3d orbitals of Co(III), a conjecture unsupported by any other evidence of which we are aware. The dynamic quadrupolar relaxation mechanism mentioned above may provide an explanation for some of the line width observations. Hydrogen bonding is a very rapid dynamic effect and might contribute in this way to the relaxation. Also, rotation of the imidazole ligands about the cobalt–nitrogen bond axis could cause a dynamic relaxation; apparently the potential barrier to such rotation is small.[60] These effects, as well as other puzzling ^{59}Co line width effects involving other substituted porphyrin and imidazole ligands[61] merit further investigation.

Acknowledgment. We are grateful to the National Institutes of Health for supporting the research (Grant no. DK30145), to Brown University for an University Fellowship to C.M.S., to Dr. James Van Epp for NMR technical assistance, to Dr. John Mitchell for line width data at 2.114 T, and to Drs. Paul O'Brien, Luigi Cassidei, Philip Rieger, and W. Robert Scheidt for helpful discussions.

Supplementary Material Available: Tables giving the influence of temperature on ^{59}Co NMR and the experimental conditions for ^{59}Co NMR studies of $[Co(TP_xP)(RIm)_2]BF_4$ and substituent effects on ^{59}Co chemical shifts and ^{59}Co line widths (4 pages). Ordering information is given on any current masthead page.

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Estimation of the H–H Distances of η^2-Dihydrogen Ligands in the Complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(PR_2CH_2CH_2PR_2)_2]^+$ [M = Fe, Ru, R = Ph; M = Os, R = Et] by Solution NMR Methods

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Abstract: The spin–lattice relaxation times, T_1, of the dihydrogen and hydride ligands in the complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(PR_2CH_2CH_2PR_2)_2]^+$ [M = Fe, Ru, R = Ph; M = Fe, R = C_6D_5; M = Os, R = Et] have been measured as a function of temperature by the ^{1}H NMR inversion–recovery method. The equations for dipolar relaxation fit the data fairly well, and from them the correlation time parameter τ_0 and the activation energy parameter E_a are obtained for the equation $\tau_H = \tau_0 e^{E_a/RT}$ where τ_H is the correlation time of the hydride ligand. It is necessary to take into account that the T_1 values average once intramolecular exchange occurs between the H and H_2 hydrogens. Reasonable H–H distances for the H_2 ligands are obtained if Woessner's relaxation equation is used, which applies for the case when the correlation time of this ligand is much shorter than that of the terminal hydride because of rapid rotation about the M–H_2 bond: for the Fe complex, 0.86 ± 0.02 Å; for Ru, 0.89 ± 0.02 Å; and for Os, 1.12 ± 0.03 Å. For the Os complex it is not possible to rule out the possibility that there is restricted rotation of the H_2 ligand because of a strong Os–H_2 interaction; in this case the H–H distance could be as long as 1.40 Å. Tunneling of H atoms between sites of approximately C_{4v} symmetry could also account for the internal motion. Calculated T_2 values do not account for breadth of the H_2 resonances in some cases.

Crabtree and Hamilton[1] have recently described how T_1 measurements can be used to determine the H–H distances of η^2-dihydrogen ligands[2] in transition-metal complexes in solution. The success of the method relies on the fact that dipolar relaxation is almost solely responsible for the short T_1 values measured for η^2-H_2 ligands because of the close proximity of one H to the other.[3] However, H–H distances determined by neutron[2] and X-ray[4] diffraction methods were found to be shorter by a correction factor (C) of about 0.9 relative to the distances calculated from the T_1 data.[1a] We describe here spin–lattice relaxation time measurements on our iron-group molecular hydrogen complexes,[4,5] which suggest that the correction factor should be 0.794 and it arises because of the rotational motion of the H_2 ligand in the complex.

We have previously reported NMR studies to order the H–H distances in the complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(dppe)_2]BF_4$, M = Fe (**1Fe**) and Ru (**1Ru**) and dppe = $PPh_2CH_2CH_2PPh_2$, and the complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(depe)_2]BPh_4$, with M = Fe (**2Fe**), Ru (**2Ru**), and Os (**2Os**) and depe = $PEt_2CH_2CH_2PEt_2$.[5a] The trend uncovered based on single T_1 determinations and ^1J(H,D) coupling constants was that the H–H bonds lengthen as Ru < Fe < Os. The complexes have a trans structure I at low temperatures, but at higher temperatures hydrogen atom exchange between the terminal hydride and dihydrogen ligands occurs.

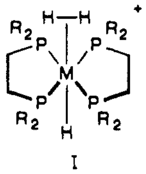
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Table I. Observed T_1 and T_2* Values (ms) of the η^2-Dihydrogen and Hydride Ligands of the Complexes in Acetone-d_6 as a Function of Temperature (Best Fit Parameters Used for the Calculations Given in Table III)

		obsd			calcd, $\alpha \gg 1$ (or $\alpha \sim 0$)		
frequency, MHz	T, K	$T_1(H_2)$	$T_2^*(H_2)$	$T_1(H)$	$T_1(H_2)$	$T_2^*(H_2)$	$T_1(H)$
1Fe[a]							
200	291	40 ± 20		40 ± 20	34	23	34
	244	11 ± 2	5.9	116 ± 10	12	10	169
	224	10 ± 2	4.0	130 ± 10	9.0	7.0	131
	204	9 ± 2	2.5	130 ± 10	8.6	4.8	121
400	295	44 ± 5		44 ± 5	40	25	40
	233	17 ± 2	11	230 ± 10	16	10	240
	213	18 ± 1	8.4	277 ± 10	19	7.8	269
	203	21 ± 2			21	6.8	313
	193	22 ± 2	4.8	337 ± 20	28	5.8	392
	183	34 ± 2			34	4.5	530
1Fe-d_{40}							
200	291	25 ± 5		25 ± 5	34	23	34
	243	11 ± 1	10	200 ± 20	12	10	>169
	205	9 ± 2	6	400 ± 30	8.6	4.8	>121
1Ru							
200	303	36 ± 2		281 ± 10	34	33	456
	285	28 ± 2	10.6	294 ± 10	27	25	357
	267	20 ± 2	12.2	239 ± 10	20	20	273
	248	14 ± 1	9.9	187 ± 10	15	14	205
	230	13 ± 1	5.8	145 ± 10	12	10	160
	210	10 ± 1	5.3	156 ± 10	10	6.9	136
400	298	33 ± 2	13	453 ± 20	35	32	465
	250	21 ± 2	11	319 ± 20	21	16	287
	230	20 ± 2	6.9	291 ± 20	20	12	270
	203	22 ± 2	6.1	308 ± 20	25	8.6	339
	189	31 ± 2	4.8	422 ± 20	33	6.8	462
2Os							
200	293	420 ± 20	105	420 ± 20	447	332	447
	254	225 ± 10	70	225 ± 10	211	155	211
	205	52 ± 5	34	260 ± 10	50	43	213
	183	44 ± 5	22	190 ± 10	40	23	171
400	296	493 ± 20	140	493 ± 20	475	351	475
	212	95 ± 5	26	311 ± 20	83	60	352
	202	85 ± 5	20	337 ± 20	80	48	340
	192	81 ± 5	14	369 ± 20	86	40	365
	184	88 ± 5	11	381 ± 20	99	34	423

[a] The T_1 values given in ref 5a refer to CD_2Cl_2 solutions of complex **1Fe**.

Our complexes provide excellent tests of the proposition that dipolar relaxation is almost solely responsible for the short T_1 values measured for η^2-H_2. The H–H distance for **1Fe** is known in the solid state: 0.89 (11) Å by X-ray diffraction at 295 K[4] and 0.82 (2) Å by neutron diffraction at 25 K.[6] H–H distances from long (**2Os**) to short (**1Ru**) are represented. Furthermore, the relaxation rate of the terminal hydride nucleus can be compared to that of the H_2 nuclei. Our finding is that, at least for our iron and ruthenium complexes as well as for $W(H_2)(CO)_3(P^iPr_3)_2$,[2c] reasonable distances are calculated by assuming that the correlation time (τ_{H_2}) for extra motion of the η^2-H_2 ligand is shorter than the correlation time (τ_H) for isotropic motion of other ^1H nuclei such as the terminal hydride ligand in the metal complex. This is likely due to the rapid spinning of the H_2 ligand[2c,7,8] and tunneling of H atoms in the ligand,[2a,9] which has been suggested for $W(H_2)(CO)_3(P^iPr_3)_2$. Such motion is consonant with unresolved rotational structure on the infrared absorption for $\nu(H_2)$ observed for some group 6 metal molecular hydrogen complexes and could explain why these absorptions are so broad.[2,10]

Experimental Section

The complexes were prepared as described elsewhere.[4,5] Acetone-d_6 solutions of **2Os** were carefully degassed and sealed under Ar. Solutions of **1Ru** and **1Fe** were sealed under H_2 gas. ^1H NMR spectra were recorded on Varian XL-400 and XL-200 spectrometers. T_1 measurements were made by the inversion–recovery method; the error in T_1 measurements is typically ±10% although the error in T_1 values measured for very broad, low-intensity peaks reaches up to ±50%. For the **1Fe** data the 90° pulse was recalibrated at each temperature by studying the relaxation of a sharp peak in the organic region of the sample. The observed T_2* values were obtained from the line widths of the H_2 peaks for **1Ru** or from the variable-temperature simulations described previously.[5a] The H_2 peaks are so broad that the T_2* values obtained in this way should be fairly reliable indicators of T_2. The T_1 and T_2* data are listed in Table I. The temperatures were calibrated by the methanol method. The chemical shifts of the H_2 and H ligands, respectively, at 210 K are as follows: **1Fe** δ −8.0 (br s), −12.9 (qnt, $^2J(P,H) = 47$ Hz); **1Ru** δ −4.6 (br s), −10.0 (qnt, $^2J(P,H) = 16$ Hz); **2Os** δ −10.0 (br s), −9.7 (qnt, $^2J(P,H) = 17.5$ Hz).

The ligand $(C_6D_5)_2PCH_2CH_2P(C_6D_5)_2$ was prepared from $Cl_2PCH_2CH_2PCl_2$ (Strem Chemical Co.) and C_6D_5MgBr in a fashion similar to $Cy_2PCH_2CH_2PCy_2$.[11]

Preparation of *trans*-$[Fe(\eta^2\text{-}H_2)(H)\{(C_6D_5)_2PCH_2CH_2P(C_6D_5)_2\}_2]BF_4$, 1Fe-$d_{40}$. Dinitrogen as well as dioxygen must be excluded at all stages by use of a hydrogen or argon atmosphere. Tetrafluoroboric acid etherate (66 μL, 0.50 mmol) was added dropwise to a yellow slurry of $FeH_2\{(C_6D_5)_2PCH_2CH_2P(C_6D_5)_2\}_2$[12] (320 mg, 0.30 mmol) in diethyl ether. A pale yellow solid immediately formed, which was then filtered to yield the product (236 mg, 80%). The NMR spectra were exactly the same as those reported for **1Fe**[4] apart from the lack of phenyl resonances in the ^1H NMR spectra and slight differences in chemical shifts and line widths (see below) of resonances in the hydride region. ^1H NMR

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(acetone-d_6, 210 K): δ −7.8 (s, br, 2 H), −12.4 (qnt, 1 H, J(H,P) = 47 Hz).

Calculations

Treatment of the Internal Motion of the H_2 Ligand. The rotation of the H_2 group in a transition-metal complex can be treated in the same fashion as a methyl group spinning in a molecule. Woessner has shown how the spectral density function for a molecule tumbling anisotropically in solution[13a] can be applied to a methyl group attached to a molecule undergoing overall isotropic motion.[13b] For the case of H_2 it is assumed relaxation along the H–H bond is perpendicular to the axis of its rotation in the molecule so that $\Delta = 90°$ in Woessner's equation.[13b] The equation then simplifies to

$$J(\omega) = 0.25\tau_A/(1 + \omega^2\tau_A^2) + 0.75\tau_C/(1 + \omega^2\tau_C^2) \qquad (1)$$

$$1/\tau_A = 6D_\perp \qquad 1/\tau_C = 4D_\parallel + 6D_\perp$$

$D_\parallel$ and $D_\perp$ are diffusion coefficients for motion about the axis of rotation of the H_2 and about a perpendicular axis, respectively. But for our case

$$D_\parallel = D_H + D_{H_2} \qquad D_\perp = D_H$$

where D_H is the diffusion coefficient for overall isotropic motion of a rigid H atom in the molecule and D_{H_2} is for internal motion of the H_2. It follows that

$$1/\tau_A = 1/\tau_H \qquad 1/\tau_C = 2/\tau_{H_2} + 1/\tau_H$$

The correlation time, τ_{H_2}, is introduced to express the additional motion of the H_2 group. Noggle and Schirmer[14] have recommended defining α as

$$\alpha = \tau_H/\tau_{H_2}$$

so that

$$\tau_C = \tau_H/(1 + 2\alpha) \qquad (2)$$

Thus, eq 2 in combination with eq 1 describes how the spectral density function changes as the relative motions of the H_2 ligand and the molecule change (assuming pure rotation of the H_2 and similar temperature dependences for both correlation times τ_H and τ_{H_2}).

In the limit of extremely rapid rotation of the H_2 ligand so that $\alpha \gg 1$ ($\tau_{H_2} \ll \tau_H$), eq 1 becomes

$$J(\omega) = A\tau_H/(1 + \omega^2\tau_H^2) \qquad (3)$$

where A is 0.25. Such a case has been described for the rapid rotation of a methyl group in a protein.[15] In the limit of no rotation, $\alpha \rightarrow 0$, so that eq 1 becomes the usual spectral density equation for isotropic motion, eq 3 with $A = 1$.

Calculation of the Temperature Dependence of T_1 and T_2. Standard equations (4 and 5) were used for the calculation of T_1 and T_2 as a function of temperature[16] where r_{HH} is the distance

$$1/T_1 = 0.3\gamma_H^4\hbar^2\{J(\omega) + 4J(2\omega)\}/r_{HH}^6 \qquad (4)$$

$$1/T_2 = 0.15\gamma_H^4\hbar^2\{3J(0) + 5J(\omega) + 2J(2\omega)\}/r_{HH}^6 \qquad (5)$$

between the nucleus of interest and the nucleus responsible for the dipolar relaxation, $J(\omega)$ refers to eq 1 or 3, and τ_0 and the energy E_a determine the temperature dependence of the correlation time (eq 6). A computer program was devised to vary the

$$\tau_H = \tau_0 e^{E_a/RT} \qquad (6)$$

parameters r_{HH}, τ_0, E_a, and α and minimize the absolute deviations between calculated T_1 and T_2 values and the measured T_1 and estimated T_2 values of both the dihydrogen and hydride resonances (Table I). Intramolecular exchange of the H atoms between H_2 and H ligands was included in the calculations where appropriate by use of eq 7 discussed below.

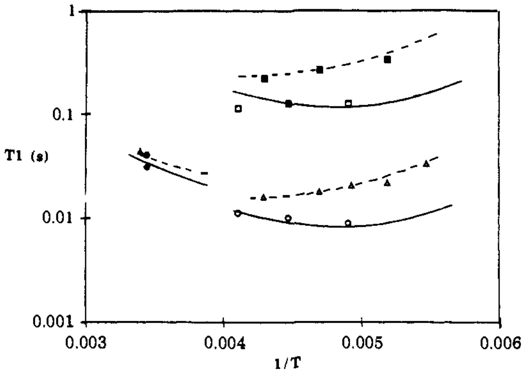

Figure 1. T_1 data from Table I for the complex *trans*-[Fe(η^2-H_2)(H)(dppe)$_2$]BF_4 in acetone-d_6 are plotted on a log scale versus $1/T$. The symbols are as follows: ○, H_2 resonance, 200 MHz; △, H_2 resonance, 400 MHz; □, H resonance, 200 MHz; ■, H resonance, 400 MHz; ●, averaging of T_1 observed at 200 MHz; ▲, averaging of T_1 observed at 400 MHz. The calculated curves from the parameters of Table III are (—) 200 MHz and (---) 400 MHz.

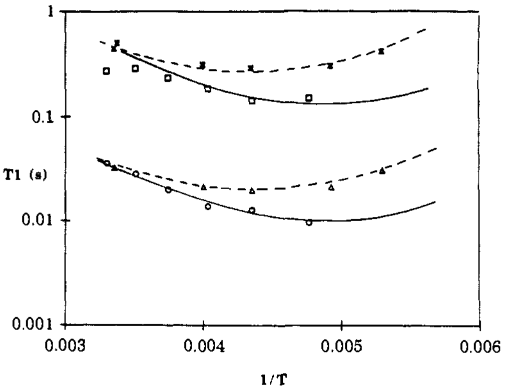

Figure 2. T_1 data from Table I for the complex *trans*-[Ru(η^2-H_2)(H)(dppe)$_2$]BF_4 in acetone-d_6 are plotted on a log scale versus $1/T$. The symbols are as follows: ○, H_2 resonance, 200 MHz; △, H_2 resonance, 400 MHz; □, H resonance, 200 MHz; *, H resonance, 400 MHz. The calculated curves from the parameters of Table III are (—) 200 MHz and (---) 400 MHz.

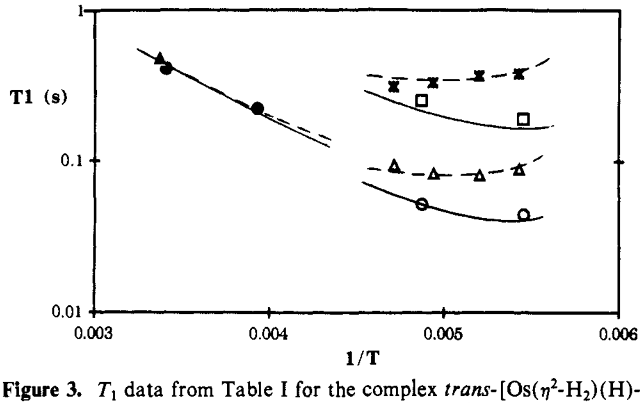

Figure 3. T_1 data from Table I for the complex *trans*-[Os(η^2-H_2)(H)(depe)$_2$]BPh_4 in acetone-d_6 are plotted on a log scale versus $1/T$. The symbols are as follows: ○, H_2 resonance, 200 MHz; △, H_2 resonance, 400 MHz; □, H resonance, 200 MHz; *, H resonance, 400 MHz; ●, averaging of T_1 observed at 200 MHz; ▲, averaging of T_1 observed at 400 MHz. The calculated curves from the parameters of Table III are (—) 200 MHz and (---) 400 MHz.

Results and Discussion

The T_1 values were measured as a function of temperature (300–190 K) by the inversion–recovery method for solutions of

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Table II. Data for the η^2-Dihydrogen Ligands[a]

complex	$T_1(H_2)$(min) (200 MHz), ms	T, K	r_{H_2}, Å $\alpha \gg 1$	$\alpha \sim 0$	^1J(H,D), Hz
$[Fe(\eta^2-H_2)(H)(dppe)_2]^+$ (**1Fe**)	8.5 ± 1	207	0.86 ± 0.02	1.09 ± 0.03	30
$[Ru(\eta^2-H_2)(H)(dppe)_2]^+$ (**1Ru**)	10 ± 1	205	0.89 ± 0.02	1.12 ± 0.04	32.9
$[Fe(\eta^2-H_2)(H)(depe)_2]^+$ (**2Fe**)	(12)	(210)	(0.91)	(1.15)	28
$[Ru(\eta^2-H_2)(H)(depe)_2]^+$ (**2Ru**)	(11)	(210)	(0.89)	(1.12)	32.0
$[Os(\eta^2-H_2)(H)(depe)_2]^+$ (**2Os**)	40 ± 5	185	1.12 ± 0.03	1.40 ± 0.03	<19[b]

[a] The r_{H_2} distances refer to cases of rapid rotation ($\alpha \gg 1$, $\tau_{H_2} \ll \tau_H$) and slow or no rotation ($\alpha \sim 0$, $\tau_{H_2} \gg \tau_H$) of the H_2 ligand, respectively. The ^1J(H,D) coupling refers to the isotopomer $[M(\eta^2-HD)(D)(diphos)_2]^+$. The values in parentheses are estimates since they are based on one determination of T_1 at 210 K. [b] Discussed in ref 5b.

1Fe, **1Ru**, and **2Os** at 200 and 400 MHz. The data are plotted in Figures 1–3. It is already known from line-shape analysis studies that the hydrogen atoms in the H_2 and H ligands exchange intramolecularly at a rate that would average the T_1 values at or above 300 K for **1Ru**, 250 K for **1Fe**, and 220 K for **2Os**.[5a] Intermolecular exchange of H atoms is negligible under the conditions of our experiments. As expected, instead of finding typical "V"-shaped plots of log T_1 vs $1/T$ for each of the H_2 and H ligands, plots are obtained with the high-temperature "arms" of the V converging to observed T_1 values averaged as in eq 7.

$$3/T_1(\text{obsd}) = 2/T_1(H_2) + 1/T_1(H) \qquad (7)$$

This convergence takes place near the temperatures noted above. Despite these deviations from the V shape, it is possible to say that the T_1 values of the H_2 and H ligands pass through minima at the same temperatures. Of course, the T_1 values for the H_2 ligands are always much shorter than those of the H ligands because of the shorter H–H distances. Observed minimum T_1 values, $T_1^{(\text{min})}$, are listed in Table II. Estimated values are given for the complexes **2Fe** and **2Ru** based on one low-temperature T_1 determination.[5a]

Two experimental observations suggest that the dipolar relaxation mechanism predominates for the hydrogens of the dihydrogen ligand and support the use of eq 4 and 5 in describing their relaxation rates. First, the temperature dependence of T_1 is described fairly well by these equations (see below). Second, there is no change in the relaxation times of the dihydrogen ligand in **1Fe** compared to **1Fe**-d_{40} when the phenyl protons are replaced by deuteriums whereas there is a large change in the terminal hydride T_1 (see Table I). The phenyl protons are the closest protons to the H and H_2 ligands (see X-ray structure of **1Fe**)[4] and are considered to be the most likely to influence the relaxation of nuclei in these ligands. Thus, as expected, the phenyl protons are major contributors to relaxation of the terminal hydride nucleus whereas the hydrogens in the H_2 ligand are solely responsible for each other's relaxation rate.

H–H Distances from the T_1 Minima. Since we were able to observe the minimum value of the relaxation time of the H_2 and H ligands in our complexes, it is a simple matter to obtain the correlation time of protons held rigidly to and tumbling with the molecule—the terminal hydride, for example. As pointed out by Hamilton and Crabtree,[1a] eq 4 requires that there be a minimum $T_1^{(\text{min})}$ value when $\omega\tau_H = 0.63$. If the H_2 ligand has no additional rotational motion ($\alpha \sim 0$), then this correlation time can be used in eq 3 with $A = 1$ to obtain $J(\omega)$, which in turn, along with $T_1^{(\text{min})}$, can be substituted in eq 4 to obtain r_{HH}. In the case of **1Fe** with $T_1^{(\text{min})} = 8.5 \pm 1$ ms and $\tau_H = 500$ ps at 200 MHz, a distance of 1.09 ± 0.03 Å is calculated (Table II).

A distance that is more compatible with the diffraction data for **1Fe** is obtained if extremely rapid rotation of the H_2 is assumed ($\alpha \gg 1$, $\tau_{H_2} \ll \tau_H$) and eq 3 with $A = 0.25$ is used. Equation 4 is still valid even though τ_{H_2} is not known; hence, r_{HH} can be determined, but it will differ from r_{HH} calculated with $A = 1$ by a factor of $(0.25)^{1/6} = 0.7937$. In this case a distance of 0.86 ± 0.02 Å is calculated for **1Fe**, which is in much better agreement with the values determined by diffraction. The distances for the other complexes are listed in Table II.

Therefore, the correction factor C reported by Hamilton and Crabtree should be 0.79 if the spinning of the dihydrogen is rapid. If τ_{H_2} is comparable in magnitude to τ_H because of restricted rotation, then eq 1 and 2 apply. Here, an intermediate value for r_{HH} would be obtained, and C could range from 0.8 to 1.0. Restricted rotation of the H_2 could result from steric interactions with the ligands or strong $d_\pi(M) \rightarrow \sigma^*(H_2)$ back-bonding. We tested this idea by attempting to fit eq 1 and 2 to the temperature-dependent T_1 data for our complexes but did not obtain evidence for an intermediate value for α (see below).

Our previous work[5a] suggested that the ordering of H–H distances should increase as **1Ru** < **2Ru** < **1Fe** < **2Fe** < **2Os** based on a variety of the properties of the complexes including ^1J(H,D) values for the corresponding isotopomers $[M(\eta^2-HD)(D)(diphos)_2]^+$ (Table II). We are now forced to conclude based on this more thorough study that the H–H bond is longer in **1Ru** than in **1Fe** and that the ^1J(H,D) values may not accurately reflect H–H bond lengths.

The dihydrogen complex $W(H_2)(CO)_3(P^iPr_3)_2$ has an H–H distance of 0.75 Å according to X-ray diffraction,[2a] 0.82 Å according to neutron diffraction,[2a] and 0.89 (1) Å according to a solid-state NMR study.[7] A T_1 value of 4 ms has been reported at 200 K, a temperature that is expected to be near the minimum T_1 value. This number gives an r_{HH} distance of 0.96C Å with Hamilton and Crabtree's approach.[1a] If $\alpha \gg 1$ so that $C = 0.79$, then the distance becomes 0.76 Å. The approximate agreement with the diffraction studies indicates that the H_2 ligand, because of its rotation, does have a shorter correlation time than the molecule as a whole. The rate of rotation has been reported to be greater than 140 KHz for the H_2 ligand in this complex, and the rotation is thought to be hindered by an energy barrier $E_{\text{rot}} = 0.3$–2 kcal mol^{-1}.[2c,8] More recent work suggests that the motion might better be described as tunneling through energy barriers between preferred H_2 orientations.[7,9] In this case the motion may not be equivalent to simple rotation if H atom sites parallel to the P–W–P axis are more populated than sites parallel to the OC–W–CO axis; thus, the Woessner treatment may not apply in this case and other cases where the H_2 binding site has low symmetry.[17] However, for our complexes, the tunneling of H atoms between sites of approximately C_{4v} symmetry should result in a motion that is indistinguishable from spinning of the H_2 ligand.

Temperature Dependence of T_1 and T_2. The case for rapid internal rotation of the H_2 ligand ($\alpha \gg 1$, $A = 0.25$) was examined by fitting to the experimental T_1 and T_2 data eq 4–6 and eq 3. The value of $A = 1$ was used in eq 3 for the terminal hydride since it is assumed to be tumbling with the molecule without additional internal motion. Equation 7 was applied for the region above the temperature where T_1 averaging occurs (see above). The best fit parameters are listed in Table III, and the calculated curves are plotted in Figures 1–3. The agreement is good for the T_1 data for the H_2 ligands. As might be expected, the calculated T_1 values for the terminal hydrides of **1Fe** (Figure 1) and **1Ru** (Figure 2) deviate from observed values at 200 MHz in the region where averaging of T_1 values starts to occur. The shape of the curves in the temperature ranges where averaging starts is not known. The τ_0 values increase as **2Os** < **1Fe** < **1Ru**, and this is the order of increasing size and rotational moment of inertia of the molecules, as expected. The E_a values are similar since they all reflect the temperature dependence of the viscosity of acetone-d_6. For **1Fe** it was difficult to obtain a precise T_1 value for the H_2 and

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(17) Zilm, K., personal communication.

Table III. Parameters Derived from a Best Fit of Equations 4 and 5 Combined with Equation 3 (A = 0.25 for Dihydrogen and A = 1 for Hydride) to the Experimental Data of Table I

complex	ν, MHz	T(min), K	τ_0, ps	E_a, kcal/mol	T_1(H)(min), ms	$r_{H\cdots H}$, Å	$T_1(H_2)$(min), ms	r_{H_2}, Å
1Fe	200	207	0.90	2.6	120	1.69	8.5 ± 1	0.86 ± 0.02
and **1Fe**-d_{40}	400	230	0.90	2.6	240	1.69	17 ± 2	0.86 ± 0.02
1Ru	200	205	1.08	2.5	135	1.72	10 ± 2	0.89 ± 0.02
	400	230	1.08	2.5	270	1.72	20 ± 2	0.89 ± 0.02
2Os	200	185	0.19	2.9	170	1.79	40 ± 5	1.12 ± 0.03
	400	203	0.19	2.9	340	1.79	80 ± 10	1.12 ± 0.03

H ligands near room temperature, 200 MHz, since intramolecular exchange causes the peaks to be very broad under these conditions. The value obtained for **1Fe**-d_{40} (Table I) is considered to be more reliable.

The fit to the T_1 and $T_2{}^*$ data for the terminal hydride was not as good, but this is expected considering that several interactions must contribute to the relaxation of this proton. Thus the calculated, averaged H···H distances ($r_{H\cdots H}$, Table III) responsible for the dipolar relaxation of the terminal hydride should be viewed with suspicion. These are likely to be averaged distances to protons on the substituents of the phosphine, which are primarily responsible for the relaxation of the terminal hydride nucleus. Nevertheless, it is very encouraging that the same temperature dependence for the correlation time (eq 6) describes the curves for both the H_2 ligand and the H ligand at both 200 and 400 MHz and that the T_1 values for both types of hydrogens pass through minima at the same temperature. This is expected since eq 4 has a minimum T_1 at the same temperature whether A = 0.25 or 1 in eq 3.

Equation 5 accounts for the $T_2{}^*$ data fairly well for **1Ru** and **1Fe**-d_{40} but predicts values that are too large by as much as a factor of 3 for the 400 MHz data for **2Os** and for 200 MHz data for **1Fe**. However, in the latter cases the terminal hydride resonances were also unusually broad. This perhaps indicates that instrumental and experimental problems may account for the extra broadening. Anomalous broadening of the H_2 resonances has also been referred to by Crabtree.[3a] In addition the T_2 values that we calculate for the complex $W(H_2)(CO)_3(P^iPr_3)_2$ are too long to explain the peak widths reported for the H_2 resonance.[2c]

As expected the r_{HH} distances for the η^2-dihydrogen ligand in Table III are shorter than averaged H···H distances ($r_{H\cdots H}$) responsible for the dipolar relaxation of the terminal hydride. The r_{HH} distances are the same as those obtained by using the values $T_1{}^{(\min)}$ (Table II). Note that the fit to the experimental data for a case where the additional motion of the H_2 ligand is much slower than the tumbling of the molecule ($\alpha \ll 1$) would be indistinguishable from our calculations, which assume very rapid rotation. However, the distances obtained by the former method are too long, at least for **1Fe** and **1Ru**, judging from the X-ray diffraction data (see Table II). For the Os complex it is not possible to rule out the possibility that there is slower rotation of the H_2 ligand because of a strong Os–H_2 interaction; in this case the H–H distance could be as long as 1.40 Å.

In summary the bulk of the experimental data is explained well by eq 3 with A = 0.25, and thus the correlation time of the H_2 ligand is much shorter than that of the terminal hydride. For iron the rotation or tunneling rate at 200 K must exceed about 10^3 MHz on the basis of the correlation time τ_{H_2}.[14]

If rotation of the H_2 is hindered by strong interactions with the metal, then the correlation time might fall in the intermediate region where intermediate values of α in eq 2 apply. Interactions between the metal and H_2 ligand are thought to decrease as **2Os** > **1Fe** > **1Ru**.[5a] In this case of restricted rotation of the H_2 ligand, the H–H distance will be only bracketed by the values of Table II. The parameter α of eq 2 was varied along with the parameters r_{HH}, τ_0, and E_a by computer to try to obtain a better fit to the data. Figure 4 shows how the calculated T_1 values for the H_2 ligand in **1Ru** change when a value of α = 2.5 is used in eq 1, 2, and 4 while parameters E_a and τ_0 are kept constant. The value of 2.5 for α gives an H–H distance of 1.01 Å, which corresponds to the value of C = 0.9 proposed previously.[1a] As Figure 4 shows, rotation of the H_2 ligand at a rate consistent with α = 2.5 or C = 0.9 would be readily distinguishable from the case of very rapid rotation.[18] Intermediate correlation times for the H_2 ligand (when α is between 0.01 and 100 or when rates of rotation are between about 0.1 and 10^3 MHz at 200 K) give curves with much flatter minima, which are shifted to lower temperatures; in addition, the curves for 200 and 400 MHz move much closer together. These features are not consistent with the experimental data for our complexes, and no good fit is obtained. We also examined the possibility of separate temperature dependences for τ_{H_2} and τ_H by using an equation like eq 6 for τ_{H_2} with E_{rot} = 0.3–2.0 kcal mol^{-1} to match proposed energy barriers for the rotation of H_2.[2a,8] When τ_{H_2} was of the same magnitude as τ_H, the curves again showed flattened minima shifted to lower temperature like those reported above for intermediate values of α and again did not match our experimental curves. Thus, the value of C of 0.9 proposed by Crabtree and Hamilton does not apply for our complexes. Perhaps there is slower rotation in the iridium and tungsten complexes where a value of 0.9 has been proposed[1a] or perhaps the low symmetry of the H_2 binding site makes eq 1 inapplicable if tunneling is the predominant process.[17]

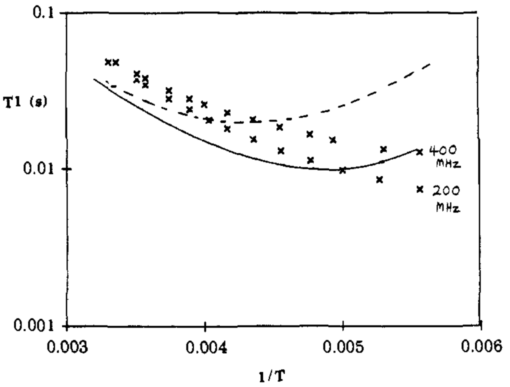

Figure 4. Calculated temperature dependences of T_1 data for the H_2 ligand in $[Ru(\eta^2\text{-}H_2)(H)(dppe)_2]BF_4$ in acetone-d_6 by use of eq 1, 2, and 4 with E_a and τ_0 and other parameters as in Table III: (—) $\alpha \gg 1$, at 200 MHz, r_{HH} = 0.89 Å (as in Figure 2); (- - -) $\alpha \gg 1$, at 400 MHz, r_{HH} = 0.89 Å (as in Figure 2); (×) α = 2.5, at 200, and 400 MHz, r_{HH} = 1.01 Å (C = 0.9).

Conclusions. The reasonable agreement between theory and experiment supports the proposal that dipolar relaxation is solely responsible for the short T_1 values measured for η^2-H_2 ligands. The H–H distances calculated for the case when the correlation time of the H_2 ligand is shorter than that of the terminal hydride due to extra motion of the H_2 ligand are in best agreement with distances determined in the solid state by diffraction. The H–H bond is found to be longer in **1Ru** than in **1Fe** despite our preliminary report to the contrary,[5a] and thus ^1J(H,D) values may not accurately reflect H–H bond lengths. There is evidence from the literature for rapid rotation and tunneling of the atoms in the H_2 ligand,[2a,c,7–9] particularly in **1Fe**.[19] Complexes where a value of C = 0.9 has been proposed[1a] may undergo slower rotation of

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(18) We interpret C as: $r_\alpha/r_0 = \{[J_\alpha(\omega) + 4J_\alpha(2\omega)]/[J_0(\omega) + 4J_0(2\omega)]\}^{1/6}$, where J_α and J_0 are given by eq 1 and 2 with α = 2.5 and α = 0, respectively, in this case.

(19) Eckert, J.; Bautista, M. T.; Morris, R. H., to be submitted for publication.

the H_2 ligand and give an intermediate value for α in eq 2. Alternatively, eq 1 does not apply in this case because of tunneling of H atoms between sites of low symmetry. Work is still required to explain the disagreement between observed and calculated line widths of the H_2 resonance in the ^1H NMR spectrum.

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Note Added in Proof. Dr. L. Field has suggested privately that $T_1^{(\min)}$ for **1Fe** may be short due to a paramagnetic state contributing to the relaxation. However, $T_1^{(\min)}$ values for the terminal hydride of **1Fe**, **1Ru**, and **2Os** are similar (Table III), a fact that goes against this suggestion.

Optical Determination of Magnetization Behavior: A Study of Unstable Metallocenes by Magnetic Circular Dichroism

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Abstract: In this paper we report the first application of magnetic circular dichroism (MCD) to determine the magnetization curves for unstable, matrix-isolated molecules. Curves are obtained by recording the MCD signal at fixed wavelength as a function of B/T over the magnetic field range 0–8 T. For each compound, the curve is recorded at 1.8 K and at another temperature between 6 and 17 K. Magnetization curves are reported for three unstable matrix-isolated metallocenes Cp_2M (M = Mo, W, Re; Cp = η^5-C_5H_5) with spin and orbitally degenerate ground states. They are compared to curves for matrix-isolated (η^5-C_5Me_5)$_2$Re reported earlier and for (tol)$_2$V (tol = η^6-toluene), which has a $^2A_1$ ground state. The data are analyzed by two methods. The first uses published methods for a random array of linear molecules. Assuming $g_\perp = 0$, values of $g_\parallel$ of 2.75 ± 0.18, 3.07 ± 0.15, and 5.34 ± 0.36 are determined for Cp_2M (M = Mo, W, and Re, respectively). The $g_\parallel$ value for Cp^*_2Re ($Cp^* = \eta^5$-C_5Me_5) and the isotropic g value for (η^6-tol)$_2$V (5.07 ± 0.19 and 1.94 ± 0.03, respectively) are in excellent agreement with determinations by EPR. In the second method of analysis, a quantum mechanical model including the effects of covalency, spin–orbit coupling, and low-symmetry distortion is used. The differential absorbance is evaluated for particular transitions as a function of B and T. A least-squares fitting procedure is then employed to determine the g values, the orbital reduction factor, and the distortion parameter at an assumed value of the spin–orbit coupling constant. The values of $g_\parallel$ determined by this method are in excellent agreement with the first method. This method also gives estimates of $g_\perp$, which prove to be as low as 0.05. These experiments demonstrate the power of optical determination of magnetization curves and g values for unstable molecules, some of which are EPR silent.

The measurement of the magnetization curve or the magnetic parameters of an unstable molecule presents many difficulties. The traditional response to this question is to use electron paramagnetic resonance, a method that has had spectacular success in many instances. However, there are drawbacks to EPR: (i) its high sensitivity compared to those of other spectroscopic methods renders it difficult to demonstrate that an EPR spectrum belongs to the same molecule as an absorption spectrum; (ii) more seriously, some molecules are EPR silent, although they are paramagnetic. EPR silence is encountered most frequently with molecules containing heavy elements and an even number of unpaired electrons. In such situations, zero-field splittings often exceed the operating frequency of the EPR spectrometer. There is also a group of molecules with orbital and spin angular momentum, which are EPR silent at room temperature, because they relax very rapidly, but which often become EPR detectable at very low temperature.[2]

We faced a combination of all these problems in studying the unstable metallocenes of tungsten, molybdenum, and rhenium, which we had generated by photolysis of the corresponding hydrides, Cp_2MH_n, and/or related Cp_2ML molecules (Cp = η^5-C_5H_5) in low-temperature matrices.[3,4] We turned instead to a quite different technique, magnetic circular dichroism (MCD).[5,6] Since the MCD spectra of these molecules exhibited the same intense, structured bands as the absorption spectra, we knew at once that we were studying the same molecules in MCD and in absorption. Moreover, the MCD signals increased in intensity as the temperature was lowered. This phenomenon, known as a *C*-term to MCD spectroscopists, is a sure indicator of paramagnetism. It arises from the increasing Boltzmann population of the lowest Zeeman state as the temperature is lowered or the magnetic flux density, B, is increased (Figure 1). We could take the analysis a stage further by examining the ratio of the integrated differential absorption to the integrated absorption (C/D).[5] When considered in conjunction with an analysis of the electronic states available to the metallocenes, this ratio gave an estimate of the value of $g_\parallel$. This approach proved beyond doubt that each of these molecules had high orbital angular momentum in the ground state, arising from the presence of a vacancy in the e_2 orbital (Figure 2).[6] Nevertheless, the use of band areas suffered from a number

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(1) (a) University of East Anglia. (b) University of York.

(2) E.g., see: Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance, Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972.

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