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Review Article

Transition metal dihydrogen complexes: isotope effects on reactivity and structure[†]

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Abstract: Complexation of dihydrogen to transition metal centers was discovered by Kubas and coworkers in 1984. The notion that the simplest molecule in chemistry can act as a ligand to form relatively stable transition metal complexes has led to a paradigm shift in coordination chemistry. Crucial to the exploration of this intriguing new chemistry has been the use of isotope substitution. Several aspects of the coordination chemistry of dihydrogen have revealed fascinating isotope effects on reactivity, spectroscopy and in some cases structure. Complexation of HD has been used to diagnose bond distances from measurements of J_{HD} and isotope effects for D_2 versus H_2 binding have been evaluated. Examples of quantum mechanical exchange coupling in H_2 complexes have been described. These effects disappear when one of the H atoms is replaced by D. In molecules with bound hydrogen adjacent to a hydride ligand, non-statistical occupancy of hydrogen versus hydride sites by deuterons has been observed. In some cases, isotope-dependent *structures* have been established by the study of HD, HT and DT complexes using NMR spectroscopy. Copyright © 2007 John Wiley & Sons, Ltd.
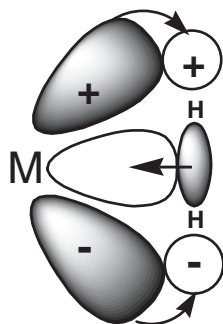
Introduction

Homogeneous transition metal catalysts play a pivotal role in hydrogenation and hydroformylation reactions. For this and other reasons, the reaction of hydrogen with soluble transition metal complexes has been extensively studied. The first molecular transition metal hydride complex to be reported was $H_2Fe(CO)_4$, described by Walter Hieber and coworkers in 1931.[1] In 1984, the first example of coordination of an intact dihydrogen molecule was reported by Greg Kubas and coworkers.[2] This revolutionary result was received with some skepticism by the coordination chemistry community. Kubas has described the difficulties that were encountered, which bear considerable resemblance to the reception accorded to the discovery of nitrogen complexes 20 years earlier.[3]

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The accepted paradigm for the binding of a Lewis basic ligand to a Lewis acidic metal center depends upon electron donation from a low lying molecular orbital of the ligand (often a lone pair) to an empty metal centered orbital of appropriate symmetry. Some ligands (such as ethylene and carbon monoxide) also gain additional binding energy by back donation from filled metal d orbitals into empty ligand centered antibonding orbitals. For the binding of hydrogen to transition metals, an adaptation of the Dewar–Chatt model for ethylene binding is generally accepted. The bonding interactions between a metal complex and hydrogen have been described in terms of donation from the filled sigma bonding orbital of H_2 into an empty orbital of sigma symmetry on the metal. This interaction is augmented by back donation from filled metal orbitals of predominant d character to the σ^* orbital of H_2. Both of these interactions weaken and lengthen the H–H bond. In the limit of strong back donation from an electron-rich metal center, bond cleavage to form a dihydride (*oxidative addition*) can result. In the diagram below, filled orbitals are shaded and M represents a metal with associated ancillary ligands. While this model is generally accepted, there is continuing discussion of the relative importance of the sigma and pi components.

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Since the initial discovery by Kubas, a large number of hydrogen complexes have been prepared, and a rich chemistry is rapidly developing. A key aspect of the structure of these complexes is the H–H distance (d_{HH}), which has been found to be in the range 0.85–1.0 Å in the vast majority of complexes reported to date. In contrast, conventional dihydride and polyhydride complexes generally have $d_{HH} \geqslant 1.5$ Å. Dihydrogen complexes which have d_{HH} values between approximately 1.1 and 1.5 Å are structurally very interesting. Such complexes have been termed 'stretched' or 'elongated' dihydrogen complexes. In the representation below, elongated dihydrogen complexes are depicted as intermediate between 'normal' dihydrogen complexes and dihydride complexes.
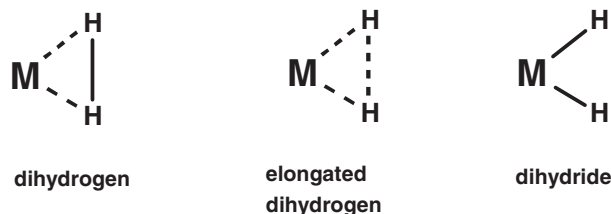
The thermal stability of these complexes varies with the strength of the interaction between H_2 and the metal center. The initial studies by Kubas and coworkers examined complexes of the group 6 metals W, Mo and Cr of the general form $(PR_3)_2M(CO)_3(H_2)$. These complexes bind hydrogen relatively weakly and have values of d_{HH} less than 1 Å. Species with stronger metal/hydrogen interactions are more robust and have longer values of d_{HH}. While the complexes discussed here have good thermal stability and are isolable at room temperature, dihydrogen complexes are reactive and like many low valent organometallic species must be stored and handled under an inert atmosphere.

Experimental methods for structure determination in dihydrogen complexes

The precise location of metal-bound hydrogen atoms by X-ray diffraction is problematic. Superior structural information is provided by neutron diffraction, but the requirement for large well-formed single crystals has limited this method to a small subset of the known complexes.[4]

The direct measurement of dipolar couplings in solid-state ^{1}H NMR is a potentially general approach to this problem which requires modest quantities of solid sample. Dipolar coupling between the bound hydrogen atoms is proportional to $(d_{HH})^{-3}$, so this method gives very precise values for d_{HH}.[5]

Crabtree and coworkers pioneered the use of dipole–dipole relaxation rates (a solution ^{1}H NMR technique) to measure HH distances.[6] This methodology was later refined by Halpern and coworkers.[7] The measurement at various temperatures of the spin lattice relaxation time (T_1) of the hydride resonance is required. If the temperature corresponding to the maximum rate of relaxation (minimum T_1) can be reached, a value for d_{HH} can be extracted.

A widely employed solution NMR method relies upon the measurement of H–D couplings in the bound dihydrogen ligand. By employing HD gas in the synthesis reaction, a single deuteron (nuclear spin $I = 1$) can be introduced into the bound hydrogen ligand. In HD gas, the coupling between H and D ($^1J_{HD}$) is 43 Hz. When HD gas reacts with a transition metal precursor to form a dihydride complex, the resulting two bond coupling between H and D ($^2J_{HD}$) is typically very small, ca. 2–3 Hz. Dihydrogen complexes have $1J_{H–D}$ values between these two limits, and the value of $^1J_{H–D}$ is inversely related to the internuclear distance d_{HH}. This empirical correlation is anchored by data from solid-state NMR and neutron diffraction determinations as outlined above.[8] For $d_{HH} \leqslant 1.2$ Å, this relationship can be easily quantified (Equation (1)):

$$d_{HH}(\text{Å}) = 1.44 - 0.0168(J_{HD}) \qquad (1)$$

A very similar inverse linear relationship between $J_{H–D}$ and d_{HH} was predicted computationally.[9] A more sophisticated analysis of the relationship between HD coupling and d_{HH} recently reported by Chaudret, Limbach and coworkers suggests that the linearity as described in Equation (1) breaks down at longer distances, but that reliable values for d_{HH} can be extracted from H–D coupling.[10] This approach has been extended by Gelabert and coworkers using a slightly different analysis, with the results shown in Figure 1.[11] A problem with both of these approaches is the relative paucity of structural data for complexes with values of $d_{HH} \geqslant 1.3$ Å. In spite of these limitations, this method is believed to give reliable values of d_{HH} up to about 1.5 Å. At longer distances, the two bond components of the coupling become dominant, leading to contributions to the coupling from factors other than d_{HH}. Implicit in any determination of d_{HH} from $^1J_{H–D}$ is the assumption that the distance is independent of
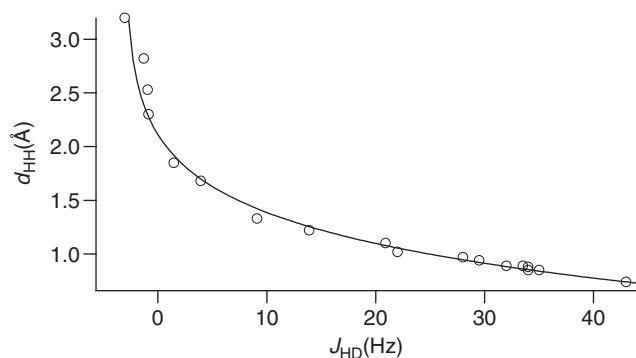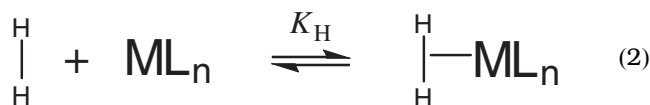
Figure 1 d_{HH} as a function of J_{HD}. Circles indicate experimental data from neutron diffraction and solid-state NMR spectroscopy. The line is fit using a published model.[11]

isotope substitution. As outlined below, this assumption is not always valid.
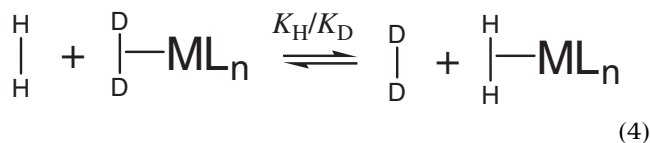
Isotope effects on hydrogen binding

Shortly after the discovery of dihydrogen complexes, attention turned to measurement of the hydrogen binding energetics and the possibility of isotope effects on hydrogen binding. In the case of the prototypical complex $(H_2)W(CO)_3(PCy_3)_2$, measurement of the heat of reaction for displacement of the bound dihydrogen with pyridine has been used in combination with other data to determine that the binding energy of H_2 to this metal center is approximately $20\,kcal/mol$.[12]

In general, the binding of hydrogen to a metal fragment ML_n can be considered in terms of Equation (2), with binding of deuterium described by Equation (3)

$$\begin{matrix} H \\ | \\ H \end{matrix} + ML_n \xrightleftharpoons{K_H} \begin{matrix} H \\ | \\ H \end{matrix}\!-\!ML_n \qquad (2)$$

$$\begin{matrix} D \\ | \\ D \end{matrix} + ML_n \xrightleftharpoons{K_D} \begin{matrix} D \\ | \\ D \end{matrix}\!-\!ML_n \qquad (3)$$
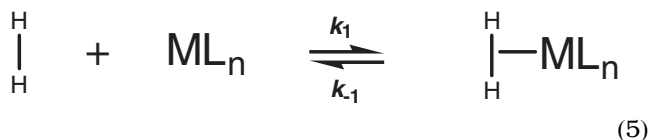
Competitive binding of hydrogen versus deuterium can be described by Equation (4), which results from combination of Equations (2) and (3). A direct measure of the deuterium equilibrium isotope effect (EIE) is provided by the ratio K_H/K_D

$$\begin{matrix} H \\ | \\ H \end{matrix} + \begin{matrix} D \\ | \\ D \end{matrix}\!-\!ML_n \xrightleftharpoons{K_H/K_D} \begin{matrix} D \\ | \\ D \end{matrix} + \begin{matrix} H \\ | \\ H \end{matrix}\!-\!ML_n \qquad (4)$$

Kubas, Bender and coworkers have used vibrational data to calculate the EIE for Equation (4) for $ML_n = W(CO)_3(PCy_3)_2$. This tungsten complex is the only dihydrogen complex for which a complete set of vibrational frequencies is available. Using the general treatment of EIEs developed by Bigeleisen and Goeppert-Mayer,[13] the calculated EIE value for Equation (4) is $K_H/K_D = 0.78(300\,K)$.[14] This inverse EIE is largely attributable to low-frequency torsional and wag modes. These modes are significantly more populated at $300\,K$ for the deuterium complex versus the hydrogen complex. These calculated values were confirmed by competition experiments, which gave $K_H/K_D = 0.70 \pm 0.15$ for the tungsten complex in THF solvent at $22°C$.[14] Similar experiments lead to $K_H/K_D = 0.65 \pm 0.15$ for the Cr analog with $ML_n = Cr(CO)_3(PCy_3)_2$. In both cases, deuterium binds more strongly than hydrogen. This is somewhat counterintuitive, since the D–D bond is stronger than the H–H bond by ca. $1.8\,kcal/mol$, suggesting that the reaction of Equation (4) should be slightly exothermic.

The study of the temperature dependence of the equilibrium of Equation (4) reveals that the isotope effect can be attributed to an unfavorable enthalpy term, $\Delta\Delta H = 1.8 \pm 1.0\,kcal/mol$. Thus, displacement of bound deuterium by hydrogen as depicted in Equation (4) above is *endothermic.* This enthalpy term overcomes a favorable entropy contribution of $\Delta\Delta S = 5.3 \pm 4.0\,cal/mol/deg$. The standard entropy of D_2 gas is $34.6\,cal/mol/deg$ versus $31.2\,cal/mol/deg$ for H_2. The greater negative entropy of binding for D_2 gas versus H_2 gas is due to a greater loss of rotational (and translational) entropy for D_2 upon binding.

Limited data are available for isotope effects on the rate of dissociation or coordination of hydrogen. Such kinetic isotope effects (KIE) can be measured in some cases. For the reaction shown in Equation (5), with $ML_n = W(CO)_3(PCy_3)_2$, Hoff and coworkers determined the values of $k_{-1} = 469\,s^{-1}$ for H_2 and $267\,s^{-1}$ for D_2.[15] This leads to the KIE for hydrogen (deuterium) dissociation $k_{-1}^H/k_{-1}^D = 1.7$

$$\begin{matrix} H \\ | \\ H \end{matrix} + ML_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{matrix} H \\ | \\ H \end{matrix}\!-\!ML_n \qquad (5)$$

Using this observation in combination with the EIE data allows the calculation of the KIE for binding (Equation (6))

$$k_1^H/k_1^D = K_H/K_D \times k_{-1}^H/k_{-1}^D = 0.7 \times 1.7 = 1.2 \qquad (6)$$

Isotope effects for hydrogen binding to $Cr(CO)_5$ to form the unstable complex $(H_2)Cr(CO)_5$ have been

determined by fast spectroscopic methods.[16] In this case, the rate of H_2 binding is 1.9 times faster than the rate of D_2 binding $(10^4 \, s^{-1})$, but the dissociation rate for H_2 is $2.5 \, s^{-1}$ compared to $0.5 \, s^{-1}$ for D_2. Overall, D_2 is bound more strongly than H_2.

Isotope effects in ^{1}H NMR spectroscopy of H_2 complexes: exchange coupling

As reviewed by Sabo-Etienne and Chaudret,[17] some transition metal polyhydride complexes exhibit quantum mechanical exchange coupling (QMEC). If two adjacent hydrogen atoms bound to a metal center are in a suitably soft potential, a pairwise tunneling process can occur. This often leads to *very* large HH couplings in the ^{1}H NMR spectra of these complexes. There is some discussion in the literature as to the possible intermediacy of a dihydrogen complex in mediating this interaction. Consistent with the symmetrization postulate, the couplings are quenched when the symmetry of the system is reduced, i.e. if one of the two H atoms is replaced by D or T.

In this context, very interesting observations have been reported by Chaudret and coworkers on a cationic H_2 complex of tantalum, $[Cp_2Ta(CO)(H_2)]^+$ (**1**, $Cp = \eta^5\text{-}C_5H_5$). The tantalum center in complex **1** has a d^2 configuration, which is expected to give a large electronic asymmetry in the back donation from Ta to the σ^* orbital of the bound H_2 ligand as the H_2 rotates. It was expected that hydrogen rotation in this complex would have a sufficiently large barrier to rotation that a 'static' spectrum would be accessible in the temperature range available to solution ^{1}H NMR spectroscopy (Figure 2).

Surprisingly, the resonance due to bound dihydrogen in **1** is invariant with temperature. In contrast the HD complex **1**-d_1 exhibits decoalescence at low temperature, allowing the two ends of the bound HD ligand to give distinct resonances (Scheme 1).[18]

This profound change in the NMR spectrum upon isotope substitution is not the result of a conventional KIE on the rotation process. Rather, Chaudret and

coworkers attribute this to the quenching of QMEC by isotope substitution.

Dihydrogen complexes with an adjacent hydride ligand

Molecules with both dihydrogen and hydride ligands adjacent in the coordination sphere of a transition metal complex have very interesting properties. Such complexes generally have barriers to hydrogen atom permutation of 5 kcal/mol or less. Such dynamic processes can be studied by ^{1}H NMR spectroscopy.
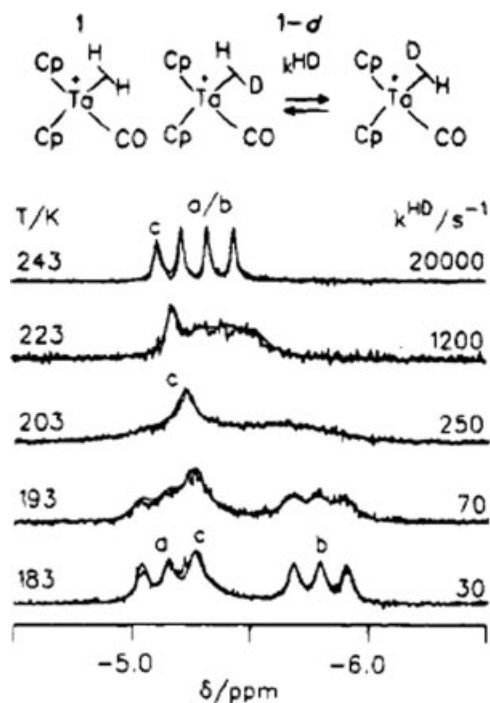

Figure 2 ^{1}H NMR spectra for the hydride region of a mixture of **1** and **1**-d_1 at various temperatures as reported by Sabo-Etienne and coworkers.[18] The signal designated as c is due to **1** and is invariant with temperature. The signals designated as b and c are due to **1**-d_1. The experimental spectra are overlaid with calculated spectra derived using the indicated value for k^{HD}, the rate constant for H atom permutation. Reproduced by permission from the American Chemical Society.

Scheme 1

$$(7)$$
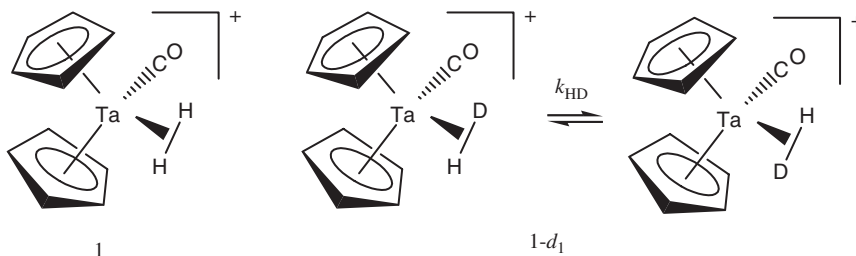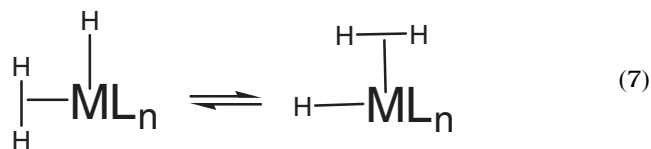
When such a molecule is partially deuterated, the expectation would be that the deuteron would be statistically distributed between the dihydrogen and the hydride ligand. In fact, non-statistical distributions of deuterium are often observed. In the case of the cationic iridium tris-pyrazolyborate complex **2**, D concentrates in the hydride ligand, leading to concentration of H in the dihydrogen ligand. In the structural diagrams for complexes **2–4**, the site of deuterium enrichment is indicated with an arrow. By studying the NMR spectra of partially deuterated samples of complex **2** as a function of temperature, the energy difference between the two different isomers of $2\text{-}d_1$ can be quantified. The species with the single deuteron in the hydride site is more stable by 125 cal/mol (Scheme 2).[19]

In contrast to **2**, partial deuteration of **3** leads to concentration of D in the dihydrogen ligand.[20] Similar results were reported for the iron complex **4**.[21] It seems that the lowest energy situation results from placing D in the strongest available bond. In the case of third row transition metals such as iridium, the M–H bond is stronger than the H–H bond. For first and second row metals such as rhodium and iron, the situation is reversed.

A somewhat different situation results in molybdenum complex **5**, which also features a dihydrogen ligand adjacent to a hydride. In this case, the metal configuration is d^2, so this molecule combines some of the features of tantalum complex **1** with the dihydrogen/hydride complexes **2–4** considered above. It could reasonably be anticipated that the d^2 configuration would lead to a substantial barrier to H_2 rotation and that the degenerate atom exchange would be slowed sufficiently at very low temperatures that three distinct hydride resonances could be observed, corresponding

to a hydride ligand and the inner/outer ends of the dihydrogen ligand.

Very low-temperature ^{1}H NMR spectroscopy of complex **5** and partially deuterated derivatives reveals that rotation of the bound HD ligand can be stopped on the NMR timescale, while the HH ligand exhibits a substantial exchange coupling. Although this dynamic process can be stopped, the atom exchange between the dihydrogen moiety and the adjacent hydride is *very* rapid at the lowest accessible temperatures (125 K), even in $5\text{-}d_2$.[22] It is also observed that partially deuterated samples of **5** exhibit non-statistical distribution of D, with a slight concentration of D in the dihydrogen ligand (Scheme 3).

Elongated dihydrogen complexes

Elongated dihydrogen complexes were initially considered as frozen structures at various points on the oxidative addition pathway of dihydrogen to the transition metal center, and were described by simply interpolating between the dihydrogen or dihydride models. However, attempts to use conventional experimental methods to determine the structure of elongated dihydrogen complexes are fraught with difficulties. In some cases, a complete description of the bonding situation in such complexes presents significant challenges to our traditional ideas of chemical bonding. Both computational and experimental approaches have been applied to these problems,
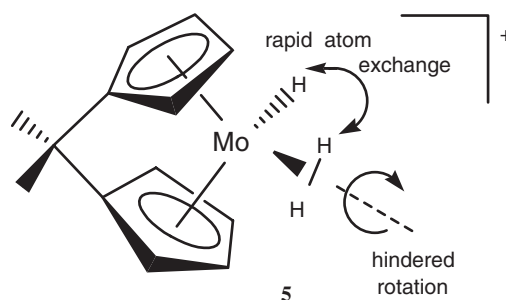
Scheme 3
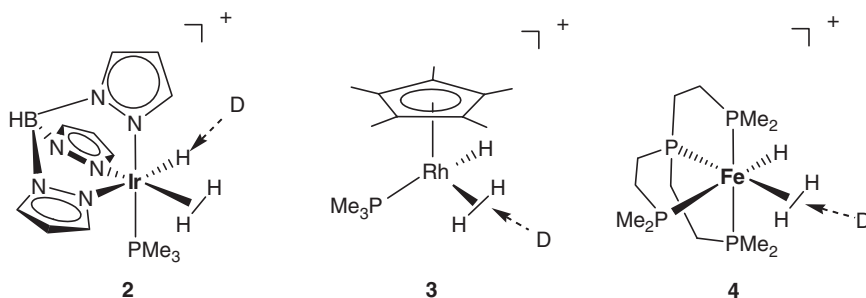
Scheme 2

and the interplay between theory and experiment has been particularly beneficial in advancing our understanding of these interesting molecules.

Ruthenium complexes: structural and computational studies

Cyclopentadienyl and phosphine ligands are widely used supporting ligands for hydride and dihydrogen complexes. There is an extensive set of cationic ruthenium dihydrogen complexes of the general form $[Cp/Cp^*Ru(P–P)(H_2)]^+$ (P−P = chelating diphosphine ligand; $Cp = \eta^5\text{-}C_5H_5$; $Cp^* = \eta^5\text{-}C_5Me_5$).[23] These robust cationic complexes can be prepared by several synthetic methods. The most convenient uses metathesis reactions of the corresponding neutral chloride with $NaBAr_4$ under hydrogen gas. When the preparations are carried out with HD gas, the HH distance can be readily extracted by measurement of J_{HD}. Depending upon the co-ligands employed, the HH distance varies greatly, from 1.0 to 1.2 Å. This extensive family of complexes is exemplified by $[Cp^*Ru(dppm)(H_2)]^+$ (**6**; dppm = bis-diphenylphosphinomethane).

The structure of **6** was determined (neutron diffraction) by Morris, Koetzle and coworkers in 1994, who found that $d_{HH} = 1.10 \pm 0.03$ Å. This is consistent with T_1 measurements and the H–D coupling. Variable temperature ^{1}H NMR spectra revealed 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 (Scheme 4).[24]

In 1997 a computational study was reported on $[CpRu(H_2PCH_2PH_2)(H_2)]^+$, which serves as a model system for complex **6**. Using DFT calculations, a two-dimensional potential energy surface (PES) was built up as a function of d_{HH} and the Ru–H distance (Figure 3).

The resulting PES is highly anharmonic and has a very slight gradient in energy as the H–H distance is increased, suggesting that the H_2 ligand is greatly delocalized. Calculations on the lowest energy state gave expectation values of 1.02 and 1.61 Å for the H–H and Ru–H_2 distances, respectively, close to the neutron diffraction distances (1.10 and 1.58 Å, respectively). Longer values of the H–H distance were obtained for vibrationally excited states. Assuming a Boltzmann-type equilibrium distribution for all the vibrational states considered, the mean thermal H–H distance is predicted to become longer at higher temperatures. This fact explains the experimentally observed decrease in J_{HD} upon increasing the temperature, which

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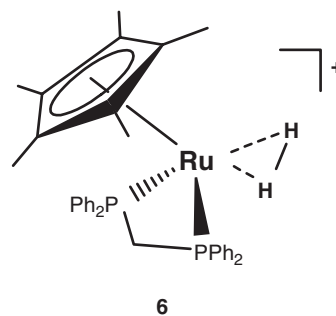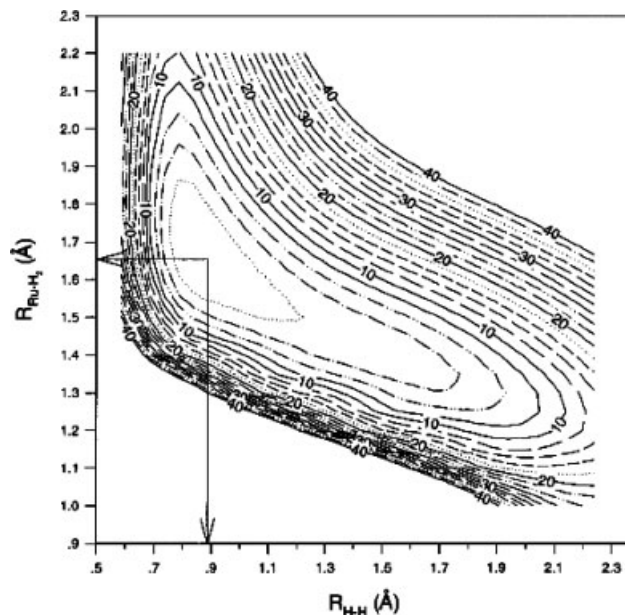
Scheme 4

Figure 3 Two-dimensional potential energy surface for the $[CpRu(H_2PCH_2PH_2)(H_2)]^+$ complex. Energies of contours are given in kcal/mol. The arrows indicate the position of the minimum potential energy structure. Reproduced by permission from the American Chemical Society.

would be due to the thermal population of vibrationally excited states involving longer H–H distances.

Importantly, these findings led to the prediction that replacement of H with D would lead to a significant structural isotope effect, with d_{DD} predicted to be 3% less than d_{HH}.[25]

Ruthenium complexes: experimental observation of structural isotope effects

While neutron diffraction studies are generally seen as definitive, the structural data on complex **6** have an unusually large uncertainty of $\pm 3\%$ in d_{HH}. This is due to thermal motion which persists even at the low temperature employed for the diffraction experiment, providing indirect verification of the soft PES computed by Lledos, Lluch and coworkers.
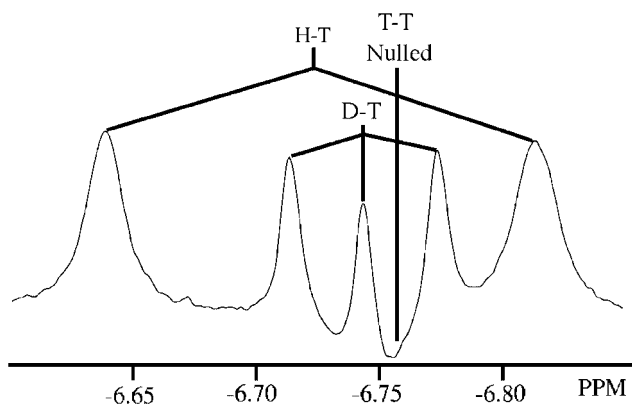
Figure 4 ^3H NMR spectrum (800 MHz) of **6** at 287 K. The resonance due to bound T_2 has been nulled by applying a 180–τ–90 pulse sequence with $\tau = 15$ ms. Coupling of T to H in HT gives the outer doublet. Coupling of T to D ($I = 1$) in bound HD leads to the central 1:1:1 pattern. Reproduced by permission from the American Chemical Society.
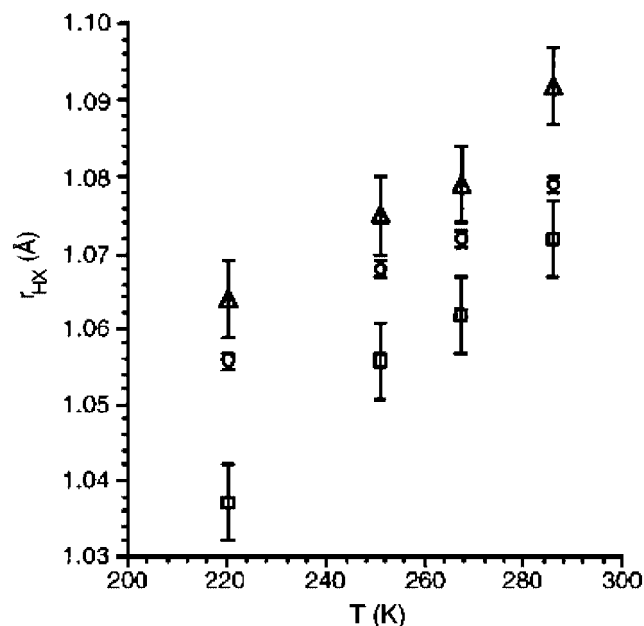

Figure 5 Bond distances derived from coupling data as a function of temperature for complex **6**. HD (triangles), HT (circles) and DT (squares). Reproduced by permission from the American Chemical Society.

Ultimately, the predicted structural isotope effect was observed experimentally by the use of NMR spectroscopy. In principle, examination of the coupling in isotopomers of **6** containing bound HD, HT and DT should reveal any changes in structure arising from changes in the mass of the bound ligand.[26] These experiments require the handling of tritium in the form of carrier-free T_2. Suitable precautions must be followed while preparing the samples and while recording NMR spectra. While bound HD and HT can be observed with a conventional ^1H NMR probe, special equipment is required to directly observe tritons. A typical triton NMR spectrum for complex **6** is shown in Figure 4.

Since couplings are directly proportional to the magnetogyric ratios of the nuclei, it was readily apparent that the bond distances are all temperature dependent and that heavier isotopes lead to significantly shorter bonds between the hydrogen (deuterium, tritium) atoms. The couplings can be converted to HX distances by application of the magnetogyric ratios and the correlation between distance and HD coupling. A summary of data for complex **6** is shown in Figure 5. Inspection of this data shows that the computational predictions of a structural isotope effect are verified. For example, a comparison of bound HD versus bound DT reveals that d_{DT} is 2–3% shorter than d_{HD}, qualitatively verifying the computational prediction. This is a remarkable isotope effect on a bond distance in a molecule which is stable at room temperature.

These observations were subsequently extended to complexes closely related to **6**. It was found that $[CpRu(dmpe)(H_2)]^+$, (dmpe = 1,2 bis-dimethylphosphinoethane) a complex with $d_{HH} = 1.07$ Å (from $J_{HD} = 22$ Hz) also exhibits a modest temperature

dependence of the H–D coupling, showing the same trend of lower coupling at higher temperatures. In contrast, $[CpRu(dppe)H_2]^+$ (dppe = 1,2 bis-diphenylphosphinoethane) exhibits a *temperature-independent* H–D coupling of 25 Hz, consistent with d_{HH} of ca. 1.02 Å. Similar temperature-independent H–D couplings were observed for $[Cp^*Ru(dmpm)H_2]^+$ (dmpm = 1,2 bis-dimethylphosphinomethane), ($J_{HD} = 16$ Hz; d_{HH} of ca. 1.16 Å). Thus, it was concluded that the phenomenon of structural isotope effects is exquisitely sensitive to the structure of the dihydrogen complexes, with the temperature- and isotope-dependent structures only observed for ruthenium complexes of this type when d_{HH} is ca. 1.1 Å.

Iridium complexes: a different temperature dependence

Dicationic iridium analogs to the cationic ruthenium complexes described above have been prepared. Complexes such as **7** have been prepared and characterized by NMR spectroscopy (Scheme 5).

Based on the observed relaxation time T_1 for the hydride resonance and the value of J_{HD} for **7**-d_1, the structure of complex **7** is best described as an elongated dihydrogen complex or compressed dihydride, with d_{HH} of ca. 1.4 Å. Interestingly, the observed values of J_{HD} in **7**-d_1 are temperature dependent, suggesting that the structure of **7** changes with
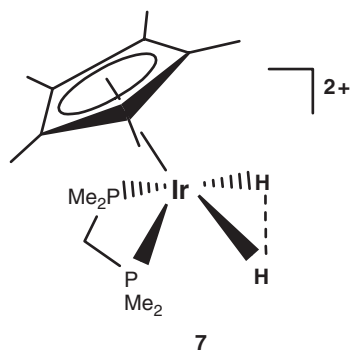
Scheme 5

temperature, but the values of J_{HD} *increase* with increasing temperature. This is precisely the opposite behavior seen in complex **6**, and suggests that d_{HH} shortens as the temperature is raised.[27] This novel experimental observation was subsequently interpreted computationally in terms of a PES with two slightly different minima, one roughly corresponding to a dihydrogen structure and the other to a dihydride.[11]

Structural isotope effects are predicted computationally for complex **7**.[11] Experimental verification of this prediction has not been realized. This experiment will require the preparation of complex **7** with HD, HT and DT bound. Since complex **7** is a dication, it is *very* acidic, readily protonating even weak bases such as triflate. The hazards of tritium containment with a complex of this acidity have so far prevented this experiment.

Conclusion

The coordination chemistry of dihydrogen continues to surprise and delight chemists with new and unexpected developments. As might be expected for a 'ligand' consisting of two H atoms, isotope substitution has played a pivotal role in understanding this chemistry. Some of these developments have been truly remarkable, and have led chemists to consider carefully what is meant by standard ideas such as *structure*. We can look forward to the preparation of many more interesting new complexes and the fruitful application of isotope studies in the elucidation of their structure and reactivity.

Acknowledgements

REFERENCES

1. Hieber W, Leutert F. *Berichte der Deutschen Chemischen Gesellschaft* 1931; **64B**: 2832.
2. Kubas GJ, Ryan RR, Swanson BI, Vergamini PJ, Wasserman HJ. *J Am Chem Soc* 1984; **106**: 451.
3. Kubas GJ. *Metal Dihydrogen and σ–Bond Complexes: Structure, Theory and Reactivity*, Chapter 2. Kluwer Academic/Plenum Publishers: NY, 2001.
4. Bau R, Drabnis MH. *Inorg Chim Acta* 1997; **259**: 27; Koetzle TF. *Trans Am Crystallogr Assoc* 1997; **31**: 57.
5. Zilm KW, Millar JM. *Adv Magn Opt Res* 1990; **15**: 163.
6. Hamilton DG, Crabtree RH. *J Am Chem Soc* 1988; **110**: 4126.
7. Desrosiers PJ, Cai L, Lin Z, Richards R, Halpern J. *J Am Chem Soc* 1991; **113**: 4173.
8. Luther TA, Heinekey DM. *Inorg Chem* 1998; **37**: 127.
9. Hush NS. *J Am Chem Soc* 1997; **119**: 1717.
10. Gründemann S, Limbach HH, Buntkowsky G, Sabo-Etienne S, Chaudret B. *J Phys Chem A* 1999; **103**: 4752.
11. Gelabert R, Moreno M, Lluch JM, Lledós A, Pons V, Heinekey DM. *J Am Chem Soc* 2004; **126**: 8813.
12. Kubas GJ, Burns CJ, Khalsa GRK, Van Der Sluys LS, Kiss G, Hoff CD. *Organometallics* 1992; **11**: 3390.
13. Bigeleisen J, Goeppert-Mayer M. *J Chem Phys* 1947; **15**: 261.
14. Bender BR, Kubas GJ, Jones LH, Swanson BI, Eckert J, Capps KB, Hoff CD. *J Am Chem Soc* 1997; **119**: 9179.
15. Zhang K, Gonzalez AA, Hoff CD. *J Am Chem Soc* 1989; **111**: 3627.
16. Church SP, Grevels W-F, Hermann H, Schaffner K. *J Chem Soc Chem Commun* 1985; 30.
17. Sabo-Etienne S, Chaudret B. *Chem Rev* 1998; **98**: 2077.
18. Sabo-Etienne S, Chaudret B, Abou El Makarim H, Barthelat JC, Daudey JP, Ulrich S, Limbach HH, Moise C. *J Am Chem Soc* 1995; **117**: 11602.
19. Oldham Jr WJ, Hinkle AS, Heinekey DM. *J Am Chem Soc* 1997; **119**: 11028.
20. Taw FL, Mellows H, White PS, Hollander FJ, Bergman RG, Brookhart M, Heinekey DM. *J Am Chem Soc* 1997; **124**: 5100.
21. Bampos N, Field LD. *Inorg Chem* 1990; **29**: 587.

22. Pons V, Conway SLJ, Green MLH, Green JC, Herbert BJ, Heinekey DM. *Inorg Chem* 2004; **43**: 3475.

23. Oldham Jr WJ, Heinekey DM. *Chem Rev* 1993; **93**: 913–926.

24. Klooster WT, Koetzle TF, Jia G, Fong TP, Morris RH, Albinati A. *J Am Chem Soc* 1994; **116**: 7677–7681.

25. Gelabert R, Moreno M, Lluch JM, Lledós A. *J Am Chem Soc* 1997; **119**: 9840.

26. Law JK, Mellows H, Heinekey DM. *J Am Chem Soc* 2001; **123**: 2085.

27. Pons V, Heinekey DM. *J Am Chem Soc* 2003; **125**: 8428.