# Dihydrogen Complexes: Some Structural and Chemical Studies

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The discovery of the dihydrogen complex $[W(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2]$ (1) (Cy = cyclohexyl) by Kubas et al.[1] was one of the most exciting results in inorganic chemistry in the 1980s. The H_2 ligand was shown to be bound as an intact molecule (structure A) rather than in the usual dihydride form (structure B). Within three

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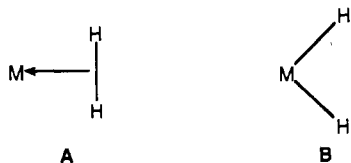
years, a large number of other H_2 complexes[2-7] had been identified, notably by the groups of Morris,[2] Heinekey,[3] Simpson,[5] Poliakoff and Turner,[7a] Grevels,[7b] and Sweany[7c] and ourselves.[6] Molecular hydrogen is the only example of a pure nonpolar covalent bond without lone pairs or other bonds in the molecule, and it is an important test bed for ideas on covalency. Principles that emerge are also likely to be relevant to other problems, such as the functionalization of unactivated C–H bonds.[6c]

Why does H_2 sometimes bind to give an $M(\eta^2\text{-}H_2)$ complex, but more often to give a classical dihydride, $M(H)_2$? The metals involved have both empty d_σ and filled d_π orbitals (Figure 1). Electron donation from the filled $H_2(\sigma)$ orbital to the empty $M(d_\sigma)$ weakens, but does not break, the H–H bond because the resulting two-electron, three-center orbital is bonding over all

three atoms. On the other hand, sufficient "back-donation" from filled d_π orbitals into the empty $H_2(\sigma^*)$ will tend to break the H–H bond, because $H_2(\sigma^*)$ is H–H antibonding in character.[8] Electron-withdrawing ligands or a net cationic charge tends to reduce the M to H_2 back-bonding and so favor $\eta^2\text{-}H_2$ binding. Lewis acids without d_π electrons (BF_3) do not seem to bind H_2, so some back-bonding is necessary. Morris[9] finds $\eta^2\text{-}H_2$ binding for electrophilic L_nM groups (L = ligand; M = metal) for which $L_nM(N_2)$ has a $\nu(N_2) > 2060$ cm^{-1}. In contrast, $L_nM(H)_2$ tends to be found where $\nu(N_2) < 2060$ cm^{-1}. The more π-basic the L_nM group, the more the N_2 π^* and H_2 σ^* orbitals are filled, leading to a

(1) Kubas, G. J. Acc. Chem. Res. 1988, 21, 120; Comments Inorg. Chem. 1988, 7, 17.
(2) (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. J. Am. Chem. Soc. 1985, 107, 5581. (b) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. J. Chem. Soc. 1987, 109, 3780.
(3) (a) Chinn, M. S.; Heinekey, D. M. J. Am. Chem. Soc. 1987, 109, 5865. (b) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. Organometallics 1989, 8, 1824.
(4) Siedle, A. R. Inorg. Chem. 1988, 27, 1593.
(5) Conroy-Lewis, F. M.; Simpson, S. J. J. Chem. Soc., Chem. Commun. 1986, 506; 1987; 1675.
(6) (a) Crabtree, R. H.; Lavin, M. J. Chem. Soc., Chem. Commun. 1985, 794, 1661. (b) Crabtree, R. H.; Lavin, M.; Bonneviot, L. J. Am. Chem. Soc. 1986, 108, 4032. (c) Crabtree, R. H. Chem. Rev. 1985, 85, 245. (d) Crabtree, R. H.; Hamilton, D. G. J. Am. Chem. Soc. 1986, 108, 124. (e) Hamilton, D. G.; Crabtree, R. H. J. Am. Chem. Soc. 1988, 110, 4126. (f) Luo, X.-L.; Baudry, D.; Boydell, P.; Charpin, P.; Nierlich, M.; Ephritikhine, M.; Crabtree, R. H. Inorg. Chem., in press.
(7) (a) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. J. Chem. Soc., Chem. Commun. 1985, 27. (b) Church, S. P.; Grevels, F.-W.; Herrman, H.; Scheffner, K. J. Chem. Soc., Chem. Commun. 1985, 30. (c) Sweany, R. L. J. Am. Chem. Soc. 1985, 107, 2374. Sweany, R. L.; Moroz, A. J. Am. Chem. Soc. 1989, 111, 3577.
(8) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. Inorg. Chem. 1987, 26, 3054. Sevin, A. Nouv. J. Chim. 1981, 5, 233. Saillard, J.-Y.; Hoffman, R. J. Am. Chem. Soc. 1984, 106, 2006. Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. J. Am. Chem. Soc. 1986, 108, 6587. Hay, P. J. J. Am. Chem. Soc. 1987, 109, 705.
(9) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. Inorg. Chem. 1987, 26, 2674.

Robert Crabtree was born in London in 1948. After research with Prof. Malcolm Green at Oxford and Prof. Joseph Chatt at Sussex, he worked as Attache de Recherche in Dr. Hugh Felkin's laboratory of the CNRS Natural Products Institute at Gif sur Yvette, near Paris. Since 1977, he has been at Yale, where he is now Professor. Other areas of study in the Crabtree group are C–H activation, especially mercury-photosensitized reactions, halocarbon complexation, and the bioinorganic chemistry of nickel and manganese. Dr. Crabtree has recently written a text on organometallic chemistry.
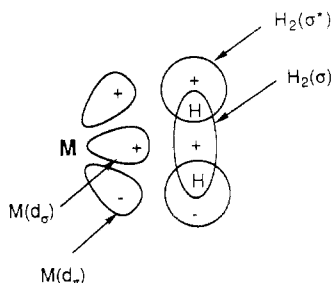
Figure 1. The M–(H$_2$) bond is believed to be dominated by electron donation from H$_2(\sigma)$ to M(d$_\sigma$). Significant M(d$_\pi$) to H$_2(\sigma^*)$ back-donation breaks the H–H bond and gives a classical dihydride M(H)$_2$.

lower ν(N$_2$) and a greater tendency to break the H–H bond.

Iridium Dihydrogen Complexes

In 1984, Maryellen Lavin[6] in our group had made **2** (L = PPh$_3$), a compound that has a labile aqua ligand that can be readily replaced by a variety of conventional ligands. Having just read Kubas's first paper,[10a] she decided to add H$_2$ to **2** (eq 1). The product, **3**, contains

$$\text{(eq 1)}$$
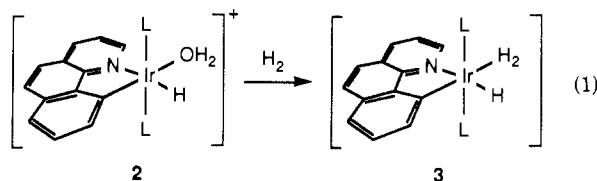
an η^2-H$_2$ as well as a terminal hydride. This became clear from the ^{1}H NMR spectrum. The single broad resonance at room temperature decoalesces at 240 K to give a sharp resonance for Ir–H and a broad one which could be assigned to Ir–(η^2-H$_2$). Kubas found that the HD analogue of **1** has an HD coupling constant of 33.5 Hz in the NMR spectrum, much closer to that for free HD (43 Hz) than for a "classical" L$_n$M(H)(D) complex (ca. 1 Hz) and consistent with a significant degree of H–H bonding in the complex. The HD analogue of **3** showed a J(H,D) of 29.5 Hz, and so **3** could be confidently assigned as an η^2-H$_2$ complex.

Complex **3** can be deprotonated by tertiary amines or butyllithium. Lavin was able to show by isotopic labeling that the site of deprotonation is the η^2-H$_2$ and not the classical Ir–H. H$_2$, a very poor acid in the absence of coordination, is therefore strongly activated by binding. Chinn and Heinekey[3a] have recently determined pK_a values of 17.6 for [CpRu(dmpe)(H$_2$)]$^+$ and −2 for [(C$_5$Me$_5$)Re(CO)(NO)(H$_2$)]$^+$.[3b] This means that η^2-binding must strongly deplete the electron density on the H$_2$ in these cases, no doubt as a result of the predominance of H$_2(\sigma)$ to M(d$_\sigma$) electron donation. Heterolytic hydrogen or C–H activation[6b] may generally occur via deprotonation of an η^2-H$_2$ or η^2-C–H intermediate or transition state.

Relaxation Studies

In 1978, Jennifer Quirk looked at the protonation of IrH$_5$(PCy$_3$)$_2$, but we were never able to characterize the

product.[11] The NMR spectrum, with sharp and broad resonances in a 1:2 ratio, so closely resembled that of **3** that we now felt it must be [IrH$_2$(H$_2$)$_2$(PCy$_3$)$_2$]$^+$ (**4**, eq 2). The HD analogue was too fluxional to show

$$\text{(2)}$$

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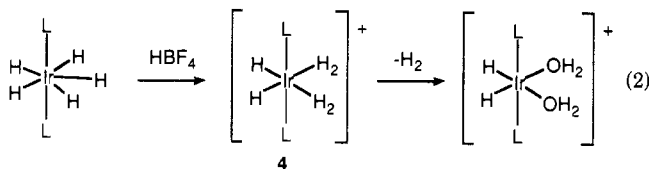
J(H,D) coupling at the lowest accessible temperatures. No other characterization method was applicable. No ν(H–H) band was observable by IR, and no crystals were obtainable for diffraction studies. Lavin and I both consulted widely within our department for ideas. Kubas[10] had noted the breadth of the η^2-H$_2$ NMR signal from **1** and had suggested that rapid dipolar relaxation might be responsible. Professor Kurt Zilm in our department also suggested to us that the T_1 for an H$_2$ complex might be short. These ideas fell on fertile ground, because Professor Richard Uriarte had already been looking at T_1 values of classical hydrides in our group for an unrelated reason.[12]

We were delighted when Lavin[6] showed that, in the authentic η^2-H$_2$ tricyclohexylphosphine analogue of **3**, the T_1 for the η^2-H$_2$ site (30 ms) is more than an order of magnitude shorter than that for the classical Ir–H site (390 ms) at −85 °C and 500 MHz. Thirty milliseconds was shorter than any T_1 we had found for classical hydrides. For the more fluxional derivative **4**, both resonances gave exceptionally short T_1 values (48 and 73 ms at 500 MHz), as a result of fluxional exchange between the sites. The intensity ratio of the peaks for the two types of hydride is 1:2, supporting the formulation [IrH$_2$(H$_2$)$_2$L$_2$]$^+$ for **4**. Instead of being a classical Ir(VI) complex, the very favorable d^6 octahedral Ir(III) state is preferred. Chaudret[13] has now shown that the isoelectronic Ru species is [RuH$_2$(H$_2$)$_2$L$_2$].

The T_1 method seemed to be a convenient qualitative test, useful even in cases where all the previous methods (neutron diffraction, J(H,D) in the proton NMR, and ν(H–H) in the IR spectrum) were inapplicable. Doug Hamilton,[6d,e] also a graduate student, then looked at many different hydrides and found values of T_1 that were intermediate between the short values we associated with nonclassical structures and the longer values typical of the classical hydrides. This forced us to be more quantitative and look more deeply into the physical origin of the T_1. We concluded that the most likely relaxation mechanism is dipole–dipole (DD). The theory of DD relaxation predicts that the T_1 values should vary with temperature and go through a minimum at a temperature θ(min). This was confirmed experimentally (Figure 2).

The reason for the appearance of this minimum is as follows. When the T_1 is measured, the spins are first inverted by a 180° pulse; the rate of their return to the initial equilibrium state is $(T_1)^{-1}$. Only if the inverted spins experience a fluctuating magnetic field at or near

(10) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (c) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. (d) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (e) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1987**, *109*, 8113.

(11) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331.
(12) Crabtree, R. H.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1985**, *24*, 1949.
(13) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598.

Table I
Calculated and Observed H–H Distances[a]

compd	T_1(min), ms	freq, MHz	r(calcd), Å	r(obsd), Å	ref
[W(H$_2$)(CO)$_3$(PCy$_3$)$_2$]	<5[b]	200	<0.96	0.84,[c] 0.89[d]	1, 10, 17
[FeH(H$_2$)(dppe)$_2$]$^+$	<7[b]	200	<1.05	0.89[c]	2, 15
[IrH(H$_2$)(bq)(PPh$_3$)$_2$]$^+$	8	200	1.04	0.92[d]	6b
[CpRu(H$_2$)(CO)(PCy$_3$)]$^+$	4	250	0.93	0.97[d]	3a, 17b

[a] For compounds for which both T_1 and solid-state structural studies have been studied. No account has been taken of H$_2$ rotation. Abbreviations: dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; bq = 7,8-benzoquinolinate. [b] At 193 K, T_1 minimum not yet attained. [c] By neutron diffraction. [d] By solid-state NMR.
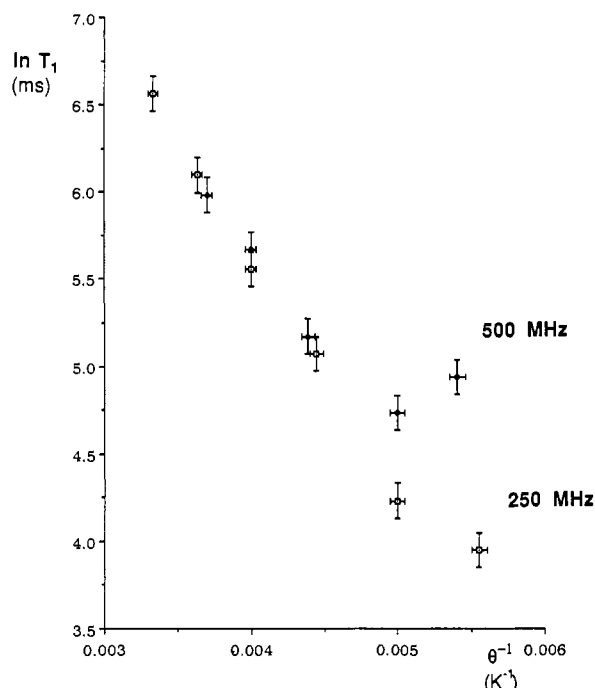

Figure 2. A plot of ln T_1 vs $1/\theta$ for ReH$_7$(PPh$_3$)$_2$, showing the pronounced minimum at 500 MHz. Note that the minimum is only just attained at 250 MHz.

the Larmor frequency will they undergo a spin flip and so be able to return to equilibrium. Several sources for the required fluctuating magnetic field have been identified.

In the DD mechanism, we consider two H nuclei, H$_a$ and H$_b$, in a rigid molecule separated by a distance r. Collisions with the solvent cause the molecule to rotate randomly (Brownian motion). H$_a$ and H$_b$ are magnetic dipoles rotating about each other with the molecular motion, and so the magnetic field of each is felt by the other. If the average rotation rate happens to be close to the Larmor frequency, then each proton becomes a source of a magnetic field fluctuating at or near the Larmor frequency which will help relax the other. H$_a$ and H$_b$ can then lose the energy of the inverted spins to the thermal bath of the solvent and reach equilibrium. A molecule will be most efficiently relaxed by the DD mechanism at some temperature θ(min) for which the molecular rotation rate best matches the Larmor frequency. Equation 3[6e] describes the behavior of T_1 with τ_c, the rotational correlation time of the molecule (a measure of the average molecular rotation rate).

$$[T_1(DD)]^{-1} =$$
$$0.3h^2\gamma^4r^{-6}[\tau_c/(1 + \omega^2\tau_c^2) + 4\tau_c/(1 + 4\omega^2\tau_c^2)] \quad (3)$$

(γ = gyromagnetic ratio, h = Planck's constant/2π, τ_c = rotational correlation time (s/rad), ω = Larmor frequency)

Since it depends on r^6, T_1 is very sensitive to the presence of a pair of protons that are abnormally close together, as in an H$_2$ complex. The DD contribution from this pair should dominate the relaxation. Contributions from the solvent nuclei and the other nuclei in the molecule should be negligible by comparison. Koetzle, Caulton, et al.[14a] reported the neutron diffraction structure of FeH$_2$(H$_2$)(PEtPh$_2$)$_3$. This confirms the nonclassical structure we originally assigned from T_1 data.[6d] Knowing the structure, we can now calculate that between 95 and 98.6%[14b] of the experimental relaxation comes from the DD coupling within the H$_2$ ligand, so DD relaxation within the H$_2$ is indeed dominant. The same is true for [FeH(H$_2$)(dppe)$_2$]$^+$.[15]

The temperature, θ(min), of the minimum T_1 [T_1-(min)] is field dependent but is usually in a convenient range (−20 to −100 °C) for T_1(min) to be measured. The choice of −80 °C in our original studies, intended to prevent fluxionality and H$_2$ loss, was fortunate because it is usually within 20 °C of θ(min).

The great advantage of T_1(min) is that it depends only on the H–H separation, r, and the magnetic field, B, but is independent of θ and the molecular size. In contrast, T_1 at a single temperature will depend on how close we happen to be to θ(min). By eq 3, T_1 measured on the high θ side of θ(min) (the fast-motion regime) should be the same at different fields, but the T_1 value at lower θ (slow-motion regime) depends on B^2. T_1(min) itself scales directly with B, so that T_1(min,250MHz) is half T_1(min,500MHz). This makes it important to cite B when reporting T_1(min), and both B and θ for nonminimum data.

By differentiating eq 3, we find that eq 4 holds at the minimum. This result allows us to calculate τ_c and so solve eq 3 for r without adjustable parameters. At 250 MHz, this leads to eq 5. We were surprised to find r(H–H) values in such good agreement with those from other methods (Table I).

$$\tau_c = 0.62/\omega \quad (4)$$

$$[T_1(min,250MHz)]^{-1} = 157.2r^{-6} \quad (5)$$

(r = H–H distance (Å), T_1 = relaxation time (s))

These r values were systematically slightly longer than the crystallographic ones for the nonclassical hydrides. Prof. Sunney Chan suggested using an empirical C factor to account for this apparent systematic error (eq 6). We estimated C to be ca. 0.9 on the basis of comparison with the crystallographic results.

$$r_{real} = C(r_{calcd}) \quad (6)$$

(14) (a) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Caulton, K. G., personal communication, 1989. (b) Depending on whether free rotation of the H$_2$ ligand is occurring (in which case, 95%) or not (98.6%).
(15) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823.

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Table II
T_1(min) Data for Some Hydride Complexes[a]

compd	temp, K	T_1(min), ms	ref
[CpRu(PPh₃)₂H]	238	300	6e
[ReH₇(dppe)]	222	67	6e
{ReH₇[P(p-FC₆H₄)₃]₂}	200	55	6e
[ReH₈(PPh₃)]⁻	200	245[b]	6e
[WH₆(PMe₂Ph)₃]	235	181	6e
[Fe(H₂)H₂(PEt₂Ph)₃]	203	24	6d
[IrH(H₂)(bq)(PPh₃)₂]⁺	200	8[c]	6b

[a] At 250 MHz. [b] The relatively high value seems to be a result of rapid free rotation of the ReH_8 group about the Re–P bond.[22] [c] Of the H_2 resonance.

Morris[16a] traced the source of this discrepancy to H_2 rotation. If H_a–H_b is rotating much more rapidly about the M–(H_2) bond than does the molecule as a whole, then this H_2 will be less efficiently relaxed, because H_a and H_b will no longer have a rotation frequency close to the Larmor frequency. On this basis,[16b] Morris[16a] predicted that C should be 0.79 for fast rotation, rising to 1.0 for a nonrotating H_2. By fitting observed T_1 data to theory, he suggested that fast rotation was probably occurring. Zilm[17] has used an elegant solid-state NMR method to measure the DD coupling directly for a variety of H_2 complexes. He finds an r(H–H) of 0.890 ± 0.006 Å for 1.

The Saga of ReH₇L₂ and the Limitations of the Method

The polyhydrides ReH_7L_2 are an extreme case of the stabilization of high oxidation states by H ligands, and they are important catalysts for alkane conversion.[18] They react by loss of H_2, which usually occurs at 60–110 °C. If $[IrH_8L_2]^+$ avoids Ir(VII) by being an H_2 complex, could something similar be true for ReH_7L_2?

At the time we first looked at the T_1 data, the H ligands had not been located crystallographically. We found T_1(min) values of 54–67 ms at 250 MHz for a series of these heptahydrides. These values are longer than those for the unambiguously identified H_2 complexes, but shorter than those for the classical cases studied up to then (Table II). Were the rhenium heptahydrides classical with a short T_1 or nonclassical with a long T_1?

To tell, we had to compare the observed T_1 with values calculated on the basis of plausible models. For the classical structure, we took a tricapped trigonal prism (TTP, shown below for 5),[19] and for the non-classical form, we took a dodecahedral (DDH) 8-coordinate [ReH₅(H₂)L₂]. We then calculated the T_1 for each hydride proton H_n by summing the contributions from all the H_n...H_m vectors in the molecule using eq 5 and averaged the results for all the hydrides to obtain the calculated T_1(min). For the TTP structure, we calculated a T_1(min,250MHz) of 107 ms. A value of 67 ms is calculated for DDH if r(H–H) is 1.07 Å and C is

(16) (a) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031. (b) Woessner, D. E. *J. Chem. Phys.* **1962**, *37*, 647.

(17) (a) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837. (b) Zilm, K. W.; Millar, J. M. *Adv. Magn. Reson.*, in press.

(18) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243; **1982**, 606. Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1235.

(19) Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *4*, 558.
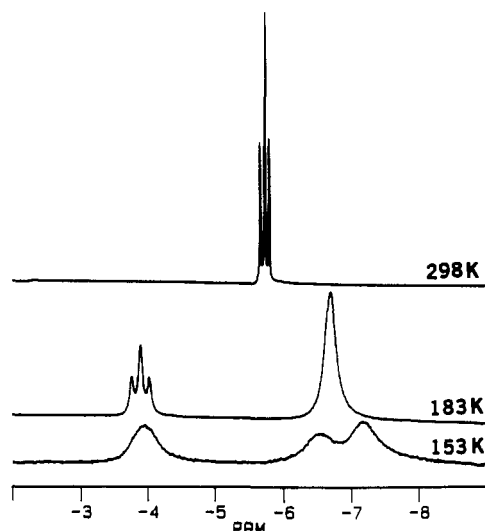
Figure 3. The ¹H NMR spectrum of ReH₇L₂ [L₂ = 1,1'bis(di-phenylphosphino)ferrocene], showing the decoalescence. The low-temperature pattern is most consistent with a classical structure.

0.79. This seemed most reasonable, and so we therefore (wrongly) proposed the nonclassical structure ReH_5-(H_2)L_2 for all the rhenium heptahydrides.

Xiao-Liang Luo then found a T_1(min,250MHz) of ca. 77 ms for [ReH₆(SiPh₃)(PPh₃)₂], a classical complex first made by Michel Ephritikhine.[6f] This led him to question the nonclassical structure for ReH_7L_2, and so he applied the isotopic perturbation of resonance (IPR) method,[20] which relies on isotopic fractionation between different types of site to distinguish, for example, MH_3 from $M(H_2)H$. It can be used even if fluxional exchange between sites is fast on the NMR time scale. First, a mixture of $MD_xH_{(3-x)}$ isotopomers is prepared. In the d_1 isotopomer, the energies of the $M(H_2)D$ and M-(HD)H isomers should differ, because of the difference in X–H and X–D zero-point energies ($\Delta\Delta E$) for the two types of site. If there is also a chemical shift difference ($\Delta\delta$) between the sites, then the d_0, d_1, and d_2 isotopomers should show different averaged chemical shifts. These shifts, unlike simple secondary isotope shifts (IS), should be temperature dependent, because the extent of any fractionation should depend on temperature. IPR is difficult to detect for most nonclassical hydrides, perhaps in part because the proton resonance is usually rather broad and in part because $\Delta\delta$ is often small; at least, it is small in the few cases[1,3] in which it can be measured. Field et al.[21] have recently seen an apparent IPR of ca. 20 ppb at 300 K for {P[(CH₂)₃PMe₂]₃FeH-(H₂)}⁺, however.

Luo did not see IPR for complexes of the ReH_7L_2 type, but only a small and temperature-independent IS of 2–8 ppb.[22] Since $\Delta\delta$ must be significant for IPR to be seen, we could still argue that a nonclassical structure is adopted but $\Delta\delta$ is small or 0. To eliminate this possibility, we needed to measure $\Delta\delta$ directly. To do this, we needed an ReH_7L_2 case in which the different sites could be frozen out by ¹H NMR at low temperature. Luo therefore made many new heptahydrides,

(20) (a) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558. (b) Calvert, B. R.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(21) Bampos, N.; Field, L. D. *Inorg. Chem.* **1990**, *29*, 587.

(22) Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3775; *J. Am. Chem. Soc.*, in press.

Table III
Observed T_1(min) Values Compared with Those Calculated from Crystallographic Data^a

compd	structural meth	T_1(min) calcd	found	field	ref
$FeH_2(H_2)(PEtPh_2)_3$	n-diff	$3.8–14.6^b$	24^c	250	14a
$ReH_7(dppe)$	n-diff	77	67	250	24
$ReH_5(PPh_3)_3$	X-ray	148	138	400	29
$Re_2H_8(PEt_2Ph)_4$	n-diff	302	140	400	35, 29
$W(H_2)(CO)_3(P\text{-}i\text{-}Pr_3)_2$	n-diff	$3.5–14.5^b$	4^d	200	1, 10
$W(H_2)(CO)_3(PCy_3)_2$	sol st NMR	$2.5–10.1^b$	$4^{d,e}$	200	17
$[FeH(H_2)(dppe)_2]^+$	n-diff	$1.9–7.5^b$	8.5^f	200	2, 15
$[IrH(H_2)bq(PPh_3)_2]^+$	sol st NMR	$4–15.5^b$	8^g	250	6
$WH_6(PMePh_2)_3$	n-diff	201	181	250	36
$Cp[Ir(PMe_3)H_3]^+$	n-diff	189	300^f	500	31b, 37
$Cp[Ir(PPh_3)H_3]^+$		$(189)^h$	200^f	500	31b, 37
$Cp[Ir(AsPh_3)H_3]^+$		$(189)^h$	210^f	500	31b, 37
$[CpRu(H_2)CO(PCy_3)]^+$	sol st NMR	$5.3–21.2^b$	4	250	3a, 17b

^{a} T_1 calculations from ref 22; n-diff = neutron diffraction; X-ray = X-ray diffraction; sol st NMR = direct observation of dipole–dipole coupling by solid-state NMR. ^{b} The first figure cited assumes no rotation of the H_2 ligand, i.e., $C = 1$. The second assumes fast H_2 rotation ($C = 0.79$). ^{c} At 203 K; T_1 minimum not observed. ^{d} At 193 K; T_1 minimum not observed. ^{e} Assuming that T_1 is essentially the same as T_1 from the P-i-Pr$_3$ analogue at the same τ_c. Cy = cyclohexyl. ^{f} At 210 K; T_1 minimum not observed. ^{g} Of the H_2 resonance. ^{h} Assuming that the structure is essentially the same as that of the PMe$_3$ analogue.

choosing ligands that he felt would favor a static structure by imposing conformational restrictions on the complex. Finally, with ReH$_7$(dppf) (5) [dppf = 1,1′-bis(diphenylphosphino)ferrocene] and related species, he was successful. As can be seen in Figure 3, 5 shows two resonances in a 2:5 ratio at 183 K. This is superficially consistent with the formulation [Re-H$_5$(H$_2$)L$_2$], but the peak of intensity two shows a substantial (32 Hz) coupling to phosphorus; this coupling is usually <5 Hz in nonclassical hydrides.[23] At 153 K, Luo was able to resolve three of the four sites of a disubstituted TTP with the dppf frozen in a C_2 conformation in a ca. 2:2:(2 + 1) ratio. This result confirms the classical structure for 5. Not only is the splitting pattern correct for TTP and not DDH, but there is a large Δδ between the peak of intensity two and the other peaks, which should lead to a substantial IPR if the complex were nonclassical.

5
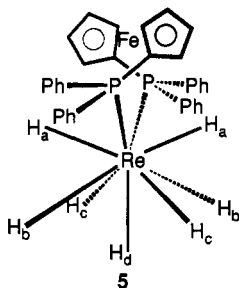
If ReH$_7$L$_2$ complexes are classical, then why do they give T_1(min) values as low as 54–67 ms at 250 MHz? The answer came from some neutron diffraction work by Dr. Judith Howard,[24] who showed in 1988 that ReH$_7$(dppe) is classical in the solid state. We obtained the coordinates from her and calculated a T_1(min),[22] by assuming (a) that the solid-state structure is retained in solution and (b) that DD relaxation is dominant. The calculated T_1(min) of 77 ms is in excellent agreement with the observed value of 67 ms.[22] These

calculations also gave very good agreement for a variety of other complexes (Table III). Only in the case of Re$_2$H$_8$L$_2$ do the calculations fail for reasons we do not yet understand. The general success of these calculations suggests that in most cases both of the assumptions hold, i.e., that (a) the solid-state structure is maintained in solution and (b) DD relaxation is dominant.

The reason the calculated value based on the neutron diffraction structure is substantially lower than the value we calculated earlier for the pure TTP polyhedron is that the presence of the large phosphorus atoms distorts the structure from the ideal TTP in such a way as to decrease the H...H distances.

Are Other Relaxation Mechanisms Involved?

Up to now, we have assumed that DD relaxation is dominant, but we need to consider whether other relaxation mechanisms are operating. For diamagnetic molecules, these are believed to be limited to DD, chemical shift anisotropy (CSA), spin rotation (SR), and scalar (SC) mechanisms.[25]

CSA[26] relaxation is only efficient for nuclei such as ^{195}Pt and ^{199}Hg, which have a large shielding anisotropy Δσ (e.g., Δσ values of 2500–10 000 ppm have been reported[27]); proton anisotropies are generally much smaller, e.g., 17 ppm for 1.[17] $[T_1(CSA)]^{-1}$ is proportional to B^2. As shown in Figure 2, the T_1 for ReH$_7$(PPh$_3$)$_2$ is essentially independent of field in the fast-motion regime, ruling out CSA.

The SR mechanism depends on molecular collisions, and $[T_1(SR)]^{-1}$ usually depends directly on the temperature. $[T_1(SR)]^{-1}$ usually rises[28] at higher temperature, but for free H$_2$, the usual temperature dependence is reversed.[17b] Since SR is an important mechanism for free H$_2$, it ought to contribute for coordinated H$_2$, but it has not yet been implicated for hydrides.

(23) (a) Bianchini et al.[23b] assign larger couplings (27–67 Hz) to J-(P,H$_2$) in certain Co and Ir hydrides, however. (b) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobi, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. Bianchini, C.; Mealli, A.; Peruzzini, M.; Zanobi, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.

(24) Howard, J. A. K.; Mason, S. A.; Johnson, O.; Diamond, I. C.; Crennell, S.; Keller, P. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1502.

(25) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Longman: Birmingham, AL, 1983.

(26) Ando, I.; Webb, G. A. *Theory of NMR Parameters*; Academic Press: New York, 1983.

(27) Keller, H. J.; Rupp, H. H. *Z. Naturforsch.* **1971**, *26a*, 785. Kennedy, J. D.; McFarlane, W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1653.

(28) Pesek, J. J.; Mason, W. R. *J. Magn. Reson.* **1977**, *25*, 519. Koole, N. J.; DeKoning, A. G.; De Bie, M. J. A. *J. Magn. Reson.* **1977**, *25*, 227. Lambert, J. B.; Netzel, D. A. *J. Magn. Reson.* **1977**, *25*, 531.

Many of the metal nuclei of polyhydrides are quadrupolar (e.g., ^{99}Ru and ^{101}Ru, $I = {}^5/_2$, 30%; ^{185}Re and ^{187}Re, $I = {}^5/_2$, 100%) and usually relax rapidly. This can influence the M–H hydride relaxation by scalar relaxation "of the second kind" (SCII). While SCII effects on T_2 and therefore on line width are relatively common, SCII effects on T_1 are extremely rare, because the Larmor frequencies of the two nuclei, M and H, have to be very close for SCII to contribute; this is not true for any transition metal, and there is no evidence that metals ever relax hydride protons by the SC mechanism.[17]

The best evidence for the dominance of the DD mechanism in the cases studied to date is the invariance of T_1 with B in the fast-motion regime, along with the general agreement between the observed T_1 data and the theoretical DD prediction (Table III). Exceptions will no doubt be found, however.

The Interpretation of T_1(min) Data

Relaxation measurements only provide a single T_1-(min) value, and assumptions need to be made in interpreting the data in terms of structure. For complexes in which there are only two H ligands, this is straightforward, because the difference in T_1 is so large (e.g.: $W(H_2)(CO)_3L_2$, 4 ms; $W(H)_2(CO)_3L_2$, 1700 ms at 200 MHz). Where more than two H ligands are present, the interpretation is still simple, provided the different sites can be frozen out and their T_1 values measured. In fluxional high coordination number polyhydrides, however, the problem is more complicated.[29] Nevertheless, up to now, the T_1(min) for a classical complex has never been less than 50 ms and for a nonclassical complex never more than 35 ms *at 250 MHz*, and so the ranges for the two structural types do not overlap. This situation is not likely to continue, because Zilm[17b] finds an r(H–H) as long as 1.02 Å in $[CpRu(dmpe)(H_2)]^+$, equivalent to a T_1(min) of 29.5 ms for $L_nM(H_2)$, assuming free H_2 rotation. This could easily lead to an averaged T_1(min) of >50 ms in a fluxional polyhydride. IPR methods provide a possible solution in such a case, but further work is needed.

Classical and Nonclassical Polyhydride Tautomers

The only nonclassical rhenium polyhydride we have found is **6** (L = PMe_2Ph) in eq 7.[30a] The ^{1}H NMR spectrum at room temperature in the hydride region

$$\mathrm{Re}(H)_4(CO)L_3 \xrightarrow{HBF_4} [\mathrm{Re}H_4(CO)L_3]^+ \rightleftharpoons [\mathrm{Re}H_2(H_2)(CO)L_3]^+ \quad (7)$$

6a **6b**
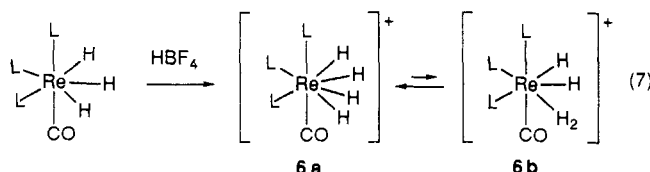
(Figure 4a) shows a single averaged quartet, but at 278 K decoalescence occurs, to give a quartet for the classical tetrahydride, $[ReH_4(CO)L_3]^+$ (**6a**), and a broad feature for $[ReH_2(H_2)(CO)L_3]^+$ (**6b**), a rare non-d^6 H_2 complex. At 208 K, there is a second decoalescence, which reveals a terminal Re–H multiplet and a broad

(29) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 6, 2181. Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 43.
(30) (a) Luo, X. L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 189. (b) Lunder, D. M.; Green, M. A.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.*, in press; personal communication, 1989.
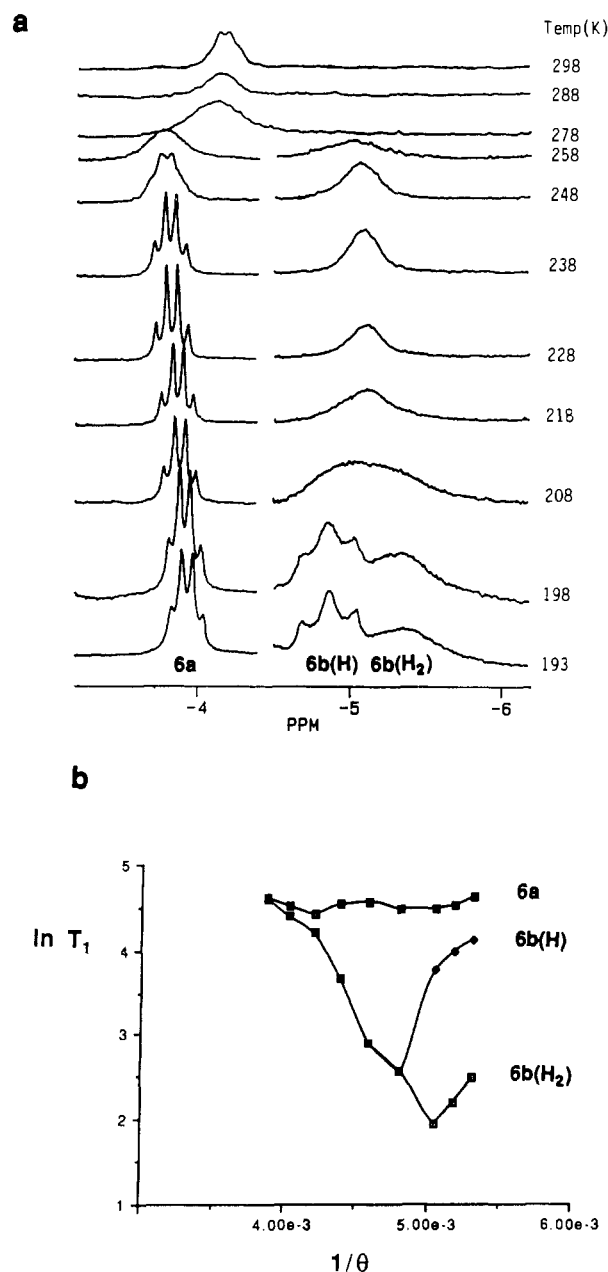

Figure 4. (a) ^{1}H NMR spectrum of $[ReH_4(CO)(PMe_2Ph)_3]^+$, showing the decoalescences. The resonances due to **6a** and the classical and nonclassical sites of **6b** can be distinguished. (b) A plot of ln T_1 vs $1/\theta$ for $[ReH_4(CO)(PMe_2Ph)_3]^+$, showing the effects of the exchange process, which perturbs the usual V-shaped curve.

feature assigned to Re–(η^2-H_2) in a 1:1 ratio. The corresponding HD complex shows a well-defined J-(H,D) of 34 Hz, as expected for Re–(η^2-HD). A plot of ln K vs θ^{-1} shows that ΔH is 1.1 kcal/mol and ΔS is 2.4 cal/(mol K) for the conversion of **6a** to **6b**. The positive charge and presence of a CO ligand in **6** makes the metal relatively electrophilic and favors nonclassical binding of H_2. Caulton[30b] finds a classical structure for $[ReH_4(PMe_2Ph)_4]^+$, where the more donor PMe_2Ph replaces CO and back-bonding is therefore enhanced. Classical and nonclassical tautomers have previously been seen only for dihydrides.[1,3a,5]

At 200 K, the H_2 resonance of **6b** shows a clear-cut T_1 minimum of 8 ms at 250 MHz (Figure 4b), as expected for an H_2 ligand. The Re–H resonance of **6b** has a T_1 of 43 ms, a value that is somewhat reduced by

fluxional exchange. At the same temperature, **6a** has an even longer T_1: 88 ms. The almost flat T_1 vs θ^{-1} curve for **6a** may be the result of the expected V-shaped curve being strongly deformed by the exchange process. As the intrinsic relaxation rate for **6a** falls with increasing θ, contributions due to the exchange steadily increase, leading to little net change in the T_1(obsd).

The two processes have different activation energies. For the intramolecular exchange, $\Delta G^{\ast}$ is 9.8 kcal/mol at 208 K, and for the fluxional process which converts **6b** to **6a**, $\Delta G^{\ast}$ is 11.6 kcal/mol at 213 K. This difference seems to be significantly larger than the experimental errors involved. Since the intramolecular exchange between the two types of sites in **6b** has a lower activation energy than does the conversion of **6b** to **6a**, the intramolecular exchange within **6b** cannot proceed via the oxidative addition product **6a**. The exchange requires an associative pathway, e.g., via an H...H...H transition state or intermediate. Such an η^3-H_3 species would be a pseudooctahedral d^6 Re(I) complex, **6c**, and so could be particularly stable. η^3-H_3 complexes have

6c
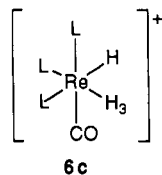
been proposed,[31] but none has yet been observed as a

stable ground-state structure. In this system, the proposed H_3 species could be no more than 10 kcal/mol above the ground state, so a stable H_3 ground state might be accessible in a suitable system.

Conclusion

The structural chemistry of metal hydrides continues to pose challenging problems, but a combination of physical methods is beginning to clarify the picture. Similar types of σ-bond complexes are probably formed with Si–H, C–H, and other species.[32-34] In the future, we can expect more surprises in hydride chemistry. We will also learn more about how to use σ-bond complexation to activate both H_2 and other covalent bonds.

(31) (a) Burdett, J. K.; Pourian, M. R. *Organometallics* **1987**, *6*, 1684. (b) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 2303. Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Demou, P. *J. Am. Chem. Soc.* **1989**, *111*, 3088. (c) Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R. *C. R. Acad. Sci., Ser. 2* **1987**, *305*, 1523.

(32) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527.
(33) Periana, R.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. Parkin, G.; Bercaw, J. *Organometallics* **1989**, *8*, 1172. Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502.
(34) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1985**, *24*, 418.
(35) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.
(36) Gregson, D.; Mason, S. A.; Spencer, J. L.; Turner, D. G. *Inorg. Chem.* **1984**, *23*, 4103.
(37) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909.

Vibrational Adiabaticity in Chemical Reactions

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The notion of *electronic adiabaticity* is well-established in many branches of chemistry. It is embodied in the Born–Oppenheimer approximation, which states that electronic and nuclear motions can be treated separately. As a result, although the wave functions and energies of electronic states depend parametrically on the relative positions of the nuclei, the electronic properties are usually independent of the nuclear momenta.

The Born–Oppenheimer separation is usually justified in terms of the large difference between the periods characteristic of electronic and nuclear motions. Even when the approximation breaks down, as in some cases of predissociation, it is usual to begin with the Born–

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Oppenheimer states and then to consider nonadiabatic transitions between these states. In fact, the Born–Oppenheimer approximation can be viewed as a special case of Ehrenfest's principle, which states that when two motions are associated with very different time scales they are, to a first approximation, separable. It follows that a motion is likely to adjust adiabatically—that is, without change of quantum state—to a force that is applied relatively slowly.

My aim in this Account is to explore the value of the concept of *vibrational adiabaticity* in collisions between species that interact chemically. It is not, of course, contended that reactions occur with complete vibrational adiabaticity. Indeed, it is necessary to examine what such a concept means in bimolecular chemical reactions. In the simplest case, typified by A + BC → AB + C, where A, B, and C are all atoms, it is possible to correlate the vibration of BC at $t = 0$ to the vibration of AB at $t = \infty$, through the bond stretching motion orthogonal to the minimum energy path (MEP) at in-