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Single Crystal Neutron Diffraction Study of the Complex $[Ru(H\cdots H)(C_5Me_5)(dppm)]BF_4$ Which Contains an Elongated Dihydrogen Ligand

Wim T. Klooster,[‡] Thomas F. Koetzle,[*,‡] Guochen Jia,[§] Tina P. Fong,[†]
Robert H. Morris,[*,†] and Alberto Albinati[⊥]

Contribution from the Chemistry Departments of Brookhaven National Laboratory, Upton, New York 11973-5000, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, and the University of Toronto, St. George and Scarborough Campuses, Toronto, Ontario, M5S 1A1, Canada; and Istituto di Chimica Farmaceutica, Università di Milano, I-20131 Milano, Italy

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Abstract: The H–H distance of the dihydrogen ligand in $[Ru(H\cdots H)(C_5Me_5)(dppm)]BF_4$ is 1.08(3) Å as determined by neutron diffraction on a crystal of volume 3.2 mm^3 at 15 K: monoclinic, space group $P2_1$, a = 10.833(3), b = 15.045(4), c = 10.781(2) Å, β = 114.47(2)°, V = 1599.3(7) Å^3, and D_c = 1.473 g cm^{-3} for Z = 2; $R(F)$ = 0.071, $R(F^2)$ = 0.151, $R_w(F^2)$ = 0.099 for 4198 reflections. The H–H distance, when corrected for the effects of thermal motion, lengthens slightly from 1.08(3) to 1.10(3) Å. The complex contains an elongated dihydrogen ligand which is symmetrically, side-on bonded to the ruthenium as one leg of a three-legged piano stool structure. The H_2 ligand lies parallel to the C_5Me_5 ligand plane, an orientation where π-overlap with an $a''d$ orbital on the metal is optimum. The T_1 NMR method gives an H–H distance of 1.10(1) Å for the case of restricted rotation. The present structure provides a model for coordinated H_2 at an intermediate stage of oxidative addition. The ^1J(H,D) coupling in the Ru(H···D) isotopomer increases with decreasing temperature; this is interpreted as a slight shortening of the H–D distance. The structural and ^{1}H NMR data are compared for dihydrogen complexes which have been studied by single crystal neutron diffraction.

Introduction

An X-ray diffraction study of the title compound failed to yield the locations of the hydrogen atoms.[1] However solution NMR data suggested that this complex contained an elongated dihydrogen ligand with an H–H distance of 1.1 Å.[1] We decided to carry out a neutron diffraction study because such a distance is intermediate to those observed so far by neutron diffraction studies of dihydrogen complexes. There is a group of complexes with short (<0.9 Å) distances: *trans,mer*-$W(H_2)(CO)_3(P^iPr_3)_2$ (0.82(2)),[2] *trans*-$[Fe(H_2)H(dppe)_2]BPh_4$ (0.82(2)),[3] and *cis,mer*-$Fe(H_2)(H)_2(PEtPh_2)_3$ (0.82(1)).[4] All of these distances may need to be lengthened by a few hundredths of an Å, because there was no correction for librational motion of the H_2 ligand. This was done for another complex of this group, *trans*-$Mo(H_2)(CO)(dppe)_2$, where the H–H distance upon correction increased from 0.74 to 0.85 Å.[5] A second group of complexes has quite long H–H distances for dihydrogen complexes as determined by neutron diffraction: $Re(H\cdots H)(H)_5(Ptol_3)_2$ (1.36(1)),[6] $Ir(H\cdots H)(H)(Cl)_2(P^iPr_3)_2$ (1.11(3)),[7] and *trans*-$[Os(H\cdots H)(OAc)(en)_2]PF_6$ (1.34(2) Å).[8] The Re complex is proposed to have a spinning H···H unit of the same distance in solution on the basis of a ^{1}H NMR T_1 study,[9,10] but little has been reported about the solution structure and dynamics of the H_2 ligands in the other two complexes. X-ray diffraction and solid state ^{1}H NMR studies suggest that some complexes have H–H distances which fall between these two groups. X-ray diffraction studies of $[ReH_6(cyttp)]^+$,[11] $ReH_2(Cl)(PMePh_2)_4$,[12,13] and $RuH_3I(PCy_3)_2$[14] suggest that H–H distances of 1.08(5), 1.17(13), and 1.03(7) are present, respectively. Complexes $[RuH_2Cp(CO)(PCy_3)]^+$ and $[RuH_2Cp(dmpe)]^+$ have d(H–H) of 0.97 and 1.02 Å, respectively, according to solid state NMR measurements.[15]

An indicator of an elongated dihydrogen ligand (denoted H···H and also referred to as "stretched" [10]) in dissolved complexes might be the ^1J(H,D) coupling of the HD complex. It has been proposed[16] that when such couplings fall between 5 and 25 Hz such a form of the ligand is present. The present work supports this idea. On the other hand, temperature and solvent dependence of the ^1J(H,D) coupling could indicate the presence of a rapid equilibrium between spinning dihydrogen and fixed dihydride forms. The complex *trans*-$[Os(H\cdots H)H(depe)_2]^+$ is the only

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[‡] Brookhaven National Laboratory.

[§] Hong Kong University of Science and Technology.

[†] University of Toronto.

[⊥] Università di Milano.

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Table 1. Crystallographic Data

formula	$C_{35}H_{39}BF_4P_2Ru$
T, K	15.0
space group	$P2_1$
Z	2
a, Å	10.833(3)
b, Å	15.045(4)
c, Å	10.781(2)
β, deg	114.47(2)
V, Å^3	1599.3(7)
fw	709.6
D_c, g cm^{-3}	1.473
μ, cm^{-1}	2.70
hkl limits	$0 \le h \le 14; 0 \le k \le 21; -14 \le l \le 14$
$(\sin\theta)/\lambda_{max}$, Å^{-1}	0.67
scan widths, deg	2.6 for $2° \le 2\theta \le 70°$ and then $0.71 + 3.70 \tan\theta$ for $70° \le 2\theta \le 102°$
reflcns measd	4872
independent reflcns	4198
$R(F_o^2)$	0.151
$R_w(F_o^2)$	0.099
goodness of fit, S	1.48
w	$1/\sigma(cs)^2$, where cs = counting statistics

proposed example of this.[17] The title complex is known to exist in solution as a slowly equilibrating mixture of $[Ru(H\cdots H)(C_5Me_5)(dppm)]^+$ and *trans*-$[Ru(H)_2(C_5Me_5)(dppm)]^+$ tautomers where the HD couplings of their isotopomers are not averaged.[1]

Experimental Section

Crystals were obtained by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of $[RuH_2(C_5Me_5)(dppm)]BF_4$. The crystals can sit in air for days without visible decomposition.

A specimen of volume 3.2 mm^3 was mounted on an aluminum pin which was sealed under a helium atmosphere in an aluminum container. This container was placed in a closed-cycle helium refrigerator[18] and mounted on a four-circle diffractometer at port H6S of the Brookhaven High Flux Beam Reactor. The neutron beam, monochromated by Ge(220) planes in transmission geometry, was of wavelength 1.158 63(8) Å as calibrated against a KBr crystal (a_0 = 6.6000 Å at 295 K). The sample temperature was maintained at 15.0 ± 0.1 K during the experiment, and unit cell dimensions were determined by least-squares fit of $\sin^2\theta$ values for 32 reflections.

Three-dimensional intensity data for 4872 reflections were obtained over one quadrant of reciprocal space by means of ω–2θ scans. The intensities of two reflections were monitored after every 50 reflections of data collection and showed no systematic variations throughout. Integrated intensities I_0 and variances $\sigma^2(I_0)$ were derived from the scan profiles. Lorentz factors were applied, but the data were not corrected for absorption. Averaging over 209 symmetry-related pairs of reflections resulted in an internal agreement factor of 0.075 and yielded 4198 independent observations. Further details are given in Table 1.

Initial coordinates for the refinement were taken from the positional parameters of the non-hydrogen atoms derived from the room temperature X-ray analysis.[1] The hydrogen atoms were then located in successive difference maps. Least-squares refinements were carried out by a full-matrix procedure,[19] minimizing $\sum w(F_0^2 - (k^2F_c^2))^2$ using all independent data. The final model included positional and anisotropic thermal parameters β_{ij} for all 82 atoms and the scale factor k of 1.053(2) for a total of 738 variable parameters. No extinction correction was necessary.

Neutron scattering lengths ($\times 10^{-12}$ cm) were taken to be b_{Ru} = 0.721, b_P = 0.531, b_F = 0.565, b_C = 0.664 84, b_B = 0.535, and b_H = −0.374 09.[20] The refinement converged with fit indices $R(F_0)$ = 0.071, $R(F_0^2)$ = 0.151; $R_w(F_0^2)$ = 0.099; S = 1.48, based on 4198 reflections. Selected bond lengths and angles are listed in Table 2.

^1H NMR spectra of $[Ru(HD)(C_5Me_5)(dppm)]BF_4$ in CD_2Cl_2 were obtained by use of a Unity 400 MHz instrument at the temperatures listed in Table 3. This complex was prepared as described previously.[1]

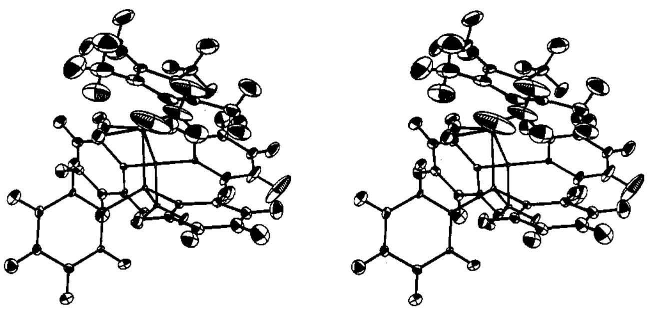

Figure 1. Stereo views of $[Ru(H\cdots H)(C_5Me_5)(dppm)]BF_4$. Thermal ellipsoids are at 30% probability.[32]

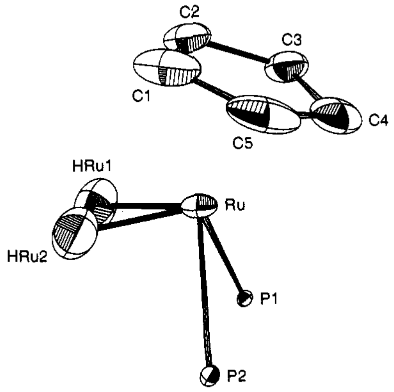

Figure 2. View emphasing the local geometry about the Ru atom.

Results and Discussion

Description of the Structure of $[Ru(H\cdots H)(C_5Me_5)(dppm)]BF_4$. The overall geometry of the cation is that of a three-legged piano stool (Figures 1 and 2) as determined by the room temperature X-ray diffraction study.[1] There are slight differences in the positions of the non-hydrogen atoms between the X-ray study and this low temperature neutron structure determination as indicated by a comparison of selected bond lengths and angles (Table 2). The differences are attributed to differences in thermal motion. For example the carbon atoms in the C_5 ring have large displacement parameters arising from ring rotation or libration effects. This is the most likely explanation for the lack of agreement between the position of ring carbon C5 determined at two temperatures. The thermal parameters determined in both studies show that atomic motion increases for atoms further from the center of the molecule. The X-ray report compared bond distances and angles defined by the non-hydrogen atoms to those of related structures,[1] and therefore only the positions of the hydrogen atoms are of concern here.

The dihydrogen ligand is η^2-bonded to the ruthenium in the usual fashion, with an H–H distance of 1.08(3) Å (Figures 2 and 3). This is intermediate in the range of 0.8–1.4 Å found for eight dihydrogen complexes studied to date by neutron diffraction. We have tried to correct the H–H distance for the effects of thermal motion by use of the program THMA14.[21] The corrected distance is 1.10 Å after applying a "rigid body" correction to the H_2 group. In complexes with short H–H distances (<0.9 Å) larger corrections are expected to account for the large torsional motion of the H_2 unit. For example in $Mo(H_2)(CO)(dppe)_2$, the H–H distance (0.74(2) Å), after correction, is in the range of 0.80–0.85 Å.[5,22]

The mean Ru–H distance of 1.66(2) Å is longer than the value of 1.58(1) Å estimated for ruthenium–hydride bonds.[23] Such metal to dihydrogen distances are longer than corresponding

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) from Neutron Diffraction at 15 K and X-ray Diffraction at 298 K (Ref 1)

	neutron	X-ray
	Bond Lengths (Å)	
Ru–HRu1	1.66(2)	
Ru–HRu2	1.67(2)	
HRu1–HRu2	1.08(3)	
Ru–C1	2.22(1)	2.210(7)
Ru–C2	2.234(8)	2.232(6)
Ru–C3	2.24(1)	2.227(7)
Ru–C4	2.21(1)	2.223(7)
Ru–C5	2.260(9)	2.222(7)
Ru–P1	2.314(9)	2.298(2)
Ru–P2	2.297(8)	2.301(2)
C1–C2	1.43(1)	1.45(1)
C1–C5	1.41(1)	1.396(9)
C2–C3	1.42(1)	1.378(8)
C3–C4	1.40(1)	1.470(9)
C4–C5	1.46(2)	1.37(1)
	Bond Angles (deg)	
P1–Ru–P2	71.4(3)	71.47(7)
P1–C11–P2	93.6(4)	94.0(3)
Ru–P1–C11	97.6(4)	97.3(2)
Ru–P2–C11	97.4(4)	97.2(2)
P1–Ru–C1	161.2(4)	165.4(2)
P1–Ru–C2	126.2(4)	128.5(2)
P1–Ru–C3	101.8(4)	103.1(2)
P1–Ru–C4	108.9(4)	109.0(2)
P1–Ru–C5	143.2(4)	140.5(2)
P2–Ru–C1	124.5(4)	121.6(2)
P2–Ru–C2	161.8(4)	159.6(2)
P2–Ru–C3	144.5(3)	147.4(2)
P2–Ru–C4	111.0(3)	111.3(2)
P2–Ru–C5	101.8(3)	101.0(2)
C1–C2–C3	108.3(6)	109.0(5)
C2–C3–C4	107.7(7)	106.7(5)
C3–C4–C5	108.8(7)	107.6(5)
C4–C5–C1	106.5(8)	110.2(6)
C5–C1–C2	108.6(9)	106.5(5)
P1–Ru–HRu1	80.3(6)	
P1–Ru–HRu2	101.7(7)	
P2–Ru–HRu1	102.4(7)	
P2–Ru–HRu2	80.0(6)	
HRu1–Ru–HRu2	38(1)	

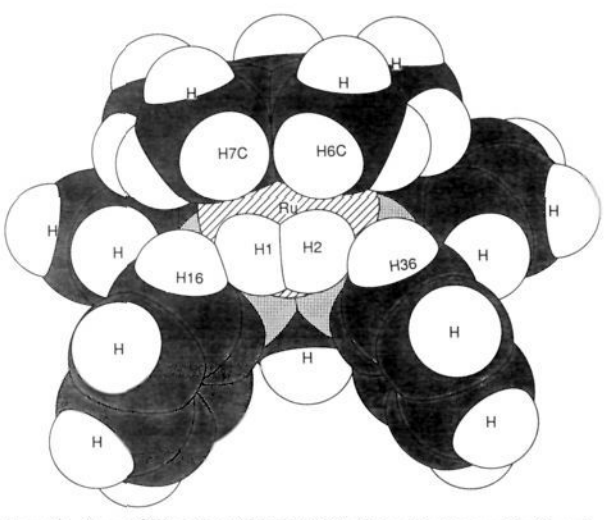

Figure 3. Space filling view (CHEM 3D) of the dihydrogen binding site emphasizing H atoms which are near-neighbors to H1 and H2 (HRu1 and HRu2 of the neutron diffraction study).

Table 3. Coupling Constants ${}^1J(H,D)$ of $[Ru(H\cdots D)(C_5Me_5)(dppm)]BF_4$ in CD_2Cl_2 as Determined by ${}^1H$ NMR Spectroscopy at 400 MHz

temp, K	${}^1J(H,D)$, Hz
295	21.1 ± 0.2
273	21.5 ± 0.1
253	21.6 ± 0.2
233	22.0 ± 0.1
213	22.3 ± 0.2

hydride distances in two iron complexes (Table 4) but marginally shorter than the one in the complex $Ir(H\cdots H)(H)(Cl)_2(P^iPr_3)_2$. The last complex has an elongated dihydrogen ligand. A large degree of backbonding into σ^*_{H-H} was the explanation given for both the elongated H–H bond and the unusually short Ir–H distances.[7] However the present ruthenium complex also has an elongated H_2 ligand but does not show a comparable M–H shortening effect. Other complexes with stretched (H···H) distances (Table 4) have metal–hydrogen distances to the (H···H) unit and metal–hydrogen distances to the terminal hydrides which are comparable.

The conformation of the dppm ligand is such that the two phenyl groups lying on the same side of the ruthenium as the H_2 are oriented roughly perpendicular to the H_2Ru plane so that there is an approximate mirror plane through the molecule (Figure 3). The H_2 hydrogens each have one close contact of about 2 Å with an *ortho* phenyl-group hydrogen: 2.00 Å for HRu1···H16 and 2.12 Å for HRu2···H36. The H_2 could have rotated by 90° to avoid these contacts; however, it would then move out of the region which is optimum for $d\pi(Ru)$–$\sigma^*(H_2)$ bonding. Calculations show that the best metal d orbital for π bonding in a three legged piano stool of this type is of a″ symmetry (in the C_s symmetry of the complex)[24] oriented exactly in the same fashion as the dihydrogen ligand in our complex. Therefore a barrier to propeller-like rotation of the H_2 unit might be expected. Solution NMR data provide evidence for this (see below). Recently the barrier to rotation of the vinylidene ligand in complexes $[Fe(=C=CR^1R^2)(C_5H_5)(dppm)]^+$ has been measured by NMR methods.[25] An X-ray structure determination showed that the vinylidene ligand also orients itself to interact with the same a″ $d\pi$ orbital.[25]

Discussion of Solution NMR Data. The title complex exists in solution as a 2:1 mixture of dihydrogen complex, *trans*-$[Ru(H\cdots H)(C_5Me_5)(dppm)]^+$, and dihydride complex, $[Ru(H)_2(C_5Me_5)(dppm)]^+$. Some of us anticipated an H–H distance of 1.10 Å for the dihydrogen complex on the basis of the medium-sized $J(H,D)$ coupling of the HD complex (21.0 ± 0.2 Hz) and the T_1(min) value of the H_2 resonance.[1] The T_1(min) value of 18 ms at 400 MHz and 220 K corresponds to an H–H distance of 1.10(1) Å if the dihydrogen ligand is restricted to rotate at a rate of much less than the spectrometer frequency ($\ll$400 MHz). If the dihydrogen ligand were rapidly spinning ($\gg$400 MHz) then an H–H distance of 0.87 Å would be more appropriate; however, complexes which have H–H distances in this range have much larger $J(H,D)$ coupling constants. For example $[Ru(H_2)H(dppe)_2]^+$ has a rapidly spinning H_2 unit with a $d(H–H)$ of 0.90 Å which results in a similar T_1(min) value of 20 ms, but its isotopomer has an $J(H,D)$ value of 33 Hz.[26] Hence we concluded that the η^2-H_2 ligand in this complex is in the slow rotation regime with an H–H distance of 1.10 Å.[1] The dihydrogen ligand is likely to be moving fast enough to average the magnetic environments of the H nuclei since the HD resonance in the analogous chiral complex $[(C_5Me_5)Ru(dmdppe)(H\cdots D)]^+$ was not broadened by the slowing of the rotation, even at 130 K.[27]

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Table 4. Structural and ^{1}H NMR Parameters for Complexes Studied by Neutron Diffraction

		dihydrogen						
complex	hydride d(M–H), Å	$d(\mathrm{M{-}H})_{\mathrm{av}}$, Å	d(H–H), Å	J(H,D), Hz	T_1(min) obs, ms	ν, MHz	T_1(min) calcd slow spin, ms	T_1(min) calcd fast spin, ms
$\mathrm{W(H_2)(CO)_3(P^iPr_3)_2}$		1.89(1)[a]	0.82(1)[a]	34[a]	4[b]	200	2	7
$\mathrm{Mo(H_2)(CO)(dppe)_2}$		1.92(1)[c]	0.80–0.85[c,d]	34[e]	20[b,e]	200	6–8	15–20
$\mathrm{[Fe(H_2)H(dppe)_2]BPh_4}$	1.53(1)[f]	1.62(1)[f]	0.82(2)[f]	32[g]	17[g]	400	3–4	12–18
$\mathrm{Fe(H_2)(H)_2(PEtPh_2)_3}$	1.538(7), 1.514(6)[h]	1.59(2)[h]	0.82(1)[h]		24[h,i]	250	4[i]	15[i]
$\mathrm{[Ru(H{\cdots}H)(C_5Me_5)(dppm)]BF_4}$		1.66(2)	1.08(2)–1.10[d]	21	18	400	16–17	66–69
$\mathrm{Ir(H{\cdots}H)(H)(Cl)_2(P^iPr_3)_2}$	1.58(1)[j]	1.54(2)[j]	1.11(3)[j]	12[j]	38[k]	200	14[k]	49[k]
$\mathrm{[Os(H{\cdots}H)OAc(en)_2]PF_6}$		1.60(1)[l]	1.34(2)[l]	9.1[l]	61[l]	400	60	241
$\mathrm{Re(H{\cdots}H)(H)_5(Ptol_3)_2}$	1.673(4)–1.697(4)[m]	1.680(4)[m]	1.357(7)[m]		66[n]	250	50[n]	68[n]
					110[o]	500	93[o]	124[o]
$\mathrm{Os(H{\cdots}H)(H)_4(P^iPr_2Ph)_2}$	1.643(4)–1.668(4)[p]	1.638(4)[p]	1.650(6)[p]					

[a] Reference 2. [b] Close to but not necessarily the minimum value. [c] Reference 5. [d] Longer distance is estimated by use of the Maverick/Trueblood correction. [e] Reference 33. [f] Reference 3. [g] Reference 26. [h] Reference 4. [i] Rapid H atom site exchange averages the relaxation rate of the (H_2) and two terminal hydride nuclei; see ref 31. [j] Reference 7. [k] Rapid H atom site exchange averages the relaxation rate of the (H_2) and one terminal hydride nucleus. [l] Reference 8. [m] Reference 6. [n] Reference 9. [o] Reference 23. [p] Reference 34.

Now that all of the H atom positions are available, the method of Desrosiers et al.[23] can be applied to calculate the dihydrogen T_1(min) value expected for such a structure and to find out what percentage of the relaxation rate of the dihydrogen nuclei is due to nuclei on the C_5Me_5 and dppm ligands. When all sources of relaxation are taken into account the T_1(min) for a nonspinning H···H ligand of bond length 1.09 Å is 17 ms at 400 MHz (Table 4); it would have to be 69 ms if there were rapid spinning.[28] Therefore the solid state and solution structures must be very similar. The total contribution from ligand nuclei is calculated to be 3%, the remaining 97% being due to one dihydrogen proton relaxing the other by the dipolar mechanism. The two short dihydrogen–ortho-hydrogen distances mentioned above account for most of the 3% ligand contribution.

The ^{1}J(H,D) coupling constants of Table 3 have a linear dependence on temperature. The coupling increases from 21.1 to 22.3 Hz as the temperature is lowered from 295 to 213 K. The coupling does not appear to be field dependent (it is 20.9 ± 0.3 Hz at 200 MHz, 295 K),[1] unlike the complex $\mathrm{Ru_2(HD)(DPB)(^{*}Im)_2}$ which tends to align with the magnetic field.[29] Such a temperature dependence was interpreted in the past as a rapid interconversion of spinning dihydrogen and dihydride tautomers for which the equilibrium constant was temperature dependent.[17] The analogous situation here would be a rapid equilibrium between a rapidly spinning dihydrogen tautomer $\mathrm{Ru(H_2)}$ with a short H–H distance (~0.8 Å) and *cis*-dihydride tautomer with a long H–H distance (1.8 Å). However this is not consistent with the observation of the elongated structure in the solid state. We conclude that a temperature dependent J(H,D) coupling can be a property of elongated dihydrogen ligands. The thermal population of vibrational modes that increase the H–D distance would explain this observation. Plots of d(H–D) versus J(H,D) for dihydrogen complexes from the literature are either linear with a slope of 0.011 Å/Hz[30] or curved with slopes ranging from 0.01 to 0.025 Å/Hz[17] depending on the interpretation of the data. Therefore an decrease in J(H,D) of 1.2 Hz with increasing temperature represents a lengthening of about 0.01 to 0.03 Å. This explanation does not apply to the complex *trans*-$\mathrm{[Os(H{\cdots}D)H(depe)_2]^+}$ in acetone-d_6 where J(H,D) *increased* from 10.5 to 11.6 Hz as the temperature increased from 220 to 325 K.[17]

There is not as good agreement between the solid state structure for other complexes (Table 4) and the solution structure anticipated on the basis of NMR data. The relaxation rate of the H_2 nuclei in Kubas' tungsten complex is primarily determined by the short dihydrogen bond distance and secondarily by longer H···H interactions with some phosphine protons. The barrier to H_2 rotation is very small for this complex, and so the fast spinning limit should apply. The calculated T_1(min) value of 7 ms at 200 MHz is in poor agreement with the one low temperature value of 4 ms measured for this complex. A more thorough VT T_1 study is needed. The agreement is better for the Mo and two Fe complexes with H–H distances of 0.82–0.87 Å at the rapid spinning limit. The T_1 calculated for each H ligand in the complex $\mathrm{Fe(H_2)(H)_2(PEtPh_2)_3}$ has to be converted to a relaxation rate, and then these have to be averaged to allow a comparison with the observed T_1 value of about 24 ms; this is because there is rapid intramolecular H atom exchange between the H_2 and hydride sites.[31] The observed T_1(min) value of 38 ms at 200 MHz for the Ir complex is most consistent with the T_1 value of 49 ms calculated with the (H···H) unit of 1.11 Å at the fast spinning limit. We wonder whether the H–H distance elongates to about 1.3 Å when this complex dissolves in solution; this might happen because of the breaking of the intermolecular H-bond between the (H···H) unit and a terminal chloride which could only exist in the crystal lattice.[7] This is proposed because the J(H,D) value of about 12 Hz for the deuterated complex in solution is closer to that of the Os complex of Table 4 with J(H,D) of 9.1 Hz and d(H···H) of 1.34 Å than to our Ru complex with J(H,D) of 21 Hz and d(H···H) of 1.09 Å. A stretching of this magnitude in the Ir complex would give a calculated T_1(min, slow spinning) value of 33 ms which is consistent with the observed value of 38 ms. The observed T_1(min) value for $\mathrm{[Os(H{\cdots}H)OAc(en)_2]^+}$ gives evidence for a slow spinning or static H···H ligand. It is difficult to calculate accurately the T_1(min) value expected from the structure for the rhenium heptahydride of Table 4 because of relaxation contributions from the rhenium, ligand protons, and other hydrides and because only an exchange-averaged T_1(min) is observed. Luo et al.[9,10] calculate a fast spinning limit value of 68 ms which is close to the observed T_1(min) value, while Desrosiers et al.[23] calculate values at the fast and slow limits which bracket the observed value. Therefore it is not definitely established for the Ir and Re complexes in solution whether the (H···H) unit is spinning rapidly or not.

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Conclusions

The complex [Ru(H···H)(C_5Me_5)(dppm)]BF_4 is one of the few dihydrogen complexes where the presence of an elongated dihydrogen ligand has been established in the solid state and in solution. The dihydrogen ligand is oriented for electronic reasons parallel to the C_5Me_5 ligand, and this creates a barrier to rotation. A comparison between the T_1(min) value calculated from the H atom positions in the solid state, and the value measured for the complex in solution reveals that there is somewhat restricted rotation of the H···H unit and that the overall structure in the solid and solution phases are the same. The ^1J(H,D) coupling in the Ru(H···D) isotopomer is found to be temperature dependent, decreasing with increasing temperature. This is interpreted as a slight lengthening of the H···D bond with increasing temperature, rather than a shift in a rapid equilibrium between the tautomers [Ru(HD)(C_5Me_5)(dppm)]$^+$ which has a spinning HD ligand and *cis*-[Ru(H)(D)(C_5Me_5)(dppm)]$^+$ which has separate *cis*-hydride and -deuteride ligands. The homolytic splitting of the HD ligand is apparently arrested between these two extremes in this complex.

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Supplementary Material Available: Tables of positional and thermal parameters (6 pages); tables of observed and calculated structure factors (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.