JAN 08 1991

Conf-9009141-8

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7-

LA-UR--90-4336

DE91 005852

TITLE: **CHEMICAL BONDING OF HYDROGEN MOLECULES
OF TRANSITION METAL COMPLEXES**

DISCLAIMER

AUTHOR(S): **Gregory J. Kubas**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SUBMITTED TO: **Proceedings of "International Symposium on Metal-Hydrogen Systems"**
Banff, Alberta, CANADA
September 2-7, 1990

MASTER

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos

Los Alamos National Laboratory

Los Alamos, New Mexico 87545

de
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CHEMICAL BONDING OF HYDROGEN MOLECULES TO TRANSITION METAL COMPLEXES

Gregory J. Kubas

Los Alamos National Laboratory

Los Alamos, NM, 87545 (U.S.A.)

Introduction

Until recently the chemistry of hydrogen in metal systems had been universally accepted to involve only its atomic form. However, our unexpected discovery of stable bonding of neutral dihydrogen (H_2) *molecules* to molybdenum and tungsten complexes in 1983 has led to a new field of inorganic chemistry and has altered the way chemists now perceive bonding and reactions on metal coordination compounds [1,2]. The discovery has been universally characterized to be one of the most significant of the past decade in inorganic chemistry. The H-H bond in the neutron diffraction structure of $W(CO)_3(PR_3)_2(H_2)$ (CO= carbonyl; PR_3 = organophosphine) is aligned side-on to the metal ($W-H = 1.89 \text{ \AA}$) and is elongated from $0.74 \text{ \AA}$ in elemental H_2 to $0.82 \text{ \AA}$ (Fig. 1). Such $M-H_2$ species had been thought to be only transients in H-H bond cleavage to metal hydrides. We have shown that this molecular tungsten complex is a stable crystalline solid under ambient conditions, but the H_2 can be *reversibly* removed in vacuum or under inert atmosphere (e. g. argon) even at 25°C to give the coordinatively unsaturated precursor, $W(CO)_3(PR_3)_2$. The dissociation pressure of H_2 is 1-10 torr depending on the phosphine R group and the binding energy of H_2 to the complex is about 15 kcal/mol. The H_2 is thus weakly bound, easily exchanges with D_2 , and can be readily displaced by other more strongly held molecules such as CO or even N_2 (the complex is decomposed by atmospheric oxygen). Complete isotopic scrambling of H_2/D_2 mixtures to give HD occurs over the solid complex or in solution (the complexes are soluble in organic solvents, such as toluene, but not water). Surprisingly, the 6-coordinate H_2 complex can exist in *dynamic equilibrium with its 7-coordinate dihydride form in the solution phase*, indicating little energy difference between these rapidly interconverting species.

The ratio of H₂ complex to dihydride is about 4:1 and thermodynamic measurements [3] show ΔH° to be only 1.5 kcal/mol and $\Delta H^\ddagger = 10$ kcal/mol. The dihydride has not been isolated or observed in the solid state but was readily observed in solution by infrared and NMR spectroscopy.

Many new examples of H₂ complexes have now been found throughout the transition metal series and even the actinides (~60 complexes) [2], and nearly 200 papers have been published on the subject. Included are several polyhydride complexes that had long been believed to contain only classical hydrides, e. g. FeH₄(PR₃)₃, which has recently been shown by neutron diffraction [4] to be actually FeH₂(H₂)(PR₃)₃ (Fig. 2). By far the most common electronic structure of dihydrogen complexes is d⁶ (metals in oxidation states containing 6 d-electrons, e. g. W(0)) with overall octahedral coordination of ligands around the metal center. Ionic dihydrogen complexes can be formed by protonation of hydride complexes in solution with both strong (e. g. HBF₄) and weak (e. g. alcohols) acids: $M-H + H^+[anion]^- \rightarrow [M-H_2]^+[anion]^-$ where M represents a metal-ligand fragment such as Fe(H)(PR₃)₄. The bound H₂ here can be very acidic, readily transferring a proton to a base and displaying aqueous pK_a values ranging from -2 (i. e. as strong as sulfuric acid!) to 18 [5]. Metal-bound H₂ was found to transfer hydrogen (as H⁺) to bases more readily than hydride ligands coexisting on the same metal center.

H₂ has also been found to molecularly bind to metal surfaces such as Ni(510) [6], palladium atoms in rare-gas matrices [7], and small metal atom clusters (e. g. Cu₂(H₂)₂, Cu₂(H₂)₃, Cu₃(H₂), Fe_x(H₂) (x= 3 or 4) at low temperatures [8]. The relevance of M-H₂ binding to catalytic hydrogenation mechanisms and hydrogen storage is readily apparent. Even the function of metal-containing biological enzymes such as nickel hydrogenases are now being considered in terms of molecular hydrogen binding [9].

Bonding and Cleavage of the H-H Bond

Importantly, the tungsten complex represented the first stable compound containing intermolecular interaction of a *sigma-bond* (H-H) with a metal and serves as a prototype for other "nonclassical" (2-electron, 3-center) complexes (e. g. the bonding of C-H bonds to metals). Searches are now on for stable methane or other alkane binding to metals (observable only at low temperature). Extensive theoretical investigations of metal-dihydrogen bonding have been carried out using primarily ab initio and Extended Huckel calculational techniques [2,10]. The bonding model is

similar to that of the Dewar-Chatt-Duncanson model of metal-olefin bonding (Fig. 3). The primary interaction is donation of electron density from the H_2 bonding electron pair (σ -orbital) to a vacant metal d-orbital. There is also, to a lesser degree, "back-donation" into the σ^* antibonding orbital of H_2 from a filled d-orbital, which is of major importance. It is responsible for the side-on bonding of H-H to metals and also represents the mechanism by which H_2 is cleaved to atomic hydride. Clearly if the amount of backdonation becomes excessive (e. g. increasing the energy of the metal d-orbital by increasing electron density on the metal), the H-H bond is ruptured because of overpopulation of the antibonding H_2 orbital. The formation of a dihydride from the tungsten- H_2 complex discussed above graphically demonstrates this cleavage process. In addition we have shown that *one can "fine tune" H_2 interaction with metal complexes to bind either as dihydrogen or dihydride by adjusting the electron-donating properties of the co-ligands* (e. g. phosphines). To effect this we synthesized a series of complexes of molybdenum of the type $Mo(CO)(H_2)(R_2PCH_2CH_2PR_2)_2$ and varied the organo phosphine substituent, R. For R= phenyl (a poorer electron donor), the complex contains molecularly bound hydrogen in the typical 6-coordinate octahedral structure (Fig. 4), but for the more inductively electron-donating substituents R= ethyl or isobutyl, the complex now exists as a 7-coordinate *dihydride* with a completely rearranged structure (pentagonal bipyramid, Fig 4) [11]. All that has been changed is the net "electron-richness" of the molybdenum, which increases the amount of $Mo \rightarrow \sigma^* H_2$ backdonation, resulting in breakage of the H-H bond. The same effect has been demonstrated by changing the metal from Mo to more electron-rich W.

The H-H bond length should be a measure of the degree of weakening of the H-H bond. So far three neutron diffraction structures of H_2 complexes have been carried out [1,4,12] and they all show distances of 0.82 Å (~0.79 Å for a preliminary refinement of the neutron structure of the above Mo complex). This is probably fortuitous because there is increasing evidence for elongated distances near or even greater than 1.0 Å. An x-ray structure [13] of a rhenium complex with three classical hydrides and a dihydrogen ligand showed an H-H distance of 1.06 Å, although x-ray determined distances are not reliable and must be confirmed by neutron diffraction. Solid state 1H NMR experiments by Zilm at Yale [14] also indicate distances near 1.0 Å for ruthenium- H_2 complexes. These same experiments showed H-H to be 0.89 Å in our tungsten complex, a distance 0.07 Å longer than in the neutron structure. This discrepancy may be rationalized by the fact that the bound H_2 undergoes rapid rotation or at the least librational motion about the metal- H_2 axis even at low

temperatures (see below). The thermal motion may result in an effective shortening of the actual H–H distance as observed by neutron diffraction. The determination of the real H–H internuclear distance is thus not straightforward, and the question of how long can an H–H bond be before it no longer can be considered a bond will be the subject of much speculation and experiment in the near future.

Infrared and NMR Spectroscopic Studies

The infrared spectrum of our tungsten-dihydrogen complex displayed the six vibrational modes that we calculated to exist for a bound H_2 (only two exist for a hydride, $\nu(M-H)$ and $\delta(M-H)$) [1]. The H–H stretch was located as a very broad, weak band near 2700 cm^{-1} for a solid sample. Symmetric and asymmetric W- H_2 modes were located at 1570 and 950 cm^{-1} , and two deformational modes (~ 650 and 450 cm^{-1}) were also located, all of which shifted as expected on deuterium substitution (for both the HD and D_2 isotopomers). Inelastic neutron scattering located the torsional (rotational) mode at $\sim 350\text{ cm}^{-1}$. Thus far our complexes are the only ones in which all of these modes have been observed, but the H–H stretch has been observed in several unstable species at low temperature [2]. It has been found to vary in the range $3100\text{--}2200\text{ cm}^{-1}$, much lower than that in free H_2 (4300 cm^{-1}). Several vibrational modes similar to those for our complexes have been seen for the $Ni(510)\text{--}H_2$ interaction by EELS spectroscopy [6] and also for $Pd\text{--}H_2$ [7].

Solution 1H NMR spectra of dihydrogen complexes typically show a broad single resonance due to the H_2 . HD complexes give a diagnostic 1:1:1 triplet pattern due to HD coupling ($I_D = 1$), which varies from 10–36 Hz ($J(HD) = 43\text{ Hz}$ for HD gas). Crabtree demonstrated that the H_2 ligand has a very short relaxation time T_1 on the order of 4–40 ms, thus giving another aid to determining whether dihydrogen binding is present in a complex [2]. The main reason for the low T_1 is dipolar H–H coupling which varies as r^{-6} and thus is strongly influenced by the short H–H distance for bound H_2 . H–H bond distances have been estimated by solution NMR and also indicate elongated distances near or greater than $1.0\text{ \AA}$ in several complexes [15].

Dynamics, Rotation, and Quantum Mechanical Phenomena of Bound H_2

Metal dihydrogen/hydride systems exhibit a remarkable variety of dynamic behavior: the bound H_2 ligand undergoes (1) reversible dissociation from the metal, (2) rapid propeller-like rotation about the $M\text{--}H_2$ axis, (3) isotopic scrambling, (4) intramolecular exchange with hydride co-ligands, and (5) cleavage to two hydride

ligands, all of which can occur simultaneously and as equilibrium processes. The energy barrier to rotation of bound H_2 has been studied experimentally and theoretically in relation to the bonding model for $M-H_2$. As discussed above, metal $\rightarrow H_2$ σ^* "backbonding" is crucial to the stability of H_2 complexes, and the extent of this bonding should be reflected by the magnitude of the rotational barrier. This is due to the anisotropy that exists in the co-ligand arrangement and therefore in metal d-orbital energies. The H-H bond axis can align parallel to either the phosphine-W-phosphine vector or the OC-W-CO vector in Fig. 1, and the energy difference between these orientations represents the rotational barrier (the H_2 σ donation to the vacant metal d-orbital has no orientational preference). Both experimental studies and ab initio calculations show that the H-H prefers to align along the P-W-P axis because the d-orbital in this direction is of higher energy (the phosphines are much better electron donors than CO), with an energy difference of 1.8 kcal/mol for $W(CO)_3(PR_3)_2(H_2)$ (R= cyclohexyl). Calculations using standard "molecular mechanics" programs also showed that nonbonding repulsive interactions between the H_2 and the bulky organophosphines were found not to be significant in hindering H_2 rotation. We have been able to experimentally determine the rotational energy barriers by inelastic neutron scattering methods, particularly rotational tunneling spectroscopy which measures the ground state splitting energy of H_2 in a standard double-minimum potential well [16]. We have determined that this type of potential is an excellent model for the H_2 rotation, with the assumption of rotation with one degree of freedom (possibly the first example of this for H_2 as first described by Pauling [17]). The barriers are quite low, ranging from 1-3 kcal/mol, and agreed well with the ab initio calculations. These results show that backbonding does exist and also that inelastic neutron scattering is a good diagnostic for H_2 binding. The barrier to rotation in the Fe complex (Fig. 2) is particularly low, 1.0 kcal/mol, and this has been ascribed to a weak interaction between the H_2 ligand and a cis hydride (H(3)) wherein there is donation of electron density from the Fe-H(3) bonding orbital to the σ^* orbital of H_2 [4]. This "cis-interaction" shown in Fig. 5 competes with the normally preferred orientation of the H-H bond parallel to the P(1)-W-H(3) axis, resulting in a rather flat potential (low barrier) and also the unusual alignment of the H_2 at a 45° angle to metal-ligand axes. Fig. 5 show that this interaction is the first step towards formation of a transient H_3 ligand which has often been proposed to be an intermediate in exchange of H_2 and hydride. H_3^+ is a known mass-spectrometer molecule and its possible stabilization on a metal complex has been proposed [18] but thus far has not been observed.

The above-mentioned rotational tunneling is a quantum mechanical effect (neutron-induced spin-flip, essentially para ($I=0$, $J=0$) to ortho ($I=1$, $J=1$) transitions within the ground librational state of the H_2) observable even in the remarkably high temperature regime of 180-200 K. An unusual solution NMR exchange coupling phenomenon has recently been observed in iridium trihydride complexes, $[C_5(CH_3)_5]IrH_3(L)$ (L = phosphine-type donor), in this temperature range which also has been determined to be a quantum mechanical process [19]. In this system, coherent motion of the three hydrides produces extraordinarily large 1H - 1H coupling constants (thousands of Hertz!) with huge temperature dependences. These phenomena emphasize that one must always be alert for novel quantum mechanical behavior in hydrogen systems, even at the "low" temperatures (relatively-speaking) at which many experiments are routinely carried out. Lastly, we are also utilizing neutron scattering measurements in the regime of the transition from quantum mechanical to classical behavior (quasi-elastic neutron scattering) to obtain information about dihydrogen/hydride exchange processes.

Conclusion

The now well-documented existence of molecularly-bound H_2 on metal complexes, metal surfaces, and metal atoms obviously gives cause for speculation about the existence of hydrogen pairing in bulk metal hydride systems. We have shown that the molecularly bound state is quite sensitive to several factors: (1) the overall electron "richness" of the metal center and electronic configuration (d^6 favored), (2) the presence of strong *trans*-influence ligands such as CO opposite the H_2 on the metal, which moderates the metal to H_2 backbonding, (3) solid versus solution state, and, only to a very small degree, temperature (4) as a corollary to (1), the charge of the metal complex (cation versus neutral), (5) oxidation state of the metal (usually low). In regard to (1), the electronics at the metal in metal complexes are highly controlled by ancillary ligands (electron donors versus acceptors), which of course are not present in bulk hydrides. However, there could exist conditions in the latter systems favoring at least partial or local formation of hydrogen pairing, perhaps at temperatures higher (>400 K) than those of the normal stability range of organo-metal- H_2 complexes. It is becoming more apparent from the now numerous studies of H_2 complexes that the possible distances between H atoms surrounding a metal may exist as a *continuum* from 0.74 Å to >1.5 Å rather than as specific ranges corresponding to either bound dihydrogen with $H-H = \sim 0.82$ Å or hydride (>1.5 Å). Also, recent evidence has been reported for a Ru-porphyrin system containing H_2 chemically bonded between two Ru

metal centers, possibly the first example of a *bridging* molecular hydrogen group [20]. Searches have been made for the elusive H₃ ligand, and novel quantum mechanical behavior of dihydrogen and hydride systems have been observed. Thus the frontiers of dihydrogen chemistry appear boundless, and new findings worldwide are now making what was initially an extraordinary chemical bonding phenomenon look to be almost commonplace.

Acknowledgements

Support from the Department of Energy, Basic Energy Sciences, Office of Chemical Sciences, and Los Alamos National Laboratory's Institutional Supporting Research and Development Fund is gratefully acknowledged.

References

1. G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, J. Am. Chem. Soc. 106, 451 (1984) and G. J. Kubas, C. J. Unkefer, B. I. Swanson, and E. Fukushima, J. Am. Chem. Soc. 108, 7000 (1986).
2. G. J. Kubas, Acct. Chem. Res. 21, 120 (1988) and R. H. Crabtree, *ibid.* 23, 95 (1990).
3. G. R. K. Khalsa, G. J. Kubas, C. J. Unkefer, L. S. Van Der Sluys, and K. A. Kubat-Martin, J. Am. Chem. Soc. 112, 3855 (1990).
4. L. S. Van Der Sluys, J. Eckert, O. Eisenstein, J. H. Hall, J. C. Huffman, S. A. Jackson, T. F. Koetzle, G. J. Kubas, P. J. Vergamini, and K. G. Caulton, J. Am. Chem. Soc. 112, 4831 (1990).
5. M. S. Chinn, D. M. Heinekey, N. G. Payne, and C. D. Sofield, Organometallics 8, 1824 (1989) and R. H. Morris, private communication.
6. A.-S. Martensson, C. Nyberg, and S. Andersson, Phys. Rev. Lett. 57, 2045 (1986) and Surface Sci. 205, 12 (1988).
7. G. A. Ozin, and J. Garcia-Prieto, J. Am. Chem. Soc. 108, 3099 (1986).
8. R. H. Hauge, J. L. Margrave, and Z. H. Kafafi, NATO ASI Ser., Ser. B 158 (Phys. Chem. Small Clusters), 787 (1986).
9. R. H. Crabtree, Inorg. Chim. Acta 125, L7 (1986) and S. P. J. Albracht, Rec. Trav. Chim. Pays-Bas 106, 173 (1987).
10. P. J. Hay, J. Am. Chem. Soc. 109, 705 (1987) and A. G. Ginsburg and A. A. Bagaturyants, Metalloorg. Khim. 2, 249 (1989) and references therein.
11. G. J. Kubas, R. R. Ryan, and C. J. Unkefer, J. Am. Chem. Soc. 109, 8113 (1987).

12. J. S. Ricci, T. F. Koetzle, M. T. Bautista, T. M. Hofstede, R. H. Morris, and J. F. Sawyer, *J. Am. Chem. Soc.* 111, 8823 (1989).
13. Y. Kim, H. Deng, D. W. Meek, and A. Wojcicki, *J. Am. Chem. Soc.* 112, 2798 (1990).
14. K. W. Zilm and J. M. Millar, *Adv. Magnetic and Optical Resonance* 15, 163 (1990) and K. W. Zilm, R. A. Merrill, M. W. Kummer, and G. J. Kubas, *J. Am. Chem. Soc.* 108, 7837 (1986).
15. D. G. Hamilton, and R. H. Crabtree, *J. Am. Chem. Soc.* 110, 4126 (1988); M. T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. T. Schweitzer, and A. Sella, *J. Am. Chem. Soc.* 110, 7031 (1988); and ref. 2 (Crabtree).
16. J. Eckert, G. J. Kubas, J. H. Hall, P. J. Hay, and C. M. Boyle, *J. Am. Chem. Soc.* 112, 2324 (1990).
17. L. Pauling, *Phys. Rev.* 36, 430 (1930).
18. J. K. Burdett, J. R. Phillips, M. R. Pourian, M. Poliakoff, J. J. Turner, and R. Upmacis, *Inorg. Chem.* 26, 3054 (1987).
19. K. W. Zilm, D. M. Heinekey, J. M. Millar, N. G. Payne, and P. Demou, *J. Am. Chem. Soc.* 111, 3088 (1989); D. M. Heinekey, J. M. Millar, T. F. Koetzle, N. G. Payne, and K. W. Zilm, *J. Am. Chem. Soc.* 112, 909 (1990); and K. W. Zilm, D. M. Heinekey, J. M. Millar, N. G. Payne, S. P. Neshyba, J. C. Duchamp, and J. Szczyrba, *J. Am. Chem. Soc.* 112, 920 (1990). See also the first citation in Ref. 14.
20. J. P. Collman, J. E. Hutchison, P. S. Wagenknecht, N. S. Lewis, M. A. Lopez, and R. Guillard, *J. Am. Chem. Soc.* 112, 8206 (1990).

Figure Captions

Figure 1. Neutron diffraction structure of $\text{W(CO)}_3(\text{PR}_3)_2(\text{H}_2)$ (R= isopropyl = *i*-C₃H₇) at 30 K (the lower phosphine ligand is disordered).

Figure 2. Neutron diffraction structure of $\text{FeH}_2(\text{H}_2)[\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)]_3$ at 27 K (H–H = 0.82 Å).

Figure 3. Bonding model for metal–H₂ σ -complex compared to model for metal-olefin π -complex.

Figure 4. Representation of the structures of the reaction products of H₂ with the unsaturated precursor $\text{Mo(CO)(R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$ to give either an H₂ complex or a dihydride depending solely on the nature of the organo-substituent R: phenyl (Ph) versus ethyl (Et) or isobutyl (*i*-Bu).

Figure 5. Cis-interaction between dihydrogen and hydride, leading to formation of a transient metal–trihydrogen complex, which can freely rotate to give site exchange of hydrogen (labelled with asterisk) from hydride to dihydrogen.

M - olefin

M - π - bond

M - H₂

M - σ - bond

cis-interaction

H₃-complex

exchanged

END

DATE FILMED

02 / 14 / 91