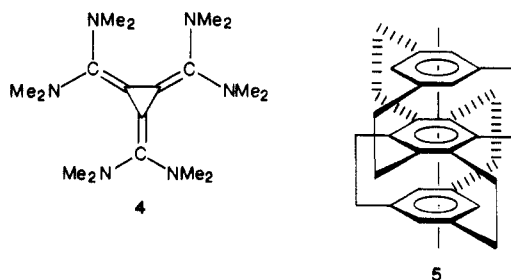


magnetic coupling nor bulk ferromagnetic behavior has been reported.³⁷

Radicals possessing D_{2d} symmetry, albeit rare, in principle may possess a doubly degenerate POMO and should be studied.¹⁵ Oxidation of D_{3h} tris(dicyanomethylene)cyanopropane should lead to a d^3 radical cation.³⁵ Since it has not been isolated, other derivatives with electron-donating groups, e.g., NR_2 , to stabilize the radical cation, e.g., 4, should be studied. Alternatively, with the goal of building a solid where adjacent chains are out-of-register by one-half of a unit cell as noted for the $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{*+}[\text{A}]^{*-}$ system, meta-substituted multilayered cyclophanes,³⁶ e.g., [2.2.2], 5, are challenging targets for synthesis. These bulky materials may provide the proper solid-state structure enabling bulk ferromagnetic behavior.



Summary

Quantitative bulk ferromagnetic behavior (spontaneous magnetization) has been established for the organic-like molecular solid $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^{*+}[\text{TCNE}]^{*-}$. It exhibits a Curie temperature, T_c , of 4.8 K, saturation magnetization of 16 300 (emu G)/mol, and a 2 K coercive field of 1 kG. Above 16 K the dominant magnetic

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(37) **Note Added in Proof:** The dication of hexaazaocatadecacyclonene has been reported to possess a triplet ground state.^{7,38b} Recent structural and magnetic data, however, show that the solid is diamagnetic. Thus, electronic-driven structural distortions are an important consideration in the design of an s/p organic ferromagnet (Miller, J. S.; Dixon, D. A.; Calabrese, J. C.; Krusic, P. J., submitted).

interactions are along a chain (1-D) and near T_c 3-D bulk effects, as evidenced by the values of the critical exponents, dominate the susceptibility. The extended McConnell model has been developed, and it provides the synthetic chemist guidance for making new molecular materials to study cooperative magnetic coupling in systems. Assuming the electron-transfer excitation arises from the POMO, to achieve ferromagnetic coupling in a molecular solid via the McConnell mechanism, a stable radical (neutral, cations/anions, or ions with small diamagnetic counterions) must possess a degenerate POMO that is not half-filled, and the lowest excited state formed via virtual charge transfer (retro or forward) possesses the same spin multiplicity and mixes with the ground state. This requirement limits the structure of a radical to D_{2d} , C_3 , or higher symmetry where symmetry-breaking distortions do not occur. Intrinsic doubly and triply degenerate orbitals are not necessary and accidental degeneracies suffice. To achieve bulk ferromagnetism, ferromagnetic coupling must be established throughout the solid. A microscopic model that accounts for the observations to data has been discussed. These requirements for ferromagnetism are met by $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^{*+}[\text{TCNE}]^{*-}$. Additionally, this model predicts that the Ni^{III} and Cr^{III} analogues should be respectively antiferromagnetic and ferrimagnetic, as preliminary data suggest.

Extensive chemical syntheses of cleverly designed radicals, as well as physical, experimental, and theoretical insight, are necessary to test and extend these concepts and establish a deeper understanding of cooperative phenomena in molecular solids.

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Molecular Hydrogen Complexes: Coordination of a σ Bond to Transition Metals

GREGORY J. KUBAS

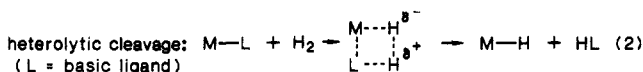
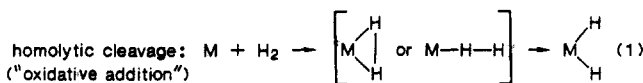
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The activation of hydrogen by metal centers is an important chemical reaction from both commercial and scientific standpoints. The H-H bond is strong (103 kcal/mol) and H_2 addition to unsaturated organic and

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other compounds must be mediated by metal centers, forming the basis for catalytic hydrogenation. In catalytic mechanisms, hydride complexes formed by cleavage of H_2 have been thought to play a key role.^{1,2}



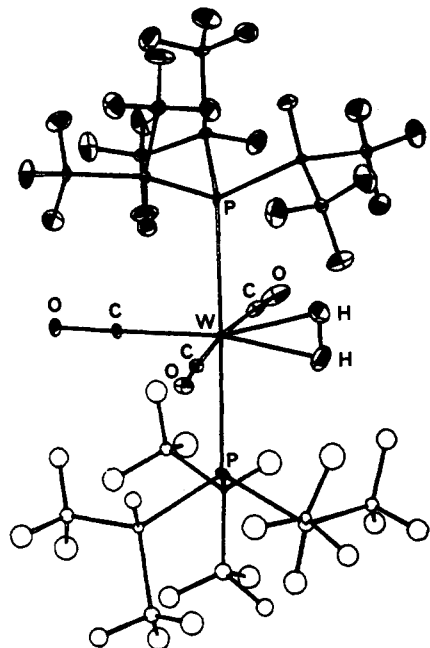


Figure 1. Structure of $W(CO)_3(PPR^i)_2(H_2)$ (neutron, 30 K). (Disorder is present in C-H positions of lower phosphine.)

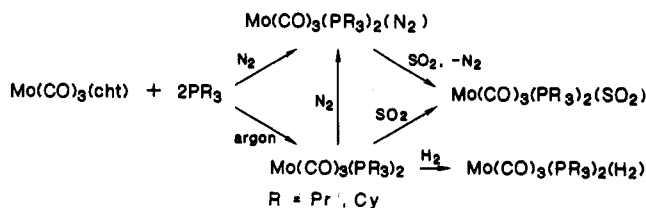
The initial interaction of H_2 with a metal center has long been discussed (e.g., H_2 as an acid vs base)^{2,3} but was regarded only as a transient in hydride formation. Reports of possible H_2 binding occasionally appeared in the literature,⁴ but lacked proof.

In 1983, as a spinoff of metal- SO_2 chemistry, we obtained clear evidence for the first stable dihydrogen complex, $W(CO)_3(PPR^i)_2(\eta^2-H_2)$ (Figure 1; η^2 denotes side-on bonding).⁵ Initially, it was viewed as an "arrested" intermediate along a reaction coordinate, stabilized by sterically demanding phosphines. However, many new H_2 complexes are being found, including complexes previously thought to be classical hydrides, and we have shown that an η^2-H_2 complex can exist in equilibrium with its dihydride tautomer.^{6,7} Thus H_2 complexes are more than reactive intermediates and should be considered to have an identity and

chemistry of their own, possibly including direct reactivity in catalytic hydrogenation. H_2 binding is the first example of stable intermolecular coordination of a σ bond and suggests that similar nonclassical binding may occur for other σ bonds (C-H, C-C, etc.).

Discovery of Dihydrogen Complexes

The establishment of H_2 coordination bears some historical perspective⁸ since, as for the discovery of dinitrogen complexes by Allen and Senoff,⁹ it is a classic example of serendipity and the importance of exploring rather than dismissing anomalous results. In 1979, we were examining structure/bonding principles in Mo- SO_2 complexes.¹⁰ In an exploration of steric effects, a complex with bulky phosphines, $Mo(CO)_3(PPR^i)_2(SO_2)$, was synthesized by replacement of labile acetonitrile ligands in $Mo(CO)_3(NCMe)_3$ by phosphine and SO_2 . As luck would have it, unsatisfactory 20% yields prompted use of $Mo(CO)_3(cht)$ (cht = cycloheptatriene) as starting material and exhaustive variation of reaction conditions. This seemingly trivial exercise led to two key observations and eventual reward. Under an N_2 atmosphere, the solution formed by addition of PPR^i_3 to cht complex evolved a gas upon SO_2 addition and, under argon (no SO_2) became purple rather than orange. It soon became clear that the gas was N_2 displaced from a yellow reversibly-bound N_2 complex and that the purple color was due to a 16-electron precursor, $Mo(CO)_3(PPR^i)_2$.



I eventually isolated $M(CO)_3(PR_3)_2$ for $M = Mo$ and W but only for specific bulky $R = Pr^i, Cy$ (cyclohexyl). The complexes readily added N_2 and other ligands sterically capable of occupying the sixth coordination site.^{11,12} X-ray studies later revealed that $W(CO)_3(PR_3)_2$ contained an "agostic" interaction¹³ of a phosphine C-H group with the metal at the sixth site, the first example for an alkyl PR_3 .¹²

It was noted that H_2 reversibly added to purple $M(CO)_3(PR_3)_2$ to give yellow complexes with properties similar to those of the N_2 adducts. The H_2 reaction was studied as part of our efforts to reduce SO_2 ¹⁴ ($M(CO)_3(PR_3)_2$ failed to catalyze SO_2 or ethylene hydrogenation under mild conditions, presumably because only one open coordination site exists). The IR frequencies of the hydrogen complexes called attention: instead of bands at $1700-2300\text{ cm}^{-1}$ (ν_{MH}) and $700-900$

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cm^{-1} (δ_{MH}) characteristic of a 7-coordinate dihydride complex, bands near 1570, 950, and 465 cm^{-1} were observed ($M = W$), shifting appropriately on D_2 substitution. These modes and the high lability of the hydrogen were the first clues that "the bonding of the hydrogen to these metal complexes may be novel", as was understated in a communication in 1980.¹¹ X-ray diffraction studies of $M(\text{CO})_3(\text{PCy}_3)_2(\text{H}_2)$ were frustrated by disorder involving the hydrogen positions and the trans CO. Encouragingly, the CO and PCy_3 ligands were in octahedral positions, with a vacancy in the sixth site presumably containing the hydrogen.

To gain proof of molecular coordination became an irresistible challenge, and efforts turned to single-crystal neutron diffraction to locate the hydrogens. The necessary large crystals (ca. 10 mm^3) of $W(\text{CO})_3(\text{PPr}^i_3)_2(\text{H}_2)$ were grown, and the first data were collected at Los Alamos by Phillip Vergamini in 1982. Although a complete structure could not be obtained, partly because of phosphine disorder, a difference-Fourier map phased on non-hydrogen atom coordinates from X-ray data demonstrated the presence of an H_2 ligand. Subsequent 173 K X-ray data confirmed a side-on-bonded H_2 (Figure 1) with H-H = 0.75 (16) Å (X-ray) and 0.84 Å (neutron).⁵ Since the usual uncertainty in X-ray hydrogen locations was destined to create skepticism, further proof was sought. An elegant suggestion by Russ Drago led to incontrovertible spectroscopic evidence for the presence of a weakened H-H bond: observation of large HD coupling in the ^1H NMR of the HD complex. The NMR of $W(\text{CO})_3(\text{PPr}^i_3)_2(\text{H}_2)$ had shown an unusual broad singlet ($\delta -4.2$) for the $\eta^2\text{-H}_2$, with no coupling to ^{31}P or ^{183}W , but the HD substitution proved to be diagnostic: a 1:1:1 triplet (^2H spin = 1) with $J_{\text{HD}} = 33.5$ Hz resulted. J_{HD} for HD gas is 43.2 Hz¹⁵ and for hydride-deuteride complexes is <2 Hz; hence an H-D bond of reduced order was indicated. The HD complexes provided added benefits: IR spectra showed bands at positions intermediate to those for the H_2 and D_2 complexes and not superimpositions of MH + MD modes as in HMD species.¹⁶ Importantly, a band at 2360 cm^{-1} was assignable to ν_{HD} (ν_{HH} and ν_{DD} were initially obscured). After Raman spectra added further evidence, we finally were able to claim $\eta^2\text{-H}_2$ binding. Ironically, in an inversion of the normal order, spectroscopic rather than crystallographic data provided the convincing evidence.

New Examples of Dihydrogen Complexes

Two questions arose: what factors stabilized dihydrogen coordination and would new examples of H_2 complexes be found. Initially it was believed that the bulky phosphines disfavored a 7-coordinate dihydride, but electronic factors now appear to primarily control whether H_2 binds molecularly or scissions. The second question was soon answered in early 1983 when Ray Sweany privately communicated to us IR evidence for matrix-isolated $\text{Cr}(\text{CO})_5(\text{H}_2)$. These results¹⁷ were published in 1985 along with related papers^{18,19} showing

that the latter is stable in liquid Xe or cyclohexane for seconds at 25 °C. There was no new stable complex until Crabtree's group reported NMR evidence for $[\text{IrH}(\text{H}_2)(\text{PPh}_3)_2(\text{bq})]^+$, formed by displacement of an H_2O ligand by H_2 .²⁰ Next, Morris found that $[\text{MH}(\text{H}_2)(\text{dppe})_2]^+$ ($M = \text{Fe}, \text{Ru}$), formed by protonating $\text{MH}_2(\text{dppe})_2$, contained $\eta^2\text{-H}_2$ from X-ray and NMR evidence.²¹ Both we⁷ and Morris found that unsaturated $\text{Mo}(\text{CO})(\text{dppe})_2$ ²² coordinated H_2 . An increasing number of new complexes, including matrix-isolated "ligand-free" $\text{Pd}(\text{H}_2)$ and small clusters, e.g., $\text{Cu}_3(\text{H}_2)$, have been shown²³⁻³⁹ (Table I) or suggested⁴⁰ to contain dihydrogen ligands. Molecular H_2 chemisorption on chromia^{4b} and stepped Ni(100) surfaces⁴¹ and intra-zeolite hydrogen complexes^{4c-e} of Ni^+ and Pd^+ have also been claimed. Binding of H_2 to the metal centers in hydrogenase (Ni) and nitrogenase (Mo) has been proposed.^{40e-g}

Remarkably, several polyhydrides known for many years to have unusually high formal oxidation states (Table I) are now being reformulated to contain H_2 ligands.³⁶⁻³⁸ NMR T_1 diagnostics³⁶ (see below) and neutron data³⁷ show that $\text{MH}_4(\text{PR}_3)_3$ ($M = \text{Fe}, \text{Ru}$) is actually $\text{MH}_2(\text{H}_2)(\text{PR}_3)_3$. The Ru complex and also $[\text{RuH}_3(\text{dppe})_2]^+$ had actually been proposed to contain "neutral dihydrogen" in 1976,^{4a} and ironically, an

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Table I
Molecular Hydrogen Complexes and Spectral Properties

complex	NMR data			$\nu(\text{HH}), \text{cm}^{-1}$	ref
	$\delta_{\text{H}_2}^a$	$[J_{\text{HD}}]^b$	$\{T_1\}^c$		
Mo(CO) ₃ (PCy ₃) ₂ (H ₂)				[~2950] ^d	5, 6
Mo(CO) ₃ (PCy ₂ Pr ⁱ) ₂ (H ₂)	-3.13				6
Mo(CO)(dppe) ₂ (H ₂)	-5.0	[34]	{20} ^e	2650	7
W(CO) ₃ (PCy ₃) ₂ (H ₂)	-3.85			2690	5, 6
W(CO) ₃ (PPr ⁱ) ₂ (H ₂)	-4.50 ^e	[33.5]	{4} ^e	2695	5, 6
W(CO) ₃ (PCy ₂ Pr ⁱ) ₂ (H ₂)	-3.90				6
[FeH(H ₂)(dppe) ₂] ⁺	-8.0 ^f		{7} ^f		21
[FeH(H ₂)(depe) ₂] ⁺	-10.5 ^h		{12} ^f		24
[RuH(H ₂)(dppe) ₂] ⁺	-4.6 ^f	[32]	{11} ^f		21
[RuH(H ₂)(depe) ₂] ⁺	-6.4 ^h		{11} ^f		24
[OsH(H ₂)(depe) ₂] ⁺	-10.0 ^h		{52} ^f		24
[Os(η^2 -OAc)(PPh ₃) ₃ (H ₂) ⁺	-8.9 ⁱ	[13.7]	{90} ^j		32
[CpRu(PPh ₃)(Bu ⁿ NC)(H ₂) ⁺	-7.92	[28.6]			25
[CpRu(CO)(PCy ₃)(H ₂) ⁺	-7.91	[28.2]	{3} ^k		26
[CpRu(dmpe)(H ₂) ⁺	-10.06 ^l	[22]			26
[CpRu(Ph ₂ PCH ₂ PPh ₂)(H ₂) ⁺	-6.98	[22]			25
[IrH(H ₂)(PPh ₃) ₂ (bq)] ⁺	-2.9 ^m		{30} ⁿ		20, 28
[IrH(H ₂)(PCy ₃) ₂ (bq)] ⁺	-4.64 ^m		{65} ⁿ		20, 28
[IrH ₂ (H ₂) ₂ (PCy ₃) ₂] ⁺	-5.04 ⁿ		{48} ^m		27, 28
[Rh[P(CH ₂ CH ₂ PPh ₂) ₃](H ₂) ⁺	-7.39 ^o	[18]	{170} ^p	q	33
Known Polyhydrides Reformulated to Contain H ₂ Ligands					
FeH ₂ (H ₂)(PEtPh ₂) ₃	-11.5		{24} ^k	~2400	36, 37
RuH ₂ (H ₂)(PPh ₃) ₃	-7.06		{38} ^k		36, 37
RuH ₂ (H ₂)(PCy ₃) ₃	-7.9		{28} ^k		38
RuH ₂ (H ₂) ₂ (PCy ₃) ₂	-9.1		{44} ^k		38
Ru ₂ H ₄ (H ₂)(PCy ₃) ₄	-12.5		{88}		38
[OsH ₃ (H ₂)(PPh ₃) ₃] ⁺			{35} ^h		36
ReH ₃ (H ₂)(PPh ₃) ₂			{78} ^r		36
ReH ₃ (H ₂)(dppe)			{79} ^r		36
Low-Temperature Stable Species					
Cr(CO) ₅ (H ₂)				3030	17-19, 29
Cr(CO) ₄ (H ₂) ₂					17, 29
Cr(CO) ₃ (PCy ₃) ₂ (H ₂)					35c
Mo(CO) ₅ (H ₂)				3080	29
W(CO) ₅ (H ₂)				2711	29
CpMH(CO) ₂ (H ₂) (M = Mo, W)					30
M(CO) ₄ (cyclooctene)(D ₂) (M = Cr, W)					34
Fe(CO)(NO) ₂ (H ₂)				2973	31
Co(CO) ₂ (NO)(H ₂)				{2976, 3100}	31
CoR(H ₂)(CO) ₃ (R = H, CH ₃)					35a
Ni(CO) ₃ (H ₂)					35b
Pd(H ₂)					23
Cu ₂ H ₂ (H ₂) _x , Cu ₃ (H ₂)					39

^a Ppm; broad singlets unless noted (bq = 7,8-benzoquinolate; dppe, depe, dmpe = R₂PCH₂CH₂PR₂, R = Ph, Et, Me, respectively. ^b For the HD complexes; Hz. ^c For the H₂ ligand, by inversion-recovery, in ms. ^d Based on $\nu_{\text{DD}} = 2180 \text{ cm}^{-1}$. ^e 183 K. ^f Below 253 K. ^g 210 K. ^h 220 K; signal for Os complex is a binomial quintet at 21 °C. ⁱ Binomial quartet, $J_{\text{PH}} = 9.5 \text{ Hz}$. ^j 193 K (57 ms at 295 K). ^k 205 K. ^l Multiplet, $J_{\text{PH}} = 3.6 \text{ Hz}$. ^m 193 K. ⁿ 188 K. ^o Multiplet, $J_{\text{PH}} = 67.0, 13.7 \text{ Hz}$, $J_{\text{RuH}} = 13.7 \text{ Hz}$. ^p 303 K. ^q Complex is a hydride in the solid but contains H₂ in solution. ^r 203 K.

unexplained IR band at 2400 cm⁻¹ in the Fe complex⁴² no doubt corresponds to ν_{HH} . Thus it is surprising that H₂ binding had not been proven earlier. Interestingly, the solid-state structure of Cp₂NbH₃ has been shown by neutron diffraction⁴³ to contain only hydrides, yet ¹H NMR data⁴⁴ of analogues with substituted Cp suggest H₂ ligands are present in solution. A similar situation exists for Cp^{*}RuH₃(PR₃), which gives H-H coupling constants as high as 130 Hz.^{44b} One must speculate that *solution and solid-state structures of hydrogen/hydride complexes can differ*, and the dihydrogen-dihydride equilibria discussed below substantiate this.

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(43) Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Kvik, A.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* 1977, 99, 1775.

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Structure and Reactivity of Dihydrogen Complexes

Three classes of H₂ complexes exist: thermally unstable complexes formed by photolytic CO loss, neutral complexes from H₂ addition to unsaturated precursors, and cationic species made by protonation of hydrides. Since H₂ is normally reversibly bound, an unsaturated precursor should exist and a stable 16-electron complex is a good candidate for stable H₂ binding, especially if it contains an agostic C-H. However, an unstable electron-poor fragment such as Cr(CO)₅ will likely lead to an unstable H₂ complex.

The structure of W(CO)₃(PPrⁱ)₂(H₂) from 30 K neutron data⁴⁵ (Figure 1) shows H-H = 0.82 (1) Å, significantly longer than in free H₂ (0.74 Å), and W-H = 1.89 (1) Å, elongated over normal W-H (~1.7 Å). The H-H in [FeH(H₂)(dppe)₂]⁺ is 0.89 (11) Å, with

(45) Vergamini, P. J.; Wasserman, H. J.; Keotzle, T.; Ryan, R. R.; Kubas, G. J., unpublished results.

Fe–H = 1.53 (8), 1.55 (7) Å (X-ray diffraction underestimates internuclear distances).²¹ In both cases the overall geometry is nearly octahedral with the hydrogen parallel to the P–M–P vector. The X-ray structure of Mo(CO)(dppe)₂(H₂) did not reveal the H₂ because of disorder, but NMR evidence ($J_{\text{HD}} = 34$ Hz) attested to an H–H bond.⁷

The H₂ generally behaves as a weak donor ligand, displaceable by N₂ and reversibly dissociating on mild heating or in vacuo ($P_{\text{dissoc}} = 1\text{--}10$ Torr; $\Delta H_{\text{dissoc}} \approx 12$ kcal/mol⁴⁶ for W(CO)₃(PR₃)₂(H₂)). Removal of H₂ gives W(CO)₃(PR₃)₂, which contains an intramolecular W···H–C interaction.¹² Thus, the H₂ displaces an agostic C–H group, an unprecedented experimental comment on the relative binding abilities of these ligands. ΔH for H₂ + W(CO)₃(PCy₃)₂ has been measured in solution to be –9.9 kcal/mol (cf. –13.5 kcal/mol for N₂).⁴⁷ The W complexes are more stable than Mo analogues, which partially dissociate in solution, and Cr(CO)₃(PCy₃)₂(H₂) is stable only under high H₂ pressures (>300 psi).^{35c} The cationic complexes can be more robust than neutral ones, being stable in donor solvents (e.g., acetone) which instantly displace H₂ in the W complexes.

As expected, facile exchange of bound H₂ with D₂ occurs in solution, even at –25 °C, but unexpectedly, M(CO)₃(PR₃)₂(H₂) and D₂ give at a slower rate statistical amounts of HD, even in the *solid state* (~1 week). Similarly, solutions of W(CO)₃(PPrⁱ)₂(HD) revert to a mixture of H₂, D₂, and HD isotopomers within 1–2 days with no involvement of solvent or phosphine protons. Thus H–H cleavage and scrambling are occurring by an unknown mechanism. Coordination of D₂ as a seventh ligand violates the 18-electron rule, and transient displacement of phosphine or CO would be unlikely in the solid. A possibility suggested by Burdett⁴⁸ is transient coordination of polyhydrogen species such as H₃ or H₄, which are known “mass spectrometer molecules”. [CpRu(PPh₃)(CNBu^t)(H₂)]⁺ has also been reported to give HD with D₂.²⁵ Cr(CO)₅(H₂) and D₂ in liquid Xe do not produce HD, but Cr(CO)₄(H₂)₂ does, implying that here the simultaneous coordination of two H₂ reduces the activation energy for the exchange.²⁹ Metal hydride–dihydrogen complexes apparently scramble via intramolecular exchange between hydride and H₂.^{21,28}

In addition to isotopic exchange, two significant demonstrations of *direct* reaction of H₂ ligands have been reported. Labeling experiments pointed to deprotonation by RLi of the η^2 -H₂ rather than the hydride in IrH(H₂)(bq)L₂⁺.²⁸ NMR showed that [CpRu(dmpe)(H₂)]⁺ was deprotonated by Et₃N in preference to the equilibrium dihydride form (see below).²⁶ Thus H₂ ligands appear to be more acidic than their hydride counterparts.

NMR Criteria for Dihydrogen Coordination

¹H NMR spectra of H₂ complexes usually display a broad singlet for the H₂ at δ –3 to –12 (Table I), comparable to or lower than δ for hydrides. Coupling to ³¹P or metal normally is not resolved, even at low temper-

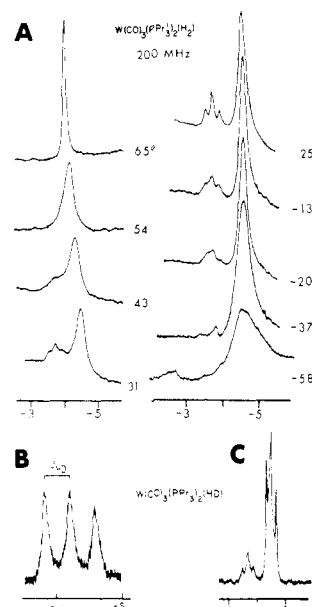


Figure 2. ¹H NMR of (A) W(CO)₃(PPrⁱ)₂(H₂) (200 MHz, methylcyclohexane-*d*₁₄) at various temperatures, (B) W(CO)₃(PPrⁱ)₂(HD) (90 MHz, toluene-*d*₈, 35 °C), and (C) W(CO)₃(PPrⁱ)₂(HD) (200 MHz, methylcyclohexane-*d*₁₄, 25 °C).

ature, due in part to large dipolar coupling between H₂ protons. Some examples of $J(\eta^2\text{-H}_2\text{,P})$ have recently been found for [OsH(H₂)(depe)₂]⁺ (calculated to be 5.8 Hz)²⁴ and [CpRu(R₂PC₂H₄PR₂)(HD)]⁺, which showed the first resolved coupling (2.0–3.6 Hz),^{25,26} tenfold lower than in classical hydrides.

As described earlier, HD complexes usually give large $J_{\text{HD}} = 28\text{--}34$ Hz (Table I, Figure 2B–C) diagnostic of H₂ binding.⁵ Recently, values as low as 13 Hz have been observed; whether this indicates elongated H–D bonds remains to be seen. Since J_{HD} is often unobservable in fluxional complexes that also contain hydrides, Crabtree developed a second criterion: proton relaxation time, T_1 .^{27,28,36} Because T_1 is dominated by dipole–dipole contribution (r_{HH}^{-6} dependence), the T_1 of η^2 -H₂ was anticipated to be unusually short. Indeed, low values (4–100 ms) were found for H₂ ligands vs >350 ms for hydrides. The temperature dependence of T_1 was found to be crucial in intermediate cases, and the minimum value, $T_1(\text{min})$, corresponded to hydrides when >150 ms and H₂ when <80 ms. $T_1(\text{min})$ values also allowed calculation of effective H–H distances, which in some cases were claimed to be as high as 1.1 Å in ReH₅(H₂)(PR₃)₂ (>1.5 Å for classical hydrides).^{36b}

Solid-state ¹H NMR can also be used to determine H–H distances.⁴⁹ The 0.890-Å value in W(CO)₃(PCy₃)₂(H₂) is intermediate to that in the PPrⁱ₃ analogue (0.82 Å) and that in FeH(H₂)(dppe)₂⁺ (0.89 Å, X-ray, underestimated). This correlates with the decreasing lability of H₂ in this series (stronger M–H₂ bond = longer H–H bond). The above work along with our solid ²H NMR⁶ of W(CO)₃(PPrⁱ)₂(D₂) and neutron scattering data also demonstrates that the H₂ ligand undergoes rapid hindered rotation (see below).

Dihydrogen/Dihydride Equilibrium in M(CO)₃(PR₃)₂(H₂)

Of major significance is the question whether η^2 -H₂ complexes truly represent the first step in H–H scission,

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(46) Zilm, K., private communication.

(47) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; de la Vega, R. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J., submitted to *Organometallics*. This ΔH is actually the enthalpy of displacement of the agostic C–H interaction, which has a binding energy estimated to be 15 kcal/mol.

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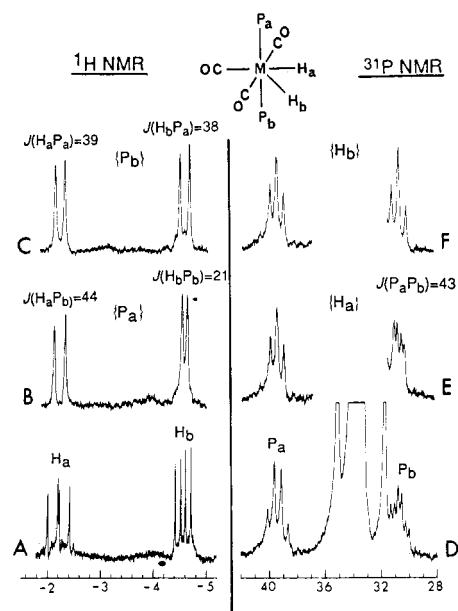
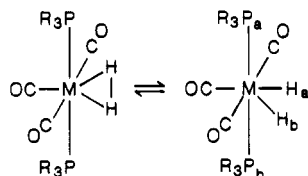


Figure 3. ^1H (A) and ^{31}P (D) NMR spectra of $\text{W}(\text{CO})_3[\text{P}(i\text{-C}_3\text{D}_7)_2]_2(\text{H}_2)$ (200 MHz, toluene- d_6 , -92°C). The ^1H - ^{31}P coupling interactions were selectively decoupled by applying a CW radio-frequency field at the resonance frequency of P_a (B), P_b (C), H_a (E), and H_b (F) in separate experiments. (The off-scale peaks in spectrum D are due to the ^{31}P signal of the H_2 complex, with ^{183}W side bands.)

and again $\text{W}(\text{CO})_3(\text{PPR}^i)_2(\text{H}_2)$ played a pioneering role. Initial 90-MHz NMR studies showed only a single broad peak for the H_2 near $\delta -4.2$, but at -30°C (or 200 MHz, 25°C) a weak triplet appeared at $\delta -3.7$. The 38-Hz ^{31}P -H coupling was typical of a metal hydride, and variable-temperature (VT) NMR and solution IR data⁶ showed that the hydride was an equilibrium species (~ 15 – 30%) and was in fact 7-coordinate $\text{WH}_2(\text{CO})_3(\text{PPR}^i)_2$ expected from H-H bond cleavage:



The equilibrium demonstrated a surprising tautomeric relation between dihydrogen and dihydride complexes. VT ^1H NMR (Figure 2A) showed coalescence of the triplet hydride signal and the H_2 signal into a singlet at 65°C , indicative of fast exchange between hydride and H_2 . The HD isotopomer (Figure 2C) showed the same triplet ($J_{\text{HD}} < 2$ Hz), consistent with a hydride-deuteride. Furthermore, the dihydride is stereochemically nonrigid, as expected for 7-coordination.⁵⁰ Upon lowering of the temperature, the triplet in Figure 2A broadened, disappeared, and reappeared in the slow-exchange limit as two separate signals, indicative of inequivalent hydrides (H_a and H_b). The H_2 signal which obscured H_b ($\delta -4.9$) was nulled by an inversion-recovery pulse sequence (T_1 for $\text{H}_2 \ll T_1$ for H_a and H_b), giving a well-resolved spectrum at -92°C (Figure 3A). The doublet of doublet patterns for H_a and H_b represent coupling to inequivalent P_a and P_b , which give multiplet ^{31}P signals due to PH and PP coupling [J -

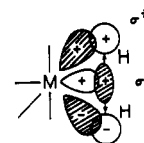
(P_a - P_b) = 43 Hz] (Figure 3D). Selective heteronuclear decoupling (Figure 3) showed that H_a is nearly equivalently coupled to (and hence positioned symmetrically with respect to) P_a and P_b ($J = 39, 44$ Hz) while H_b is inequivalently coupled ($J = 38, 21$ Hz).

Importantly, the T_1 's for H_a and H_b are 1.67 s (at -92°C), consistent with hydrides, and 400 times higher than that (4 ms) for the H_2 ligand in dynamic equilibrium. At 25°C , as a result of the tautomeric exchange, the T_1 's become nearly equal and intermediate in value, although still quite short: 31 ms for the dihydrogen peak and 35 ms for the hydrides.

A second striking example of dihydrogen/dihydride ($\sim 6:1$) equilibrium has been found by Chinn and Heinekey in $[\text{CpRu}(\text{dmpe})(\text{H}_2)]^+$, wherein the ΔG of activation was calculated from NMR data to be 20.4 kcal/mol.²⁶ This barrier to oxidative addition is higher than that for our system (~ 15 kcal/mol) and both values are indicative of a much deeper well for $\text{M}-\text{H}_2$ along the potential surface for $\text{M} + \text{H}_2$ reaction than originally imagined. The rate of oxidative addition in the Ru complex is surprisingly low: a solution prepared at -30°C showed only H_2 form, and equilibrium was reached only on warming to -10°C ($t_{1/2} = 10$ min). This is also clear evidence for structural differences in solution and solid states.

Metal-Dihydrogen Bonding and H-H Bond Cleavage: Theoretical Studies

Two early views of hydrogen activation were taken: either transfer of σ -electrons of H_2 into a vacant metal d orbital^{2a,e} or transfer of electrons from an occupied metal d orbital to the antibonding orbital of H_2 .^{2b-d} Orchin and Rupilius,^{3c} in examining hydroformylation catalysis by cobalt carbonyls, proposed initial $\eta^2\text{-H}_2$ bonding involving both of these interactions, analogous to the Dewar-Chat-Duncanson model for metal-olefin π -bonding:



H_2 binding and eventual H-H cleavage would then be aided by back-donation of electrons from metal to σ^* of H_2 . Theoretical treatments of H_2 activation were not initiated until 1979,^{1e,2g,3d,e,48,51-54} coincidentally the year we prepared $\text{M}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$. One of these studies was prompted by the known reaction of $(\text{C}_5\text{R}_5)_2\text{ZrHR}'$ with H_2 to give $(\text{C}_5\text{R}_5)_2\text{ZrH}_2$ and $\text{R}'\text{H}$, which was difficult to reconcile because the d^0 metal center would preclude formal oxidative addition of H_2 . Accordingly, transient H_2 adduct formation followed by transfer of either H^{+3f} or H atom^{3d} ("direct hydrogen transfer") to alkyl was invoked. Extended-Hückel calculations by Brintzinger^{3d} on $(\text{C}_5\text{R}_5)_2\text{ZrH}_2 + \text{H}_2$ gave an energy

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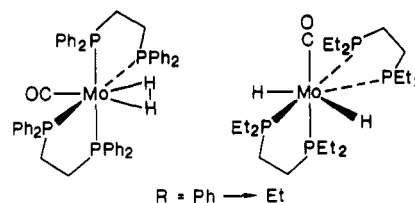
minimum corresponding to an $\eta^2\text{-H}_2$ complex. Examination of charges and overlap populations indicated that both $\text{H}_2 \rightarrow \text{M}$ and $\text{M} \rightarrow \text{H}_2$ σ^* -donation occurred. Bagatur'yants³⁶ showed that a Pd atom- H_2 interaction is stable, with side-on bonding (small Pd $\rightarrow \text{H}_2$ back-donation) slightly favored over end-on bonding. These calculations and our synthesis of H_2 complexes were performed nearly simultaneously, without mutual knowledge, resulting in a beautiful match of experiment and theory. Ozin's²³ observation of Pd(H_2) complexes in rare-gas matrices confirmed Bagatur'yants' and related calculations.⁵¹

More refined studies followed the discovery of stable H_2 complexes, notably ab initio calculations by Hay⁵² on H_2 addition to a fixed idealized $\text{W}(\text{CO})_3(\text{PH}_3)_2$ fragment with structural parameters based on $\text{W}(\text{CO})_3(\text{PPr}^i)_2(\text{H}_2)$. A stable $\eta^2\text{-H}_2$ complex resulted (17 kcal/mol bond energy, $\text{H-H} = 0.79 \text{ \AA}$ (vs 0.82 \AA actual)) with preference (0.3 kcal/mol) for alignment of the H_2 axis parallel to P-W-P, as in the actual structure. Orbital population analysis showed that the primary interaction is $\text{H}_2 \rightarrow \text{M}$, with a small amount of $\text{M} \rightarrow \sigma^*$ back-bonding. Hoffmann and others have extensively analyzed the activation of H-H and C-H bonds on metal complexes, metal surfaces, and Sc^+ .⁵³

An important consideration is the electronic and steric influences of ancillary ligands in stabilizing H_2 coordination versus dihydride formation. Assuming the above bonding model, increasing the basicity of the metal center in H_2 complexes would be expected to lead to H-H cleavage because of higher $\text{M} \rightarrow \sigma^*$ donation. Indeed in $\text{Mo}(\text{CO})_x(\text{PR}_3)_{5-x}\text{H}_2$ H_2 ligands are present until the strong π -acceptor CO's are totally substituted by basic PR_3 ($\text{MoH}_2(\text{PMe}_3)_5$ is a 7-coordinate hydride⁵⁵). Calculations show that mixtures of σ -donor and strong π -acceptor coligands favor $\eta^2\text{-H}_2$ since acceptors, particularly when trans to H_2 , interact with the d orbital that populates σ^* H_2 .^{48,54} Complexes with all acceptors, e.g., $\text{Mo}(\text{CO})_5(\text{H}_2)$, are thermally unstable to H_2 loss, presumably because back-bonding is too small. Although $[\text{FeH}(\text{H}_2)(\text{dppe})_2]^+$ contains no stabilizing acceptors, H_2 binds because of the low basicity of Fe,^{54b} the trans effect of the hydride, and the positive charge.

Stereochemical Control of H_2 Coordination versus Dihydride Formation

In order to define the steric and electronic requirements for H_2 vs hydride binding, we synthesized a series of complexes, $\text{Mo}(\text{CO})(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)_2\text{H}_2$, wherein the coordination mode was found to depend primarily upon the donor strength of the phosphine.⁵⁶ For $\text{R} = \text{Ph}$, an H_2 trans to the CO in an octahedral geometry was present. ^1H NMR showed a characteristic broad H_2 resonance with $T_1 = 20 \text{ ms}$ and $J_{\text{HD}} = 34 \text{ Hz}$. However, the complex with more basic⁵⁷ alkyl donors ($\text{R} = \text{Et}$) gave a quintet at $\delta -5.4$ ($J_{\text{PH}} = 34 \text{ Hz}$), $T_1 = 370 \text{ ms}$, and unobservable J_{HD} characteristic of hydrides rather than $\eta^2\text{-H}_2$. X-ray studies of $\text{MoH}_2(\text{CO})(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)_2$ confirmed a 7-coordinate pentagonal-bipyramidal structure similar to that for $\text{MoH}_2(\text{PMe}_3)_5$,⁵⁵ with the CO in an axial position cis to distal hydrides:



VT NMR showed characteristic stereochemical non-rigidity⁵⁰ (collapse of the quintet to an A_2BCX_2 multiplet at the slow-exchange limit ($-66 \text{ }^\circ\text{C}$)). In order to determine if steric effects are important, the complex with bulkier $\text{R} = \text{Bu}^i$ (size of $\text{PBu}_3 \approx \text{PPh}_3$) was prepared. Its NMR and IR spectra were similar to those of the Et complex, indicating it is also a dihydride (a lower T_1 (200 ms) and higher H_2 lability possibly indicated small equilibrium amounts of H_2 complex in solution). Thus increasing the basicity of the ancillary ligands is the prime factor in promoting oxidative addition of the dihydrogen, in agreement with theoretical models, and ligand size is of much less consequence. Whether bulky coligands add thermal stability to H_2 complexes has yet to be tested.

Since a binding site for dinitrogen is also a potential binding site for dihydrogen, Morris⁵⁸ has proposed that when ν_{NN} of N_2 complexes falls in the range 2060–2150 cm^{-1} the corresponding H_2 complex will be stable vs thermally unstable complexes for $\nu > 2150 \text{ cm}^{-1}$ (electron-poor metal center) and hydrides for $\nu < 2060 \text{ cm}^{-1}$ (electron rich). For example, the N_2 analogue of the dihydride $\text{MoH}_2(\text{PMe}_3)_5$ has $\nu_{\text{NN}} = 1950 \text{ cm}^{-1}$. ν_{NN} for $\text{Mo}(\text{CO})(\text{N}_2)(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2$, 2090 cm^{-1} , is well within the frequency range for stable H_2 complexes, that for $\text{R} = \text{Bu}^i$ (2060 cm^{-1}) is on the dihydrogen/dihydride borderline, and that for $\text{R} = \text{Et}$ (2050 cm^{-1}) is just inside the hydride range. These data fit remarkably well with the observed structures.

Other studies of ligand/metal variations have been carried out by Morris' group on $[\text{MH}(\text{H}_2)(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)_2]^+$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}; \text{R} = \text{Ph}, \text{Et}$).^{21,24} In all cases the H_2 ligand remained intact, and it is surprising that $[\text{OsH}(\text{H}_2)(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)_2]^+$ is a dihydrogen complex since $[\text{OsH}_3(\text{PPh}_3)_4]^+$ with less basic monodentate phosphines is a trihydride.⁵⁹ Constraints imposed by the chelating phosphines may override phosphine basicity arguments here. Chelate ring size has in fact been shown to determine whether protonation of $\text{CpRu}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{H}$ yields a dihydrogen ($n = 1$) or dihydride ($n = 3$) complex or a mixture of both tautomers ($n = 2$).²⁵ Once again H_2 coordination is favored in the more constrained system.

Vibrational Studies of Coordinated H_2 and Its Hindered Rotation

$\text{W}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$ is thus far unique in that all of the vibrational modes associated with the dihydrogen have been located while none have been observed in the cationic complexes. If the M-H_2 fragment is considered to be a triangular unit, six fundamental modes are expected: $\nu(\text{HH})$, $\nu_s(\text{MH}_2)$, $\nu_a(\text{MH}_2)$, two $\delta(\text{MH}_2)$, and a torsion, $\tau(\text{MH}_2)$ (Table II). Nujol mull IR spectra of $\text{W}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$ and its D_2 and HD isotopomers displayed bands (Figure 4) for all modes except the

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Table II
Vibrational Frequencies for Dihydrogen Complexes^a

	$W(CO)_3(PCy_3)_2(H_2)^b$	$Mo(CO)_3(PCy_3)_2(H_2)^b$	$Mo(CO)(dppe)_2(H_2)^b$	$W(CO)_5(H_2)^c$	$Pd(H_2)^d$	$Co(CO)_2(NO)(H_2)^d$
$\nu(HH)$	2690	[2950] ^e	2650	2711		3100
$\nu_a(MH_2)$	1568	[1420] ^e				1345
$\nu_s(MH_2)$	951	885	875	919	960	868
$\delta(MH_2)$	~650 ^f					
$\delta(MH_2)$	462	471	400 ^g			
$\tau(H_2)$	{ 325 } { 370 }		430			

^aIn cm^{-1} . IR data, except for $\tau(H_2)$ (INS). ^bFor Nujol mulls. ^cFor liquid xenon solutions at $-70^\circ C$. ^dFor Xe matrix at 12 K. ^eCalculated based on observed frequency for D_2 complex. ^fBased on INS and calculated IR frequency shift from D_2 complex. ^gTentative assignment; possibly this peak corresponds to the INS peak at 430 cm^{-1} .

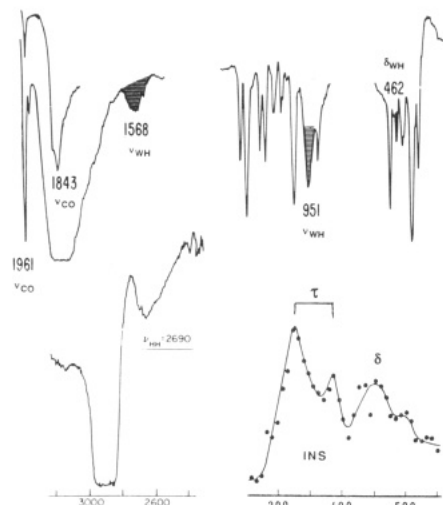


Figure 4. Nujol mull IR and inelastic neutron scattering (INS) spectra of $W(CO)_3(PCy_3)_2(H_2)$ in regions of $W-H_2$ modes. Lower left spectrum shows ν_{HH} for perdeuteriophosphine complex.

torsion (observed by inelastic neutron scattering).⁶ Raman spectra of solid samples exhibited only one strong mode, $\nu_s(MH_2)$.

The vibration of most interest, ν_{HH} , was located in $W(CO)_3[P(C_6D_{11})_3]_2(H_2)$ at 2690 cm^{-1} , using $P(C_6D_{11})_3$ to remove ν_{CH} interference (Figure 4). It has now been seen in several complexes as a broad, weak band at $2400\text{--}3100\text{ cm}^{-1}$ (cf. 4300 cm^{-1} for free H_2) (Table I), with a large metal dependence. The 370 cm^{-1} lower ν_{HH} for $W(CO)_5(H_2)$ vs $Mo(CO)_5(H_2)$ may reflect differences in metal basicity while the 430 cm^{-1} lower ν_{HH} for $Mo(CO)(dppe)_2(H_2)$ vs $Mo(CO)_5(H_2)$ correlates with $H-H$ weakening by a more basic center.

ν_{MH} also shows metal dependence (Table II). The weak, broad $\nu_a(MH_2)$ at 1570 cm^{-1} in $W(CO)_3(PR_3)_2(H_2)$ is not observed for the Mo analogue (possibly obscured), and the symmetric stretch at 950 cm^{-1} is weaker and $\sim 70\text{ cm}^{-1}$ lower in the Mo species. These data combined with the higher ν_{HH} for Mo species suggest weaker coordination of H_2 to Mo than W, in line with thermal stabilities. ν_{MH} for the Fe and Co nitrosyl species are also lower than those for W complexes, while that for $Pd(H_2)$ is nearly identical with the latter's.

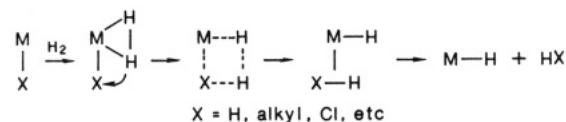
Inelastic neutron scattering (INS) is a powerful technique to locate vibrations involving hydrogen, particularly large-amplitude motions such as torsions. Excellent spectra (Figure 4) of $W(CO)_3(PR_3)_2(H_2)$ have been obtained at LANL and Grenoble.⁶⁰ The 450 cm^{-1} band coincides with a δ_{MH} in the IR, and the prominent peaks at 330 and 370 cm^{-1} are assignable to a split

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torsional (rotational) mode, $\tau(H_2)$. The data show the barrier to rotation of the H_2 to be 762 cm^{-1} ($\sim 2\text{ kcal}$). Analysis also predicts a librational ground-state splitting of $\sim 1\text{ cm}^{-1}$, observed to be 0.95 cm^{-1} in essentially a neutron-induced nuclear spin flip (para \rightarrow ortho- H_2 transition). The temperature dependence of this "tunneling" mode shows that at 2 K spin conversion is quite slow (as in solid H_2) and that tunneling persists to remarkably high temperatures ($\sim 200\text{ K}$). This is perhaps the highest temperature at which a quantum mechanical phenomenon has been observed.

Conclusions

The discovery of hydrogen complexes has significantly altered the way chemists must now perceive bonding and transformations at metal centers. Few would have believed that H_2 complexes would be stable relative to free H_2 or metal hydrides; now one must ask if there is any limit to the ability of metals to bind other σ -bonded molecules, e.g., CH_4 .⁶¹ The electron-deficient bonding (two-electron, three-center) in these systems resembles that in nonclassical carbonium ions and boron hydrides. The H_2 /hydride equilibrium gives an unprecedented opportunity to study the most fundamental bond-breaking/forming process at a metal. It appears that the H_2 ligand has a chemistry of its own and that complete $H-H$ rupture at a metal center may not be initially necessary in catalytic hydrogenation since deprotonation of H_2 ligands has been demonstrated. Indeed, hydrogenolysis of d^0 metal alkyl complexes had been suggested^{3f} to occur by direct transfer of H from a transiently bound H_2 to the alkyl via a four-center cyclic transition state⁶² as proposed in heterolytic H_2 cleavage^{2e} (eq 2). The proven existence of H_2 coordination now enhances this view:



" σ -bond metathesis", a term recently employed by

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Bercaw,^{62b} aptly fits. Future exploration includes range of H-H distances, η^1 -H₂ binding (a Pt- η^1 -I₂ complex has been found⁶³), and polyhydrogen ligands (H₃⁺ or H₃⁻). Evidence for the latter and related interactions resembling the four-center transition state in the above scheme has already begun to appear as of this writ-

ing.^{44b,64}

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Time-Resolved Studies of Solvation in Polar Media

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1. Introduction

Interest in the molecular motions associated with chemical reactions in solution has prompted an effort to understand the dynamics of solvation. The effect of macroscopic solvent parameters (i.e., viscosity, polarity) on chemical dynamics has been extensively studied for many decades.¹ Correlations between rate constants and such solvent variables have been reported.²⁻⁴ These studies indicate that to some extent, solvent effects on chemical reactions can be accounted for by the changes the solvent induces in the potential energy barrier and free energy of reaction.

However, for reactions in which the rates are comparable to or faster than solvent fluctuations, the details of the motion and structure of the surrounding solvent can play a deterministic role in the rates of chemical reaction. In order to understand these phenomena, major issues must be addressed: (a) how are the intermolecular forces and molecular motions of solvent perturbed by the chemically reacting system and (b) how do solvent fluctuations couple to the reactive potential energy surface.

In recent years, these issues have received more theoretical⁵⁻¹² than experimental¹³⁻¹⁵ attention. Advances in statistical mechanics have resulted in new treatments for equilibrium solvation which take into account molecular details of the solvent.^{16,17} For non-equilibrium phenomena, the subject of this Account, the solvent is generally modeled as a dielectric continuum.^{18,19} In this treatment the solvent is modeled as a structureless fluid with a frequency-dependent dielectric constant, $\epsilon(\omega)$. Usually $\epsilon(\omega)$ is expressed in the Debye form (eq 1):

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau_D} \quad (1)$$

In eq 1, ϵ_{∞} and ϵ_0 are the high-frequency and zero-frequency dielectric constants, respectively; τ_D is the Debye relaxation time. Dielectric dispersion experiments

on simple liquids (i.e., DMSO²⁰ show that $\epsilon(\omega)$ is well described by eq 1. In contrast, most solvents have more complex dielectric response than given in eq 1. In the case of the normal alcohols, $\epsilon(\omega)$ is generally expressed in terms of multiple regions of Debye-like behavior.^{21,22}

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_{10} - \epsilon_{1\infty}}{1 + i\omega\tau_{D1}} + \frac{\epsilon_{20} - \epsilon_{2\infty}}{1 + i\omega\tau_{D2}} + \frac{\epsilon_{30} - \epsilon_{3\infty}}{1 + i\omega\tau_{D3}} \quad (2)$$

The Debye relaxation times are commonly associated with the following molecular motions:²¹ hydrogen-bonding dynamics in molecular aggregates (τ_{D1}), monomer rotation (τ_{D2}), and rotation of the terminal C-OH group (τ_{D3}). In addition to τ_D , a second relaxation time, the longitudinal relaxation time, or constant charge relaxation time, τ_L , is commonly invoked to gauge dynamical solvent effects. The functional form for τ_L varies slightly depending on the nature of the perturbation and the value used for ϵ_{∞} (n^2 or $\epsilon_{1\infty}$;^{15,25} for the case of a point charge, τ_L is related to τ_D by $\tau_L = (\epsilon_{\infty}/\epsilon_0)$

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