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H−H Distances in Elongated Transition Metal Dihydrogen Complexes: Effects of Temperature and Isotopic Substitution

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Since the isolation and characterization of the first transition metal dihydrogen complexes by Kubas and co-workers,[1] several hundred dihydrogen complexes have been reported.[2] The key structural parameter in these complexes is the H−H distance r_{HH}, which is difficult to determine by X-ray diffraction. Solution NMR techniques such as the measurement of H−D couplings in partially deuterated samples have proven to be very useful in determining r_{HH}. There is increasing empirical[3,4] and theoretical[5] evidence that an inverse linear relationship exists between the J_{HD} value of the H−D complex and r_{HH}, at least for 0.8 Å $\leq r_{HH} \leq$ 1.35 Å. Determination of r_{HH} from J_{HD} values has the advantage over relaxation based methods that correction factors concerning the rotation regime of the dihydrogen ligand and other sources of relaxation do not have to be considered.[6,7] While the vast majority of complexes studied to date have $r_{HH} \leq 1$ Å, there are a small number of examples of dihydrogen complexes with longer values of r_{HH}, which seem to be intermediate between dihydrogen and normal dihydride complexes. Such species may represent arrested intermediate states in the very important oxidative addition reaction.

Reports of temperature-dependent values of J_{HD} in certain dihydrogen complexes are perplexing and may seem to reduce the utility of the H−D coupling measurement in determining the H−H distance. In the well-characterized cationic ruthenium complex $[Cp^*Ru(dppm)(H_2)]^+$ (**1**), $r_{HH} = 1.10(3)$ Å has been determined by low-temperature neutron diffraction.[8] In solution, complex **1**-d_1 exhibits a small decrease in J_{HD} upon increasing the temperature from ca. 200 K to room temperature, which may signal a slight increase in the H−H (H−D) bond distance. Thermal population of vibrationally excited states was proposed to account for the decreased coupling at higher temperatures.[8] A computational study using Density Functional Theory (DFT) calculations has confirmed this hypothesis, and also leads to the intriguing suggestion that the bond distance in complex **1** will be sensitive to isotopic substitution, with the distance in the H−H complex predicted to be approximately 10% longer than that in the corresponding T−T complex.[9] We sought to obtain additional coupling data for complex **1** and related complexes to verify this intriguing hypothesis.

Since the reported variation in J_{HD} values with temperature in complex **1** is very subtle, we first sought to confirm the effect of temperature by repeating the measurements at a variety of magnetic fields. This is important to rule out the possibility that residual dipolar coupling arising from partial alignment in the field is responsible for the observed variation in the coupling with temperature.[10] Such effects are usually only observable in very high magnetic fields. While Morris and co-workers[8] had reported that J_{HD} values were field independent at 200 and 400 MHz, we needed to verify that very high fields would not lead to partial alignment. We find that the measured value of J_{HD} in complex **1** is independent of magnetic field within experimental error (300, 500, and 750 MHz) when spectra were recorded at a variety of temperatures between 220 and 300 K[11] (see Figure 1). The estimated uncertainty in the J_{HD} values is ±0.3 Hz, so the observed effect of temperature is real, but only slightly larger than experimental uncertainty.

To verify the temperature dependence of the coupling and to probe for the predicted isotope effects on bond distance, the use of tritium NMR spectroscopy is advantageous. The magnetogyric ratio of ^3H is 6.949 times larger than that of ^2H, so couplings between H and T should be correspondingly larger than couplings between H and D, making the detection of small changes in the coupling much more reliable. A sample of complex **1** (1 mg) was dissolved in CD_2Cl_2 and equilibrated under 1 atm of HD gas for several hours, giving a mixture of isotopomers with a deuterium content of ca. 50%. Exposure to T_2 gas (200 Torr) for 2 h affords a sample containing about 20% tritium in the bound dihydrogen.[12] ^1H NMR spectra were recorded at 500 and 750 MHz and ^3H NMR spectra were recorded at 533 and 800 MHz. A typical ^1H NMR spectrum is shown in Figure 2. The coupling data for the various isotopomers of complex **1** are summarized in Table 1.

An analysis based on those complexes where the H−H distance is accurately known from neutron diffraction or solid-state NMR spectroscopy has previously led to the conclusion that the observed J_{HD} couplings have an inverse linear relationship to the H−H bond distance with $r_{HH}(\text{Å}) = 1.44 - 0.0168(J_{HD})$.[13] To derive distances from J_{HT} and J_{DT} values, these couplings can be converted to the corresponding H−D couplings by using $\gamma_T/\gamma_D = 6.949$ and $\gamma_T/\gamma_H = 1.067$. Distances so derived are tabulated in Table 1. The most precise data arise from the H−T coupling measurements, where the experimental uncertainty is estimated as ±0.4 Hz, corresponding to an uncertainty in the bond distance of ±0.001 Å. The bond distance data for bound H−D, H−T, and T−D as a function of temperature are shown in Figure 3.

The derived bond distances at the higher temperatures are in agreement with the value of $r_{HH} = 1.10(3)$ Å for complex **1** reported by neutron diffraction. It is clear from our data that substitution with heavier isotopes leads to a significant shortening of the bond distance, as predicted by the DFT study of Lledós, Lluch, and co-workers.[9]

An alternative explanation for the observed temperature dependence of the coupling constants described above postulates

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(11) Samples of $[Cp^*Ru(dppm)(H-D)]^+$ (**1**-−d_1) were prepared by treatment of methylene chloride solutions of **1** with D_2 gas until ^1H NMR spectroscopy indicated approximately 90% deuteration. This allows for the observation of the hydride resonances of **1**-d_1 without interference from the resonances due to **1**.

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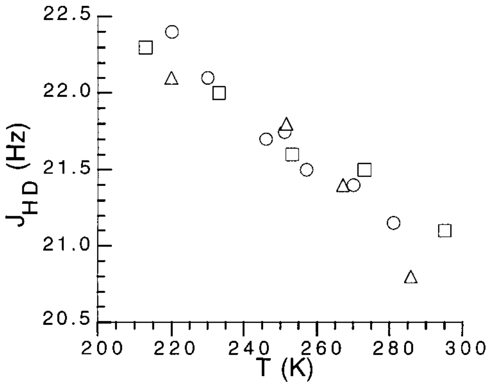

Figure 1. J_{HD} versus temperature at various magnetic fields: (squares) 400 (ref 8), (triangles) 500, and (circles) 750 MHz.

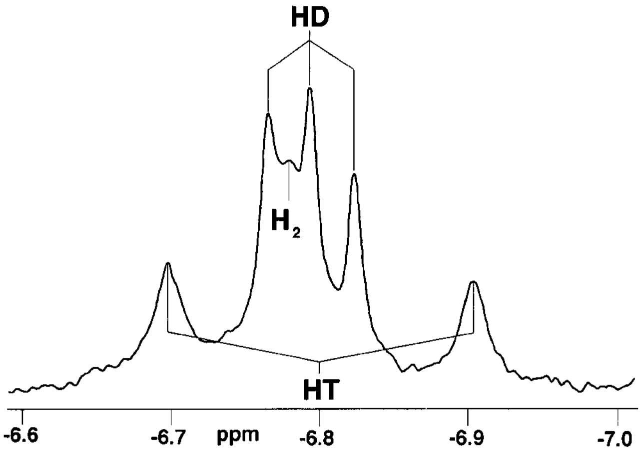

Figure 2. Partial ^{1}H NMR spectrum (750 MHz) of **1** at 251 K with incorporation of deuterium and tritium. The chemical shift of the bound dihydrogen in **1** is −6.779 ppm. Isotope shifts for **1**-d_1 and **1**-t_1 are 15 and 22 ppb, respectively.

Table 1. Couplings (Hz) and Derived Distances (Å) in Isotopomers of **1**

T (K)	J_{HD}[a]	r_{HD}[b]	J_{HT}[c]	r_{HT}[d]	J_{DT}[a]	r_{DT}[b]
286	20.7	1.092	149.1	1.079	23.4	1.072
267	21.5	1.079	151.8	1.072	24.0	1.062
251	21.7	1.075	153.6	1.068	24.4	1.056
220	22.4	1.064	158.7	1.056	25.6	1.037

[a] ±0.3 Hz. [b] ±0.005 Å. [c] ±0.4 Hz. [d] ±0.001 Å.

a rapid equilibrium between the predominant dihydrogen form (as seen in the low-temperature neutron structure) and a minor cis dihydride tautomer. If this hypothesis is correct, the observed couplings and chemical shifts would represent a population weighted average of these two isomers, which would be expected to shift with temperature. If such an equilibrium prevails, a temperature-dependent chemical shift for the resonance due to bound H_2 would be expected. Careful measurement shows that the chemical shift due to the bound dihydrogen in **1** is essentially independent of temperature, moving upfield by only 10 ppb upon changing the temperature from 220 to 300 K.

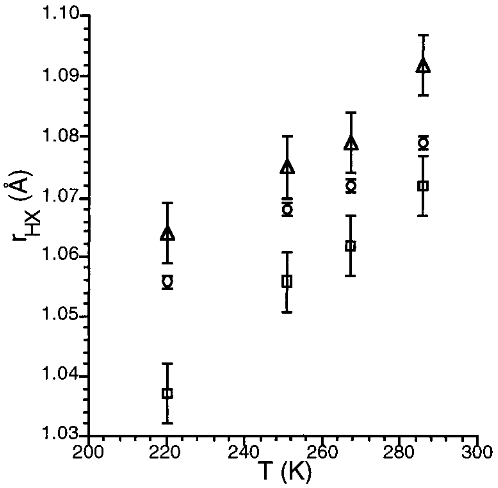

Figure 3. Bond distances as a function of temperature: (triangles) HD, (circles) HT, and (squares) DT. Error bars indicate the estimated uncertainty.

Another signature of the possible equilibrium would be isotopic perturbation effects arising from nonstatistical distribution of deuterium (and tritium). These effects will be manifested by large and temperature-dependent values of the isotope shift. However, the isotope effects on the chemical shifts of the hydride resonance in **1** are small and temperature independent. For example, $\delta_{\mathrm{HD}} - \delta_{\mathrm{HH}} = 15$ ppb and $\delta_{\mathrm{HT}} - \delta_{\mathrm{HH}} = 22$ ppb (see Figure 2). The former of these values is actually in the low end of the range of isotope effects reported for bound dihydrogen.[14] On the basis of these observations, the equilibrium hypothesis seems unlikely, but cannot be definitively ruled out.

The results described here provide direct experimental verification of the conclusions of the DFT study of Lledós and Lluch.[9] The remarkable isotope dependence of the bond distance in the bound dihydrogen ligand of **1** is attributed to the extremely flat and highly anharmonic potential energy surface that defines the H−H and M−H interactions in this complex, which allows the zero point energy differences among the various isotopomers to be directly reflected in the bond distances.[15] The striking change of the bond distance upon small changes in temperature is due to thermal population of vibrational excited states which are only slightly higher in energy than the ground state. That these effects are exhibited by a molecule that is readily isolable is without precedent.

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(14) Cf.: Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175.

(15) A reviewer has pointed out that the model of Lledós and Lluch only includes the H−H stretching coordinate and neglects other softer vibrational coordinates of the M(H_2) fragment.