations on $[(MeS)(CO)(CN)Fe(\mu\text{-}S)_2(\mu\text{-}CO)Fe(CO)(CN)]^z$ ($z = 0$ to −2) models show that the μ-CO can easily shift like a gate, where the O atom moves little but the carbon swings left or right to form *semibridging* CO ligands that are well-known in organometallic chemistry. Also, the μ-S can join via S−S bonds, a variable not even considered above (Scheme 23).[406] Remarkably, the transformations between six different isomers at three possible redox levels are virtually barrierless. The active site possesses a relatively flat potential energy surface for geometrical changes at Fe, CO, S, and bound H, which is consistent with the extremely rapid rates of H_2 production in the enzymes. H_2 weakly binds to Fe in the position of the H_2O ligand in the enzyme as in the model (**5**), but calculations indicate the H_2 complex is stabilized by a CO gate shift to the right (**6**). In the reduced states of



(**5**) (**6**) (**7**)

these models, ($\mathbf{5}^{2-}$) undergoes a mechanistically significant barrierless transfer of one H atom from Fe−H_2 to form SH ($\mathbf{7}^{2-}$).

The above CO movements and overall coordination-sphere "rotations" about the iron centers were also examined theoretically by Darensbourg.[248b] Both this author and Rauchfuss have recently structurally characterized mixed-valent Fe(II)Fe(I) dithiolato complexes that feature semibridging CO ligands, e.g., $(\mu\text{-pdt})[Fe(CO)_2(PMe_3)][Fe(CO)_2(IMes)]^+$ (pdt = propanedithiolate; Imes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) [407a] and $[Fe_2(S_2C_2H_4)(CO)_3(PMe_3)(dppv)][BF_4]$ (dppv = *cis*-1,2-$C_2H_2(PPh_2)_2$).[407b] A protected open site with structural similarity to the active site of FeFe H_2ases for possible H_2 binding and activation was found in these complexes, and the latter complex adds CO to this site with a concomitant shift of the semibridging CO to a normal bridging position.

8.2.12. Summary of the above Relationships

The important structure/bonding/reactivity relations between the active sites of H_2ases and organometallic systems can be summarized as follows.

(1) Octahedral Fe(II) d^6 centers are favorable for reversible molecular H_2 binding and heterolytic cleavage. The binding strength of H_2 in organometallic systems can be competitive with that for aqua ligands, depending on the electrophilicity versus nucleophilicity of the metal center.

(2) The CO ligands are presumed to be present to increase the electrophilicity of the metal center to promote reversible H_2 binding rather than irreversible formation of catalytically inactive hydride complexes. Such electron-withdrawing ligands, especially when positioned trans to the H_2 ligand, are also known to favor heterolytic cleavage of H_2. The CO ligands can easily shift between terminal, semibridging, and bridging positions, and it is thus crucial that the exact stereochemistry of a complex or an enzyme active site is known in order to understand H_2 activation. Electrophilic metal centers are also known to disfavor binding of atmospheric dinitrogen that could inhibit H_2 activation.

(3) Cyanide ligands may be present because of their very strong ligand-field strength that helps to maintain the metal centers in a low-spin (diamagnetic) state necessary to keep the CO ligands tightly bound. It is significant that cyanide can be formed biologically along with CO, unlike organophosphines or most other strong field ligands in inorganic and organometallic complexes.

(4) The M−M bonds in H_2ases may be present to facilitate initial protonation of the active site. Such bonds can be fairly basic (perhaps more than the proposed amino groups in the

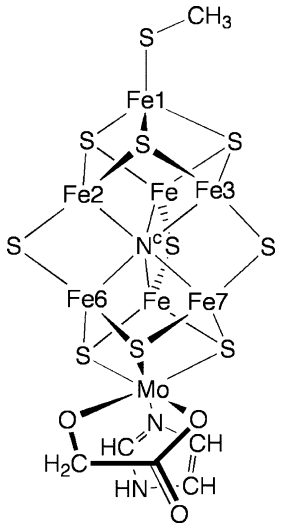


Figure 5. Model for the crystal structure of FeMo-co in *Azotobacter vinelandii*, as used in density functional calculations.[421]

sulfido linker) and readily form hydride-bridged structures that are proposed to be a step in the mechanism of H_2 formation. They may also facilitate electron transfer from the site of H_2 heterolyis to the attached Fe−S cubane cluster in the Fe−Fe H_2ases.

Biomimetic production of hydrogen fuel is being intensely studied, and many of the above principles could be relevant to homogeneous catalytic cycles for formation of H_2 from protons and electrons. Splitting of water photochemically or otherwise on inexpensive first-row transition metals such as iron is ideally needed to avoid use of valuable hydrocarbons and precious metals.

9. Hydrogen Activation in Nitrogenases

Hydrogen conversion is again of prime importance in nitrogen fixation to ammonia by nitrogenase enyzmes (N_2-ases)[408] and can be at least partially understood in terms of inorganic chemistry. Massive research efforts[241,242,244,336,409−425] have been directed at determination and modeling of the structure and function of N_2ase, rationalized partially on improving or providing alternate methods of ammonia production. Hundreds of million of tons of NH_3 are produced annually worldwide by the Haber process (eq 85).

$$N_2 + 3H_2 \xrightarrow[\text{Fe catalyst}]{400-500\ ^\circ\text{C}} 2NH_3 \qquad (85)$$

Although the industrial catalyst is iron based, its chemistry is not comparable to that in biological systems, since it takes place under very high pressures and temperatures. Nitrogenase catalyzes this under much milder conditions, but the mechanism is still enigmatic. The structure of the iron−molybdenum cofactor (FeMo-co) that is the site of catalysis is a NFe_7MoS_9(homocitrate) cluster linked to the protein through a cysteine residue.[410] A model of the site simplified for computational analysis[421] is shown in Figure 5. There is an unusual central trigonal prism of six iron atoms (Fe2−Fe7) linked by three doubly bridging sulfur atoms and centered by a small atom, initially speculated to be nitrogen (Nc), although there is more recent spectroscopic evidence[419] that it is not nitrogen. Recent biochemical investigations have provided strong evidence that the Fe4 face of FeMo-co involving atoms Fe2, Fe3, Fe6, and Fe7 is where alkynes and alkenes are bound, implicating this as the site of dinitrogen activation.

Nitrogenase uses electrons and protons to hydrogenate N_2, requiring careful chemical control to direct electrons and protons toward difficult to reduce N_2 while avoiding the facile combination of electrons and protons to form H_2. There is always some diversion to form H_2 (obligatory hydrogen evolution), however. At least one H_2 is produced for every N_2 reduced, seemingly as a waste of reducing equivalents.

$$8e^- + 8H^+ + N_2 \rightarrow 2NH_3 + H_2 \qquad (86)$$

There are extensive studies concerning the hydrogen reactivity of nitrogenase, much of which was developed by Thorneley and Lowe from their detailed kinetic data.[424] Their scheme involved eight stages of linked electron- and proton-transfer processes, and the earlier stages of reduction are the more intriguing, involving the accumulation of H atoms on FeMo-co, the evolution of H_2, and the initial binding of N_2. There are equilibria involving interchange of N_2 with H_2, reflecting the fact that H_2 is a competitive inhibitor of the reduction of N_2.

Insight into the nature of the intermediates comes from kinetic analysis of the HD formation reaction of nitrogenase, i.e., the N_2-dependent formation of HD in the presence of D_2.[334,408a,423,424] When nitrogenase turns over under D_2, HD is formed, but only in the presence of N_2: other substrates such as acetylene do not enable the formation of HD. The HD formation is not catalyzed H_2/D_2 exchange but is a reduction, with the stoichiometry shown in eq 87.

$$2H^+ + D_2 + 2e^- \rightarrow 2HD \qquad (87)$$

Furthermore, during turnover under HD, D_2 is not formed, and when T_2 is used, there is negligible leakage of tritium label into the aqueous phase. This phenomenon implies that the H and D that form HD come from different sources that do not mix their hydrogen atoms, and that this reaction is facilitated only when N_2 is bound. This in turn implies that the displacement of H_2 by N_2 at a single active site must be an associative process. A reasonable explanation for this is that N_2 binds to a trihydride species, MH_3 or $MH(H_2)$, with displacement of H_2. Subsequent loss of N_2 by reaction with protons toward NH_3 formation or by dissociation, followed by binding of D_2, would generate MHD_2, an obvious source of HD (section 8.2.8). The Lowe−Thorneley[424] model of the nitrogenase mechanism is consistent with generation of a trihydride species by protons binding to the reduced site prior to N_2 binding. Some H_2 is released during this process, as in labile H_2 complexes that readily exchange N_2 and H_2. Hughes et al. propose a scheme for H_2 evolution, H_2 binding, and reduction at the Mo site of the enzyme wherein a Mo dihydride species eliminates H_2 on reaction with N_2.[425] However, this model does not explain why, in the comparable experiment performed under HD, no D_2 forms, nor why substrates other than N_2 do not promote HD formation. Also, if H_2 can interact with the active site, why is a substrate of any kind needed to promote HD formation? Displacement of H_2 is not a necessity for binding N_2, but why does HD form only when N_2 is being reduced? One simple answer proposed by Helleren et al. is that HD formation and N_2 binding occur at different places.[423] It is possible that different substrates bind to and are transformed at different parts of the large FeMo-co site of N_2ases (a separate P-cluster may also be involved). CO inhibits nitrogen fixation in N_2ases

but *not H_2 evolution*. A single site that binds H_2 and N_2 equivalently should be poisoned by CO for both H_2 and N_2 activity, and evidence increasingly points to multisite processes in the FeMoco cluster.

ENDOR spectroscopy showed that the cofactor covalently bound two chemically equivalent $H^{+/-}$, giving the first experimental insights into the structure of an intemediate formed during H_2 evolution catalyzed by N_2ase.[420] A species with three hydrogenic species bound to one Fe was considered as a model for an intermediate state, and a dihydrogen−hydride structure was considered. However, the ENDOR patterns showed two ^1H that appeared to be chemically equivalent, which would seem to be inconsistent with a FeH-(H_2) structure (although this possibility was not precluded in other reaction steps or reduction states). At about the same time (2005), the coordination chemistry of H_2 on FeMo-co was examined calculationally by Dance, who found that molecular H_2 coordination at iron is energetically and mechanistically reasonable. Key principles, some of which are summarized below, were derived for the coordination chemistry of hydrogenated FeMo-co modeled as in Figure 5.[421]

(1) Both Fe−H and molecular Fe−H_2 coordination can occur in exo- and endo-coordination positions at the central Fe atoms, with exo-coordination energetically better.

(2) FeMo-co has ample capacity to bind multiple H atoms and/or H_2 molecules. Two H_2 molecules can be bound to the one Fe atom if either the Fe−Nc bond or the Fe−(μ_3-S) bond is severed.

(3) FeMo-co is able to distort substantially to accommodate binding of H and H_2, but is subject to coordinative allosteric influences.

(4) S−H to Fe−H transfers have barriers of 9−16 kcal/mol.

(5) Association of H_2 at Fe is generally endergonic, but the presence of endo-Fe6-H causes exo-Fe6-H_2 association to be exergonic.

(6) Barriers for dissociation of Fe−H_2 are generally ca. 5 kcal/mol.

(7) One very favorable process for generation of H_2 is formation of exo-Fe−H_2 by transfer from proximal sulfides: the reaction is strongly exergonic, and the barrier is as low as ca. 3 kcal/mol.

(8) H atoms in endo and exo positions on the same Fe atom convert exergonically to H_2 in the exo position, with small (ca. 3 kcal/mol) barriers.

(9) Nondissociative atom exchange between H and H_2 can occur readily at one Fe site.

Clearly, the above features have similarities to established H_2 coordination chemistry, but whether H_2 ligation is important mechanistically remains open to debate.

10. Biomimetic Hydrogen Production

Production of H_2 fuel, e.g., from water via solar energy, is of high interest.[263,426] Catalysis may involve H_2 complexes at least as intermediates, and, e.g., H_2 complexes have been implicated in solar energy conversion schemes based on photoreduction of water.[264] Industrially important water gas shift and related H_2-producing reactions undoubtedly proceed via transient H_2 complexes.[141] DuBois and co-workers have found that dicationic nickel(II) complexes with two pendant amine ligands similar to that in Scheme 13 heterolyzed H_2 to form two protonated amines and were highly efficient electrocatalysts for both H_2 evolution and oxidation.[270]

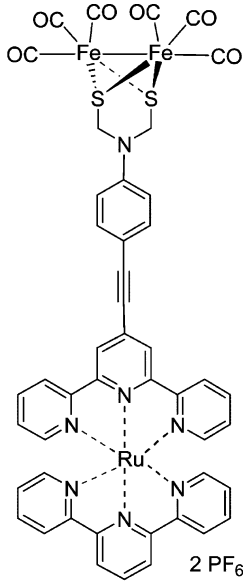


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Figure 6. Schematic representation of light-driven proton reduction.[262]

Importantly, cooperative interactions of dihydrogen ligands with both the metal center and proton relays incorporated in the second coordination sphere contribute to the high activity observed for these Ni-based molecular catalysts that rival H_2ases in reaction rates. Electrochemical production of H_2 occurred at turnover frequencies as high as 350 s^{-1}, comparable to that of Ni−Fe H_2ases (700 s^{-1}).[270b]

Biomimetic H_2 production, particularly solar driven (photocatalysis), is taking cues from modeling of the active sites of hydrogenases coupled with models of Nature's photosystems.[234,262,263,427] Here, the formation of H−H bonds from protons and electrons, the microscopic reverse of H_2 heterolysis, will be crucial in leading to formation of H_2 and is very rapid at the Fe sites in H_2ases. Coupling model catalysts with photochemical water splitting will require fine-tuning of electrochemical potentials for tandem catalysis schemes. Homogeneous catalysts are advantageous, and studies are underway in this arena, e.g., by Sun et al. in their work on linking ruthenium photoreceptor complexes to dimetallic iron complexes modeling the H_2ase active site (Figure 6).[262,427] Electrons photochemically generated from the Ru−bipy complex were designed to travel down a "molecular wire" linker to a di-iron center for combination with protons to form H_2. However, the electrochemical potentials for the processes (photochemical production of electrons and proton reduction) must be compatible, which was a barrier to progess in the Sun system. A more promising alternative process has recently been described using a triad reaction system with a stronger reductant, $Ru(bipy)_3^+$.[427]

It should also be possible to study similar monometallic iron(II) complexes with octahedral geometry with CO, CN^-, and thiolate ligands as the site of H_2 production. One key to designing such functional catalysts for hydrogen formation via, for example, water splitting is having a proper electrochemical reduction/oxidation (redox) potential for the sequential electron addition steps. In the bimetallic model complexes for H_2ases, catalysis by the diiron units is quite sensitive to electronic effects; that is, the nature of the ligands controls the electrochemical potentials for oxidation/reduction (as in most metal complexes).[235] This could partially explain

why cyanide (CN) ligands are used by hydrogenases. It is a strong electron donor (synthesizable biochemically) and would increase the electron-richness of the metal, which would facilitate protonation of the metal and lower the potential required for the electrochemical production of hydrogen. Interestingly, Sun's biomimetic dimetallic iron system did not have CN ligands and the potential was too high.[262] On the other hand, the metal center cannot be too electron-rich and must retain some electrophilic character; otherwise, release of hydrogen would not be facile, and a fine balance of electronics is needed. Thus, variation of ligands would be used to adjust the potentials, and there are well-defined parameters to predict this calculationally by assuming a structure for the complex and applying an additive ligand parameter via the methodology developed by Lever.[428] In addition to ligand effects, overall charge, i.e., cationic ($[L\text{-}M-H_2]^+$) or anionic ($[L\text{-}M-H_2]^-$), has a powerful effect on the binding and reactivity of H_2 ligands as well as electrochemistry. The nature of the metal is, of course, critical, and Rauchfuss found that platinum-group metal (e.g., Ru) mimics of the Fe-only hydrogenase active sites yield catalysts *less* effective for proton reduction, although many aspects of the associated reactivity are quite analogous.[429] Thus, there are many factors and options for exploring homogeneous catalysts for biomimetic H_2 production (as can be seen in other articles in this thematic issue), and the work is still in its infancy.

11. H_2 Coordination Chemistry Relevant to Hydrogen Storage

11.1. Introduction

In addition to enzymatic hydrogen activation and biomimetic hydrogen production, the nature of dihydrogen coordination on metal complexes and other compounds is relevant to possible new materials for *hydrogen storage*. The reversible binding of H_2 to metal complexes and the low energies for hydrogen uptake and release as H_2 gas under near ambient conditions are ideal properties for hydrogen storage. Importantly, there would be little heat released on hydrogen uptake at a fueling station and little heat needed to release the weakly held H_2 molecules from the storage vessel. This may be the most important feature of utilizing molecular hydrogen binding for hydrogen storage. The binding energy of hydrogen molecules to stable transition metal complexes was determined to be 15−20 kcal/mol and may be as low as a few kcal/mol for the weakly bound systems under pressure. On the other hand, metal *hydrides* such as $NaAlH_4$ may have M−H bond energies as high as 60 kcal/mol, a potential waste of energy. However, intermediate interactions are also known in elongated H_2 complexes and in certain intermetallic rare-earth hydrides[71−73] where d_{HH} is ∼1.5 Å, indicating additional avenues may exist in the gray area between dihydrogen and dihydride complexes. Also, multimetallic hydrides (often clusters with μ-H) are known to dissociate and re-add H_2 reversibly.[45c]

Materials that bind H_2 in the realm between physisorption and chemisorption are thus desirable, but there are severe challenges here. The main obstacle to overcome is the low gravimetric content of hydrogen (typically less than 1% in known complexes and 6% or greater is needed) because of the relatively high molecular weight of coligands. Only a few metal complexes are known to contain two H_2 ligands (none with more). The best known and most studied are $RuH_2(H_2)_2(PR_3)_2$ [R = cyclohexyl (Cy) and cyclopentyl (Cyp)] and $RuHX(H_2)_2(PCy_3)_2$ (X = Cl, I), as shown in Figure 2 and eq 3.[35,57,58,65] Up to ten hydrogens (including hydrogens from the phosphines) can be *reversibly* removed from the former (R = Cyp) under mild conditions.[65b] Although this represents only 1.71% of the weight of the complex, this demonstrates that H_2 binding to transition metal centers could be useful in hydrogen storage materials, *particularly if the metals are incorporated into nanoporous materials*, as will be discussed below. Limiting the number of "heavy ligands" (e.g., phosphine) on the metal would obviously be beneficial. Computational studies reviewed by Heben in this thematic issue[430] indicate that even complexes of the type $M(H)_x(H_2)_n$ containing multiple H_2 ligands (up to $n = 6$) could be thermodynamically stable, even devoid of ligands other than hydrogen. Although multi-dihydrogen species with few or no ancillary ligands such as $Cr(H_2)_6$ and $UH_4(H_2)_6$ have been theoretically calculated to be stable,[431] they would undoubtedly be highly reactive. Such species might be stabilized when imbedded in nanoporous media, however. Although the uranium species would clearly not be a practical storage material, the calculation suggests that up to 16 H's could surround a single metal center. A buckyball can theoretically bind up to 12 metals on all of its faces (and thus up to 48 H_2),[430,432] but again, synthesis of such species would be problematic. Nonetheless, design of such hydrogen-rich metal species is one area for exploration. As will be discussed below, unsaturated "naked" transition metal cations capable of binding multiple H_2 and/or hydride ligands may be able to be generated, since species such as $[M(H_2)_n]^+$ are known in the gas phase with up to *ten* H_2 molecules "solvating" a first-row transition metal cation.[433−449] Protonation of anionic metal polyhydrides is another possible pathway to such poly-H_2 complexes with few or no coligands, which may be stable under moderate H_2 pressures. As shown in Table 2, there are many metal−H_2 complexes with minimal or lightweight coligands. Although nearly all are unstable at room temperature, there may be means to stabilize such systems, as discussed below.

The binding of H_2 would be expected to be highly reversible in the above systems, which would be ideal for facile hydrogen storage. The above theoretically accessible multi-H_2 species would likely be unstable in the condensed phase, but they and complexes such as those in Table 2 could possibly be incorporated into nanoporous materials such as zeolites or fullerenes. As will be discussed below, metal organic framework compounds (MOFS) with very high surface areas are known to bind large numbers of H_2 primarily via physisorption within the open lattice (Figure 7). Inelastic neutron scattering spectroscopic measurements are valuable here to differentiate between the latter type of binding and coordination of H_2 to the metal, which will also be described below. Reversible binding of H_2 to main group compounds and nonmetal centers, e.g., oxides, will also be discussed. The structure and bonding properties of dihydrogen are important, and H_2 can behave as either a weak Lewis base or a weak Lewis acid toward main group compounds (Figure 8). This versatile, amphoteric-like behavior may be able to be exploited for facile reversible storage of hydrogen as molecular H_2 rather than chemical hydrides. The inability of main group compounds to backdonate electrons to H_2 σ^* (section 3.2) ensures that the H_2 is bound molecularly and reversibly rather than as a hydride, but as a result, the interaction is weak.

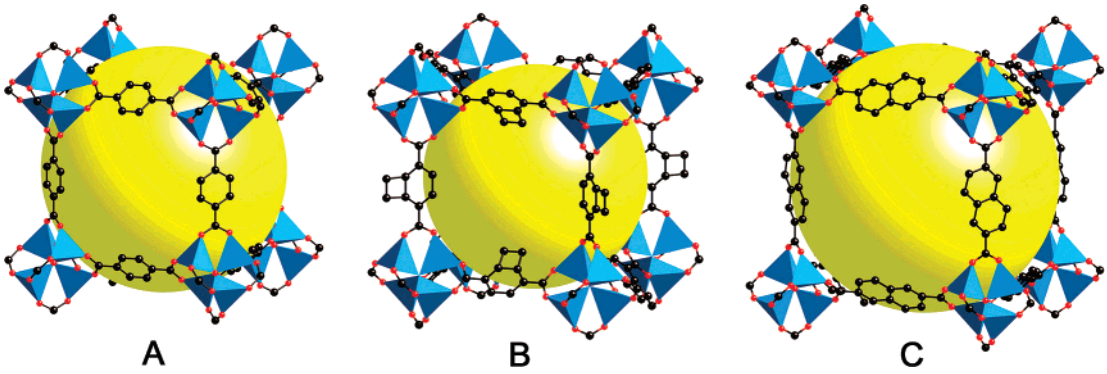


Figure 7. Single-crystal X-ray structures of MOF-5 (**A**), IRMOF-6 (**B**), and IRMOF-8 (**C**) illustrated for a single cube fragment of their respective cubic three-dimensional extended structures. On each of the corners is a cluster $[OZn_4(CO_2)_6]$ of an oxygen-centered Zn_4 tetrahedron that is bridged by six carboxylates of an organic linker. The large spheres represent the largest sphere that would fit in the cavities without touching the van der Waals atoms of the frameworks. Hydrogen atoms have been omitted. From ref 510 (http://www.sciencemag.org). Reprinted with permission from AAAS.

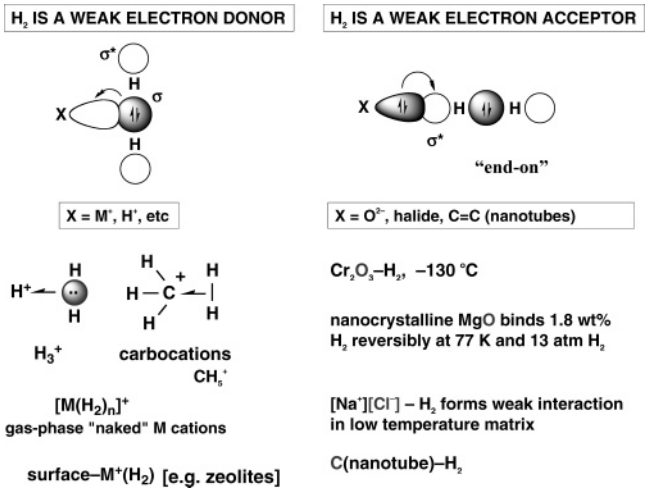


Figure 8. Examples of the ability of H_2 to behave either as a weak Lewis base or as a weak Lewis acid toward main group compounds.

Summarizing, the key advantages of molecular hydrogen binding for H_2 storage in vehicle tanks are as follows:

(1) The reversible binding of dihydrogen on a solid material would use only moderate pressure swings to fill the tank and release hydrogen. The H_2 could be added rapidly; that is, there is a small kinetic barrier for H_2 on/off and no need for catalysts or chemical conversions.

(2) Minimal heat is released on fueling the tank or is needed for hydrogen release from the tank.

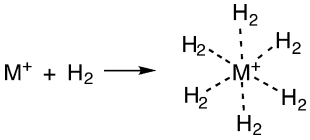
(3) Inexpensive materials can be designed to bind hydrogen.

(4) The density of hydrogen bonded to solid materials may be greater than that of liquid hydrogen.

(5) Although pressure may be needed to fill the storage vessel, the pressure of the solid-bound hydrogen will not be anywhere near as high as that of liquid hydrogen or pure pressurized gas.

11.2. H_2 Binding to Naked Metal Ions

Significant theoretical and experimental investigations of molecular H_2 binding to metals have also been devoted to systems other than discrete transition metal complexes and rudimentary species such as Pd−H_2. A large class of "naked" metal cations, $[M(H_2)_n]^+$ (M = first row transition metal) studied by ion-beam and mass spectrometric techniques, give H_2 dissociation energies and are excellent systems for H_2 and alkane binding because of their high electrophilicity and reluctance to oxidatively add these molecules.[433] These species are formed and studied, for example, by electron-impact ionization of organometallic precursors such as $CpCo(CO)_2$, injection of the resulting Co^+ into a reaction cell containing H_2, and mass spectrometric analysis. Alternately, "naked" metal ions can be produced by sputtering them off a metal cathode in a flow tube where H_2 molecules (or other small molecules) are added downstream in a guided ion-beam tandem mass spectrometer. These experiments are useful for determining M−H_2 binding energies on extremely electrophilic fragments. Neutral M on surfaces nearly always transfers electrons to approaching H_2 molecules to split the H−H bond to gives hydrides, analogous to excessive backdonation (BD) causing oxidative addition in metal complexes (Scheme 3). However, when H_2 approaches a bare M^+, the BD bonding component is less energetically favorable because the second ionization potential of M^+ is quite high. Instead, the cation polarizes the H_2 and the M^+−H_2 bonding takes on a dipole character. Calculations indicate that M^+ can in essence be "solvated" sequentially by up to ten H_2 molecules, as in eq 88.[433]



(88)

Binding energies for all first-row clusters $[M(H_2)_n]^+$ (n = 1−6) and several small molecule analogues have been determined by temperature-dependent equilibrium measurements[434−443] of mass-selected M^+ ions reacting with H_2 or by collision-induced dissociation (CID) in a guided ion-beam mass spectrometer (Table 5).[444−446] Although noncovalent electrostatic interactions (charge-induced dipole and charge quadrupole) are present, they normally comprise a small fraction of the total bond strength because the purely electrostatic attraction in $[Na(H_2)_{1,2}]^+$ and $[K(H_2)_{1,2}]^+$ is only 1.3−2.5 kcal/mol.[439,443] The presence of covalent forces in the bonding is shown by the strong influence of the nature of M^+ on both bonding energies and structures. The four covalent forces include the main interaction: electron donation from the H_2 σ orbital to M^+ that stabilizes the ion charge. Most of this donation is to the M 4s orbital with a minor amount to a 3d orbital of proper symmetry. Second, some BD to the H σ^* orbital still occurs in the later M^+

Table 5. Comparison of Experimental Binding Energies (±0.4−1.4 kcal/mol) for $[M(L)_{n-1}]^+ + L \rightarrow [M(L)_n]^+$ for L = H_2, CH_4, and N_2 up to $n = 4$

		binding energy			
ion	L	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$[Ti(L)_n]^+$	H_2	10.0	9.7	9.3	8.5
$[V(L)_n]^+$	H_2	10.2	10.7	8.8	9.0
$[Cr(L)_n]^+$	H_2	7.6	9.0	4.7	3.4
$[Mn(L)_n]^+$	H_2	1.90	1.65	1.4	1.2
$[Fe(L)_n]^+$	H_2	16.5	15.7	7.5	8.6
	CH_4	13.6	23.2	23.7	17.7
	N_2	12.9	19.8	10.8	13.6

Table 6. Interaction of H_2 with Neutral and Charged Fe

system	d_{FeH}, Å	d_{HH}, Å	binding energy, kcal/mol
$[FeH_2]^+$	1.92	0.73	−33.8
$[FeH_2]^0$	2.01	0.77	−5.0
$[FeH_2]^-$	2.25	0.86	−42.4

with filled 3d orbitals, despite the highly electron-deficient M here. In ions with half-filled 3dσ orbitals, a hybridization between the $3d_{z^2}$ and the 4s orbital reduces on-axis Pauli repulsion. Last, minor contributions from hybridization with the 4p orbitals can occur, despite their significantly higher energy. The relative importance of these and the electrostatic factors depends strongly on the valence configuration of M^+.

The observed binding energies for $[M(H_2)_n]^+$ as well as CH_4 analogues for comparison generally decrease with n, as shown in Table 5, which lists energies for $[M(L)_n]^+$ for $n = 1-4$ and L occupying octahedral sites. Computations show good agreement; that is, in $[Ti(H_2)_n]^+$, the bond energies at the DFT level are less than 1 kcal/mol lower than experimental values.[440] In general, d_{HH} is near that in free H_2, 0.74−0.77 Å, for $n = 1-6$, although in some cases the distance can approach the 0.82 Å value seen crystallographically in organometallic complexes. For Sc^+, oxidative addition of H_2 to form two hydride ligands occurs for $n = 1$, followed by molecular H_2 binding to give $[ScH_2(H_2)_n]^+$.[438] The bond strengths for $[M(H_2)_n]^+$ are greater for the later metals (Fe, Co, Ni) primarily because of greater BD and, secondarily, smaller ion size (much of the attraction is due to charge-induced dipole potential, which varies as $1/r^4$). The binding energies for Mn and Zn are by far the weakest because of repulsion between the singly occupied 4s orbital and the H_2 σ orbital.[441−443] All other first-row metals, in contrast, have a $3d^n$ valence electron configuration for the $[M(H_2)_n]^+$ species.

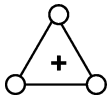
CID measurements for CH_4 binding to $[Co(CH_4)_n]^+$ exhibit parallel behavior to that for $[Co(H_2)_n]^+$ (Table 5).[447,448] Ab initio calculations show similar bond energies and predict that CH_4 binds in an η^2-H,H fashion. The trend in bond energies is rationalized by electronic changes at M (e.g. s−d hybridization) on coordination of the third and successive molecules. The different trends for the Fe^+ system for L binding are ascribed to changes in the electronic structure of M with sequential coordination of ligands of varying field strengths.[449]

Calculations on the interaction of H_2 with Fe^0, Fe^+, and Fe^- atoms show that positive charge on M favors η^2-H_2 binding while negative charge promotes OA to dihydride (Table 6).[450] This corresponds well with organometallic systems where positive charge favors η^2-H_2 coordination. The H_2 binding energy for the positively charged molecule is much greater than that for the neutral species. An energy barrier of 35 kcal/mol for H_2 OA on Fe^0 is calculated, but excitation to a quintuplet $3d^64s^14p^1$ state leads to OA without a barrier, as is experimentally known. This large dependence on electronic state may relate to that for $FeH_2(CO)_4$, where H_2 is bound in dihydride form rather than as dihydrogen, which would have been expected because of the electron-poor metal center (section 3.2). Other calculations reiterate that metal cations bind H_2 with rather large binding energies while neutral metal atoms cleave H_2.[451−454] For neutral atoms, the hydridic binding results from transfer of charge to the hydrogens that limits the number of H atoms that can subsequently be bound. However, in the cations, the binding is due to polarization of the H_2 molecule, and a large number of H_2 molecules can bind.

11.3. Interaction of H_2 with Metal Surfaces, Metal Oxides and Hydrides, and Non-transition-Metal Compounds

While the above ion species have been frequently observed spectroscopically, definitive observation of molecular binding of H_2 to metal surfaces and small metal clusters is both rare and nontrivial experimentally. Chemisorbed H_2 is observed on a stepped Ni(510) surface,[195] and calculations for H_2 on a Ni_{13} cluster,[455] triatomic NiH_2,[455] and a Ni(100) surface[456] indicate such molecularly bound states are possible, as well as hydride states. For H_2 on Ni_{13}, d_{HH} is 0.89 Å and ν(HH) is 2600 cm^{-1}, but no η^2-H_2 state is found on Cu(100) because of differences in 3d orbital occupation. Evidence for $Cu_2H_2(H_2)_x$ ($x = 1, 2$) and $Cu_3(H_2)$ in an Ar matrix exists however,[457] and it should be noted that CuCl−H_2 is also known in an Ar matrix, as shown in Table 2. This table also lists other known low-temperature stable complexes with minimal or no coligands as well as surface-bound H_2 species.

Weak Lewis acid−base interactions of H_2 with main group compounds as shown in Figure 8 are known but are usually unstable and often studied only theoretically. Calculations predict H_2 binding to several types of Lewis acidic sites, including non-transition-metal cations and ionic solids such as BeO.[458−467] The simplest such species is H_3^+, a well-known but unstable species that is formed by protonation of H_2 and has a triangulo structure with $d_{HH} = 0.87$ Å. Similar

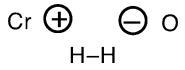


species are formed with M^+ with all outer electrons removed and include $Li(H_2)^+$ and $Be(H_2)^{2+}$.[458] $Be(H_2)^{2+}$ is much more stable than the Li complex because Be^{2+} can accommodate two electrons in degenerate $n = 2$ empty orbitals, and the energy of these LUMOs (lowest unoccupied molecular orbitals) lies closer to the energy of the occupied σ_g H_2 orbital. This extends to neutral complexes involving light metal atoms such as $OBe(H_2)$ and $SBe(H_2)$[461−465] or $F_2Mg(H_2)$[466]and its dimer,[467] where the "effective" positive charge on the M atom must be significant, e.g., metals with electronegative substituents such as O or F. Calculations[465] show that *monomeric* BeO is a substantially stronger Lewis acid than $AlCl_3$ (BeO is actually a polymeric solid like alumina).

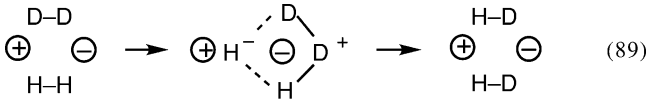
Transition metal oxides are vital heterogeneous catalysts and/or supports in many processes involving H_2 such as hydrotreatment of crude oils. Oxides studied theoretically include hematite (Fe_2O_3), modeled as a simple $Fe(\mu\text{-}O)_3Fe$

cluster with H_2 binding to an apical Fe.[468] The binding energy for $(Fe_2O_3)(H_2)$ is calculated to be relatively high, 37.6 kcal/mol, with $d_{HH} = 0.80$ Å, but placing a negative charge on the cluster decreases it to −10.1 kcal/mol and d_{HH} to 0.75 Å. This is unlike the situation for Fe atoms above (Table 6) because the negative charge on $[(Fe_2O_3)(H_2)]^-$ resides mainly on oxygen, reducing the Lewis acidity of Fe without increasing the BD that activates H_2 toward OA on Fe atoms. DFT studies of the reaction surface of $FeO^+ + H_2$ show η^2-H_2 on Fe with $d_{HH} = 0.77-0.81$ Å depending on Fe spin state.[469]

Experimental counterparts for the above computations are rare because the surface of metal oxides usually does not contain exposed unsaturated metal sites. Only very recently have coordinatively unsaturated sites (cus) been identified on an oxide surface: $RuO_2(110)$ can be seen to bind CO to Ru cus by scanning tunneling microscopy.[470] $RuO_2(110)$ has recently been found to also bind H_2 nondissociatively at 85 K ($\nu_{HH} = 2960$ cm^{-1}).[471,472] Calculations indicate that $\delta_{HH} = 0.89$ Å and that the H_2 is 1.8 Å from the Ru^{cus} atoms (cf. 0.94 Å and 1.81 Å, respectively[473] in *trans*-$[RuH(H_2)(Ph_2PC_2H_4PPh_2)_2]^+$). These data suggest that, as for H_2 on Ni surfaces, the binding of H_2 to Ru^{cus} is similar to that in organometallics. Dehydroxylated chromia (Cr_2O_3) had much earlier been proposed by Burwell to contain cus in 1969, and the Cr^{3+}(cus) and O^{2-}(cus) ion pairs chemisorb H_2 nondissociatively below −130 °C.[474,475] Pulses of D_2 at −196



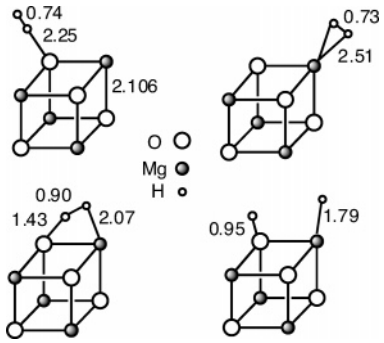
°C completely and rapidly displace adsorbed H_2 without formation of HD, although above −163 °C substantial HD is formed. This is consistent with molecular binding of H_2 to the metal center at −196 °C, with *heterolytic H_2 splitting* taking place on $Cr^{3+}\cdots O^{2-}$ sites at higher temperatures. A proposed mechanism for scrambling of $H_2 + D_2$ to HD involves a transient containing H^- associated with the Cr^{3+} and HD_2^+ with O^{2-}. A reverse situation in eq 89 with HD_2^-



(89)

associated with Cr^{3+} and H^+ with O^{2-} is also possible. Burwell points out that many other oxides adsorb and activate H_2 at low temperatures, including Co_3O_4, V_2O_3, MnO, and even main group oxides such as MgO.[474,475] Calculations show that NiO weakly binds (3.7 kcal/mol) H_2 at the metal ($d_{HH} = 0.805$ Å)[294,476] but ScO heterolytically cleaves H_2 to HScOH exothermically by 14 kcal/mol without forming an H_2 adduct as a local minimum on the potential energy surface.[477] Computations also suggested that H_2 molecules adhere to the (111) surface of MgO with a much higher binding energy of 30 kcal/mol.[478] Earlier ab initio studies of H_2 interaction and cleavage on a MgO surface using a cuboidal $(MgO)_4$ cluster as a model identified two types of interaction: η^1-H_2 on the oxygen site and η^2-H_2 at Mg.[479] Because the calculated d_{HH} (0.73 Å) in both cases is nearly the same as that for free H_2, the H_2 is most likely physisorbed. These weak complexes lead to a common transition state (TS) featuring a bridging H_2 unit with $d_{HH} = 0.90$ Å, followed by heterolytic cleavage of H_2 (Scheme 24). The estimated energies relative to the reactants are −2, +2, and −21 kcal/mol for the physisorbed complexes, the TS, and the product. Similar results were found for an analogous

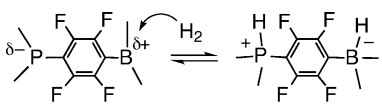
Scheme 24



$(ZnO)_4$ system as a model for H_2 adsorption and heterolytic dissociation on Zn(II) zeolites.[480] We have found experimentally that H_2 binds to commercial nanocrystalline MgO at 77 K and 13 atm up to 2% by weight,[481] although it mostly dissociates at room temperature. Using surface area = 600 m^2/g and the theoretical monolayer hydrogen density of 1.3×10^{-5} mol-H/m^2, the MgO adsorbs the equivalent of 2.5 H_2 monolayers. This indicates crevices store additional hydrogen. The enhancement storage factor of 2.5 is ∼4 times smaller than that found in carbon, e.g., nanotubes studied by Heben and others.[430] The light weight of MgO and similar main group oxides would make them attractive candidates for H_2 storage but probably only at low temperature.

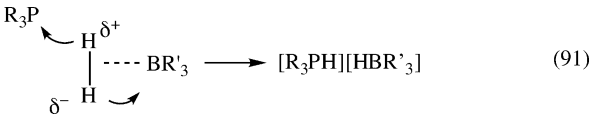
In addition to binding of H_2 to naked metal cations, neutral hydrides can interact with H_2. Calculations show that H_2 weakly binds to a large variety of binary hydrides (MH_n),[482,483] which have only rarely been observed, e.g., matrix-isolated $CrH_2\cdot(H_2)$.[484] The binding energies for $MH_2\cdot(H_2)$ decrease with increasing atomic number for M = Ti, V, and Cr, and BD is the dominant reason. Comparisons of calculated and experimental[484] vibrational frequencies support the existence of these species in matrices formed by cocondensation of M and H_2. Hydrogen exchange is calculated to occur on these systems via a trefoil-type $M-H_3$ transition state as in organometallic systems, which for alkali metal systems approximate ion pairs of M^+ and H_3^-.[482] The transition states for the exchange with group 3 transition metals have an energy of 8−10 kcal/mol relative to the reactants, which is lower than those for the alkali metal systems (16−22 kcal/mol) and group 4 metal hydrides (32−46 kcal/mol).

The metal-free aspect of most of the above systems for activation of H_2 is important because precious metals such as platinum are often used in catalysis and can be environmentally unfriendly as well as costly or in short supply. As discussed in section 8.2.5, H_2 can be cleaved at nonmetal centers, e.g., apparently on the bridging sulfides in $Cp_2Mo_2S_4$ that Rakowski DuBois found to react with H_2 to form SH ligands, perhaps via a four-center S_2H_2 transition state (eq 46). Metal-free hydrogenation of ketones on strong bases such as *t*-BuOK occurs under harsh conditions, apparently via base-assisted[350] heterolysis of H_2.[485,486] Thus, H_2 is a very weak acceptor (Lewis acid) via electron donation to its σ^* orbital and can thus interact with the O in alkoxide or metal oxides and can undergo heterolysis. Significantly, the first example of *reversible* splitting of H_2 on a *nonmetal center* has been found (eq 90).[487] The phosphine borane has a strong



(90)

Lewis acidic center (boron) linked to a Lewis basic site (phosphorus). It is likely that H_2 heterolysis takes place at the electrophilic boron center where proton transfer from a transient $R_3B\cdots H_2$ complex to the basic phosphorus site occurs to form the phosphonium borate.[487,488] Related formation of phosphonium borate salts $[R_3PH][HBR'_3]$ from reaction of sterically demanding phosphines, boranes, and H_2 was also reported.[488] Equation 91 shows a possible mechanism for the heterolyses. Theoretical and experimental



(91)

evidence indicates that H_2 can interact with a boron center. BH_5 exists calculationally as a very weak Lewis acid−base complex H_2-BH_3 with a very low dissociation energy of 1−5 kcal/mol depending on methodology.[489−491] Charge density analyses show that H_2 (and ethylene in $C_2H_4-BH_3$) are stronger donors than acceptors.[491] The barriers for hydrogen migration and rotation are very low, and the zero-point vibrational energy is similar to the binding energy so that H_2-BH_3 is barely a bound species. The dissociation energies for X_3B-H_2 (X = F, Cl) are even lower, 0.7−0.9 kcal/mol, indicative of van der Waals complexes.[491] Attempts to observe binding of H_2 to the latter in low-temperature matrixes by Sweany apparently led to heterolysis of H_2 to form B−H bonds.[492] A structure has been calculated for $[H_3C]^+[BH_2(H_2)^-]$ and indicates interaction of H_2 with boron.[493]

Other weak interactions of H_2 with main group species shown in Table 7 help to define the Lewis acid−base strength of H_2 as a *pure σ donor or acceptor*. Significantly, complexes where H_2 can act only as a pure Lewis base are unstable, attesting to the vital role of BD from metal d orbitals in stabilizing σ-ligand binding. Hypervalent main group species such as CH_5^+, CH_6^{2+}, CH_7^{3+}, $SiH_3(H_2)_2^+$, and analogous B and Al series starting with BH_6^+, AlH_4^+, and AlH_6^+ are rationalized theoretically as highly dynamic H_2 complexes of main group cations (see section 3.1). In regard to materials for hydrogen storage, some of the species in Table 7 have very high gravimetric percentages of hydrogen, e.g., $LiH(H_2)_2$ (42%), but have been characterized only under low-temperature conditions and/or are unstable.

11.4. Inelastic Neutron Scattering (INS) Studies of H_2 Coordination and Rotation

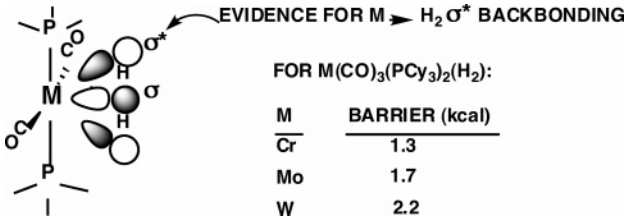
The H_2 ligand undergoes rapid two-dimensional hindered rotation about the $M-H_2$ axis; that is, it spins (librates) in propeller-like fashion with little or no wobbling. This phenomenon has been extensively studied by inelastic neutron scattering (INS) methods by Eckert because it *unequivocally distinguishes molecular H_2 binding from classical hydride binding*, where there is no such rotation.[173,494−500] Furthermore, weak physisorption of H_2, e.g., van der Waals interaction with main group atoms, can be distinguished from the much stronger binding of H_2 to metal centers. This is particularly important in solid-state hydrogen-storage materials that cannot easily be studied by NMR or other conventional methods (see section 11.5). These discriminating features arise because there is always at least a small to moderate barrier to rotation, ΔE, in metal coordination brought about by $M\rightarrow H_2$ σ* backdonation (BD) (Scheme 3). The σ-donation from H_2 to M cannot give rise to a

Table 7. Weak Interactions of H_2 with Main Group Compounds

compound	evidence	ref
$[PH_2(H_2)_2]^{3+}$, $[AsH_2(H_2)_2]^{3+}$	theory	*a*
$[SiH_3(H_2)_2]^+$	IR (ν_{HH} = 3866 cm^{-1})	*b*
$[SiH_2(H_2)]^+$; $[PH(H_2)]^+$	theory	*c*
$Na^+/K^+(H_2)_{1,2}$	surface ionization	439
$MH(H_2)_2$ (M = Li, Na, K)	solid hydrogen, theory	*d*
$Al^+(H_2)$	theory	451
$AlH_x(H_2)$; $x = 1-3$	argon matrix	*e, f*
$[AlH_x]^{n+}$; $x = 4-8$; $n = 1-3$	theory	*g*
$AlH_3(H_2)$	theory	*h*
$BH(H_2)$	solid argon	490
$BH_2(H_2)$	esr, theory	*i, j*
$BH_3(H_2)$	theory, solid argon	490[k]
$[BH_6]^+$; $[BH_7]^{2+}$; $[BH_8]^{3+}$	theory	*l*
$[BH_4L]^+$; L= NH_3, H_2O, etc.	theory	*m*
$[BXH_5]^+$; $[BX_2H_4]^+$; X= F, Cl	theory	*n*
Lewis base$-H_2$	solid argon	*o*
halide$-H_2$	argon matrix	*p−s*
$[HnGe(H_2)]^+$	$n = 0, 1$	theory, mass spec
$[GeH_3(H_2)]^+$	theory	*u, v*
$BeO-H_2$; $BeS-H_2$	theory	462−464
X_3B-H_2	theory	491
$MgO-H_2$	theory, experiment	478, 479, 481
C(nanotube)(η^1-H_2)	theory, experiment	430, 432[w−z]
Li-ZSM-5-H_2	IR (ν_{HH} = 4092 cm^{-1})	*aa*

[a] Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1997**, *119*, 12984. [b] Cao, Y.; Choi, J.-H.; Haas, B.-M.; Johnson, M. S.; Okumura, M. *J. Phys. Chem.* **1993**, *97*, 5215. [c] Gil, A.; Bertran, J.; Sodupe, M. *J. Am. Chem. Soc.* **2003**, *125*, 7561. [d] Wang, X.; Andrews, L. *J. Phys. Chem. A* **2007**, *111*, ASAP. [e] Chertihin, G. V.; Andrews, L. *J. Phys. Chem.* **1993**, *97*, 10295. [f] Pullumbi, P.; Bouteiller, Y.; Manceron, L. *J. Chem. Phys.* **1994**, *101*, 3610. [g] Olah, G. A.; Rasul, G. *Inorg. Chem.* **1998**, *37*, 2047. [h] Schreiner, P. R.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Chem. Phys.* **1995**, *103*, 5565. [i] Saxon, R. P. *J. Phys. Chem.* **1993**, *97*, 9356. [j] Van Zee, R. J.; Williams, A. P.; Weltner, W., Jr. *J. Chem. Phys.* **1997**, *107*, 4756. [k] Schreiner, P. R.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Chem. Phys.* **1994**, *101*, 7625. [l] Rasul, G.; Olah, G.A. *Inorg. Chem.* **1997**, *36*, 1278. [m] Rasul, G.; Prakash, G. K. S.; Olah, G. A. *Inorg. Chem.* **1999**, *38*, 1814. [n] Rasul, G.; Olah, G. A. *Inorg. Chem.* **2001**, *40*, 2453. [o] Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *J. Phys. Chem.* **1990**, *94*, 1352. [p] Ogden, J. S.; Rest, A. J.; Sweany, R. L. *J. Phys. Chem.* **1995**, *99*, 8485. [q] Sweany, R. L.; Ogden, J. S. *Inorg. Chem.* **1997**, *36*, 2523. [r] McKee, M. L.; Sweany, R. L. *J. Phys. Chem. A* **2000**, *104*, 962. [s] Sweany, R. L.; Vuong, L.; Bishara, J. *J. Phys. Chem. A* **2002**, *106*, 11440. [t] Jackson, P.; Sandig, N.; Diefenbach, M.; Schroder, D.; Schwarz, H.; Srinivas, R. *Chem.—Eur. J.* **2001**, *7*, 151. [u] Schreiner, P. R.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Chem. Phys.* **1994**, *101*, 2141. [v] Archibong, E. F.; Leszczynski, J. *J. Phys. Chem.* **1994**, *98*, 10084. [w] Lee, E.-C.; Kim, Y.-S.; Jin, Y.-G.; Chang, K. J. *Phys. Rev. B.* **2002**, *66*, 073415. [x] Han, S. S.; Lee, H. M. *Carbon* **2004**, *42*, 2169. [y] Yildirim, T.; Ciraci, S. *Phys. Rev. Lett.* **2005**, *94*, 175501. [z] Cheng, H.; Pez, G. P.; Cooper, A. C. *J. Am. Chem. Soc.* **2001**, *123*, 5845. [aa] Arean, C. O.; Manoilova, O. V.; Bonelli, B.; Rodriguez-Delgado, M.; Palomino, G. T. *Chem. Phys. Lett.* **2003**, *370*, 631.

Scheme 25



rotational barrier since it is completely isotropic about the $M-H_2$ bond. In $M(CO)_3(PCy_3)_2(H_2)$, the barrier actually arises from the *disparity* in the BD energies from the d orbitals when H_2 is aligned parallel to P−M−P versus parallel to OC−M−CO, where BD is less (though not zero; Scheme 25).

ΔE varies with M, coligands, and other factors and can be analyzed in terms of the BD and other forces that lead to it, both calculationally and by a series of experiments where

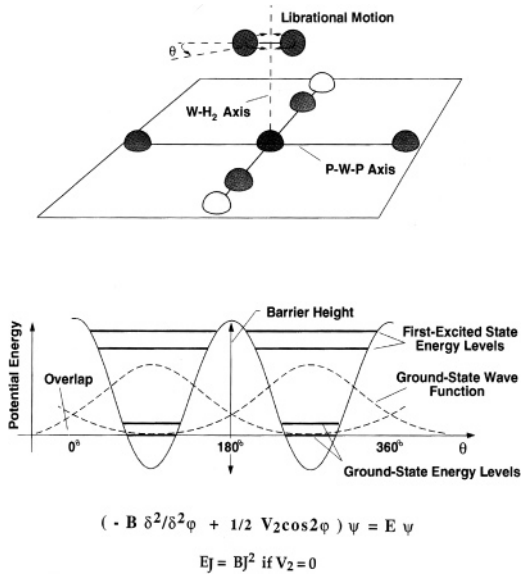


Figure 9. Model for the hindered rotation of the H_2 ligand in metal complexes. (top) Schematic of H_2 rotation in $W(CO)_3(\eta^2\text{-}H_2)P_2$ about the axis from the W atom to the midpoint of the H−H bond. (bottom) Double-minimum potential $V_2(\varphi)$. The transitions indicated are for $W(CO)_3(H_2)(PCy_3)_2$, where B is taken to be 49.5 cm^{-1}.

metal−ligand (M/L) sets are varied. In most "true" H_2 complexes with $d_{HH} < 0.9$ Å, the barrier is only a few kcal/mol and observable only by neutron scattering methods. It can be as low as 0.5 kcal/mol for symmetrical ligand sets, for example all cis L are the same, but has never been measured to be zero because minor geometrical distortions or crystal lattice-related effects are usually present. In the case of complexes with elongated H−H bonds or where rotation is sterically blocked as in $[Cp'_2M(H_2)(L)]^+$ (M = Nb, Ta), much higher barriers of 3−12 kcal/mol are observed by INS or even solution NMR methods.[222,501] Interactions of η^2-H_2 with cis ligands can significantly lower the barriers, as was shown in section 6. The hindered rotation of η^2-H_2 is thus governed by a variety of forces, which can be divided into bonded (electronic) and nonbonded interactions ("steric" effects). The direct electronic interaction between M and H_2 results from overlap of the appropriate molecular orbitals. Nonbonded interactions such as van der Waals forces between the η^2-H_2 atoms and the other atoms on the molecule may vary as η^2-H_2 rotates.

The geometry and height of the barrier can be derived by fitting the rotational transitions observed by INS techniques to a model for the barrier. The simplest possible model for the rotations of a dumbbell molecule is one of planar reorientation about an axis perpendicular to the midpoint of the H−H bond in a potential of twofold symmetry (Figure 9). Application of a barrier to rotation rapidly decreases the separation between the lowest two rotational levels, which may then be viewed as a split librational ground state. Transitions within this ground state as well as those to the excited librational state (often called torsions) may be observed by INS. The former occur by way of rotational tunneling,[502] since the wave functions for the H_2 in the two wells 180° apart overlap. This rotational tunneling transition has an approximately exponential dependence on the barrier height, and is therefore extremely sensitive to the latter and thus to even very minor changes in H_2 environment (e.g., crystal packing forces). It is this property that is exploited to gain information on the origin of the barrier and to easily distinguish even small variations in H_2 binding sites in materials (section 11.5).

Both the rotational tunneling transition and the transitions to the first excited librational state can readily be observed by INS techniques.[173,494−500,502] Neutrons are extremely well suited as probes for molecular rotations when the motion involves mainly H atoms. The INS studies allow observation of low-lying transitions within the ground librational state of the η^2-H_2 (tunnel splitting), which corresponds to the para (I= 0, J= 0) to ortho (I= 1, J= 1) transition for free H_2 (120 cm^{-1} in liquid hydrogen). INS measurements are typically carried out at ∼5 K using ∼1 g of polycrystalline H_2 complex sealed under inert atmosphere in aluminum or quartz sample holders. This measurement can be performed without regard to other hydrogen-containing ligands, which do not have observable excitations at low temperatures in the energy range of those of the H_2. In most cases, the ground-state rotational tunnel splitting, as well as the two transitions to the split excited librational state, are observed. Because the tunnel splittings (typically 1−10 cm^{-1}) can be measured with much better accuracy than the librational transitions, the value for the barrier height V_2 is usually extracted from the former. Prior to the discovery of H_2 complexes, the only systems known containing hydrogen molecules were H_2 gas or H_2 that was barely affected by its surroundings (as in physisorbed H_2). The smallest splittings between the ortho and para H_2 states that had previously been observed were 4.8−10.5 cm^{-1} for H_2 in K-intercalated graphite[503] and 30.6 cm^{-1} for H_2 in Co ion-exchanged NaA zeolite.[504] In both of these cases, H_2 is in all likelihood physisorbed as no indication of H−H bond activation could be found. However, for the M(η^2-H_2) ground librational state, splittings between 17 and 0.6 cm^{-1} are observed at temperatures as high as 200 K. The signals shift to lower energy and broaden but remain visible into the quasielastic scattering region. Observation of rotational tunneling, which is a *quantum mechanical* phenomenon, at such a high temperature is extraordinary: in all previous studies of this type involving CH_3 or $[NH_4]^+$, the transition to classical behavior occurs well below 100 K.

Considerable molecular level detail on the interaction and binding of H_2 with both metal centers and nonmetal substances can be obtained by inelastic neutron scattering from the hindered rotor states of the bound molecule. The transition energies between these quantum mechanical rotational states for an adsorbed hydrogen molecule are very sensitive to the shape and height of the barrier to rotation, which in turn is a reasonably direct measure of the guest−host interactions. For low to medium barrier heights (as in, for example, the MOF hydrogen storage materials discussed below), the transition between the lowest two states (rotational tunneling transition) decreases approximately exponentially with an increase of the barrier to rotation from the molecule's chemical environment. Moreover, the very large inelastic scattering cross section of ^1H compared to that of any other atoms present in such systems makes rotational tunneling spectroscopy by INS a highly specific method to characterize the interaction between H_2 and its host.

In addition to studies of H_2 rotational motion, the low-frequency to midfrequency (200−1000 cm^{-1}) region of the neutron vibrational spectrum can be probed to investigate the nature of dihydrogen bonding. This measurement is only possible by use of a differential technique[505] involving subtraction of the spectrum observed for a sample with a

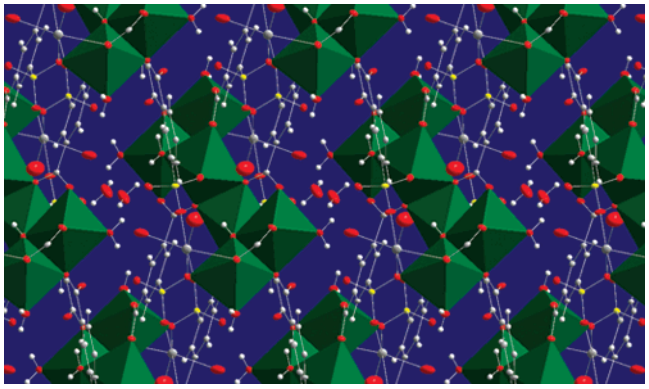


Figure 10. Crystal structure for hydrated $NaNi_3(SIPA)_2(OH)(H_2O)_5 \cdot H_2O$, viewed in the *ab* plane. NiO_6 octahedra are illustrated as green polygons. Sodium, sulfur, carbon, oxygen, and hydrogen atoms are shown as blue, yellow, gray, red, and white spheres, respectively.

D_2-ligand (or another suitable "blank") from that of an identical sample with the H_2 ligand, which leaves only the vibrational modes for the $M-(H_2)$ fragment. For example, deformational modes in $W(CO)_3(PCy_3)_2(H_2)$ have been identified by this technique (section 5). It is also useful for studies of almost any low-energy vibration involving hydrogen in the solid phase, e.g., in ammonia−borane, NH_3BH_3. The latter has received a great deal of interest recently as a solid-state hydrogen storage material ("chemical hydrogen storage"), since it was discovered to release hydrogen under mild thermal conditions in the presence of acids or transition metal catalysts.[506] The unique "dihydrogen bonding" interactions (see eq 53) between the adjacent protic NH and hydridic BH groups in NH_3BH_3 are important in both the dynamics of hydrogen motion and the reaction chemistry here.

11.5. Binding of H_2 to Highly Porous Solids and INS Studies

Nonmetal highly porous compounds such as carbon-based substances, e.g., fullerenes, and metal organic framework (MOF) materials have been intensely studied as possible lightweight materials for H_2 storage.[507−523] This subject has been reviewed in this thematic issue by Heben and will not be discussed in detail except for relevance to the structure/bonding principles and methods developed for studying metal−H_2 complexes, such as neutron scattering. Techniques such as inelastic neutron scattering discussed above provide a unique tool for investigating the structure, dynamics, and chemical environment of hydrogen in potential hydrogen storage materials. This method as well as other neutron spectroscopy methods (powder and single-crystal neutron diffraction) has been applied to H_2 adsorption at low temperatures (typically 77 K) in porous carbons,[507] zeolites,[504,508,518] nickel phosphates,[509] Prussian blue anaogues,[514] and hybrid inorganic−organic compounds (e.g., MOFs).[510−513,515−517,519−523] These methods have been described in more detail in a study of hybrid materials that will be discussed below.[516] IR spectroscopy has also been used, and the presence of a doublet at 4029 and 4008 cm^{-1} has been ascribed to H_2 adsorbed on available surface Zn^{2+} ions on MOF-5.[520]

An excellent recent example of the value of INS studies on H_2−MOF interaction that will be discussed in detail is H_2 adsorbed in $NaNi_3(SIPA)_2(OH)(H_2O)_5 \cdot H_2O$, a MOF synthesized by Cheetham shown in Figure 10.[516] The organic linker here is 5-sulfoisophthalate (SIPA). At the lowest

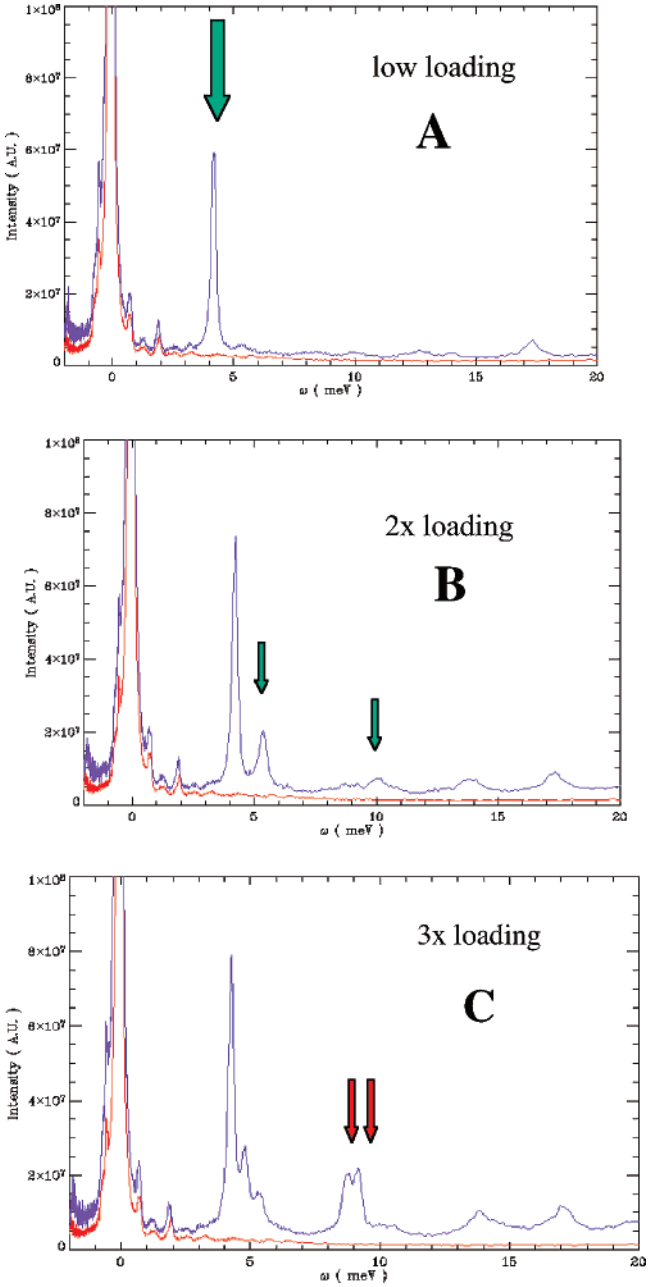


Figure 11. Inelastic neutron spectra of H_2 in $NaNi_3(SIPA)_2(OH)(H_2O)_5 \cdot H_2O$ for different loading levels. Various loadings are shown in purple, with an unloaded measurement in red for comparison. The intensity is expressed in arbitrary units (A.U.). Several well-defined binding sites with strong guest−host interactions (much greater than carbons) or MOF-5 sites with planar rotation (green arrows in A and B) indicate peaks for chemisorbed H_2 at unsaturated Ni sites. 3-D rotation (physisorbed H_2) is seen in part C (two new peaks shown by red arrows).

loading of H_2, a strong peak is observed in rotational tunneling spectra (Figure 11) at 4.2 meV along with a weaker peak at 17.3 meV from hindered rotational transitions of the bound H_2 molecule. This value of 4.2 meV for the energy of the lowest rotational transition (or the rotational tunnel splitting) may be compared with about 1.5 meV for H_2 in VSB-5,[509] where it must be kept in mind that a lower energy indicates a larger barrier to rotation. A larger barrier to rotation may not necessarily be equivalent to stronger binding of the sorbed hydrogen, but in a general sense this seems to be the case and these results provide a good confirmation of this general trend. The INS spectra of H_2 in NiSIPA appear

to strongly suggest that binding of molecular hydrogen first occurs by molecular chemisorption at the unsaturated Ni(II) binding sites created by dehydration (Figure 11), as the series of transitions at 4.1 and 17.3 and 22 meV (not shown) cannot be assigned on the basis of a model for physisorbed H_2 (i.e., double-minimum with *two* rotational degrees of freedom) but can be fitted to the model used for coordinated dihydrogen (*planar* rotation in a double-minimum potential) with a barrier height $V/B = 3.1$, where the rotational constant B for H_2 is 7.35 meV. A second site becomes occupied when the H_2 loading is increased to twice the initial loading (Figure 11) with a set of transitions at 5.4 meV and about 10 meV that again fit to the model for planar rotation ($V/B = 1.7$) indicative of molecular chemisorption. Two additional binding sites for H_2 become evident at three times the lowest loading, another strong binding site characterized by peaks at 4.8 and 13.8 meV and a second one characterized by a doublet at 8.5 and 9.2 meV. This latter set of transitions, however, corresponds to that for a physisorbed molecule (two-dimensional reorientation) and a barrier of 3.4*B*. Another site for physisorbed H_2 becomes progressively occupied at four and five times the original loading with transitions at 10.8 meV and 7 meV and a shoulder at approximately 17.2 meV, which correspond to a barrier of 2.2*B*. At the highest loading (5×, not shown), a peak is also observed close to the free rotor value (14.7 meV) that would suggest some agglomeration of hydrogen molecules into bulk solid particles.

The above data suggest that several accessible, coordinatively unsaturated Ni(II) sites exist in $NaNi_3(SIPA)_2(OH)(H_2O)_5 \cdot H_2O$ when it is dehydrated at sufficiently high temperature to remove aqua ligands from the Ni octahdedra. Additional sites in the structure, where H_2 is thought to be physisorbed, bind the molecule much more strongly than do carbon supports. Remarkably detailed information has also been obtained on the primary binding sites of H_2 in a series of metal−organic frameworks composed of $Zn_4O(O_2C^-)_6$ secondary building units (Figure 7) with the use of INS.[510,511b] Five primary binding sites had been identified for gases in IRMOF-1, including three on the inorganic cluster and two solely on the phenylene link.[517] Each $(CO_2)_3$ site is surrounded trigonally by $(ZnO)_2$ sites at 4 Å, and so each cluster can accommodate at most 16 adsorbed molecules per formula unit. In the INS spectra, two unique 0−1 transitions for these sites, in a 1:3 intensity ratio, were expected, saturating at approximately 16 H_2 per formula unit. Aside from variance in peak positions, and possible overlap in the case of IRMOF-8, this is what was observed, and it was concluded that sites I and II for H_2 adsorption are $(CO_2)_3$ and $(ZnO)_2$. Despite their chemical similarities, the variation in INS peak positions associated with sites I and II of each MOF is significant and clearly indicates that the organic links play an active role in defining the nature of the adsorption sites for H_2. This is reasonable given the variety of links employed in these materials, which strongly affect the local structure of the $Zn_4O(O_2C^-)_6$ clusters and thus the charge transfer between the Zn^{2+} and the aryl carboxylates. In contrast, features assigned to H_2 bound to primarily organic sites cover a more narrow energy range and show low barriers to rotation consistent with the weaker binding on those sites. These sites show much larger increases in INS intensity with higher H_2 loading, as their capacity for adsorption at the low temperature of these experiments is significantly higher.

Direct evidence for strong side-on H_2 binding to metal centers as in organometallic dihydrogen complexes (so-called Kubas complexes) has been obtained. Binding to exposed Cu coordination sites has been seen by neutron diffraction and INS methods in a Cu-exchanged zeolite ZSM-5[518] and in the Prussian blue analogue, $Cu_3[Co(CN)_6]_2$.[514] The INS study on Cu−ZSM-5 showed H_2 rotational barriers of 1.8 and 2.1 kcal/mol, similar to those seen in metal−dihydrogen complexes, indicating side-on bonding of H_2 to Cu. This is in marked contrast to what has been observed for open Cu binding sites in MOFs or partially Cu^{2+} exchanged zeolite A.[524]

The development of such highly porous solids for reversible molecular H_2 binding in the above Ni, Cu, Zn, and other systems is a major challenge in materials science. The difficulty arises because a sufficiently strong affinity toward H_2 for room-temperature storage applications is needed, but the interaction cannot be so strong that it leads to irreversible dissociative binding, slows kinetics, or results in large energy losses associated with cycling. The MOFs and other highly porous materials containing coordinatively unsaturated metal sites are a realistic and promising means of achieving this goal. In order to bind molecular H_2, it is necessary to design compounds with high surface areas or mimic the nanotube structures of carbon fullerenes, but using much less expensive materials. There is a great opportunity for design of, for example, supramolecular cagelike structures of light main group elements such as boron, oxygen, nitrogen, lithium, etc. that would help trap molecular hydrogen. As discussed above, H_2 molecules have the ability to bind to a large variety of materials as either a Lewis acid or a Lewis base, albeit weakly, and this is the key feature to be explored for new hydrogen storage methods.

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