Dihydrogen complexes as prototypes for the coordination chemistry of saturated molecules

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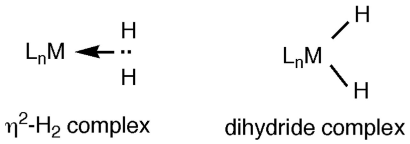
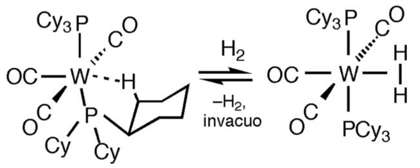
The binding of a dihydrogen molecule (H_2) to a transition metal center in an organometallic complex was a major discovery because it changed the way chemists think about the reactivity of molecules with chemically ''inert'' strong bonds such as H–H and C–H. Before the seminal finding of side-on bonded H_2 in $W(CO)_3(PR_3)_2(H_2)$, it was generally believed that H_2 could not bind to another atom in stable fashion and would split into two separate H atoms to form a metal dihydride before undergoing chemical reaction. Metal-bound saturated molecules such as H_2, silanes, and alkanes (σ-complexes) have a chemistry of their own, with surprisingly varied structures, bonding, and dynamics. H_2 complexes are of increased relevance for H_2 production and storage in the hydrogen economy of the future.

Dihydrogen (H_2) and hydrocarbons are vital in chemical processes such as hydrogenation and conversions of organic compounds. Catalytic hydrogenations are the largest-volume chemical reactions: all crude oil is treated with H_2 to remove sulfur/nitrogen, and >100 million tons of ammonia fertilizer are produced annually to support much of the world's population. The H_2 molecule is married together by a very strong two-electron H–H bond but is only useful chemically when the two H atoms divorce in controlled fashion. This also applies to other strong σ-bonds such as C–H in alkanes. However, the mechanism at the molecular level by which the union splits was established only relatively recently because such electronically saturated molecules were never caught in the act of chemically binding to a metal or other "third party," usually the first step in breaking apart a strong bond. The discovery by Kubas and coworkers (1) in 1984 of coordination of a nearly intact H_2 molecule to a metal complex (L_nM; L = ligand) caught this in intimate detail and led to a new paradigm in chemistry (1–4) (see Sketch 1).

The H_2 binds side-on (η^2) to M primarily through donation of its two σ electrons to a vacant metal orbital to form a stable H_2 complex. It is remarkable that the electrons already strongly bonded can donate to a metal to form a nonclassical 2-electron, 3-center bond, as in other "electron-deficient" molecules such as diborane (B_2H_6). M–H_2 and other "σ-complexes" (3, 5), encompassing interaction of any σ-bond (C–H, Si–H, etc) with a metal center, are the major theme of this special feature.



Sketch 1.



Eq. 1.

Introduction and Historical Perspective

Certain discoveries and how they came about are fascinating sagas, e.g., that for buckminsterfullerene (C_{60}) (6). That its existence remained hidden for so long adds to the lore, and our unexpected revelation of metal–H_2 complexes has some commonality. Metal dihydrides formed by oxidative addition (OA) of the H–H bond to a metal center had been known early on to be a part of catalytic cycles (7), as documented in a 1980 retrospective on catalytic hydrogenation by a pioneer in the field, Jack Halpern (8). Although some form of metal–H_2 interaction was assumed to participate in dihydride formation, it was thought to be unobservable. We were fortunate to observe it in the complex $W(CO)_3(PR_3)_2(H_2)$, as detailed by this author (2, 3). This was the first molecular compound synthesized and isolated entirely under ambient conditions that contained the H_2 molecule (albeit "stretched") other than elemental H_2 itself. The H–H bond length in $W(CO)_3(P^iPr_3)_2(H_2)$ (0.89 Å) is stretched ≈20% over that in H_2 (0.74 Å), showing that H_2 is not physisorbed but rather chemisorbed, where the bond is "activated" toward rupture. Like H_2, other saturated molecules such as alkanes were thought to be inert to such binding, although their C–H bonds somehow could also be broken on metals. The "somehow" is why the finding of an H_2 complex was important: it is the prototype for activation of all σ-bonds.

This discovery of $W(CO)_3(P^iPr_3)_2(H_2)$ ensued the serendipitous synthesis of its novel, "unsaturated" 16-e precursor, $M(CO)_3(PCy_3)_2$ (M = Mo, W; Cy = cyclohexyl) (9). Its unusual purple color changed instantly and reversibly to yellow on exposure to N_2 and H_2 in both solution and solid states, signifying adduct formation (Eq. **1**).

Crystallography later revealed a phosphine C–H bond weakly occupying the sixth binding site in $W(CO)_3(PCy_3)_2$ (10). This type of "agostic" interaction (11) relieves electronic unsaturation in coordinatively unsaturated complexes and is entropically favorable because it is "intramolecular." "Intermolecular" binding of a C–H bond as in an alkane σ-complex (often also termed "agostic") is less stable. Irrefutable evidence for H_2 binding in Eq. **1** came slowly because pinpointing H positions crystallographically is difficult, even by neutron diffraction. A consultant, Russ Drago, suggested an experiment elegant in its simplicity: synthesize the HD complex and look for a large HD coupling constant in the proton NMR that would show that the H–D bond was mostly intact. It worked beautifully: the ^1H NMR of $W(CO)_3(P^iPr_3)_2(HD)$ showed a 1:1:1 triplet (deuterium spin = 1) with J_{HD} = 33.5 Hz, nearly as high as in HD gas, 43.2 Hz. Observation of J_{HD} higher than that for a dihydride complex (>2

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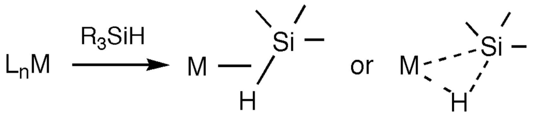
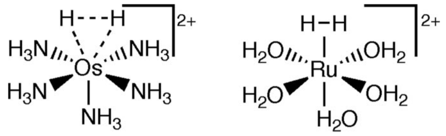


Eq. 2.



Scheme 1.

Hz) became the premier criterion for an H_2 complex.

One reason that H_2 complexes were so well hidden was the notion that such complexes could not be stable relative to classical dihydrides, as exemplified by the controversy over our initial findings. This paralleled the discovery of metal–dinitrogen complexes by Allen and Senoff, whose seminal paper was initially rejected (12). At the time of our finding, spectroscopic evidence for unstable $M–H_2$ interactions was found by photolysis of $Cr(CO)_6$ in the presence of H_2 at low T (13–16). $Cr(CO)_5(H_2)$ was postulated based on IR CO stretching frequencies but could not be conclusively demonstrated; only recently has its ^1H NMR spectrum been observed at low T (17, 18). Even theoretical bases for interaction of H_2 and other σ-bonds with a metal was still in its infancy at the time of our discovery. Ironically, a computational paper by Saillard and Hoffmann (19) in 1984 on the bonding of H_2 and CH_4 to metal fragments such as $Cr(CO)_5$ was published shortly after our publication (1) of the $W–H_2$ complex, without mutual knowledge. Such interplay between theory and experiment has continued as one of the most valuable synergistic relations in all of chemistry (3, 4, 20). The innate simplicity of H_2 was attractive computationally, but the structure/bonding/dynamics of H_2 complexes turned out to be unimaginably complex and led to extensive study (>300 computational publications).

Initially, H_2 binding in $M(CO)_3(PR_3)_2(H_2)$ seemed unique because the bulky phosphines sterically inhibited formation of a 7-coordinate dihydride through OA. Kaesz and coworkers (21) viewed this as "arrested OA," a descriptive term for the bonding in a silane complex, $CpMn(CO)_2(\eta^2\text{-}HSiPh_3)$. Silane complexes (22, 23) were among the first examples of σ-bond complexes but were initially unrecognized as such because the asymmetrically bound silane ligand (Eq. **2**) lacked the superb clarity of the H_2 ligand, which has electrons only in the H–H bond.

The hundreds of H_2 complexes synthesized after our discovery could not initially have been imagined, and it was difficult to know where to search for new ones. It would take more than a year before others were identified, notably by Morris, Crabtree, Chaudret, and Heinekey. This quartet has since performed elegant synthetic, reactivity, and NMR studies on H_2 and silane complexes (5, 25–30) and was eventually joined by >100 investigators worldwide. Remarkably, several complexes initially believed to be hydrides were revealed to be H_2 complexes by Crabtree and Hamilton in 1986 (5, 31), by using as criteria the short proton NMR relaxation times of H_2 ligands ($T_1 < 100$ msec). Particularly interesting was $RuH_2(H_2)(PPh_3)_3$ first reported in 1968 (32); it possessed unusual H_2 lability that Singleton in 1976 commented was characteristic of "H_2-like bonding" (33). However, attempts to prove H_2 binding here was problematic, even long after H_2 binding was established (34).[‡]

More than 600 H_2 complexes are known (most of them stable) for nearly every transition metal and type of coligand and are the focus of 1,500 publications, dozens of reviews, and three monographs (2–5, 20, 25–30, 35–43). The view on H_2 complexes has shifted from significance in basic science to a more practical bent, e.g., H_2 fuel production and storage. Two frequent questions after their discovery were as follows. Are H_2 complexes relevant in catalysis, i.e., does direct transfer of hydrogen from an H_2 ligand to a substrate occur? And could methane bind to metal complexes? The answer to both is yes, and although a stable methane complex has not been isolated, alkane binding has been observed.

Synthesis and Diagnosis of H_2 Complexes

Most H_2 complexes contain low-valent metals with d^6 electronic configurations that favor side-on binding of σ-bonds. Reversibility of H_2 binding is often a key feature, i.e., H_2 can be removed simply upon exposure to vacuum and readded many times at ambient temperature/pressure, as in Eq. **1**. Virtually all σ-complexes are diamagnetic, with one exception (44). σ-Ligands have not been definitively shown to bridge metals. Surprisingly, the coligands on H_2 complexes can be simple classical nitrogen-donor ancillary ligands such as ammonia, as in $[Os(NH_3)_5(H_2)]^{2+}$ (45), which has a very long H–H distance (d_{HH}), ≈1.34 Å (46), more characteristic of a dihydride, which it was initially believed to be (47). Complexes containing only H_2O (48) or CO (17, 18) coligands are also known, but are marginally stable (Scheme 1).

Determining the presence of a H_2 ligand and its d_{HH} is nontrivial because even neutron diffraction has limited applicability and can give foreshortened d_{HH} because of rapid H_2 rotation/libration (49). $^1J_{HD}$ is the best criterion, and values determined in solution correlate well with d_{HH} in the solid state through Eqs. **3** and **4** (50, 51).

$$d_{HH} = 1.42 - 0.0167 J_{HD}\ \text{Å [Morris]} \qquad \textbf{[3]}$$

$$d_{HH} = 1.44 - 0.0168 J_{HD}\ \text{Å [Heinekey].} \qquad \textbf{[4]}$$

Data include d_{HH} from crystallography and also solid-state NMR measurements by Zilm and Millar (52) that gave the most accurate d_{HH} (direct measure of internuclear HH separation). For $W(CO)_3(P^iPr_3)_2(H_2)$, J_{HD} = 34 Hz, giving d_{HH} = 0.86–0.88 Å vs. 0.89 Å from solid-state NMR and 0.82(1) Å from neutron diffraction [uncorrected for H_2 libration (49)]. Short T_1 values for the H_2 ligand (27) are also diagnostic (e.g., 4 msec for the W complex), although care must be exercised in interpretation (53–55). A powerful spectroscopic tool developed by a colleague at Los Alamos, Juergen Eckert, is inelastic neutron scattering studies of rapid H_2 rotation in solid H_2 complexes that provide unequivocal evidence for molecular H_2 binding and also the presence of $M{-}{>}H_2$ backdonation (56).

Several synthetic routes to H_2 complexes are available; the simplest is reaction of H_2 with an unsaturated complex such as $W(CO)_3(PR_3)_2$ (Eq. **1**). Displacement of weakly bound "solvento" ligands such as CH_2Cl_2 (57) or H_2O from $[Ru(H_2O)_6]^{2+}$ (Scheme 1) is also effective. Protonation of a hydride complex by acids is most often used (28, 38) and is widely applicable because it does not require an unsaturated precursor that may not be available. Neutral polyhydrides L_nMH_x are convenient targets for protonation to cationic H_2 complexes, $[L_nM(H_2)H_{x-1}]^+$, which can be more robust than complexes

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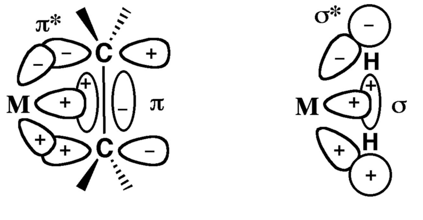
[‡] In 1993 Zilm obtained solid-state ^1H NMR evidence for H_2 coordination (d_{HH}= 0.93 Å) on a sample we prepared.



M–π bond   M–σ bond

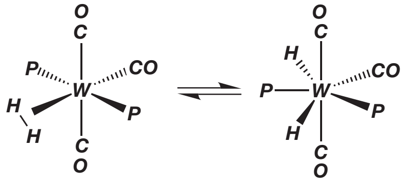
Scheme 2.

prepared from H_2. Only a few stable solid *bis*-H_2 complexes are known, e.g., $[RhH_2(H_2)_2(PCy_3)_2]^+$ (58), $Tp^*RuH(H_2)_2$ (59), and $RuH_2(H_2)_2(PR_3)_2$; R = Cy (30) and cyclopentyl (60), for which the neutron structure shows unstretched cis–H_2 ligands.

Structure, Bonding, and Dynamics of H_2 Complexes

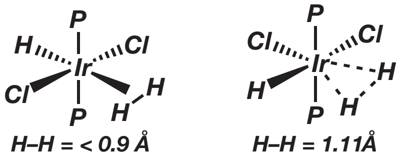
The 3-center metal–H_2 interaction complements classical Werner-type coordination complexes where a ligand donates electron density through its nonbonding electron pair(s) and π-complexes such as olefin complexes in which electrons are donated from bonding π-electrons (Scheme 2). It is remarkable that the bonding electron pair in H_2 can further interact with a metal center as strongly as a nonbonding pair in some cases. The resulting side-on bonding in M-H_2 and other σ-complexes is "nonclassical," by analogy to the 3-center, 2-electron bonding in carbocations and diborane. The M center may be considered to be isolobal with H^+ and CH_3^+ (61), mimicking carbocation chemistry; i.e., a σ-complex such as M^+–CH_4 is related to CH_5^+, which is viewed as a highly dynamic H_2 complex of CH_3^+ (62). 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" of electrons from a filled metal d orbital to the σ* antibonding orbital of H_2 (Scheme 2), a critical interaction unavailable to main group atoms (3, 4, 20). The backdonation is analogous (4) to that in the Dewar–Chatt–Duncanson model (63, 64) for π-complexes, e.g., M–ethylene.

A large variety of σ-bonds X–H interact inter- or intramolecularly with metal centers (3, 42). In principle any X–Y bond can coordinate to a metal center, providing substituents at X and Y do not interfere. Backdonation of electrons from M to H_2 (or to σ* of any X–Y bond) is crucial not only in stabilizing σ-bonding but also in activating the bond toward homolysis (3, 4, 20). If it becomes too strong, e.g., by increasing electron-donor strength of coligands on M, the σ-bond cleaves to form a dihydride because of overpopulation of the H_2 σ* orbital. There is often a fine line between H_2 and dihydride coordination, and in some cases equilibria exist in solution for $W(CO)_3(PR_3)_2(H_2)$ (Eq. **5**), showing that side-on coordination of H_2 is the first step in H–H cleavage (2).



Eq. **5**.

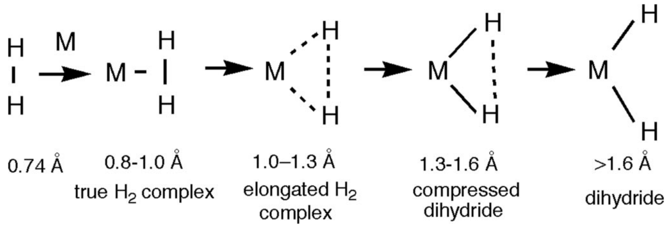
Although electronic factors for OA are well established, the role of steric factors is less clear. Bulky phosphines can inhibit H_2 splitting: for less bulky R = Me the equilibrium lies completely to the right, i.e., the complex is a "dihydride" (65). However, as shown above, H_2 complexes are also stable with only small coligands L such as NH_3 (Scheme 1), in some cases with greatly elongated d_{HH}, two further paradigm shifts. This led to extensive efforts to vary M, L, and other factors to study stretching of the H–H bond. Within the large regime of hundreds of L_nM–H_2 complexes, the reaction coordinate for the activation of H_2 on a metal (Scheme 3) shows d_{HH} varying enormously, from 0.82 to 1.5 Å (3, 18, 25–31, 35–38, 44–60, 65–68). This "arresting" of bond rupture along its entire reaction coordinate is unprecedented. Although the d_{HH} ranges shown are arbitrary, each category of complexes has distinct properties. The d_{HH} is relatively short (0.8–1.0 Å), and H_2 is 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 (d_{HH} = 1–1.3 Å) (29, 46, 66–69) 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 (67). Complexes with $d_{HH} > 1.3$ Å are now viewed as "compressed hydrides," with NMR features differing from elongated H_2 complexes, e.g., J_{HD} increases with T for the former and decreases for the latter (69). These are terms because a near continuum of d_{HH} has been observed.



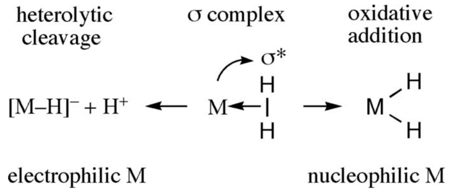
Scheme 4.

Activation of H_2 is very sensitive to M, L, and charge, e.g., changing R from phenyl to alkyl in $Mo(CO)(H_2)(R_2PC_2H_4PR_2)_2$ leads to splitting of H_2 (49). Strongly donating L, third-row M, and neutral charge favor elongation or splitting of H–H, whereas first-row M, electron-withdrawing L, and positive charge (cationic complex) favor H_2 binding and shorten d_{HH}. 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 backdonation and normally keep $d_{HH} < 0.9$ Å. Thus one can favor a σ-complex by placing the potential σ-ligand trans to a strong π-acceptor. 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 in Scheme 4 (70). The *cis*-dichloro complex is actually a "compressed trihydride" ($d_{HH} \sim 1.5$ Å) in solution, but in the solid state it 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 (71). Exceptions exist: the isomers of an "electron-poor" system, $Cr(CO)_4(PMe_3)(H_2)$, have similar J_{HD} (≈34 Hz, hence $d_{HH} \approx 0.86$ Å) whether H_2 is trans to CO or PMe_3 (18).

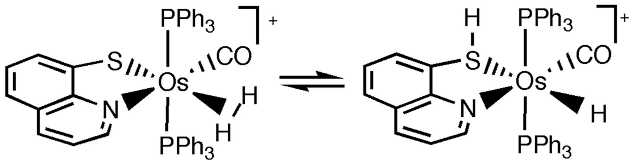
At what point is the H–H bond "broken"? Theoretical analyses suggest 1.48 Å, i.e., twice the normal length (72), but little H–H bonding interaction remains for $d_{HH} > 1.1$ Å (29). In certain "elongated" H_2 complexes, e.g., $[OsCl(H_2)(dppe)_2]^+$, the energy barrier for stretching the H–H bond from 0.85 Å all of the way to 1.6 Å is calculated (29, 69) to



Scheme 3.



Scheme 5.



Eq. 6.

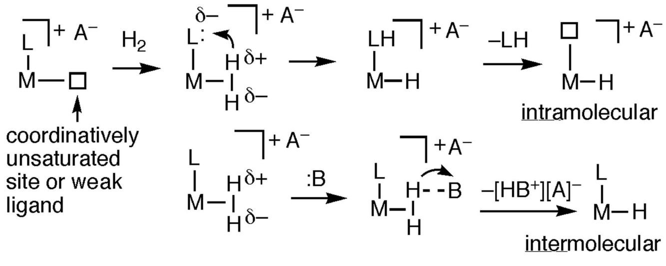
be astonishingly low, ≈1 kcal/mol. The H_2 is highly delocalized: the H atoms undergo large amplitude vibrational motion along the reaction coordinate for H–H breaking. Remarkably, d_{HH} is both temperature and isotope dependent in $[CpM(diphosphine)(H_2)]^{n+}$ (M = Ru, Ir; $n = 1, 2$) (73, 74). These phenomena illustrate the highly dynamic behavior of coordinated H_2 (40), which can exhibit quantum-mechanical phenomena such as rotational tunneling (56) and exchange coupling (75). M–H_2 and other σ-bond interactions are among the most dynamic, complex, and enigmatic chemical topologies known. The H_2 ligand can bind/dissociate, reversibly split to dihydride, rapidly rotate, and exchange with cis hydrides, all on the same metal. Often these dynamics cannot be frozen out on the NMR time scale even at low T.

It is clear that H_2 binding followed by OA serves as a prototype for other σ-bond activation processes, e.g., C–H and Si–H. Silanes (H_nSiR_{4-n}) bind in η^2-Si-H fashion (as in Eq. **2**) (21–24, 42, 76). The η^2-SiH_4 structure in *cis*-$Mo(CO)(SiH_4)(Et_2PC_2H_4PEt_2)_2$, the first transition metal complex of SiH_4, exists in equilibrium with its OA tautomer, $MoH(SiH_3)(CO)(Et_2PC_2H_4PEt_2)_2$, analogous to that for the $W(\eta^2\text{-}H_2)$ system (Eq. **5**), with similar structures and thermodynamic parameters (77). SiH_4 binding and Si–H cleavage directly model that believed to occur for CH_4 activation. Si–H distances in hydrosilane complexes vary widely, analogous to H_2 complexes (3). A valuable yardstick for measuring activation in $M(\eta^2\text{–}X\text{–}H)$ bonds is the value of the NMR coupling constant J_{XH} compared with that in the free ligand. There is typically a 50–80% reduction in J_{HD} in unstretched HD complexes, a 74% reduction in $J(^{13}CH)$ for low-temperature cyclopentane coordination in $CpRe(CO)_2(C_5H_{10})$ (78), and 65% in $J(^{11}BH)$ in complexes of neutral borane ligands (79). J_{SiH} in $M(\eta^2\text{–}Si\text{–}H)$ are normally closer to those in OA products. η^2–Ge–H bonds undergo OA much more easily than Si–H, and in general, the ease of OA of H_2 lies between that of germanes and silanes (80). Backdonation is critical: silanes bind more strongly than alkanes and cleave much like H_2 because the Si–H bond is a good acceptor whereas C–H is not (the much higher energy of its σ* orbital reduces interaction with M *d* orbitals). However, the situation is more complex than for H_2 activation because substituents at C or Si alter both electronics and sterics.

Reactivity of σ-Complexes: Acidity and Heterolysis of X–H Bonds

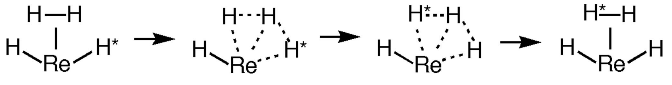
Aside from loss of H_2, reactions of M–H_2 are dominated by homolytic cleavage of H_2 (OA) and heterolytic cleavage, essentially deprotonation of bound H_2 on electrophilic metal centers (Scheme 5) (25). σ-Complexes have several advantages in catalytic and other reactions. Foremost is that the formal oxidation state of M does not change on binding of H_2, whereas formation of a dihydride formally increases the metal oxidation state by two. H_2 ligands can also have far greater thermodynamic and kinetic acidity than hydrides, which is important in the ability of acidic H_2 ligands to protonate substrates such as olefins and N_2. In heterolytic cleavage (25, 40, 81, 82), the H_2 ligand is deprotonated, and the remaining hydrogen ligates to the metal as a hydride. Both pathways have been identified in catalytic hydrogenation and also may be available for other σ-bond activations, e.g., C–H cleavage. Heterolysis of X–H bonds through proton transfer to a basic site on a cis ligand or to an external base is a crucial step in many industrial and biological processes involving direct reaction of H_2, silane, borane, and (possibly) alkane ligands.

H_2 complexes can undergo heterolysis in two distinct ways (Scheme 6). Intramolecular heterolysis is extremely facile for proton transfer to a cis ligand L (e.g., H or Cl) or to the counteranion of a cationic complex. The proton can also end up at a trans ligand (Eq. **6**) (83).



Scheme 6.

Intermolecular heterolysis involves protonation of an external base B, e.g., an ether solvent, to give a metal hydride (H^- fragment) and the conjugate acid of the base, HB^+. This is the reverse of protonation reactions used to synthesize H_2 complexes (all reactions in Scheme 6 can be reversible), and the $[HB]^+$ formed can relay the proton to internal or external sites (base-assisted heterolysis). Crabtree and Lavin (84) first demonstrated heterolysis of H_2 by showing that the H_2 in $[Ir^IH(H_2)(LL)(PPh_3)_2]^+$ is deprotonated by LiR in preference to the hydride ligand. A milder base, NEt_3, was shown by Heinekey and Chinn (85) to more rapidly deprotonate the η^2-H_2 tautomer in an equilibrium mixture of $[CpRuH_2(dmpe)]^+$ and $[CpRu(H_2)(dmpe)]^+$. The H_2 ligand has greater kinetic acidity because deprotonation of an H_2 complex involves no change in coordination number or oxidation state. Thus, H_2 gas can be turned into a strong acid: free H_2 is an extremely weak acid [pK_a ~ 35 in THF (86)], but binding it to an electrophilic cationic metal increases the acidity spectacularly, up to 40 orders of magnitude. The pK_a can become as low as −6, i.e., η^2–H_2 can become more acidic than sulfuric acid as shown by Morris (25, 26, 82) and later Jia (36). Electron-deficient cationic H_2 complexes with electron withdrawing ligands such as CO and short H–H bonds (<0.9 Å), i.e., $[Re(H_2)(CO)_4(PR_3)]^+$ (87) are among the most acidic. Positive charge increases acidity: $W(CO)_3(PCy_3)_2(H_2)$ is deprotonated only by strong bases (88), but on oxidation to $[W(CO)_3(PCy_3)_2(H_2)]^+$ becomes acidic enough to protonate weakly basic ethers (89). Such ability is relevant to processes such as ionic hy-



Eq. 7.

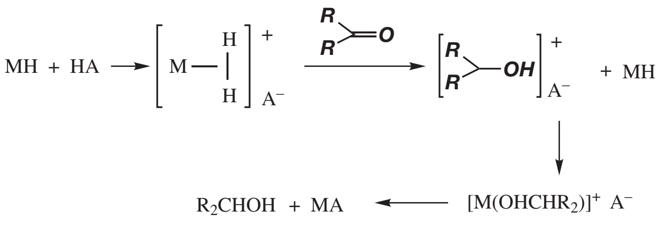
drogenation and the function of metalloenzymes such as hydrogenases (H_2ases).

Complexes with H_2 ligands are highly dynamic, and cis interactions, which are hydrogen-bonding-like interactions between η^2–H_2 and a cis hydride observable in the solid state (3, 20, 42, 90), facilitate solution exchange processes (Eq. **7**). The intermediate is a "trihydrogen" complex (91, 92). Although not isolated, evidence exists for its intermediacy in facile H-atom exchange in $ReH_2(H_2)(CO)(PR_3)_3$ (93), which can be exceedingly fast even at −140°C in hydrido(H_2) complexes (94–99). The barrier for hydrogen exchange in $IrClH_2(H_2)(P^iPr_3)_2$ is only 1.5 kcal/mol even in the solid state (95, 96).

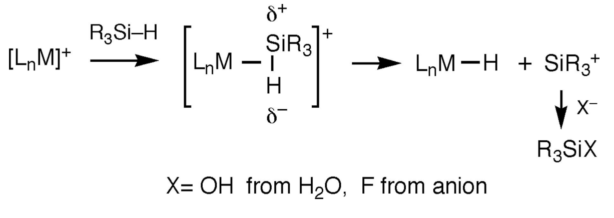
Can direct transfer of hydrogens from an H_2 ligand occur in catalytic hydrogenation? Although difficult to prove conclusively, there is evidence in ionic hydrogenation where an organometallic hydride, e.g., $CpMoH(CO)_3$, plus a strong acid, e.g., HO_3SCF_3, reduce ketones (100, 101). An acidic H_2 complex is involved in proton transfer (Scheme 7). An impressive example of catalysis employing heterolysis of H_2 is the asymmetric hydrogenation of ketones to alcohols catalyzed by the ruthenium system of Nobel Laureate Ryoji Noyori (102, 103). Other σ-bonds can be cleaved heterolytically, particularly on electrophilic metals (3, 40, 42). For coordinated Si–H bonds, the bond becomes polarized $Si(\delta^+)$–$H(\delta^-)$, i.e., the Si becomes positively charged (Scheme 8). Very reactive silylium ions are eliminated; they scavenge nucleophiles such as water or abstract fluoride from anions such as $B(C_6F_5)_4^-$ (104). Similarly, a coordinated B–H bond in a $BH_3{\cdot}PMe_3$ ligand in $[Mn(CO)_4(PR_3)(BH_3{\cdot}PMe_3)]^+$ cleaves to give H^- (forming $MnH(CO)_4(PR_3)$) and "$[BH_2{\cdot}PMe_3]^{+}$" (105).

Can C–H bonds in alkanes bind to electrophilic M to form a σ-alkane complex that can be split heterolytically? Proton transfer to a cis ligand (or anion) could take place followed by functionalization of the resultant methyl complex. Increased acidity of C–H bonds in transient alkane complexes analogous to that for coordinated H–H bonds may be important in alkane activation such as conversion of methane to methanol, a holy grail in chemistry well addressed in this special feature and the prolific work of Bercaw, Periana, and Bergman. In 1965, Chatt discovered OA of an arene C–H bond to a metal complex and in 1976 predicted that "in 25 years methane will be the most popular ligand in coordination chemistry," as noted by Shilov (106). As can be seen, this prediction has become true. As in H_2 activation, alkane σ-complexes should be intermediates, astonishingly even in reaction media as harsh as sulfuric acid at 200°C in Pt^{II}-catalyzed methane to methanol conversions (107, 108), despite the weak binding energy of CH_4 to metals [≈10 kcal/mol (109)].

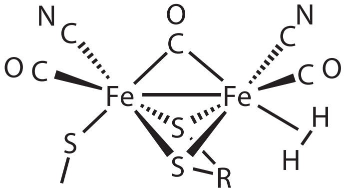
Molecular binding and heterolysis of H_2 on metal surfaces and small metal clusters is rarely observed because formation of hydrides is favored. H_2 binding to a stepped Ni(510) surface containing unsaturated sites was seen by electron energy-loss spectroscopy (110) and is the first step in hydriding other surfaces (111, 112). H_2 also ligates at low T in small clusters such as $Cu_3(H_2)$ (113), $Pd(H_2)$ (114), and similar species (115). Oxides adsorb and activate H_2, including Cr_2O_3, MgO, and ZnO even at 25°C; some of these could involve molecular binding. $(\eta^2$–$H_2)CrO_2$ has been prepared by cocondensation of CrO_2 molecules with H_2 in Ar at 11 K and photoisomerized to HCrO(OH), ostensibly through H_2 heterolysis (116). RuO_2 (111) has also been found to bind H_2 at 85 K (ν_{HH} = 2960 cm^{-1}; calcd d_{HH} = 0.89 Å) (117) suggesting that, as for H_2 on Ni surfaces, the binding of H_2 is similar to that in organometallics. Zeolites can bind H_2 (118, 119), notably to the extraframework iron in Fe–ZSM5 at 110 K. Research at the interface between heterogeneous and homogeneous catalysis (41) includes employing H_2 interactions as probes for the catalytic sites in both regimes (120–122). An elegant example is the demonstration that $Ir(CO)Cl(PPh_3)_2$ catalyzes hydrogenation of unsaturated compounds both in solution and solid state through an H_2 complex (123).



Scheme 7.



Scheme 8.

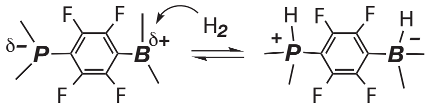


Sketch 2.

Activation of H_2 on Biological and Nonmetal Systems

H_2ases are redox enzymes in microorganisms that catalyze $H_2 \rightleftharpoons 2H^+ + 2e^-$ to either use H_2 as an energy source or dispose of excess electrons as H_2 (124–127). Biologically unprecedented CO and CN ligands are present in the dinuclear active site of iron-only H_2ases (128) that are remarkably organometallic-like and have been extensively modeled for biomimetic H_2 production (126, 127, 129–132) (see Sketch 2).

This site presumably transiently binds and heterolytically splits H_2, most likely at a site trans to bridging CO, where a proton transfers to a thiolate ligand as in Eq. **6** or other Lewis-basic site (127). Such heterolysis has recently been shown to occur on a mononuclear Fe complex with a pendant nitrogen base (132). Nature apparently designed these enzymes billions of years ago to use the CO ligand, whose strong trans influence



Scheme 9.

favors reversible H_2 binding and heterolysis (3, 40). An H_2 complex of a H-ase model, $[Ru_2(\mu\text{-}H)(\mu\text{-}S_2C_3H_6)_2(H_2)(CO)_3(PCy_3)_2]^+$, is known, albeit with Ru instead of Fe (133).

H_2 can also be activated at nonmetals, e.g., the bridging sulfides in $Cp_2Mo_2S_4$ that react with H_2 to form SH ligands perhaps via a 4-center S_2H_2 transition state (134). Metal-free hydrogenation of ketones on strong bases such as *t*-BuOK occurs under harsh conditions, apparently through base-assisted heterolysis of H_2 (135, 136). Thus, H_2 is a very weak acceptor (Lewis acid) through electron donation to its σ^* orbital and can interact with the O in alkoxide or metal oxides and undergo heterolysis (3). Significantly, the first example of reversible splitting of H_2 on a nonmetal center has been found (137). The phosphine borane in Scheme 9 has a strong Lewis acidic center (boron) linked to a Lewis basic site (phosphorus). It is likely that H_2 heterolysis takes place at boron where proton transfer from an H_2-like complex to the basic phosphorus site occurs to form a phosphenium–borate.

H_2 Storage and Production: A Glance to the Future

H_2 is a fuel of the future, but vexing challenges exist. Materials for H_2 storage are difficult to design because, although H_2 can readily be extruded from a variety of compounds, it can be difficult to add back. The materials also must be light and contain >6% by weight H_2, reducing prospects for known facile reversible systems such as metal–H_2 or hydride complexes. Amine borane, H_3NBH_3, is a popular candidate and also combines both Lewis acidic (B) and basic (N) centers. Here, however, these centers are directly bonded, whereas the acidic and basic sites are separated by linkers in the phosphine-borane in Scheme 9. The metal-free aspect is relevant because precious metals such as platinum are often used in catalysis and can be environmentally unfriendly as well as costly or in short supply. Materials such as metal-organic frameworks (MOFS) (138–140) are now being examined for H_2 storage and have huge surface area capable of binding large numbers of H_2 molecules. Neutron scattering studies by Eckert are critical in determining whether H_2 binds to unsaturated metal centers as in organometallics and/or is physisorbed in the framework. Calculations indicate complexes with multiple H_2, i.e., $Cr(H_2)_6$ may be stable (141), and species such as $[M(H_2)_n]^+$ have a fleeting gas phase existence (142), but isolation in condensed phases will be problematic.

Production of H_2 fuel from water by means of solar energy is of high interest (143). Catalysis may involve H_2 complexes at least as intermediates, and H_2 complexes have been implicated in solar energy conversion schemes based on photoreduction of water (144). Industrially important water gas shift and related H_2-producing reactions undoubtedly proceed through transient H_2 complexes (145). Biomimetic H_2 production, particularly solar driven (photocatalysis), is also a challenge and may take a cue from models of the active site of H_2ase coupled with models of nature's photosystems (129–131, 143). 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_2-ases. Coupling model catalysts with photochemical water splitting will require fine-tuning of electrochemical potentials for tandem catalysis schemes.

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