

Coordination Chemistry of Dihydrogen

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I. Introduction

Transition-metal hydride complexes have been intensively studied due to their important role as intermediates in a number of catalytic hydrogenation processes.¹ Given their long history of study, it is surprising that isolable dihydrogen species have not been generally recognized until very recently. While dihydrogen complexes have been invoked along the reaction coordinate for oxidative addition of dihydrogen on an unsaturated metal center, these speculations have been put on a more secure foundation since the initial report of the first isolable dihydrogen complex (Figure 1) by Kubas and co-workers in 1984.² This seminal discovery has led to intense activity by several research groups worldwide, although the initial report was met with some skepticism, and convincing characterization data for these very novel complexes was only obtained with difficulty. These events have been described by Kubas.³ The 1992 American Chemical Society Inorganic Award was presented to Kubas in recognition of his outstanding contributions in this field.

The bonding in these complexes has been described using a model that is reminiscent of the familiar concepts developed to describe binding of ethylene and



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other related ligands. The H-H σ orbital donates electron density to an empty metal d orbital of σ symmetry. This interaction is augmented by back-donation from filled metal d orbitals. The bonding picture is represented schematically in Figure 2.

While the initial focus of workers in the field has been the synthesis of new dihydrogen complexes as well

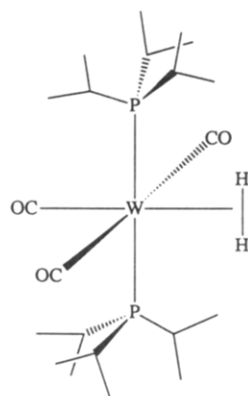


Figure 1. Sketch of the structure of $[W(\eta^2-H_2)(CO)_3(P\text{-}i\text{-}Pr_3)_2]$, shown by diffraction data to contain intact dihydrogen bound in a side-on manner.

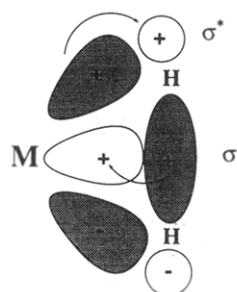
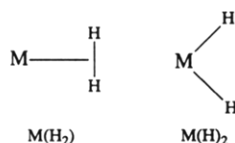


Figure 2. Bonding model in transition metal dihydrogen complexes illustrating the synergistic flow of electrons.

as describing their structure and bonding, more recent work has addressed reactivity of these interesting molecules. A wide variety of reactions have been described and many more will no doubt be discovered in the near future. There is some indication that dihydrogen complexes may be important in biological systems. Crabtree has proposed their involvement in the action of the hydrogenase and nitrogenase enzymes.⁴

At the present time more than 170 dihydrogen complexes have been reported. The very rapid development of this field is remarkable. In less than seven years the study of dihydrogen complexes has become a significant branch of coordination chemistry. This review will summarize in a comprehensive fashion the synthesis, characterization, structure, and reactivity of dihydrogen complexes. Coverage of the literature is up to the end of 1992. Various reviews of the field have appeared previously, but rapid developments have rendered these outdated.⁵ A very recent review has appeared which highlights the reactivity of dihydrogen complexes.⁶

In order to distinguish between dihydrogen complexes and classical dihydrides, the chemical formulas of the former will henceforth be presented as $M(H_2)$, as shown below.



The abbreviations employed in this review are tabulated at the end of the text.

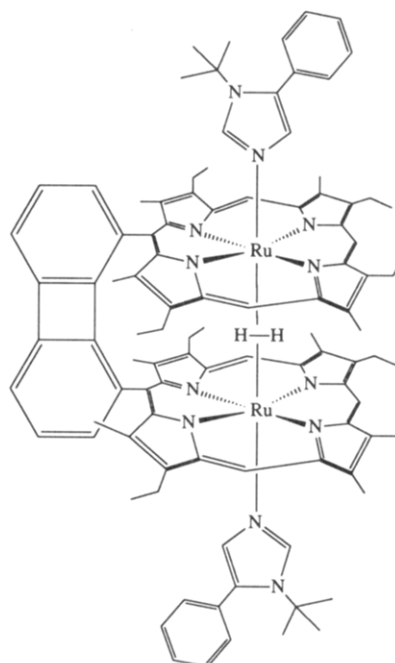


Figure 3. Proposed structure of $Ru_2(DPB)(*Im)_2(H_2)$.

II. Synthetic Methods

A. Reaction with Hydrogen

Reaction of a coordinatively unsaturated metal fragment with hydrogen was employed by Kubas and co-workers in the preparation of the first dihydrogen complexes. The precursor complexes are formally 16-electron species of the form $M(CO)_3(PR_3)_2$ ($M = Cr, Mo, W$; $R = Cy, i\text{-}Pr$) formed in situ from $[M(CO)_3\text{(cycloheptatriene)}]$ ($M = Mo, W$)^{2,7,8} or $[M(CO)_3\text{(naphthalene)}]$ ($M = Cr$)^{9,10}. An agostic interaction between the metal center and a C-H bond of a cyclohexyl group in the precursor molecules has been established by X-ray crystallography for the tungsten complex and more recently for the chromium analogue. This chemistry can be thought of as displacement of a weakly bound ligand (the agostic C-H bond) by the incoming dihydrogen ligand. A similar strategy was employed by Crabtree and Lavin to prepare the cationic iridium complex $[Ir(PPh_3)_2(bq)(\eta^2-H_2)H]^+$ by displacement of bound water from the aquo complex $[Ir(bq)(PPh_3)_2(OH_2)(H)]^+$.¹¹

This methodology was also exploited by Morris and co-workers in the synthesis of compounds of the general formula, $[MH(H_2)(L_2)_2]^+$, where $M = Fe, Ru, Os$, and L_2 is a variety of chelating diphosphines. For example, the homologous series of complexes $trans\text{-}[MH(H_2)\text{(depe)}_2]^+$ ($M = Fe, Ru, Os$) was prepared by reacting the precursor complexes $trans\text{-}M(H)(Cl)(depe)_2$ with sodium tetraphenylborate in acetone under 1 atm of hydrogen gas.¹² The labile chloride ligand is easily displaced to form the dihydrogen complexes under mild conditions.

A very exciting extension of the hydrogen reaction was reported recently by Collman and co-workers. Reaction of $Ru_2(DPB)$ with H_2 in the presence of a hindered imidazole ligand *Im affords the hydrogen complex $Ru_2(DPB)(*Im)_2(H_2)$, in which the bound hydrogen is bridging between the two Ru centers¹³

Table I. Photolytically Generated Dihydrogen Compounds

compound	$\nu(\text{H-H})$, cm^{-1}	ref	compound	$\nu(\text{H-H})$, cm^{-1}	ref
$\text{Cr}(\text{CO})_5(\text{H}_2)$	3030	16	<i>cis</i> - $\text{CpWH}(\text{H}_2)(\text{CO})_2$		20
<i>cis</i> - $\text{Cr}(\text{CO})_4(\text{H}_2)_2$		15	<i>trans</i> - $\text{CpWH}(\text{H}_2)(\text{CO})_2$		20
$\text{Cr}(\text{CO})_4(\text{H}_2)$		15	<i>cis</i> - $\text{Cp}^*\text{MoH}(\text{H}_2)(\text{CO})_2$		20
$\text{Mo}(\text{CO})_5(\text{H}_2)$	3080	17	<i>trans</i> - $\text{Cp}^*\text{MoH}(\text{H}_2)(\text{CO})_2$		20
$\text{W}(\text{CO})_5(\text{H}_2)$	2711	17	<i>cis</i> - $\text{Cp}^*\text{WH}(\text{H}_2)(\text{CO})_2$		20
<i>cis</i> - $\text{W}(\text{CO})_4(\text{H}_2)_2$		15	<i>trans</i> - $\text{Cp}^*\text{WH}(\text{H}_2)(\text{CO})_2$		20
<i>cis</i> - $\text{Cr}(\text{CO})_4(\text{COE})(\text{D}_2)$		25	$\text{CpMn}(\text{CO})_2(\text{H}_2)$		21
<i>trans</i> - $\text{Cr}(\text{CO})_4(\text{COE})(\text{D}_2)$		25	$\text{Cp}^*\text{Mn}(\text{CO})_2(\text{H}_2)$		26
<i>cis</i> - $\text{W}(\text{CO})_4(\text{COE})(\text{D}_2)$		25	$(\text{C}_5\text{Et}_5)\text{Mn}(\text{CO})_2(\text{H}_2)$		27
<i>trans</i> - $\text{W}(\text{CO})_4(\text{COE})(\text{D}_2)$		25	$\text{CpV}(\text{CO})_3(\text{H}_2)$	2642	22
<i>mer</i> -(C_2H_4) $_2\text{Cr}(\text{CO})_3(\text{H}_2)$		28	$\text{CpIr}(\text{CO})(\text{H}_2)$		29
<i>mer</i> -(C_2H_4) $_2\text{Mo}(\text{CO})_3(\text{H}_2)$		28	$\text{CpNb}(\text{CO})_3(\text{H}_2)$	2600	23
<i>mer</i> -(C_2H_4) $_2\text{W}(\text{CO})_3(\text{H}_2)$		28	$\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$	2973	30
<i>cis</i> -(C_2H_4) $_2\text{Cr}(\text{CO})_3(\text{H}_2)$		28	$\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$	3100	30
<i>cis</i> -(C_2H_4) $_2\text{Mo}(\text{CO})_3(\text{H}_2)$		28	$\text{Pd}(\eta^1\text{-H}_2)$		24
<i>cis</i> -(C_2H_4) $_2\text{W}(\text{CO})_3(\text{H}_2)$		28	$\text{Pd}(\eta^2\text{-H}_2)$		24
$(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{H}_2)$		26	$\text{CoH}(\text{H}_2)(\text{CO})_3$		31
$(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$		26	$\text{Co}(\text{CH}_3)(\text{H}_2)(\text{CO})_3$		31
$(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_2(\text{H}_2)$		26	$\text{Ni}(\text{CO})_3(\text{H}_2)$		32
$(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{H}_2)$		26	$\text{Cu}(\text{H}_2)\text{Cl}$	3222	33
<i>trans</i> - $\text{CpMoH}(\text{H}_2)(\text{CO})_2$		19	$\text{CrH}_2(\text{H}_2)$		34

(Figure 3). Subsequent determination of the dipolar coupling in high-field NMR experiments suggests that the H-H axis is perpendicular to the Ru-Ru vector.¹⁴

A number of dihydrogen complexes can be generated photochemically and studied spectroscopically in various low temperature conditions as well as in hydrocarbon solvent at room temperature (Table I). This area of investigation developed simultaneously in several laboratories beginning in 1985. Sweany and Poliakoff, Turner, and co-workers reported the observation of $\text{Cr}(\text{CO})_5(\text{H}_2)$ formed upon photolysis of $\text{Cr}(\text{CO})_6$ in H_2 -doped argon matrices and in liquid xenon solutions respectively.¹⁵⁻¹⁷ Poliakoff and Turner were also able to observe the compound in *n*-heptane at room temperature under 100 atm of hydrogen. Grevels and co-workers reported the same compound formed by flash photolysis of $\text{Cr}(\text{CO})_6$ in cyclohexane at room temperature.¹⁸ Sweany reported the formation of the first bis-dihydrogen complex, $\text{Cr}(\text{CO})_4(\text{H}_2)_2$, as well as $\text{Cr}(\text{CO})_4(\text{H}_2)$ and $\text{Cr}(\text{CO})_5(\text{H}_2)$ in low-temperature argon matrices. This class of dihydrogen species has been expanded to include $\text{Mo}(\text{CO})_5(\text{H}_2)$ and $\text{W}(\text{CO})_5(\text{H}_2)$, observed in liquid xenon.¹⁷

Sweany has reported a series of dihydrogen compounds of the general formula $\text{CpMH}(\text{H}_2)(\text{CO})_2$ and $\text{Cp}^*\text{MH}(\text{H}_2)(\text{CO})_2$ ($\text{M} = \text{Mo}$ and W) in argon matrices.^{19,20} Similar compounds including $\text{CpMn}(\text{CO})_2(\text{H}_2)$ (formed in supercritical xenon),²¹ $\text{CpV}(\text{CO})_3(\text{H}_2)$,²² and $\text{CpNb}(\text{CO})_3(\text{H}_2)$ ²³ have been added more recently to this class of dihydrogen compounds.

Ozin and Garcia-Prieto reported infrared evidence for the formation of both η^1 and η^2 forms of ligand-free $\text{Pd}(\text{H}_2)$ in both krypton and xenon matrices at 12 K.²⁴

B. Protonation of Hydride Complexes

Protonation of a neutral hydride complex to give a cationic dihydrogen complex was first reported by Crabtree and Lavin in 1985. $[\text{Ir}(\text{PPh}_3)_2(\text{bq})(\eta^2\text{-H}_2)\text{H}]^+$, initially prepared by displacement of bound water as described above, was shown to react with MeLi to generate $\text{Ir}(\text{PPh}_3)_2(\text{bq})\text{H}_2$. The dihydrogen species can be regenerated quantitatively upon addition of 1 equiv

of $\text{PhCH}(\text{SO}_2\text{CF}_3)_2$.³⁵ Subsequent work has demonstrated that the protonation of neutral hydrides to give cationic H_2 complexes is a fairly general reaction of considerable utility. Morris initially employed this particular methodology to prepare $[\text{MH}(\text{H}_2)(\text{dppe})_2]^+$ ($\text{M} = \text{Fe}$ and Ru). Protonation of the neutral dihydrides $[\text{MH}_2(\text{dppe})_2]$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was found to give the same cationic dihydrogen complexes as can be prepared from the monohydrides, $[\text{MH}(\text{dppe})_2]\text{BF}_4$, and hydrogen gas.³⁶ The synthesis of a wide variety of dihydrogen complexes of this type via protonation reactions has been reported by Morris and co-workers and by Field and co-workers (see Table I). Contributions have also been made by Rigo and co-workers³⁷ and Suburi and co-workers.^{38,39} Albertin and co-workers have prepared a series of related compounds using the protonation methodology. The compounds of general formula $[\text{MH}(\text{H}_2)(\text{P})_4]^+$ ($\text{M} = \text{Fe}$, Ru , Os ; $\text{P} = \text{PPh}(\text{OEt})_2$, $\text{P}(\text{OEt})_3$, and $\text{P}(\text{OMe})_3$) can be isolated upon treatment of the corresponding dihydrides with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$.^{40,41}

Subsequent extension of the protonation methodology to ruthenium half sandwich complexes has led to a wide variety of cationic complexes of the type $[\text{CpRu}(\text{L})(\text{L}')(\text{H}_2)]^+$. The first synthesis of this type was reported in 1986 by Conroy-Lewis and Simpson. Protonation of $\text{CpRu}(\text{PPh}_3)(\text{CN-}t\text{-Bu})\text{H}$ affords the stable, isolable complex $[\text{CpRu}(\text{PPh}_3)(\text{CN-}t\text{-Bu})(\text{H}_2)]^+$.⁴² An extensive series of compounds of this type have been reported by Heinekey and co-workers.⁴³⁻⁴⁵ Additional examples have recently been reported by Jia and Morris.⁴⁶

Protonation of anionic hydride complexes allows access to neutral dihydrogen complexes. An example of this is provided by the work of Collman and co-workers, who reported that protonation of $\text{K}[\text{Os}(\text{OEP})\text{H}]$ in THF affords $\text{Os}(\text{OEP})(\text{H}_2)(\text{THF})$.⁴⁷

C. Dihydrogen Complexes Formed under Reducing Conditions

Li and Taube have reported an interesting series of compounds of the general formula, *trans*- $[\text{Os}(\text{NH}_3)_4(\text{H}_2)(\text{L})]^{+2/+3}$ where $\text{L} = \text{acetonitrile}$, pyridine, imidazole, iodide, chloride, water, acetone, and

Table II. Dihydrogen Complexes

complex ^a	J_{H-D} , Hz	T_1 , ms ^b	ref(s)	complex ^a	J_{H-D} , Hz	T_1 , ms ^b	ref(s)
Cr(CO) ₃ (PCy ₃) ₂ (H ₂)			9, 50	[(tetraphos-II)Co(H ₂)] ⁺	27.8	19 (300)	75
Mo(CO) ₃ (PCy ₃) ₂ (H ₂)			2	[(tetraphos-II)Rh(H ₂)] ⁺	18	120 (300)	76
Mo(CO) ₃ (P- <i>i</i> -Pr) ₃ (H ₂)			2				
W(CO) ₃ (PCy ₃) ₂ (H ₂)			2	[Os(NH ₃) ₅ (H ₂)] ⁺ 2	15.2	345 (400)	77
W(CO) ₃ (P- <i>i</i> -Pr) ₃ (H ₂) (x,n)	33.5	4 (200)	2	[Os(NH ₃) ₅ (H ₂)] ⁺ 3			77
W(CO) ₃ (PCy ₃) ₂ (H ₂) (x)			51	[Os(NH ₃) ₄ (H ₂)(CH ₃ CN)] ⁺ 2	20.3	62 (400)	48
[Re(CO) ₃ (PCy ₃) ₂ (H ₂)] ⁺	28		52	[Os(NH ₃) ₄ (H ₂)(py)] ⁺ 2	19.6	38 (400)	48
				[Os(NH ₃) ₄ (H ₂)(Im)] ⁺ 2	17.1	63 (400)	48
Mo(CO)(dppe) ₂ (H ₂) (x, n)	34		53,54	[Os(NH ₃) ₄ (H ₂)] ⁺	12.5	129 (400)	48
MnH(H ₂)(dmpe) ₂		22 (400)	55	[Os(NH ₃) ₄ (H ₂)] ⁺	10.2	125 (400)	48
MnH(H ₂)(depe) ₂		25 (400)	55	[Os(NH ₃) ₄ (H ₂)(D ₂ O)] ⁺ 2	8.1	77 (400)	48
ReCl(H ₂)(PMePh ₂) ₄ (x)		25 (200)	49,56	[Os(NH ₃) ₄ (H ₂)(CD ₃ CO)] ⁺ 2	4.0	74 (400)	48
[FeH(H ₂)(dppe) ₂] ⁺ (x, n)	32	8.5 (200)	36,57	[Os(NH ₃) ₄ (H ₂)Br] ⁺	<2.5	107 (400)	48
[FeH(H ₂)(depe) ₂] ⁺	28	12 (200)	12	[Os(en) ₂ (H ₂)Cl]Cl (x)	7.2	61 (400)	48
[FeH(H ₂)(dedppe) ₂] ⁺	32	7 (200)	58	[Os(en) ₂ (H ₂)Br]Br (x)			48
[FeH(H ₂)(dmpe) ₂] ⁺	31.0		59	[Os(en) ₂ (H ₂)py] ⁺ 2 (x)			48
[FeH(H ₂)(d(<i>i</i> -Pr)pe) ₂] ⁺			59				
[FeH(H ₂)(PPh(OEt)) ₂] ⁺		3 (80)	40	Ru(OEP)(THF)(H ₂)	29.5	25 (400)	14
[FeH(H ₂)(P(OEt) ₃) ₄] ⁺		4 (80)	40	Ru ₂ (DPB)(*Im) ₂ (H ₂)	15	132 (400)	13,14
[FeH(H ₂)(<i>meso</i> -tetraphos)] ⁺	32.3	32 (200)	60	Os(OEP)(THF)(H ₂)	12	110 (400)	14,47
[RuH(H ₂)(dppe) ₂] ⁺	32.9	11 (200)	36	Os(OEP)(*Im)(H ₂)	27.5	28 (400)	14
[RuH(H ₂)(depe) ₂] ⁺	32	11 (200)	12				
[RuH(H ₂)(binap) ₂] ⁺	30		61	[IrH(H ₂)(PPh ₃) ₂ (bq)] ⁺	29.5	8 (250)	11,78
[RuH(H ₂)(dppp) ₂] ⁺	32	6 (400)	38	[IrH(H ₂)(PCy ₃) ₂ (bq)] ⁺	29	65 (250)	79
[RuH(H ₂)(dppb) ₂] ⁺		10 (400)	38	[Ir(dipph ₂ H)(H)(H ₂)(PPh ₂ Me) ₂] ⁺	33.5		80
[RuH(H ₂)(diop) ₂] ⁺		<10 (400)	39	[Ir(dipph ₂ H)(H)(H ₂)(P- <i>n</i> -Bu) ₂] ⁺	32		80
[RuH(H ₂)(PPh(OEt)) ₂] ⁺	34	7 (80)	41	[Ir(dipph ₂ H)(H)(H ₂)(PPh ₃) ₂] ⁺			80
[RuH(H ₂)(P(OMe) ₃) ₄] ⁺	31	4 (80)	62	[Ir(dipph ₂ H)(H)(H ₂)(P- <i>p</i> -tolyl) ₂] ⁺	29		80
[RuH(H ₂)(P(OEt) ₃) ₄] ⁺		3 (80)	62	[Ir(dipph ₂ H)(H)(H ₂)(P(C ₆ H ₄ F) ₃) ₂] ⁺			80
[RuCl(H ₂)(depe) ₂] ⁺		28 (400)	63	[Ir(ditolph ₂ H)(H)(H ₂)(PPh ₃) ₂] ⁺			80
[RuCl(H ₂)(dcpe) ₂] ⁺	16 ^c	4 (80)	37				
[RuH(H ₂)(dcpe) ₂] ⁺	31.5	3 (80)	37	[MoH ₄ (H ₂)(dppe)] ⁺ 2			81
[RuH(H ₂)(CO)(triphos)] ⁺		8 (250)	64	[WH ₃ (H ₂)(PMePh ₂) ₄] ⁺			82
[RuH(H ₂)(P(OCH ₃) ₃ CEt)(triphos)] ⁺	32.8	13 (250)	64	[WH ₃ (H ₂)(PMePh ₂) ₄] ⁺			82
[RuH(H ₂)(PMe ₂ Ph)(triphos)] ⁺	32.2	9 (250)	64	ReH ₅ (H ₂)(P(<i>p</i> -C ₆ H ₄ F) ₃) ₂		55 (250)	78
[OsH(H ₂)(dedppe) ₂] ⁺	19	30 (200)	58	ReH ₅ (H ₂)(PCy ₃) ₂		<60 (250)	78
[OsH(H ₂)(depe) ₂] ⁺ (x)		52 (200)	58,65	[Re(H ₂ H ₂ (CO)(PMe ₂ Ph) ₃)] ⁺	34	8 (250)	83,84
[OsH(H ₂)(dppe) ₂] ⁺ (x)		39 (400)	66,67	[Re(H ₂ H ₂ (Cyttrp)] ⁺ (x)		27 (250)	85
[OsH(H ₂)(PPh(OEt)) ₂] ⁺		10 (80)	41	[Re(H ₂)(CO) ₂ (PMe ₂ Ph) ₃] ⁺	31	7 (250)	86
[OsH(H ₂)(P(OEt) ₃) ₄] ⁺		10 (80)	62	[ReH _{5-2x} (H ₂) _x (P- <i>t</i> -Bu ₂ Me) ₂] ⁺			87
[OsCl(H ₂)(depe) ₂] ⁺		60 (400)	63	[ReH _{5-2x} (H ₂) _x (PPh ₃) ₂] ⁺			87
[OsCl(H ₂)(dcpe) ₂] ⁺	10.5 ^c	10 (80)	37	[ReH _{5-2x} (H ₂) _x (PCy ₃) ₂] ⁺			87
[OsH(H ₂)(<i>meso</i> -tetraphos)] ⁺	26.4	49 (200)	60	FeH ₂ (H ₂)(PEtPh ₂) ₃ (n)		24 (250)	88,89
[OsH(H ₂)(<i>rac</i> -tetraphos)] ⁺		160 (200)	60	ReH ₂ (H ₂)(PPh ₃) ₃		30 (250)	78
				ReH ₂ (H ₂) ₂ (PCy ₃) ₂		28 (200)	90
[(tetraphos-II)FeH(H ₂)] ⁺	28.3	6 (300)	68,69	ReH ₂ (H ₂)(PCy ₃) ₃		44 (200)	90
[P(CH ₂ CH ₂ CH ₂ PM ₂) ₃ FeH(H ₂)] ⁺	11.0	55 (400)	70	RuH ₂ (H ₂)(Cyttrp)		16 () ^d	91
[(tetraphos-II)RuH(H ₂)] ⁺	29.7		71	RuH(H ₂)(I)(PCy ₃) ₂ (x)		30 (200)	92
				RuH(H ₂)Cl(PCy ₃) ₂		30 (200)	92
[Cp*Re(CO)(NO)(H ₂)] ⁺	27	5 (500)	44	RuH(H ₂)(OCOCF ₃)(PCy ₃) ₂		20 (250)	93
[Cp*Fe(dppe)(H ₂)] ⁺	27	7 (300)	72	Ru(H ₂)(OCOCF ₃) ₂ (PCy ₃) ₂			93
[CpRu(PPh ₃)(CN- <i>t</i> -Bu)(H ₂)] ⁺	28.6		42	RuH(H ₂)Cl(CO)[P(<i>i</i> -Pr) ₃] ₂	34.5	16 (200)	94
[CpRu(CO)(PPh ₃)(H ₂)] ⁺			43,45	RuH ₂ (H ₂)(CO)[P(<i>i</i> -Pr) ₃] ₂		15 (200)	94
[CpRu(CO)(PMe ₃)(H ₂)] ⁺	28.5		43,45	Ru ₂ (H ₂)H ₄ (PCy ₃) ₄		88 (250)	90
[CpRu(CO)(PMe ₂ Ph)(H ₂)] ⁺			43,45	(P- <i>tol</i>) ₂ RuH(μ-H)(μ-Cl) ₂ Ru(H ₂)(P- <i>tol</i>) ₃		44 (300)	95
[CpRu(CO)(PCy ₃)(H ₂)] ⁺	28.5	4 (250)	43,45	[(H ₂)(dppb)Ru(μ-Cl) ₂ RuCl(dppb)]	29.4	12 (300)	96
[CpRu(H ₂)(dmpe)] ⁺	22		43,45	(P-N)(H ₂)Ru(μ-H)(μ-Cl) ₂ RuH(PPh ₃) ₂ (x)		13.8 (300)	97
[CpRu(H ₂)(dppe)] ⁺	24.9	30 (300)	73	OsHCl(CO)(P- <i>i</i> -Pr) ₂ (H ₂)		18 (200)	98,99
[CpRu(H ₂)(dppm)] ⁺	21.9		73	[OsH ₃ (H ₂)(PPh ₃) ₃] ⁺		35 (250)	78
[Cp*Ru(H ₂)(dppm)] ⁺	20.9	50 (300)	46	[OsH _{5-2x} (H ₂) _x (PMe ₂ Ph) ₃] ⁺		68 (360)	100
[Cp*Ru(H ₂)(dppp)] ⁺			67	[Os(PPh ₃) ₃ (H ₂)(OAc)] ⁺ (x)	13.7	41 (400)	101
[CpRu(H ₂)(dape)] ⁺	24.3		46	Os(SiEt ₃)Cl(H ₂)(CO)(P- <i>i</i> -Pr) ₂		17 (200)	102
[CpRu(H ₂)(dtfpe)] ⁺	25.3		46,74	{HB(3,5-Me ₂ pz) ₃ Rh(H ₂)H ₂ }		42 (400)	103
[Cp*Ru(CO) ₂ (H ₂)] ⁺	32		44	[IrH ₂ (H ₂)(PMe ₂ Ph) ₃] ⁺		20 (360)	104,105
[CpRu(dmdppe)(H ₂)] ⁺	23.8		45	IrH(H ₂)Cl ₂ (P- <i>i</i> -Pr) ₂			106
[Cp*Ru(dmdppe)(H ₂)] ⁺	23.0		45	IrH ₂ (H ₂)Cl(P- <i>i</i> -Pr) ₂ (x)		22 (300)	106,107
[CpRu(R)-prophos](H ₂)] ⁺			45	IrClH ₂ (PCy ₃) ₂ (H ₂)		27 (300)	107
[CpRu(PPh ₃) ₂ (H ₂)] ⁺	26.5		45	IrClH ₂ (P- <i>t</i> -Bu) ₂ (H ₂)			107
[Cp*Ru(PPh ₃) ₂ (H ₂)] ⁺	24.0		45	[IrH ₄ (H ₂)(PCy ₃) ₂] ⁺		48 (250)	35
[Cp*Ru(CO)(PCy ₃)(H ₂)] ⁺	29.2		45	Cp* ₂ Eu(H ₂)			108

^a X-ray and neutron diffraction structural data indicated by (x) or (n), respectively. ^b Spectrometer frequency (in MHz) indicated in parentheses. ^c J_{H-D} obtained by computer simulation. ^d No spectrometer frequency reported.

bromide.⁴⁸ These are prepared by reducing Os(NH₃)₄(O₃SCF₃)₃ with zinc amalgam in the presence of water.

Cotton and Luck found that reduction of ReCl₅ with sodium amalgam in the presence of PMePh₂ under a

hydrogen atmosphere affords ReCl(H₂)(PMePh₂)₄.⁴⁹

Although the number of dihydrogen complexes has now become quite large, the structural types are rather limited. The table of dihydrogen complexes below (Table II) has been organized to reflect these structural

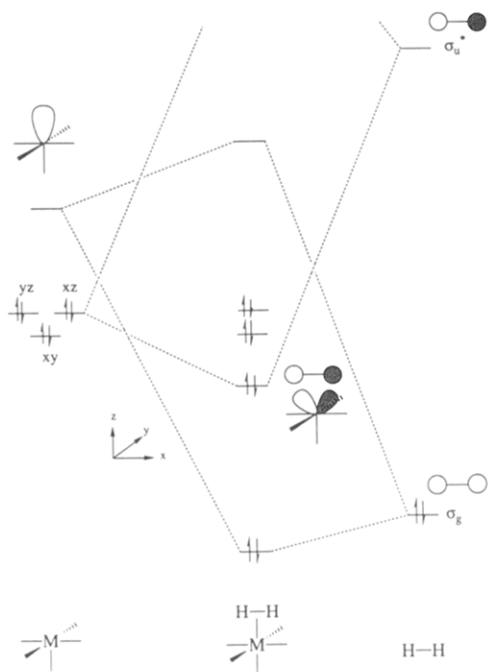


Figure 4. Interaction diagram of H_2 interacting with a ML_5 metal fragment.

classes. J_{H-D} and T_1 data including spectrometer field have been included when available.

III. Computational Studies

Computational chemistry has played an important role in understanding structure and bonding, as well as dynamic processes in dihydrogen complexes. Four neutron diffraction structures of dihydrogen complexes have been solved, providing an interesting opportunity to compare theory and experiment. The four complexes are each d^6 octahedral structures of either W, Mo or Fe; $W(CO)_3(P\text{-}i\text{-}Pr)_2(H_2)$, *trans*- $Mo(CO)(dppe)_2(H_2)$, *trans*- $[Fe(H)(H_2)(dppe)_2]^+$, and $Fe(H)_2(H_2)(PEtPh_2)_3$.

Theoretical considerations of the bonding interaction between d^6 ML_5 fragments and H_2 provide a framework in which to consider experimental results. The interaction diagram¹⁰⁹ below (Figure 4) reveals the important bonding interactions. The filled σ_g orbital of H_2 is stabilized upon mixing with the LUMO of the metal fragment, also of σ symmetry. A second symmetry-allowed interaction is mixing of the filled d_{xz} orbital with the σ_u^* orbital of the H_2 ligand. Theoretical studies¹¹⁰ indicate that the primary interaction is donation of electron density from the H_2 σ orbital to the metal center and to a lesser extent back-donation from metal d orbital to H_2 σ^* . Structural parameters from recent *ab initio* calculations¹¹¹ of the model compound, $W(CO)_3(PH_3)_2(H_2)$, compare favorably to experimental data for $W(CO)_3(P\text{-}i\text{-}Pr)_2(H_2)$. The calculated M-H and H-H distances are 1.911 and 0.812 Å (1.89 and 0.82 Å by neutron diffraction). The H_2 ligand undergoes hindered rotation with a calculated rotational barrier of 2.2 kcal/mol in agreement with the value obtained by inelastic neutron scattering (*vide infra*). An important conclusion from this study was that steric effects are negligible but that electron donation from the metal to H_2 σ^* accounts for the hindered motion.

Theoretical analysis has confirmed that the ground-state structure of dihydrogen complexes is intimately

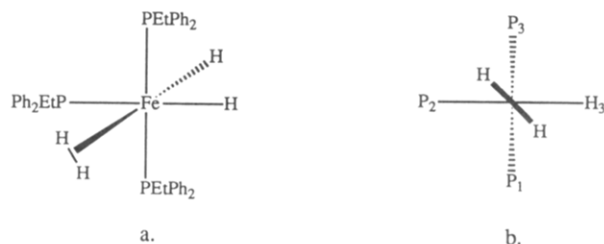


Figure 5. (a) Idealized structure of $Fe(H)_2(H_2)(PEtPh_2)_3$ and (b) ground-state orientation of the H_2 ligand as viewed down the H_2 -M bond axis.

linked with metal to σ^* back-bonding. Generally the metal t_{2g} set contains two orbitals which are directed toward the H_2 ligand. These are the two HOMO's which are expected to define the rotational orientation of the H_2 ligand. Calculated ground-state structures of $W(CO)_3(P\text{-}i\text{-}Pr)_2(H_2)$,¹¹¹ *trans*- $Mo(CO)(dppe)_2(H_2)$,⁵⁴ and *trans*- $[Fe(H)(H_2)(dppe)_2]^+$ ¹¹² revealed that the H_2 ligand preferentially aligned along one of the P-M-P vectors in agreement with structural data. Subtle considerations required for the Mo and Fe examples showed that distortions of the equatorial phosphorus ligands removed the degeneracy of the two d_π orbitals directed toward H_2 . *Trans* phosphorous ligands, bent back away from the H_2 ligand, allowed d_π in that plane greater ability to donate into H_2 σ^* .

$Fe(H)_2(H_2)(PEtPh_2)_3$ displays an unprecedented structure as revealed by neutron diffraction.⁸⁹ The dihydrogen ligand in this complex is positioned in a staggered conformation (Figure 5) with respect to the ligands lying in the equatorial plane of the distorted octahedron. Qualitative expectations would predict the dihydrogen ligand to eclipse the P_1 -Fe- P_3 vector to maximize back donation to σ^* . Yet the staggered conformation can be understood by considering that close in energy to the d_π orbitals is also an Fe-H σ orbital capable of donating into σ^* of the H_2 ligand. This novel interaction referred to as the "cis effect" causes a stabilization of H_2 along the P_2 -Fe- H_3 vector. The staggered ground-state structure is a compromise between the two bonding interactions. The "cis effect" is an interesting result of theoretical analysis which may be a general phenomenon in transition metal polyhydrides.¹¹³ The "cis effect" may provide a mechanism for hydrogen-atom exchange in which an H-H bond is cleaved with simultaneous H-H bond formation at the cis site.^{89,114}

Theory has been less successful in predicting the energy differences between classical and nonclassical structures of polyhydrides. The energy difference between the classical and nonclassical forms of $W(CO)_3(P\text{-}i\text{-}Pr)_2H_2$ is less than 1.0 kcal/mol as determined by NMR methods. The seven-coordinate dihydride structure was found to be 11 or 17 kcal/mol higher in energy than the dihydrogen complex by *ab initio* calculation methods.^{110b} Other systems studied theoretically include MH_7L_2 ($M = Re$ and Tc),¹¹⁵⁻¹¹⁷ IrH_5L_2 ,^{118,117} and $MH_nL_{4-n}Cp$ ($M = Ru, Rh, Os$, and Ir and $L = PH_3$ and CO).¹¹⁹

IV. Characterization of Dihydrogen Complexes

A. Diffraction Studies

Definitive characterization of hydrogen complexes is a challenging problem. In this section, a brief

Table III. Structural Data

compounds	H-H, Å ^b	M-H, Å ^b	ref(s)
W(CO) ₃ (P- <i>i</i> -Pr) ₃ (H ₂)	0.82 (n); 0.75(16) (x)	1.95(23) (x); 1.89 (n)	2, 120
FeH(H ₂)(dppe) ₂]BF ₄	0.816(16) (n); 0.87(3) (x)	1.67(2) (x); 1.616(10) (n)	57
FeH ₂ (H ₂)(PEtPh) ₃	0.821(10) (n)	1.576(9), 1.607(8)	89
ReH ₇ (P- <i>p</i> -tolyl) ₃	1.357(7) (n)		121
Mo(CO)(dppe) ₂ (H ₂)	0.80–0.85 ^a (n)	1.920(15), 1.924(15)	54
(P-N)(H ₂)Ru(μ-H)(μ-Cl) ₂ RuH(PPh ₃) ₂	0.80(6) (x)	1.50(4), 1.47(4)	97
ReCl(H ₂)(PMePh) ₂	1.17(13) (x)	1.49(9), 1.98(9)	56
[Re(H ₂)H ₄ (Cytpp)]SbF ₆	1.08(5) (x)		85
[CpRu(H ₂)(dppm)] ⁺	1.01 (x)		122
RuH(H ₂)(I)(PCy ₃) ₂	1.03(7) (x)	1.605(5), 1.59(4)	92
X-ray Structures in Which H ₂ Ligand Was Not Located			
[Os(PPh ₃) ₃ (H ₂)(OAc)][HC(SO ₂ CF ₃) ₂]			101
<i>trans</i> -[OsH(H ₂)(depe) ₂]BF ₄			65
<i>trans</i> -[OsH(H ₂)(dppe) ₂]BF ₄			123
W(CO) ₃ (PCyp) ₃ (H ₂)			51
IrH ₂ (H ₂)Cl(P- <i>i</i> Pr) ₃			124
[Os(en) ₂ (H ₂)Cl]Cl			48
[Os(en) ₂ (H ₂)Br]Br			48
[Os(en) ₂ (H ₂)py][PF ₆] ₂			48

^a The H-H bond length determined to be 0.736(10) Å was corrected for large librational motion which causes underestimation of the true value. ^b X-ray and neutron diffraction structure data indicated by (x) or (n), respectively.

summary is given of techniques which have been employed to date in both solution and solid-state investigations.

In some cases X-ray diffraction has given useful data. The difficulties associated with precise location of hydrogen atoms, particularly on second- and third-row metals, limit the usefulness of this method. While neutron diffraction is perhaps the most definitive technique, the requirement for large high-quality crystals has so far limited this method to a small number of examples (Table III). In all cases so far studied by neutron diffraction methods, the H₂ ligand is bound in a side-on fashion with an H-H distance of ca. 0.82 Å. The M-H distances to the H₂ ligand are comparable to M-H distances observed in classical hydride complexes. One example of asymmetric binding has been reported on the basis of X-ray diffraction data of Re(H₂)Cl(PMePh)₂, in which H₂ may be bound in an η¹ fashion.⁵⁶ The two Re-H distances in this complex are 1.49(9) and 1.98(9) Å. A neutron diffraction study would be most beneficial in this case.

In contrast to the short H-H distances noted above, a large body of neutron diffraction data reported prior to 1991 indicates that the shortest H...H distance in polyhydride complexes is 1.650 Å, reported for OsH₆(P-*i*-Pr)₂Ph.¹²⁵ In 1991, Howard and co-workers reported very interesting neutron diffraction results for [ReH₇-{P(*p*-tolyl)₃}₂]. This complex exhibits one H-H distance with an intermediate value of 1.357 Å.¹²¹ It seems likely that further examples of such intermediate distances between adjacent hydride ligands will be found in the future. It is not clear at this time whether such complexes should be formulated as H₂ complexes or as dihydrides.

B. Solid-State NMR

Of more general utility is the solid-state ¹H NMR experiment pioneered by Zilm.¹²⁶ In this experiment, which requires small amounts of powder sample, measurement of the dipolar coupling between the two protons allows the H-H distance to be determined directly. Use of a weak pulse prior to a dipolar echo

sequence obviates the need for deuteration of the ancillary ligands. This technique was first applied to the Kubas complex W(CO)₃(PCy₃)₂(H₂), where an H-H distance of 0.89 Å was found, in reasonable agreement with the distance of 0.82 Å determined for the P(*i*-Pr)₃ analog by neutron diffraction.¹²⁰ It should be noted that the distance determined by the NMR technique is believed to be very accurate. There is some possibility that motion of the H₂ ligand could lead to a very slight overestimation of the distance, but correction for these effects is expected to be at most 0.01 Å. Several different complexes have subsequently been studied by this method, and a range of H-H distances from 0.87–1.02 Å has been observed. The longest distance was seen in [CpRu(dmpe)(H₂)]⁺.¹²⁷ The distances observed seem to show the expected inverse correlation with *J*_{H-D}, in those cases where the comparison was possible (vide infra).

C. Vibrational Spectroscopy

Vibrational spectroscopy has played an important role in the characterization of dihydrogen complexes. As early as 1980 Kubas and co-workers reported that the formally 16-electron compounds, M(CO)₃(PR₃)₂ (M = Mo and W) would bind various small molecules including dihydrogen. The IR spectra of these M(CO)-(PR₃)₂(H₂) species did not exhibit bands at 1700–2300 cm⁻¹ ν(M-H) and 700–900 cm⁻¹ δ(M-H) as expected for terminal metal hydrides but instead bands at 1570, 950, and 460 cm⁻¹, which in turn shifted to 1150, 700, and 315 cm⁻¹ upon substitution with D₂. These bands are now readily explained given the η² binding of dihydrogen in these complexes. The triangular M(H₂) unit of a dihydrogen complex is expected to exhibit six vibrational modes: H-H stretch, symmetric and asymmetric M-H₂ modes, two deformation modes, and the torsional mode. In only one compound have all six modes been identified; W(CO)₃(PCy₃)₂(H₂) displays ν(H-H) at 2690 cm⁻¹, ν_s(M-H₂), and ν_{as}(M-H₂) at 1568 and 951 cm⁻¹, two deformation modes at 650 and 462 cm⁻¹ and the rotational mode (detected by inelastic neutron scattering) at approximately 350 cm⁻¹. Consistent with considerable weakening of the H-H interaction upon

binding, $\nu(\text{H-H})$ shifts from 4300 cm^{-1} in free hydrogen to ca. 2700 cm^{-1} in the bound complex. A range of $\nu(\text{H-H})$ values from 2400 to 3100 cm^{-1} has now been reported for H_2 complexes. Unfortunately, in the vast majority of hydrogen complexes reported to date, $\nu(\text{H-H})$ has not been detected, limiting the utility of this parameter. Although it would seem reasonable that lower $\nu(\text{H-H})$ values would correlate with greater bond activation and thus greater thermal stability, this is not always the case. For example the $\nu(\text{H-H})$ stretch of the thermally unstable $\text{CpV}(\text{CO})_3(\text{H}_2)$ complex appears at 2642 cm^{-1} while the corresponding stretch in the isolable $\text{W}(\text{CO})_3(\text{PCy}_3)_2(\text{H}_2)$ complex is 48 cm^{-1} higher.

An important distinguishing feature of dihydrogen complexes is the effect of isotopic substitution on the vibrations of the $\text{M}(\text{H}_2)$ unit. Dihydrogen complexes exhibit distinct $\nu(\text{H-H})$ stretches for the HD isotopomer approximately halfway between the H_2 and the D_2 analogs.¹²⁰ Terminal dihydride complexes on the other hand reveal distinct M-H and M-D vibrations.

As a consequence of the bonding model presented above, the dihydrogen ligand bound to a metal center is in effect a hindered rotor. Since the σ component of the bonding is expected to have no directional character, any hindrance to rotation must arise from metal d to σ^* back-bonding. Thus a measurement of the barrier to rotation will give an indication of the strength of this back-donation.

A powerful method to probe the nature of the vibrational potential experienced by the bound H_2 is provided by inelastic neutron scattering (INS) experiments. Large amplitude, low energy torsional motions in molecules such as $\text{W}(\text{CO})_3(\text{P-}i\text{-Pr}_3)_2(\text{H}_2)$, which are difficult to detect by infrared spectroscopy are readily identifiable by INS. In this case, bands at 325 and 370 cm^{-1} are assigned to a split torsional (rotation) mode. Analysis indicates a barrier to rotation of 2.4 kcal/mol . Quantum mechanical rotational tunneling is manifested by a librational ground-state splitting of 0.95 cm^{-1} . Studies of the temperature dependence of this tunneling process indicate that it persists up to ca. 185 K . That this phenomenon, which is analogous to a transition from para to ortho hydrogen, persists at such high temperatures is remarkable. Studies of several other H_2 complexes have revealed a wide range of rotational barriers, from 0.8 to 2.4 kcal/mol . These investigations have been recently reviewed by Eckert.¹²⁸

D. Solution NMR Methods

The proton NMR spectra of dihydrogen complexes generally give a single resonance of highly variable line width to high field of TMS. If other spin active nuclei are present in the molecule, coupling to the bound H_2 is in most cases not resolvable. Although there are many examples of H_2 complexes with phosphine coligands, coupling to ^{31}P has rarely been reported. The first case of resolved coupling between bound H_2 and adjacent ^{31}P nuclei was reported in the ruthenium cations of the form $[\text{CpRu}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)(\text{H}_2)]^+$. For $\text{R} = \text{Me}$, $J_{\text{H-P}} = 3.6\text{ Hz}$;⁴³ for $\text{R} = \text{Ph}$, $J_{\text{H-P}} = 2\text{ Hz}$.⁷³ These values of $J_{\text{H-P}}$ are much lower than those observed in comparable hydride complexes. A $J_{\text{H-P}}$ of 7.5 Hz has been reported in the dinuclear ruthenium complex $(\text{H}_2)(\text{dppb})\text{Ru}(\mu\text{-}$

$\text{Cl})_3\text{RuCl}(\text{dppb})$.⁹⁶ The only examples of phosphine-containing H_2 complexes with large values of $J_{\text{H-P}}$ are the cationic cobalt and rhodium complexes of the form $[(\text{tetraphos-II})\text{M}(\text{H}_2)]^+$, which have $J_{\text{H-P}} = 28\text{ Hz}$ for $\text{M} = \text{Co}$ ⁷⁵ and $J_{\text{H-P}} = 67\text{ Hz}$ for $\text{M} = \text{Rh}$.⁷⁶ A moderately large value of $J_{\text{H-P}} = 19\text{ Hz}$ has been reported for $\text{ReCl}(\text{H}_2)(\text{PMePh}_2)_4$.⁵⁶

1. H-D Coupling

It has often proven quite difficult in the absence of diffraction data to definitively establish the presence of the intact H_2 ligand. A very useful experiment that was first employed by Kubas is the partial substitution of deuterium in the H_2 ligand, which allows the direct measurement of the coupling between hydrogen and deuterium. Since $J_{\text{H-D}}$ in H-D gas is 43.2 Hz ,²⁹ the observation by Kubas of $J_{\text{H-D}} = 33.5\text{ Hz}$ in $\text{W}(\text{CO})_3(\text{P-}i\text{-Pr}_3)_2(\text{HD})$ was taken as evidence of the intact dihydrogen ligand. It is important to keep in mind that the alternative dihydride form is presumed to have a very small H-D coupling. This assumption is based on the expectation that proton-proton couplings in metal dihydrides are typically less than 20 Hz , so the corresponding values of $J_{\text{H-D}}$ would be at most $2\text{--}3\text{ Hz}$. While this assumption seems reasonable, it should be pointed out that there is in fact very little data on H-H couplings in metal hydride complexes (vide infra).

The measurement of $J_{\text{H-D}}$ values has proven to be a very important characterization tool, with over 65 values reported to date in a wide variety of complexes. The range of values reported up to 1991 was 11 to 34 Hz . In 1991 a very interesting series of osmium complexes of the form $\text{trans-}[\text{Os}(\text{NH}_3)_4(\text{L})(\text{HD})]^{+2}$ were reported by Taube and Li.⁴⁸ For a variety of ligands L, a wide range of values for $J_{\text{H-D}}$ were reported, including some extraordinarily low values of the coupling. For example, with $\text{L} = \text{H}_2\text{O}$, $J_{\text{H-D}} = 8.1\text{ Hz}$ and for $\text{L} = \text{acetone}$, $J_{\text{H-D}} = 4.0\text{ Hz}$. While the exact structure of these complexes is not known at this time, it is tempting to speculate that they may exhibit a range of fairly long H-H distances, depending on the ancillary ligands.

In related work, Morris and co-workers have studied the cationic osmium complex $\text{trans-}[\text{Os}(\text{H}_2)\text{H}(\text{depe})_2]^+$, which exhibits $J_{\text{H-D}} = 11.5\text{ Hz}$.⁶⁶ This value was derived from careful analysis of low-temperature NMR data. This coupling shows an unprecedented temperature and solvent dependence, which is consistent with a rapid equilibrium between a dihydrogen/hydride tautomer and a trihydride tautomer. Importantly, H-D coupling was retained at high temperatures, where site exchange is very rapid. Similar retention of H-D coupling at high temperatures in $[\text{Fe}\{\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3(\text{H}_2)\text{H}\}]^+$ has been reported by Field and co-workers.⁷⁰ These two observations are the only examples reported to date of what might be expected to be a fairly general phenomenon. In fluxional polyhydrides thought to contain a dihydrogen ligand, some residual H-D coupling should be observed at the high-temperature limit. Well-resolved NMR spectra will be required for detection of this coupling, since the couplings will not in general be very large.

2. Relaxation Time Measurements

In 1985 Crabtree and Lavin reported that the broadness of the NMR resonances due to bound H_2 was largely attributable to rapid dipole-dipole relaxation (short T_1)³⁵ The rapid relaxation is due to the short H-H distance in the bound H_2 ligand. Since dipole-dipole relaxation is proportional to the inverse sixth power of the internuclear distance, the measurement of T_1 values could in principle allow the definitive detection of dihydrogen complexes by a simple solution NMR method. The observation of short T_1 values is particularly useful in diagnosing the presence of H_2 ligands in fluxional polyhydride complexes, where J_{H-D} is generally not observable. An example of this situation is provided by a study of the protonation of $Ir(PCy_3)_2H_5$, which affords a cationic species of the empirical formula $Ir(PCy_3)_2H_6^+$. It was proposed by Crabtree and co-workers⁷⁹ that the short T_1 measured for the hydride protons in this molecule was due to the presence of bound dihydrogen.

Subsequently Crabtree and Hamilton developed a quantitative treatment of this problem which allows the H-H distance in the coordinated H_2 ligand to be extracted from T_1 measurements.⁷⁸ Due to the temperature dependence of the relaxation process, the method requires that data be collected over a range of temperatures so that the maximum rate of relaxation ($T_1(\text{min})$) can be determined. It is important to note that this approach assumes that H-H relaxation is the dominant relaxation mechanism.

Subsequent investigations by Morris and co-workers showed that the rapid rotation of the dihydrogen ligand has the effect of reducing the relaxation rate and must also be taken into account in the analysis of T_1 data. It was also noted by Morris that there is a significant contribution to the rate of relaxation by the ortho hydrogen atoms of adjacent arylphosphine ligands. This was established by ligand deuteration studies on the cationic complex $[Fe(H_2)(H)(dppe)_2]^+$.¹³⁰

Since relatively little precise structural data was available, it remained difficult to assess the validity of the T_1 method in the detection of H_2 complexes. Some reservations were expressed by Pregosin,¹³¹ and by Cotton,¹³² and a significant discrepancy was reported when Howard and co-workers determined the structure of (diphos)ReH₇ by neutron diffraction.¹³³ It was found that the closest H-H contact is 1.77 Å. On the basis of T_1 values, this complex had been formulated by Crabtree as (diphos)Re(H_2)(H_5). Subsequent work by Albertin⁴¹ demonstrated that very short T_1 values are found for cobalt monohydride complexes and that there was very little change upon protonation. Bakhmutov¹³⁴ suggested that proton-metal dipole-dipole relaxation is a significant contributor to the relaxation rate of cobalt hydride complexes. Crabtree and co-workers reached a similar conclusion regarding polyhydrides of rhenium.¹³⁵

In a very thorough study Halpern and co-workers made a careful analysis of the problem, pointing out the importance of taking into account all sources of relaxation. It was concluded that metals having a high magnetogyric ratio (γ) such as cobalt, rhenium, and manganese can make substantial contributions to relaxation. It is also important to evaluate relaxation by bound ³¹P nuclei and ligand protons. Additionally,

Table IV. Correlation of J_{H-D} with Structural Data

compound	H-H, Å	J_{H-D}	ref
Mo(H_2)(CO)(dppe)	0.88 (ss NMR); 0.82 (n)	34	127
W(CO) ₃ (P- <i>i</i> -Pr) ₂ (H_2)	0.89 (ss NMR); 0.82 (n)	33.5	127
[FeH(H_2)(dppe) ₂] ⁺	0.82 (n); 0.86 (T_1)	32	57
[RuH(H_2)(dppe)] ⁺	0.89 (T_1)	32.9	130
[RuH(H_2)(dcpe) ₂] ⁺	0.85 (T_1)	31.5	37
[IrH(H_2)(PPh) ₂ (bq)] ⁺	0.94 (ss NMR); 0.82 (T_1)	29.5	127
(H_2)(dppb)Ru(μ -Cl) ₂ RuCl(dppb)	0.85 (T_1)	29.4	96
[CpRu(H_2)(CO)(PCy ₃)] ⁺	0.97 (ss NMR); 0.93 (T_1)s	28	127
Os(OEP)(*Im)(H_2)	0.94 (T_1)	27.5	14
[Cp*Fe(H_2)(dppe)] ⁺	0.98 (T_1)s	27	72
[OsH(H_2)(<i>meso</i> -tetrachos)] ⁺	0.95 (T_1)	26	66
[OsH(H_2)(dppe)] ⁺	1.0 (T_1)	25.5	66
[CpRu(H_2)(dmpe)] ⁺	1.02 (ss NMR)	22	127
[CpRu(H_2)(dppm)] ⁺	1.01 (x)	21.9	122
[Cp*Ru(H_2)(dppm)] ⁺	1.1 (T_1)s	20.9	46
[Os(NH ₃) ₄ (H_2)(py)] ⁺²	0.99 (T_1)	19.6	48
[OsH(H_2)(dedppe) ₂] ⁺	1.06 (T_1)	19	66
[Os(NH ₃) ₄ (H_2)(Im)] ⁺²	1.07 (T_1)	17.1	48
[Os(PPh ₃) ₃ (H_2)(OAc)] ⁺	1.00 (T_1)	13.7	101
Os(OEP)(THF)(H_2)	1.18 (T_1)	12	14
[OsH(H_2)(depe) ₂] ⁺	1.2 (T_1)	11	66
[Os(NH ₃) ₄ (H_2)(D ₂ O)] ⁺²	1.11 (T_1)	8.1	48
[Os(en) ₂ (H_2)Cl] ⁺	1.07 (T_1)	7.2	48

^a ss NMR = solid state NMR; n = neutron diffraction; x = X-ray diffraction; T_1 = calculated from T_1 (min) data; (T_1)s = T_1 data interpreted in slow motion regime.

in polyhydride complexes, *all* hydride-hydride interactions must be considered.¹³⁶ An important conclusion of this study is that while a relaxation rate can be accurately calculated from a known structure, the converse is not necessarily true for polyhydride complexes.

3. Correlation of H-H distance with J_{H-D}

It seems reasonable that there should be an inverse relationship between the H-H distance in a hydrogen complex and the observed value of J_{H-D} observed for the H-D complex. As the H-H bond is lengthened by stronger interactions with the metal, the coupling between the two nuclei should be reduced. Early efforts by Morris to establish such a correlation based on molecules of the type $[M(\text{diphosphine})_2(H_2)H]^+$ using distances derived from T_1 measurements were inconclusive.¹³⁰ We have now tabulated data for 23 compounds where J_{H-D} is known and some structural information is available (Table IV). The H-H distance has been reported by neutron diffraction and/or solid-state NMR for six of these complexes. One X-ray structure was included. For the remaining complexes, the H-H distances were calculated from the reported value of T_1 (min). Fast rotation of the H_2 ligand was assumed except for complexes of the form $[CpM(L)(L')(H_2)]^+$ ($M = Fe, Ru$). Recent work by Morris and co-workers indicates that these molecules are likely in the slow rotation regime.⁶⁷ Contributions to relaxation due to adjacent ³¹P nuclei were neglected. Complexes containing rhenium or cobalt were excluded from the group of complexes where T_1 data was employed. A plot of H-H distance as a function of J_{H-D} is shown in Figure 6.¹³⁷ The expected inverse correlation is indeed observed, although there is considerable scatter in the data, particularly for the lower values of J_{H-D} .

A note of caution is appropriate regarding the interpretation of values of J_{H-D} at the low end of the

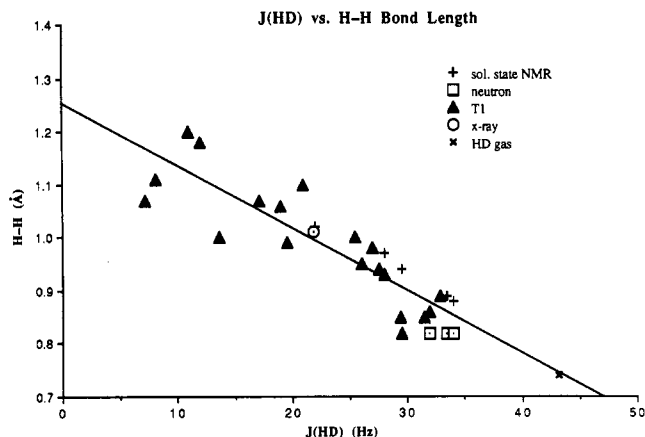


Figure 6. Plot of H-H bond length in angstroms versus J_{HD} in hertz. The symbols are as follows: +, solid-state NMR; □, neutron; ▲, T_1 ; ○, X-ray; ×, H-D gas.

range, since there may be some overlap emerging with couplings that have been previously reported for polyhydride complexes in which no H-H bonding is believed to exist. For example, Davies and co-workers have observed $J_{H-D} = 2.8$ Hz in the partially deuterated trihydride $\text{CpRu}(\text{PPh}_3)\text{H}_2\text{D}$.¹³⁸ This complex is believed to be a normal capped-square-pyramidal trihydride. The hydride ligands are rapidly permuted by a fluxional process, and the observed couplings were reported at the high-temperature limit. After taking into account statistical factors resulting from this exchange, the actual H-D coupling between adjacent hydride sites is 4.2 Hz. (The H-D coupling between nonadjacent or transoid hydrides in complexes of this type is very close to zero, based on observations on cationic iridium analogs.¹³⁹) A similar situation prevails with $\text{Cp}^*\text{Fe}(\text{PMe}_3)\text{H}_2\text{D}$, reported by Bercaw and Paciello¹⁴⁰ to have $J_{H-D} = 4.8$ Hz, corresponding to an H-D coupling between adjacent sites of 7.2 Hz. Thus it appears that *two bond* H-D coupling can be as large as some of the values which have been attributed to *one bond* H-D couplings. An alternative explanation of these moderately large values for J_{H-D} in molecules thought to be normal trihydrides is to invoke a rapid equilibrium with some quantity of a dihydrogen/hydride structure. Such an explanation was advanced by Bercaw to explain the relatively large H-D coupling in $\text{Cp}^*\text{Fe}(\text{PMe}_3)\text{H}_2\text{D}$.

This collection of data demonstrates clearly the broad range of H-H distances that are possible. There has been an interesting evolution in the types of complexes studied as the field has developed since the pioneering work of Kubas. The original Kubas complexes have H-H distances of ca. 0.82 Å, only about 10% longer than free H_2 . Neutron diffraction results show similar distances for two quite disparate iron complexes, $\text{FeH}_2\text{-(H}_2\text{)}(\text{PETPh}_2)_3$ and the cationic $[\text{FeH}(\text{H}_2)(\text{dppe})]^+$. The lack of variation in the H-H bond length despite widely varying oxidation states and ligand environments has been interpreted as evidence that the reaction coordinate for oxidative addition of H_2 is rather flat, leading to a sudden cleavage of the H-H bond late in the reaction sequence. Subsequent developments, particularly in cationic complexes, has extended the range to a current upper limit of ca. 1.1 Å, (solid-state NMR and T_1 data) corresponding to an elongation of 50% versus free H_2 . This effect is quite striking in comparison to

the relatively minor perturbations in bond distances that occur upon side-on binding of other small molecules such as N_2 or ethylene to metal centers. This is perhaps not unreasonable since all (both) of the bonding electrons in H_2 are involved in metal binding and back-donation from filled metal d orbitals into the hydrogen σ^* orbital will also weaken and lengthen the H-H bond. A useful comparison to organic chemistry is to note that a C-C single bond is only ca. 20% longer than a triple bond.

Future work will doubtless establish that there is a smooth continuum of bond distances in these complexes. As additional structural data becomes available, further examples of "intermediate" H-H distances will probably be found in addition to $[\text{ReH}_7\{\text{P}(p\text{-tolyl})_3\}_2]$. No doubt the conclusive characterization of such complexes as dihydrogen or dihydride species will be difficult, a problem which is compounded by the large angular motion of the H_2 ligand.

V. Reactivity of Coordinated Dihydrogen

A. Kinetics and Thermodynamics of H_2 Binding and Displacement

While H_2 displacement is a seemingly trivial reaction, study of this reaction and the reverse, H_2 binding, is important in understanding the basis of the interaction of H_2 with metal centers. Qualitative observations indicate that there is a wide range of lability of the H_2 ligand in various types of complexes. The original tungsten complexes discovered by Kubas are somewhat labile to loss of H_2 and must be crystallized under an H_2 atmosphere. Only hydrocarbon or aromatic solvents may be employed. The molybdenum and chromium analogs are even more labile in solution, and the chromium complex can only be observed under H_2 pressure¹⁴¹ or in the solid state.⁹ In contrast to the relatively weak binding of H_2 in these neutral complexes, some cationic complexes seem to bind hydrogen very strongly. For example, $[\text{CpRu}(\text{dmpe})\text{H}_2]^+$ is indefinitely stable in hot THF and H_2 is displaced only slowly in refluxing acetonitrile. It is important to keep in mind that the lability of a complex toward H_2 loss is not a definitive indicator of a dihydrogen versus dihydride structure. For example, Kubas has reported that the dihydride complex $\text{MoH}_2(\text{CO})(\text{depe})_2$ loses hydrogen slowly under vacuum. There are several examples of confirmed dihydrogen complexes in which the H_2 ligand is much less labile.

Quantitative studies of ligand binding to the prototypical complexes $\text{M}(\text{CO})_3(\text{PR}_3)_2\text{H}_2$ ($\text{M} = \text{Cr}, \text{Mo}$, and W) by calorimetric and equilibrium methods have been carried out by Hoff and coworkers.¹⁴² The bound dihydrogen is readily displaced from the tungsten complex by ligands such as pyridine and $\text{P}(\text{OMe})_3$, but not by THF. The latter observation is believed to be due to steric effects. Enthalpies of binding for H_2 to the metal centers $\text{M}(\text{CO})_3(\text{PCy}_3)_2$ are (in kcal/mol) -10.0 ± 1.0 for $\text{M} = \text{W}$, -6.5 ± 0.2 for $\text{M} = \text{Mo}$, and -7.3 ± 0.1 for $\text{M} = \text{Cr}$. Estimation of absolute bond strengths from this data depends upon the bond strength of the agostic interaction to the cyclohexyl ring which is present in the precursor complexes. An estimate of the strength of this interaction is provided by photoacoustic calorimetry studies of binding of heptane to

$W(CO)_5$, which indicate that the enthalpy of the agostic interaction is ca. 13.4 kcal/mol.¹⁴³ Thus the enthalpy of addition of H_2 to the "naked" $W(CO)_3(PCy_3)_2$ moiety would be about -25 kcal/mol. In related work the enthalpy of binding of H_2 to $Cr(CO)_5$ has been estimated at 17 kcal/mol from the photoacoustic calorimetry measurements of the enthalpy of substitution of $Cr(CO)_6$ with H_2 .¹⁴⁴

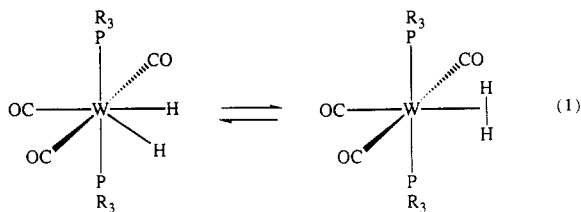
The enthalpy of binding N_2 to $M(CO)_3(PCy_3)_2$ is slightly greater than that for hydrogen, but H_2 binding is favored entropically. Thus the position of the equilibrium in the presence of both H_2 and N_2 varies with temperature. Equal binding of H_2 and N_2 is observed at -69, +28, and +50 °C for Cr, Mo, and W, respectively.

Another example of the importance of entropy effects is provided by recent studies on the binding of water to $W(CO)_3(PCy_3)_2$.¹⁴⁵ While binding of H_2O to the tungsten center is favored enthalpically, the entropy of binding for H_2O is very unfavorable, so the equilibrium favors H_2 binding at room temperature and H_2O binding at low temperature.

There is currently relatively limited thermodynamic data available for hydrogen complexes. The expansion of this data base is very important, and should be a high priority for future investigations.

B. Dihydrogen/Dihydride Interconversion

Several examples of dihydrogen complexes have now been reported where a reversible equilibrium exists between the dihydrogen form and a dihydride form. Such complexes provide a unique opportunity to study the detailed mechanism of oxidative addition of H_2 to metal centers. The first examples of such equilibria were reported by Kubas and co-workers in the tungsten complexes of the form $W(CO)_3(PR_3)_2(H_2)$ ($R = i\text{-Pr}$ and Cy).^{53,7b} A detailed study of the kinetics and thermodynamics of this equilibrium for the tungsten complexes with $R = i\text{-Pr}$ and cyclopentyl has recently been reported.⁵¹

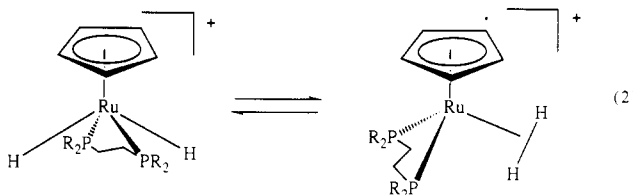


Thermodynamic parameters for the formation of the dihydrogen complex from the dihydride complex with $R = i\text{-Pr}$ are $\Delta H^\circ = -1.2 \pm 0.6$ kcal/mol, $\Delta S^\circ = -1.2 \pm 2.1$ eu, and $\Delta G^\circ = -0.80 \pm 0.12$ kcal/mol (298 K). Similar results were obtained for $R = \text{cyclopentyl}$. These observations demonstrate quantitatively some features of these systems that were qualitatively apparent. In solution, the dihydrogen form predominates at equilibrium, comprising ca. 80% of the mixture, but the dihydride form is only very slightly higher in energy. The small enthalpy of reaction indicates that the sum of the two W-H bonds is very nearly equal to the total of the H_2 binding enthalpy and the remaining H-H interaction. The significance of the small negative entropy of reaction is less clear, since this value has a large uncertainty. It might have been expected that

conversion of the dihydride species to the dihydrogen complex would lead to a slight increase in the entropy of the system since the H_2 ligand is virtually a free rotor. Such a result has been reported for a ruthenium complex (vide infra).

The kinetics of interconversion between the dihydrogen and the dihydride form of $W(CO)_3(PR_3)_2H_2$, $R = i\text{-Pr}$ were also studied by Kubas and co-workers, using spin saturation transfer techniques.⁵¹ The rate constant for oxidative addition of H_2 to produce the dihydride form of the complex is 12.4 s^{-1} at 300 K, corresponding to $\Delta G^\ddagger = 16.0$ kcal/mol. Consistent with the equilibrium data mentioned above, the reductive elimination process to produce the dihydrogen complex is even more rapid, with a rate constant of ca. 63 s^{-1} ($\Delta G^\ddagger = 15.2$ kcal/mol). These results derived from NMR methods are consistent with rates obtained in stopped-flow kinetic studies by Hoff and co-workers on the PCy_3 analog.¹⁴⁶ An important point from the kinetics study by Hoff is that oxidative addition is the rate-determining step in H_2 activation. It was found that hydrogen associates/dissociates on the metal center ca. 10 times before it actually cleaves.

Another example of dihydrogen/dihydride equilibria is provided by cationic ruthenium complexes of the form $[CpRu(R_2PCH_2CH_2PR_2)(H_2)]^+$, which are found to be in reversible equilibrium with the dihydride form.⁴⁵



The thermodynamic parameters for this equilibrium are in general similar to those reported above for the tungsten system, with the exception of the entropy of reaction. In the ruthenium complexes, there is a slight increase in entropy ($\Delta S^\circ = 4.5 \pm 0.3$ eu) in going from the dihydride to the dihydrogen form, consistent with the additional rotational degree of freedom in the hydrogen complex. The rate of approach to equilibrium was found to be significantly slower for the ruthenium system, with a free energy of activation at 300 K of ca. 20 kcal/mol, as measured by spin saturation transfer experiments.

In contrast to the relatively high barriers for rearrangement discussed above, more rapid interconversion is seen in the cationic rhenium complexes $[Cp^*\text{Re}(\text{CO})(\text{NO})(H_2)]^+ / [Cp^*\text{Re}(\text{CO})(\text{NO})H_2]^+$, (93:7 mixture of isomers) where $\Delta G^\ddagger = 10.2$ kcal/mol has been reported.⁴⁴ Another pair of cationic rhenium complexes, $[Re(\text{CO})_2(\text{PMe}_2\text{Ph})_3(H_2)]^+ / [Re(\text{CO})_2(\text{PMe}_2\text{Ph})_3H_2]^+$ has been recently reported by Crabtree and co-workers.⁸⁶ The complexes lose hydrogen irreversibly above 233 K, but the thermodynamics and kinetics of the isomerization were successfully studied at lower temperatures. The dihydride form is predominant at low temperature (183 K), but increasing amounts of the dihydrogen form are observed as the temperature is increased to 218 K, consistent with the reported values of $\Delta H = 1.7 \pm 0.4$ kcal/mol, and $\Delta S = 8 \pm 3$ eu for the dihydride to dihydrogen interconversion. The free energy of activation is 11.5 ± 0.3 kcal/mol at 223 K.

All of the examples mentioned above involve significant rearrangement of ancillary ligands to achieve the dihydride/dihydrogen interconversion. Although in none of these cases is the structure of the dihydride form known, presumably the two hydride ligands are relatively well separated. Complexes where less substantial rearrangements are required should have lower barriers to reaction. Some evidence that this may be the case is provided by the work of Bianchini and co-workers on the cationic cobalt group complexes of the form [(tetraphos)MH₂]⁺ (M = Co, Rh, and Ir). While the iridium complex is apparently a dihydride and the Co complex is thought to be a hydrogen complex,⁷⁵ the rhodium complex is reported to exist as a temperature-dependent mixture of the two forms.⁷⁶ No quantitative data is available regarding the thermodynamics and kinetics of this equilibrium, and further study is certainly indicated for these very interesting complexes.

Other data available regarding this problem is provided by the work of Morris and co-workers⁶⁶ on *trans*-[Os(H₂)H(depe)₂]⁺, which was briefly mentioned above. In this case, a long H-H bond is indicated by relaxation data and J_{H-D} , and the temperature dependence of J_{H-D} is consistent with a rapid equilibrium with a trihydride tautomer.

An additional aspect of the dihydride/dihydrogen interconversion problem which is important when the two forms are close in energy is that differences in solid-state and solution structure are often noted. In the solid state, diffraction methods have clearly demonstrated that W(CO)₃(P-*i*-Pr)₃(H₂) is entirely in the dihydrogen form. In solution an equilibrium mixture consisting of ca. 20% dihydride is observed. Similarly, [CpRu(dmpe)(H₂)]⁺ is in equilibrium with [CpRu(dmpe)H₂]⁺ in solution with the dihydrogen form predominant. From this mixture the dihydrogen form crystallizes exclusively, as shown by low temperature dissolution and subsequent examination by NMR at low temperature.⁴³ A very interesting example of this structural dichotomy has been recently reported by Bianchini and co-workers, who reported that the nature of the counterion used to crystallize a cationic cobalt complex influences the structure observed. Thus the dihydrogen complex [(tetraphos-II)Co(H₂)]⁺ was obtained as the PF₆⁻ salt, while the dihydride complex [(tetraphos-II)Co(H₂)]⁺ results when the counterion is BPh₄⁻.¹⁴⁷

In summary, there seems to be a wide variation in the position of the dihydrogen/dihydride equilibrium and in the rates of interconversion, depending on the nature of the metal and ligand set employed. At this stage relatively little quantitative data is available, and this area is certainly one that is deserving of further study.

C. Acidity of Coordinated Dihydrogen

The above section dealing with cleavage of bound H₂ to give dihydride species can be likened to homolytic cleavage of the H-H bond, a process analogous to the well-known oxidative addition reaction. Heterolytic cleavage of H₂ is also well known, but is normally achieved only by very strong bases, since H₂ is a very weak acid. The reported pK_a of H₂ in THF is 35.¹⁴⁸ When hydrogen is coordinated in a metal complex, particularly to a cationic metal center, H₂ can be

dramatically activated with respect to heterolysis. This possibility was first realized by Crabtree and Lavin, who demonstrated using isotope labeling experiments that the H₂ ligand in [Ir(PPh₃)₂(bq)(η^2 -H₂)H]⁺ is deprotonated by alkyl lithium reagents in preference to the hydride ligand.¹¹ Deprotonation of bound H₂ in [CpRu(dmpe)(H₂)]⁺/[CpRu(dmpe)H₂]⁺ by the mild base NEt₃ was demonstrated by Chinn and Heinekey.⁴³ The observed pK_a is 17.6 (acetonitrile). In this system, both the dihydride and dihydrogen form of the complex are present in equilibrium, but the dihydrogen form is found by spin saturation transfer experiments to be deprotonated more rapidly, demonstrating the greater kinetic acidity of the dihydrogen form. A consequence of this observation and the principle of microscopic reversibility is that the reverse reaction, protonation of the neutral hydride, must give as the initial kinetic product only the dihydrogen complex. Subsequent isomerization establishes the equilibrium mixture of dihydride and dihydrogen complexes. This behavior has in fact been observed for a number of ruthenium complexes of this type.⁴⁵

As pointed out by Norton,¹⁴⁹ the assessment of thermodynamic acidities of the species present at equilibrium must take into account the equilibrium constant of the system. The CpRu(dmpe)H₂⁺ system exists in an 84:14 ratio of the dihydrogen to dihydride form, respectively. Thus the pK_a of the dihydride complex [CpRu(dmpe)H₂]⁺ is 16.8, and it is a thermodynamically stronger acid than the dihydrogen form [CpRu(dmpe)(H₂)]⁺, (pK_a = 17.6).

The range of pK_a values for ruthenium complexes of the type [CpRu(L)₂(H₂)]⁺ (L = various phosphines) and several Cp* analogs has been greatly extended by Morris and co-workers using a variety of bases in methylene chloride or THF as solvent. A range of pK_a values from 4.6 to 16.3 (THF) has been reported, which show the expected correlation to the donor abilities of the ligand set.⁶⁷

In light of the above results, it is anticipated that coordination of H₂ to a less electron-rich metal center should lead to a very substantial activation to heterolysis. This has been demonstrated in the case of [Cp*Re(CO)(NO)(H₂)]⁺ and [Cp*Ru(CO)₂(H₂)]⁺. These complexes are deprotonated by diethyl ether and have estimated pK_a values of ca. -2.⁴⁴ These results demonstrate that binding of H₂ to formally 16-electron cationic metal centers which are strong Lewis acids can dramatically increase the propensity for heterolytic cleavage.

In the case of neutral complexes, there is also evidence for deprotonation of bound H₂. Collman and co-workers have observed this reaction for (OEP)Ru(THF)(H₂), which is deprotonated by strong bases such as KOH.¹⁴ This reaction is a key step in the action of this ruthenium complex as a catalyst for isotope exchange between hydrogen and water. The neutral FeH₂(H₂)(PEtPh₂)₃ and W(CO)₃(PCy₃)₂(H₂) complexes can also be deprotonated¹⁵⁰ as evidenced by their reactions with [Cu(O-*t*-Bu)(PEtPh₂)₂]₂ to form the mixed metal dimers, (PEtPh₂)₃FeH₃Cu(PEtPh₂) and (PCy₃)₂(CO)₃WHCu(PEtPh₂), respectively, along with HO-*t*-Bu.

Similar isotope exchange reactions between H₂O and D₂ have been recently reported by Kubas to occur slowly in solutions of W(CO)₃(P-*i*-Pr)₃(D₂) in the presence of

H₂O. After careful study of this and the related catalysis of isotope exchange between H₂ and D₂ to form HD it was concluded that deprotonation of bound H₂ in these complexes was unlikely to be involved.¹⁴⁵ The precise mechanism of these isotope exchange reactions, which seem to occur at metal complexes having only one ligand binding site, remains unclear at this time. Isotope exchange reactions between gaseous hydrogen and alcohols mediated by cationic metal dihydrogen complexes have recently been reported by Albinez and co-workers.¹⁵¹

The scope and utility of the heterolytic activation of hydrogen has barely been explored at this point. There are myriad possibilities for research in this area. For example, an efficient, water-soluble catalyst for the isotopic equilibration of hydrogen and water could be useful in production of heavy water and the detritiation of contaminated water from reactors.

D. Hydrogenation and Reduction Reactions

Several dihydrogen complexes have been reported to hydrogenate various olefins and ketones. For example Bianchini and co-workers found that [(tetraphos-II)Rh(H₂)]⁺ hydrogenates dimethyl maleate. Some isomerization of the olefin (to dimethyl fumarate) was also noted. The cobalt analog gave exclusively isomerization of the same substrate. A possible mechanism to explain these results involving initial protonation of the olefin followed by hydride transfer was suggested.⁷⁵

Caulton and co-workers have reported that [IrH₄P₃]BF₄ (P = PMe₂Ph), which is believed to contain a dihydrogen ligand, reacts readily with 2-butyne to afford a *cis*-2-butene complex, [Ir(MeC₂Me)P₃]BF₄, together with some *cis*-2-butene and 1-butene. Reaction of the butene complex with H₂ affords butane and regenerates the starting iridium complex.¹⁵² The mechanism of this hydrogenation reaction is not known.

In a detailed study of the photochemistry of group 6 metal carbonyl derivatives carried out in liquid xenon, Poliakoff and co-workers have found that *trans*-(C₂H₄)M(CO)₄ and (NBD)M(CO)₄ (M = Cr, Mo and W; NBD = norbornadiene) react with H₂ under photolysis conditions.²⁸ The products are dihydrogen complexes, such as *fac*-(NBD)Cr(CO)₃(H₂), which gives hydrogenation of norbornadiene to nortricyclene upon warming. Deuteration experiments are consistent with an intramolecular transfer of hydrogen to the bound norbornadiene. In contrast, *mer*-(NBD)Mo(CO)₃(H₂) affords norbornene upon warming, again by a stereospecific intramolecular reaction.

Hydrogenation of acetone to 2-propanol is effected by [Os(NH₃)₅(H₂)]³⁺.⁷⁷ The trication was generated by chemical or electrochemical oxidation of the corresponding dication, which is a known dihydrogen complex. The dication itself does not reduce acetone. Separate experiments using cyclic voltammetry indicate that the pK_a of the trication species is quite low, so the apparent hydrogenation may proceed via proton transfer followed by hydride transfer, as was suggested by Bianchini for the reduction of dimethyl maleate mentioned above.

VI. Future Perspectives

The study of hydrogen complexes has developed very rapidly since the pioneering work of Greg Kubas. What

is superficially the simplest molecule in chemistry is now proving to have a rich coordination chemistry. Synthesis of new complexes has been advanced rapidly by a large number of research groups. The challenging problems of characterization have largely been solved although more structural data is clearly needed, particularly on complexes believed to have long H-H distances. The rich dynamics and quantum mechanical effects exhibited by bound hydrogen will continue to pose fundamentally interesting problems for physical chemists and may provide important insights relevant to catalysis by metal surfaces. As is the case with other small molecules, binding of hydrogen to metals dramatically alters its reactivity, and exploration of these reactivity patterns promises to be a fruitful area of study.

Since hydrogen is now well established as a ligand, it is tempting to speculate that polyhydrogen species may be stabilized by coordination to metals. Theory suggests that H₃ complexes may be possible,¹⁵³ and recent experimental work by Crabtree and co-workers provides compelling evidence for the intermediacy of an H₃ complex in a facile tautomerization reaction of a rhenium complex.⁸⁴ The possible synthesis of an H₃ complex as a ground-state structure is an exciting prospect.

Acknowledgements

The open exchange of ideas and results in the dihydrogen community is an important part of this rapidly developing area. In particular D.M.H. thanks Greg Kubas, Ken Caulton, Bob Crabtree, Kurt Zilm, Bob Morris, and Bruno Chaudret for many helpful discussions. We thank the Petroleum Research Foundation, administered by the American Chemical Society, for support of this work.

VII. Abbreviations

binap	(<i>R</i>)- or (<i>S</i>)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
bq	7,8-benzoquinolato
Cp	cyclopentadienide anion
Cp*	pentamethylcyclopentadienide anion
COE	cyclooctene
Cyttp	PPh(CH ₂ CH ₂ PCy ₂) ₂
Cyp	cyclopentyl
dape	(P(<i>p</i> -C ₆ H ₄ OMe) ₂)CH ₂ CH ₂ (P(<i>p</i> -C ₆ H ₄ -OMe) ₂)
dcpe	1,2-bis(dicyclohexylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
dedppe	1-(diethylphosphino)-2-(diphenylphosphino)ethane
d(<i>i</i> -Pr)pe	1,2-bis(diisopropylphosphino)ethane
diop	(<i>R,R</i>)-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane
diphyH	2-(Ph)-6-(<i>o</i> -C ₆ H ₄)(C ₅ H ₃ N)
ditolpyH	2-(<i>p</i> -tol)-6- <i>o</i> -[<i>p</i> -C ₆ H ₃ (CH ₃)]C ₅ H ₃ N
dmpe	1,2-bis(dimethylphosphino)ethane
dmdppe	1-(dimethylphosphino)-2-(diphenylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
dppb	1,4-bis(diphenylphosphino)butane
DPB	diporphyrinatobiphenylene tetraanion
dtfpe	(P(<i>p</i> -C ₆ H ₄ CF ₃) ₂)CH ₂ CH ₂ (P(<i>p</i> -C ₆ H ₄ -CF ₃) ₂)

HB(3,5Me ₂ pz) ₃	tris(3,5-dimethylpyrazolyl)borate
*Im	3-tert-butyl-4-phenylimidazole
THF	tetrahydrofuran
TMS	tetramethylsilane
OEP	octaethylporphyrin
(R)-prophos	(R)-PPh ₃ CH(Me)CH ₂ PPh ₂
py	pyridine
(P-N)	Fe(η-C ₅ H ₅ (CHMeNMe ₂)P(i-Pr) ₂ -1,2)(η-C ₅ H ₅)
tetraphos-I	(C ₆ H ₅) ₂ P(CH ₂ CH ₂ P(C ₆ H ₅)) ₂ CH ₂ CH ₂ P(C ₆ H ₅) ₂
tetraphos-II	tris[2-(diphenylphosphino)ethyl]phosphine
triphos	PPh(CH ₂ CH ₂ PPh ₂) ₂

VIII. References

- James, B. R. *Homogeneous Hydrogenation*: Wiley: New York, 1973.
- Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452.
- Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17-40.
- Crabtree, R. H. *Inorg. Chim. Acta* **1986**, *125*, L7-L8.
- Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120-128. Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299-339. Henderson, R. A. *Transition Met. Chem.* **1988**, *13*, 474-480. Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95-101. Crabtree, R. H.; Luo, X.; Michos, D. *Chemtracts-Inorg. Chem.* **1991**, *3*, 245-252. Kubas, G. J. *J. Less-Common Met.* **1991**, *172-174*, 475-484.
- Morris, J. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155-289.
- (a) Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 61-62. (b) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000-7009. (c) Kubas, G. J. *Inorg. Synth.* **1991**, *27*, 1-8.
- Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294-2301.
- Eckert, J.; Kubas, G. J.; White, R. P. *Inorg. Chem.* **1992**, *31*, 1550-1551.
- Zhang, K.; Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Hoff, C. D.; Kubat-Martin, K. A.; Barnhart, D.; Kubas, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 9170-9176.
- Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794-795.
- Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780-3782.
- Collman, J. P.; Hutchison, J. E.; Wagenknecht, P. S.; Lewis, N. S.; Lopez, M. A.; Guillard, R. *J. Am. Chem. Soc.* **1990**, *112*, 8206-8208.
- Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; Lopez, M. A.; Guillard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654-5664.
- Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374-2379.
- Upmacis, R. K.; Gadd, G. E.; Poliakov, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27-30.
- Upmacis, R. K.; Poliakov, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645-3651.
- Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30-32.
- Sweany, R. L. *Organometallics* **1986**, *5*, 387-388.
- Sweany, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 6986-6991.
- Howdle, S. M.; Poliakov, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1099-1101.
- Haward, M. T.; George, M. W.; Howdle, S. M.; Poliakov, M. *J. Chem. Soc., Chem. Commun.* **1990**, 913-915.
- Haward, M. T.; George, M. W.; Hamley, P.; Poliakov, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1101-1103.
- Ozin, G. A.; Garcia-Prieto, J. *J. Am. Chem. Soc.* **1986**, *108*, 3099-3100.
- Jackson, S. A.; Upmacis, R. K.; Poliakov, M.; Turner, J. J.; Burdett, J. K.; Grevels, F.-W. *J. Chem. Soc., Chem. Commun.* **1987**, 678-680.
- Howdle, S. M.; Healy, M. A.; Poliakov, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804-4813.
- Johnson, F. P. A.; George, M. W.; Bagratashvili, V. N.; Vereshchagina, L. N.; Poliakov, M. *Mendeleev Commun.* **1991**, *1*, 26-28.
- Jackson, S. A.; Hodges, P. M.; Poliakov, M.; Turner, J. J.; Grevels, F.-W. *J. Am. Chem. Soc.* **1990**, *112*, 1221-1233.
- Bloyce, P. E.; Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1988**, 846-848.
- Gadd, G. E.; Upmacis, R. K.; Poliakov, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547-2552.
- Sweany, R. L.; Russell, F. N. *Organometallics* **1988**, *7*, 719-727.
- Sweany, R. L.; Polito, M. A.; Moroz, A. *Organometallics* **1989**, *8*, 2305-2308.
- Plitt, H. S.; Bär, M. R.; Ahlrichs, R.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 832-834.
- Xiao, Z. L.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* **1992**, *96*, 636-644.
- Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661-1662.
- Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581-5582.
- Mezzetti, A.; Del Zotto, A.; Rigo, P.; Farnetti, E. *J. Chem. Soc., Dalton Trans.* **1991**, 1525-1530.
- Saburi, M.; Aoyagi, K.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1990**, 601-604.
- Saburi, M.; Aoyagi, K.; Takeuchi, H.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1990**, 991-994.
- Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072-2077.
- Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229-230.
- Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506-507.
- Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865-5867.
- Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824-1826.
- Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166-5175.
- Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875-883.
- Collman, J. P.; Wagenknecht, P. S.; Hembre, R. T.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 1294-1295.
- Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946-8947.
- Cotton, F. A.; Luck, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1277-1278.
- Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.; Kai, Z.; Hoff, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 4419-4421.
- Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855-3860.
- Crocker, L. S.; Heinekey, D. M. Unpublished results.
- Kubas, G. J.; Ryan, R. R.; Wroblewski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339-1341.
- Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569-581.
- Perthuisot, C.; Fan, M.; Jones, W. D. *Organometallics* **1992**, *11*, 3622-3629.
- Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1991**, *30*, 767-774.
- Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823-8827.
- Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124-1126.
- Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546-548.
- Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4056-4057.
- Tsukahara, T.; Kawano, H.; Ishii, Y.; Takahashi, T.; Saburi, M.; Uchida, Y.; Akutagawa, S. *Chem. Lett.* **1988**, 2055-2058.
- Amendola, P.; Antoniutti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318-324.
- Cappellani, E. P.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Steele, M. R. *Inorg. Chem.* **1989**, *28*, 4437-4438.
- Michos, D.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4245-4250.
- Earl, K. A.; Morris, R. H.; Sawyer, J. F. *Acta Crystallogr.* **1989**, *C45*, 1137-1139.
- Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027-3039.
- Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161-171.
- Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19-C22.
- Bianchini, C.; Peruzzini, M.; Polo, A.; Vacca, A.; Zanobini, F. *Gazz. Chim. Ital.* **1991**, *121*, 543-549.
- Bamos, N.; Field, L. D. *Inorg. Chem.* **1990**, *29*, 587-588.
- Bianchini, C.; Perez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279-287.
- Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429-1431.
- Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675-1676.
- Jia, G.; Morris, R. H.; Schweitzer, C. T. *Inorg. Chem.* **1991**, *30*, 593-594.
- Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725-8726.
- Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548-5549.
- Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261-2263.
- Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126-4133.
- Crabtree, R. H.; Lavin, M.; Bonnevot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032-4037.

- (80) Albéniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 242–249.
- (81) Henderson, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1670–1672.
- (82) Oglieve, K. E.; Henderson, R. A. *J. Chem. Soc., Chem. Commun.* **1992**, 441–443.
- (83) Luo, X.-L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 189–190.
- (84) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912–6918.
- (85) Kim, Y.; Deng, H.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798–2800.
- (86) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Organometallics* **1992**, *11*, 237–241.
- (87) Fontaine, X. L. R.; Fowles, E. H.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1988**, 482–483.
- (88) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124–3125.
- (89) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Kowitz, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831–4841.
- (90) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598–599.
- (91) Jia, G.; Meek, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 757–758.
- (92) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314–2316.
- (93) Arliguie, T.; Chaudret, B. *J. Chem. Soc., Chem. Commun.* **1989**, 155–157.
- (94) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1–2.
- (95) Hampton, C.; Dekleva, T. W.; James, B. R.; Cullen, W. R. *Inorg. Chim. Acta* **1988**, *145*, 165–166.
- (96) Joshi, A. M.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1785–1786.
- (97) Hampton, C.; Cullen, W. R.; James, B. R. *J. Am. Chem. Soc.* **1988**, *110*, 6918–6919.
- (98) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563–1564.
- (99) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431–7437.
- (100) Johnson, T. J.; Huffman, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073–2074.
- (101) Siedle, A. R.; Newmark, R. A.; Korba, G. A.; Pignolet, L. H.; Boyle, P. D. *Inorg. Chem.* **1988**, *27*, 1593–1598.
- (102) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1991**, *10*, 462–466.
- (103) Bucher, U. E.; Lengweiler, T.; Nanz, D.; von Philipsborn, W.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 548–549.
- (104) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165–1167.
- (105) Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 855–863.
- (106) Gusev, D. G.; Bakhmutov, V. I.; Gruchin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *175*, 115–120.
- (107) Mediat, M.; Tachibana, G. N.; Jensen, C. M. *Inorg. Chem.* **1992**, *31*, 1827–1832.
- (108) Nolan, S. P.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8538–8540.
- (109) Saillard, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.
- (110) (a) Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466–469. (b) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705–710. (c) Jean, Y.; Lledos, A.; Maouche, B.; Aiad, R. *J. Chim. Phys.* **1987**, *84*, 806–808. (d) Volatron, F.; Jean, Y.; Lledos, A. *New J. Chem.* **1987**, *11*, 651–656.
- (111) Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324–2332.
- (112) (a) Maseras, F.; Duran, M.; Lledós, A.; Bertrán, J. *J. Am. Chem. Soc.* **1991**, *113*, 2879–2884. (b) Riegl, J.-F.; Péliissier, M.; Eisenstein, O. *J. Am. Chem. Soc.* **1992**, *31*, 3344–3345.
- (113) (a) Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1990**, *112*, 7203–7207. (b) Jackson, S. A.; Eisenstein, O. *Inorg. Chem.* **1990**, *29*, 3910–3914.
- (114) Maseras, F.; Duran, M.; Lledós, A.; Bertrán, J. *J. Am. Chem. Soc.* **1992**, *31*, 2922–2928.
- (115) Haynes, G. R.; Martin, R. L.; Hay, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 28–36.
- (116) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 6102–6108.
- (117) Lin, Z.; Hall, M. B. *Inorg. Chem.* **1992**, *31*, 4262–4265.
- (118) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 2928–2932.
- (119) Lin, Z.; Hall, M. B. *Organometallics* **1992**, *11*, 3801–3804.
- (120) Kubas, G. J.; Ryan, R. R. *Polyhedron* **1986**, *5*, 473–485.
- (121) Brammer, L.; Howard, A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 241–243.
- (122) Litster, S. J.; Redhouse, A. D.; Simpson, S. J. *Proceedings of the Conference Chemistry of the Platinum Group Metals*; Cambridge University, 1990; C-48.
- (123) Farrar, D. H.; Maltby, P. A.; Morris, R. H. *Acta Crystallogr.* **1992**, *C48*, 28–31.
- (124) Mediat, M.; Tachibana, G. N.; Jensen, C. M. *Inorg. Chem.* **1990**, *29*, 3–5.
- (125) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930–2933.
- (126) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837–7839.
- (127) Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163–200.
- (128) Eckert, J. *Spectrochim. Acta* **1992**, *48A*, 363–378.
- (129) Nageswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112.
- (130) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031–7036.
- (131) Ammann, C.; Isaia, F.; Pregosin, P. S. *Magn. Reson. Chem.* **1988**, *26*, 236–238.
- (132) Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 43–47.
- (133) 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**, 1502–1503.
- (134) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1991**, *30*, 3116–3118.
- (135) Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Magn. Reson. Chem.* **1991**, *29*, S89–S93.
- (136) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173–4184.
- (137) A similar figure with 13 compounds has appeared previously in ref 66.
- (138) Baird, G. J.; Davies, S. G.; Moon, S. D.; Simpson, S. J.; Jones, R. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1479–1486.
- (139) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909–919.
- (140) Paciello, R.; Manriquez, J. M.; Bercaw, J. E. *Organometallics* **1990**, *9*, 260–265.
- (141) Millar, J. M.; Kastrop, R. V.; Nelchior, M. T.; Horváth, I. T.; Hoff, C. D.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 9643–9645.
- (142) Gonzalez, A. A.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Khalsa, G. R. K.; Kubas, G. J. *ACS Symp. Ser.* **1990**, *428*, 133 and references therein.
- (143) Morse, J. M.; Parker, G. H.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471–2474.
- (144) Nayak, S. K.; Burkey, T. J. *Book of Abstracts*, 204th National Meeting of the American Chemical Society, Washington, DC, Fall 1992; American Chemical Society: Washington, DC, 1992; Abstract Inorganic Division no. 48.
- (145) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390–3404.
- (146) Zhang, K.; Gonzalez, A. A.; Hoff, C. D. *J. Am. Chem. Soc.* **1989**, *111*, 3627–3632.
- (147) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1992**, *114*, 5905–5906.
- (148) Buncel, E.; Menon, B. *J. Am. Chem. Soc.* **1977**, *99*, 4457–4461.
- (149) Kristjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydride: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1991; Chapter 9.
- (150) Van Der Sluys, L. S.; Miller, M. M.; Kubas, G. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 2513–2520.
- (151) Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632–3635.
- (152) Marinelli, G.; Rachidi, I. E.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 2346–2347.
- (153) (a) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakov, M.; Turner, J. J. *Inorg. Chem.* **1987**, *26*, 3054–3063. (b) Burdett, J. K.; Pourian, M. R. *Organometallics* **1987**, *6*, 1684–1691.