Determination of the H−H Distance in Transition-Metal Dihydrogen Complexes: Effects of High Magnetic Fields

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Since the isolation and characterization of the first transition-metal dihydrogen complexes,[1] there have been more than 300 complexes reported.[2] Only a very limited number of these have been structurally characterized by neutron diffraction or solid state NMR. While these techniques provide for an accurate measurement of the H−H distance, ranging from 0.82 to 1.34 Å, more routine solution NMR techniques have broader applicability. In solution NMR, a bound H_2 ligand will exhibit a fast spin−lattice relaxation rate (T_1^{-1}). The spin−lattice relaxation rate is comprised of various contributions to the relaxation process, including the homonuclear dipolar interaction, dipolar interactions from ancillary ligands, chemical shift anisotropy, spin-rotation, quadrupolar interactions, and others.[3] Assuming that the molecule is tumbling isotropically in solution and the rate of relaxation of the dihydrogen ligand is primarily due to the homonuclear dipolar interaction (R_{HH}), the internuclear H−H distance (r_{HH}) can be determined from the observed maximum rate of relaxation (minimum value of T_1).[4]

There is an increasing amount of empirical[5,6] and theoretical[7] evidence that an inverse relationship exists between the J_{HD} value of the HD complex and r_{HH}. Determination of r_{HH} from the J_{HD} value has the advantage that correction factors concerning the rotation regime of the dihydrogen ligand and other sources of relaxation do not have to be considered.[8,9]

We have recently reported the synthesis and characterization of $[Os(H_2)(PPh_3)_2(bpy)(CO)](OTf)_2$ (**1**) (bpy = bipyridyl, OTf = OSO_2CF_3).[5] The measured T_1 of the dihydrogen resonance in complex **1** exhibits a minimum value of 15.2 ms at 263 K in a 11.75 T field (^{1}H: 500 MHz). The measurement of the T_1 minimum of the hydride resonance in the monohydride precursor to **1**, $[OsH(PPh_3)_2(bpy)(CO)]OTf$, allows us to determine that the interactions with the ancillary ligands contribute approximately 3% to the rate of relaxation of the dihydrogen ligand. Based on the corrected T_1 minimum value, the r_{HH} in **1** is calculated to be 1.03 Å.[10]

We have now measured the T_1 of the dihydrogen ligand in complex **1** in a magnetic field of 17.63 T (^{1}H: 750 MHz). The increase in magnetic field was expected to cause an increase in the temperature of the T_1 minimum and an increase in its value that is directly proportional to the increase in field.[8] The T_1 minimum of the dihydrogen resonance of **1** at 750 MHz is found
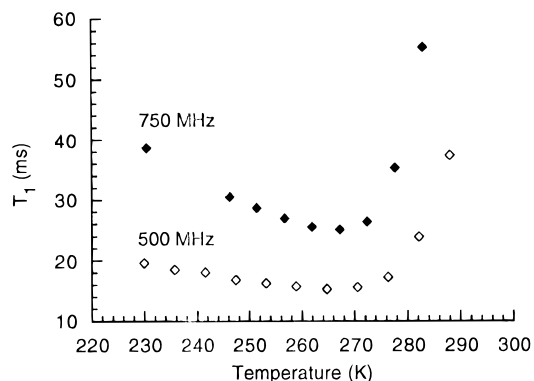

Figure 1. Variable temperature relaxation studies of the dihydrogen resonance of $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**1**) performed in magnetic fields of 11.75 and 17.63 T (^{1}H: 500 and 750 MHz) (CD_2Cl_2).

to be 25.2 ms which is slightly longer than the expected value of 22.8 ms as extrapolated from the 500 MHz data.[5] The temperature of maximum relaxation was found to be essentially identical to that observed at 500 MHz (Figure 1).[11]
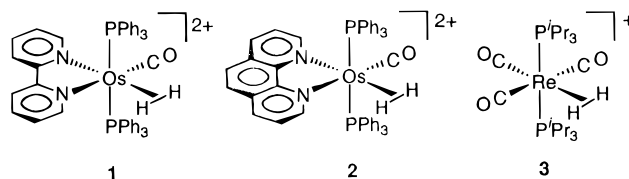
Since the expected increase in temperature of the T_1 minimum did not occur and the value of the T_1 minimum is slightly longer than expected, sources of relaxation other than R_{HH} seem to be affecting the rate. The unexpected behavior was manifested by an increase in magnetic field strength, indicating that anisotropic behavior resulting from partial alignment of complex **1** in the magnetic field may be significant.

Other indications may be apparent in the NMR spectra if partial alignment is occurring.[12] In solution NMR, the rapid molecular tumbling averages the dipolar tensors with respect to the magnetic field so that the dipolar couplings are not observable. However, interaction of the magnetic field with the anisotropic diamagnetic susceptibility ($\Delta\chi$) of the molecule can result in partial alignment with the magnetic field. Such effects become appreciable at very high fields.[13] Small residual dipolar couplings of the hydrogen atoms of the H_2 ligand in transition metal dihydrogen complexes or of the HD ligand in the partially deuterated complexes may be observable in solution NMR in high magnetic fields if the degree of alignment is large enough. The HD resonance in the ^{1}H NMR spectrum will exhibit a coupling that is comprised of the field independent spin coupling (J_{HD}) and the field dependent residual dipolar coupling (D_{HD}).[13] The residual dipolar coupling is proportional to the square of the magnetic field strength; therefore, the measurement of the H−D coupling at several field strengths allows the straightforward determination of the sign and the magnitude of D_{HD} and the magnitude of J_{HD}. Plotting the total splitting versus the square of the frequency of the magnetic field will produce a linear relationship with the intercept of the y axis (zero field) yielding the magnitude of J_{HD}, while the slope

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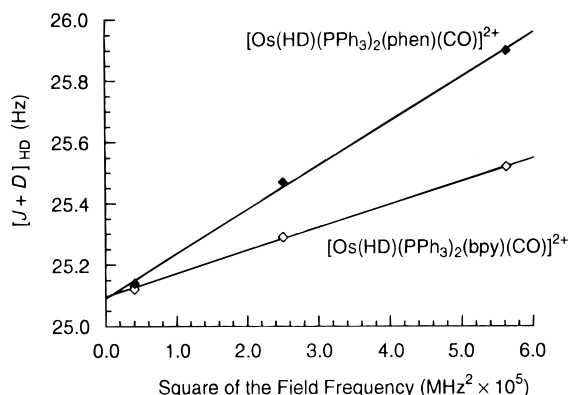
(11) Temperature calibration for the probes in the 500 and 750 MHz spectrometers was achieved using the ^{1}H chemical shifts of pure methanol: Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679−680.

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Figure 2. Total splitting, $[J + D]_{HD}$, of $[Os(HD)(PPh_3)_2(bpy)(CO)]^{2+}$ (**1**-d_1) and $[Os(HD)(PPh_3)_2(phen)(CO)]^{2+}$ (**2**-d_1) versus the square of the frequency. Values of $[J + D]_{HD}$ were measured at 200, 500, and 750 MHz (CD$_2$Cl$_2$).

of the line affords the sign of the dipolar coupling. Since the one bond J_{HD} (and J_{HH}), is always positive,[3] a negative slope indicates a negative D_{HD} (and D_{HH}) and a positive slope is indicative of a positive value of the dipolar coupling.

The partially deuterated species, **1**-d_1, and an analogue, [Os-(HD)(PPh$_3$)$_2$(phen)(CO)](OTf)$_2$ (**2**-d_1) (phen = phenanthroline), were studied in several magnetic fields to determine the field dependence of the total splitting of the HD resonance. Since the bidentate ligands are rigidly bound to the metal center, a greater degree of alignment will result at higher fields. Due to the similarity of the complexes, the spin coupling of the HD complexes is expected to be the same for **1**-d_1 and **2**-d_1, with only the field dependent residual dipolar coupling exhibiting the influence of alignment with respect to magnetic field strength. The maximum difference in the anisotropic diamagnetic susceptibility ($\Delta\chi$) of these complexes can be estimated by the difference of the measured values of magnetic susceptibilities for the bipyridyl and phenanthroline ligands.[14] The larger value of $|\Delta\chi|$ of **2**-d_1 in comparison to **1**-d_1 is expected to add slightly to the observed effects of alignment. The $[J + D]_{HD}$ of the HD resonance in **1**-d_1 measured at 750 MHz is 25.52 (±0.02) Hz and in **2**-d_1 is 25.90 (±0.05) Hz. Careful measurement of the total splitting in other fields allows the determination of the sign and magnitude of the residual dipolar coupling (D_{HD}) and the magnitude of the spin coupling (J_{HD}) for these complexes. At 750 MHz the values of D_{HD} in **1**-d_1 and **2**-d_1 are +0.42 and +0.80 Hz, respectively. The field independent value of J_{HD} is found to be +25.10 Hz in both complexes (Figure 2). The inverse relationship between J_{HD} and r_{HH} allows us to determine the H$-$H distance of the dihydrogen ligand in **1** and **2** to be 1.00 Å.[6]

We can estimate the residual dipolar coupling of **1** and **2** at 750 MHz since D_{HH} should be D_{HD} times γ_H/γ_D or +2.7 Hz for **1** and +5.2 Hz for **2**. The splitting of the H$_2$ resonances in the ^{1}H NMR spectra are therefore only expected to be 4.1 Hz for **1** and 7.8 Hz for **2** at 750 MHz[15] and thus were not detected due to the relatively broad lines observed for the dihydrogen resonances in **1** and **2**.[16]

We sought to verify the source of the partial alignment effects by examining a complex lacking ligands with significant

diamagnetic susceptibilities. To this end, we have measured the T_1 of the H$_2$ resonance as a function of temperature in [Re(H$_2$)(P^{i}Pr$_3$)$_2$(CO)$_3$]BAr$'_4$ (**3**) (Ar$'$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) at 500 and 750 MHz.[17] The expected increases in value and temperature of the T_1 minimum with the increase in field are observed. Measurements of the total splitting of the HD resonance of **3**-d_1 at varying field strengths indicate that the magnetic field has no effect on the H-D coupling.

Collman and co-workers have reported a unique transition-metal dihydrogen compound, Ru$_2$(H$_2$)(DPB)(*Im)$_2$ (DPB = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]bi-phenylene, *Im = 1-*tert*-butyl-5-phenylimidazole) that has two
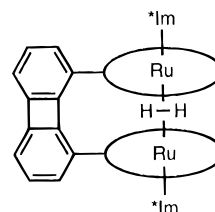
porphyrin rings that are parallel to each other and perpendicular to the Ru$-$Ru axis.[18] The extensive aromatic ring system of this complex provides for a large anisotropic diamagnetic susceptibility leading to a significant degree of alignment in the magnetic field. The partial orientation allows for the observation of residual dipolar H$-$H and H$-$D couplings in high field NMR spectra of Ru$_2$(H$_2$)(DPB)(*Im)$_2$ and Ru$_2$(HD)-(DPB)(*Im)$_2$. This is the only reported observation of partial alignment with the magnetic field of a transition metal dihydrogen complex.

The proximity of the hydrogen atoms in the H$_2$ ligand in transition metal dihydrogen complexes provide for dipolar couplings of 100$-$300 kHz as measured by solid state NMR.[19] Such large couplings allow the possibility of observable residual H$-$H dipolar couplings by solution NMR that are several orders of magnitude smaller. Accurate measurement of the total splitting of the HD resonance is important since the effect is small and the observation could be easily overlooked. Low temperature combined with relatively high magnetic fields may enhance the partial alignment, thereby affecting the relaxation data and the observed spin coupling values. The field dependence of J_{HD} values or T_1 minimum studies should be considered for the determination of the H$-$H bond distance. The growing availability of NMR spectrometers with high magnetic fields increases the possibility of observing the effects of partial alignment in solution.[13]

The observations presented here demonstrate that partial alignment can have a small but significant effect on the solution NMR parameters of transition-metal dihydrogen complexes with commonly employed coligands. Such observations of field dependent partial alignment are not restricted to complex porphyrin ligands.[18]

(14) $\Delta\chi$ values of -1.64×10^{-28} cm^3 and -2.98×10^{-28} cm^3 were used for the bipyridine and phenanthroline ligands, respectively: Bastiaan, E. W.; MacLean, C.; van Zijl, P. C. M.; Bothner-By, A. A. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1987; Vol. 19, pp 35$-$77.

(15) The splitting in the ^{1}H NMR spectrum is equal to $3D_{HH}/2$.

(16) The line widths of the H$_2$ resonances are in excess of 100 Hz. It has been noted that H$_2$ resonances may exhibit some anomalous broadening in addition to what is expected from the T_1 relaxation: Crabtree, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1987; Vol. 2, p 704.

(17) [Re(H$_2$)(P^{i}Pr$_3$)$_2$(CO)$_3$]BAr$'_4$ supplied by Dr. Catherine Radzewich for 750 MHz variable temperature NMR spin$-$lattice relaxation study. 500 MHz data: Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 4172$-$4181.

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