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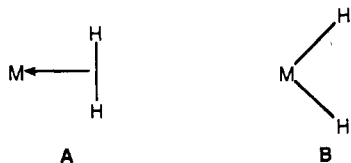
Dihydrogen Complexes: Some Structural and Chemical Studies

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The discovery of the dihydrogen complex $[W(\eta^2-H_2)(CO)_3(PCy_3)_2]$ (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



years, a large number of other H_2 complexes²⁻⁷ 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 $M(\eta^2-H_2)$ 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.⁵ Electron-withdrawing ligands or a net cationic charge tends to reduce the M to H_2 back-bonding and so favor η^2-H_2 binding. Lewis acids without d_π electrons (BF_3) do not seem to bind H_2 , so some back-bonding is necessary. Morris⁹ finds η^2-H_2 binding for electrophilic L_nM groups (L = ligand; M = metal) for which $L_nM(N_2)$ has a $\nu(N_2) > 2060\text{ cm}^{-1}$. In contrast, $L_nM(H)_2$ tends to be found where $\nu(N_2) < 2060\text{ cm}^{-1}$. The more π -basic the L_nM group, the more the $N_2\ \pi^*$ and $H_2\ \sigma^*$ orbitals are filled, leading to a

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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.

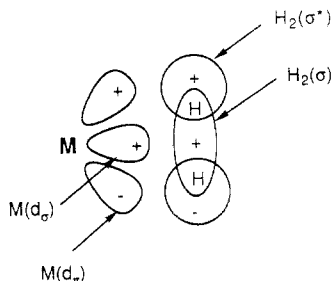
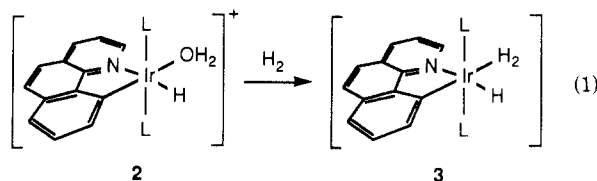


Figure 1. The M–(H₂) bond is believed to be dominated by electron donation from H₂(σ) to M(d_σ). Significant M(d_π) to H₂(σ*) back-donation breaks the H–H bond and gives a classical dihydride M(H)₂.

lower $\nu(\text{N}_2)$ and a greater tendency to break the H–H bond.

Iridium Dihydrogen Complexes

In 1984, Maryellen Lavin⁶ in our group had made 2 (L = PPh₃), 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 H₂ to 2 (eq 1). The product, 3, contains



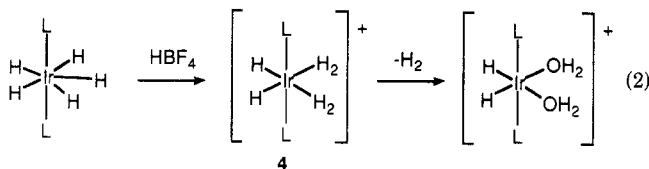
an $\eta^2\text{-H}_2$ as well as a terminal hydride. This became clear from the ¹H NMR spectrum. The single broad resonance at room temperature decoalesces at 240 K to give a sharp resonance for Ir–H and a broad one which could be assigned to Ir–($\eta^2\text{-H}_2$). Kubas found that the HD analogue 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_nM(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 $J(\text{H},\text{D})$ of 29.5 Hz, and so 3 could be confidently assigned as an $\eta^2\text{-H}_2$ 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 $\eta^2\text{-H}_2$ and not the classical Ir–H. H₂, a very poor acid in the absence of coordination, is therefore strongly activated by binding. Chinn and Heinekey^{3a} have recently determined $\text{p}K_{\text{a}}$ values of 17.6 for [CpRu(dmpc)(H₂)]⁺ and –2 for [(C₅Me₅)Re(CO)(NO)(H₂)]⁺.^{3b} This means that η^2 -binding must strongly deplete the electron density on the H₂ in these cases, no doubt as a result of the predominance of H₂(σ) to M(d_σ) electron donation. Heterolytic hydrogen or C–H activation^{6b} may generally occur via deprotonation of an $\eta^2\text{-H}_2$ or $\eta^2\text{-C-H}$ intermediate or transition state.

Relaxation Studies

In 1978, Jennifer Quirk looked at the protonation of IrH₅(PCy₃)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 [IrH₂(H₂)₂(PCy₃)₂]⁺ (4, eq 2). The HD analogue was too fluxional to show



$J(\text{H},\text{D})$ coupling at the lowest accessible temperatures. No other characterization method was applicable. No $\nu(\text{H-H})$ band was observable by IR, and no crystals were obtainable for diffraction studies. Lavin and I both consulted widely within our department for ideas. Kubas¹⁰ had noted the breadth of the $\eta^2\text{-H}_2$ 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 H₂ 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 Lavin⁶ showed that, in the authentic $\eta^2\text{-H}_2$ tricyclohexylphosphine analogue of 3, the T_1 for the $\eta^2\text{-H}_2$ 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 [IrH₂(H₂)₂L₂]⁺ for 4. Instead of being a classical Ir(VI) complex, the very favorable d⁶ octahedral Ir(III) state is preferred. Chaudret¹³ has now shown that the isoelectronic Ru species is [RuH₂(H₂)₂L₂].

The T_1 method seemed to be a convenient qualitative test, useful even in cases where all the previous methods (neutron diffraction, $J(\text{H},\text{D})$ in the proton NMR, and $\nu(\text{H-H})$ 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 $\theta(\text{min})$. 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

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Table I
Calculated and Observed H-H Distances^a

compd	$T_1(\text{min})$, ms	freq, MHz	$r(\text{calcd})$, Å	$r(\text{obsd})$, Å	ref
$[\text{W}(\text{H}_2)(\text{CO})_3(\text{PCy}_3)_2]$	<5 ^b	200	<0.96	0.84, ^c 0.89 ^d	1, 10, 17
$[\text{FeH}(\text{H}_2)(\text{dppe})_2]^+$	<7 ^b	200	<1.05	0.89 ^c	2, 15
$[\text{IrH}(\text{H}_2)(\text{bq})(\text{PPh}_3)_2]^+$	8	200	1.04	0.92 ^d	6b
$[\text{CpRu}(\text{H}_2)(\text{CO})(\text{PCy}_3)]^+$	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 = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, bq = 7,8-benzoquinolate. ^b At 193 K, T_1 minimum not yet attained. ^c By neutron diffraction. ^d By solid-state NMR.

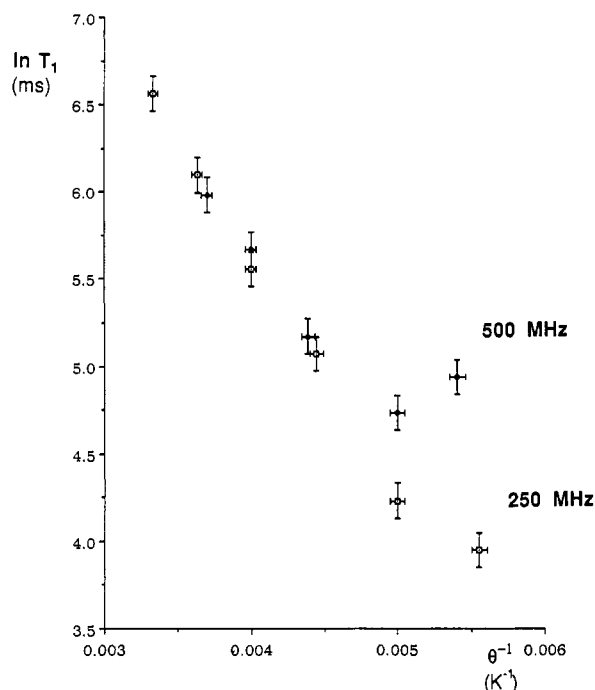


Figure 2. A plot of $\ln T_1$ vs $1/\theta$ for $\text{ReH}_7(\text{PPh}_3)_2$, showing the pronounced minimum at 500 MHz. Note that the minimum is only just attained at 250 MHz.

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 $\theta(\text{min})$ 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).

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

(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 $\text{FeH}_2(\text{H}_2)(\text{PEtPh}_2)_3$. 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 $[\text{FeH}(\text{H}_2)(\text{dppe})_2]^+$.¹⁵

The temperature, $\theta(\text{min})$, of the minimum T_1 [$T_1(\text{min})$] is field dependent but is usually in a convenient range (-20 to -100 °C) for $T_1(\text{min})$ 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 $\theta(\text{min})$.

The great advantage of $T_1(\text{min})$ 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 $\theta(\text{min})$. By eq 3, T_1 measured on the high θ side of $\theta(\text{min})$ (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 . $T_1(\text{min})$ itself scales directly with B , so that $T_1(\text{min}, 250\text{MHz})$ is half $T_1(\text{min}, 500\text{MHz})$. This makes it important to cite B when reporting $T_1(\text{min})$, 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 $r(\text{H-H})$ values in such good agreement with those from other methods (Table I).

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

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

(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.

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

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

compd	temp, K	T_1 (min), ms	ref
[CpRu(PPh ₃) ₂ H]	238	300	6e
[ReH ₇ (dpppe)]	222	67	6e
[ReH ₇ [P(<i>p</i> -FC ₆ H ₄) ₃] ₂]	200	55	6e
[ReH ₆ (PPh ₃) ⁻]	200	245 ^b	6e
[WH ₆ (PMe ₂ Ph) ₃]	235	181	6e
[Fe(H ₂)H ₂ (PEt ₂ Ph) ₃]	203	24	6d
[IrH(H ₂)(bq)(PPh ₃) 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 ReH₆ group about the Re-P bond.²² ^c Of the H₂ resonance.

Morris^{16a} traced the source of this discrepancy to H₂ rotation. If H_a-H_b is rotating much more rapidly about the M-(H₂) bond than does the molecule as a whole, then this H₂ 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 H₂. By fitting observed T_1 data to theory, he suggested that fast rotation was probably occurring. Zilm¹⁷ has used an elegant solid-state NMR method to measure the DD coupling directly for a variety of H₂ complexes. He finds an $r(\text{H-H})$ of 0.890 ± 0.006 Å for 1.

The Saga of ReH₇L₂ and the Limitations of the Method

The polyhydrides ReH₇L₂ 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 H₂, which usually occurs at 60–110 °C. If [IrH₆L₂]⁺ avoids Ir(VII) by being an H₂ complex, could something similar be true for ReH₇L₂?

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 H₂ 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 nonclassical 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 $r(\text{H-H})$ is 1.07 Å and *C* is

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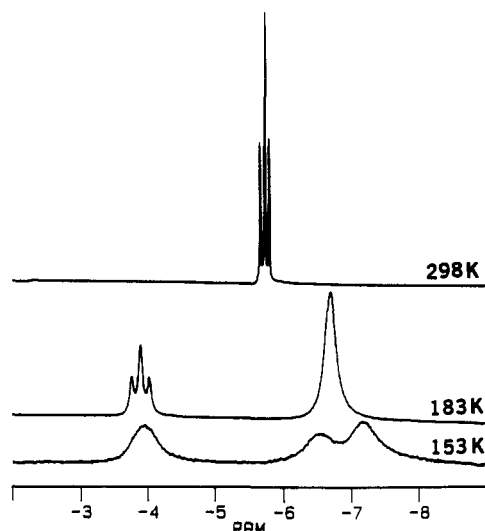


Figure 3. The ¹H NMR spectrum of ReH₇L₂ [L₂ = 1,1'-bis(diphenylphosphino)ferrocene], showing the deoalescence. The low-temperature pattern is most consistent with a classical structure.

0.79. This seemed most reasonable, and so we therefore (wrongly) proposed the nonclassical structure ReH₅(H₂)L₂ 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 ReH₇L₂, 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, MH₃ from M(H₂)H. It can be used even if fluxional exchange between sites is fast on the NMR time scale. First, a mixture of MD_{*x*}H_(3-*x*) isotopomers is prepared. In the d₁ isotopomer, the energies of the M(H₂)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 d₀, d₁, and d₂ 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 ReH₇L₂ 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 ReH₇L₂ case in which the different sites could be frozen out by ¹H NMR at low temperature. Luo therefore made many new heptahydrides,

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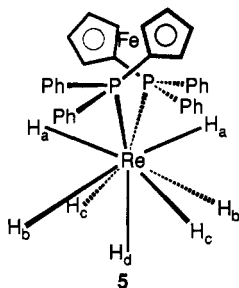
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Table III
Observed T_1 (min) Values Compared with Those Calculated from Crystallographic Data^a

compd	structural meth	T_1 (min)		field	ref
		calcd	found		
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 ₂ H ₈ (PEt ₂ Ph) ₄	n-diff	302	140	400	35, 29
W(H ₂)(CO) ₃ (P- <i>i</i> -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 H₂ ligand, i.e., $C = 1$. The second assumes fast H₂ 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*-Pr₃ analogue at the same τ_c . Cy = cyclohexyl. ^f At 210 K; T_1 minimum not observed. ^g Of the H₂ resonance. ^h Assuming that the structure is essentially the same as that of the PMe₃ analogue.

choosing ligands that he felt would favor a static structure by imposing conformational restrictions on the complex. Finally, with ReH₇(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 [ReH₅(H₂)L₂], 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 di-substituted TTP with the dppf frozen in a C₂ 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 $\Delta\delta$ between the peak of intensity two and the other peaks, which should lead to a substantial IPR if the complex were nonclassical.



If ReH₇L₂ 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 ReH₇(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

(23) (a) Bianchini et al.^{23b} assign larger couplings (27–67 Hz) to J(P,H₂) 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.

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calculations also gave very good agreement for a variety of other complexes (Table III). Only in the case of Re₂H₈L₂ 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

CSA²⁶ relaxation is only efficient for nuclei such as ¹⁹⁵Pt and ¹⁹⁹Hg, which have a large shielding anisotropy $\Delta\sigma$ (e.g., $\Delta\sigma$ values of 2500–10 000 ppm have been reported²⁷); proton anisotropies are generally much smaller, e.g., 17 ppm for 1.¹⁷ $[T_1(\text{CSA})]^{-1}$ is proportional to B^2 . As shown in Figure 2, the T_1 for ReH₇(PPh₃)₂ is essentially independent of field in the fast-motion regime, ruling out CSA.

The SR mechanism depends on molecular collisions, and $[T_1(\text{SR})]^{-1}$ usually depends directly on the temperature. $[T_1(\text{SR})]^{-1}$ usually rises²⁸ at higher temperature, but for free H₂, the usual temperature dependence is reversed.^{17b} Since SR is an important mechanism for free H₂, it ought to contribute for coordinated H₂, but it has not yet been implicated for hydrides.

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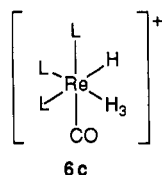
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fluxional exchange. At the same temperature, **6a** has an even longer T_1 : 88 ms. The almost flat T_1 vs θ^{-1} curve for **6a** may be the result of the expected V-shaped curve being strongly deformed by the exchange process. As the intrinsic relaxation 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, ΔG^\ddagger is 9.8 kcal/mol at 208 K, and for the fluxional process which converts **6b** to **6a**, ΔG^\ddagger 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 -H₃ species would be a pseudooctahedral d⁶ Re(I) complex, **6c**, and so could be particularly stable. η^3 -H₃ complexes have



been proposed,³¹ but none has yet been observed as a

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stable ground-state structure. In this system, the proposed H₃ species could be no more than 10 kcal/mol above the ground state, so a stable H₃ 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 H₂ and other covalent bonds.

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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–

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 $A + BC \rightarrow AB + C$, 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-

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