

# Elongated dihydrogen complexes: what remains of the H–H Bond?

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Of the several hundred examples of transition metal dihydrogen complexes that have been reported to date, the vast majority have H–H distances of less than 1.0 Å. A small number of complexes have been reported with distances in the range of 1.1 to 1.5 Å. These complexes have been termed elongated dihydrogen complexes. In this review, experimental methods for structure determination of such complexes are summarized, along with computational approaches which have proven useful in understanding the structures of these molecules.

## 1 Introduction

The structure and dynamic behaviour of transition metal complexes involving multiple hydride ligands have been studied intensively for many years, due to the importance of these species in homogeneous catalytic processes. The structures of these complexes are very interesting, and their dynamic behaviour has been intensively studied using <sup>1</sup>H NMR spectroscopy. Many such complexes exhibit *stereochemical non-rigidity* or *fluxional* behaviour, with rapid ( $\Delta G^\ddagger = 40\text{--}100\text{ kJ}\cdot\text{mol}^{-1}$ ) permutation of the hydride ligands.

It has been appreciated since 1984<sup>1</sup> that dihydrogen can act as a ligand in transition metal complexes without cleavage to form the well known dihydride structure. In some complexes of H<sub>2</sub>, the interaction with the metal center is weak, while others bind H<sub>2</sub> tightly and give robust complexes. The bonding interactions

between a metal complex and hydrogen have been described in terms of donation from the filled sigma bonding orbital 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  $\sigma^*$  orbital of H<sub>2</sub>. 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.

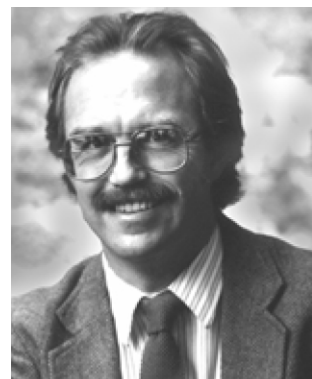
A very large number of hydrogen complexes have been prepared, and a rich chemistry is rapidly developing.<sup>2</sup> A key aspect of the structure of these complexes is the H–H distance ( $d_{\text{HH}}$ ), which has been found to be in the range 0.8–1.0 Å in the vast majority of complexes reported to date. In contrast, conventional dihydride and polyhydride complexes have  $d_{\text{HH}} \geq 1.5\text{ Å}$ . However, an increasing

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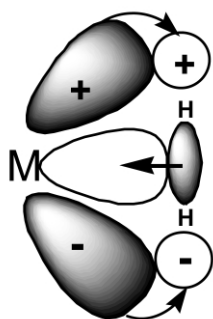


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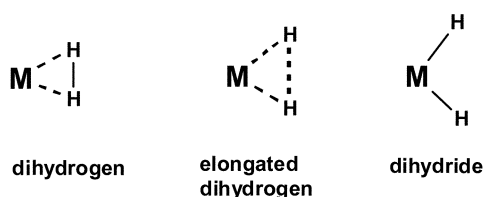


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number of species where the H–H distance falls between these limits is now known. Such complexes have been termed “stretched” or “elongated” dihydrogen complexes. This review focuses on the group of dihydrogen complexes which have  $d_{\text{HH}}$  values between 1.1 and 1.5 Å. In the representation below, elongated dihydrogen complexes are depicted as intermediate between “normal” dihydrogen complexes and dihydride complexes.



Early work in this field suggested that the structures depicted above on the left and right were possible, but that intermediate structures did not occur. More recent experimental and theoretical results suggest that a continuum of structures are possible spanning the three approximate representations shown above. The analysis of the electron density of a series of  $\text{ML}_n\text{H}_2$  complexes with a wide range of H–H values within the “atoms in molecules” formalism gave theoretical support to this bonding scheme.<sup>3</sup>

Initially, elongated dihydrogen complexes were 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 determine the structure of elongated dihydrogen complexes show that these molecules have very novel properties. In some cases, a complete description of the bonding situation in such complexes presents significant challenges to our traditional ideas of chemical bonding. Both theoretical and experimental approaches have been applied to this problem, and the interplay between theory and experiment has been particularly beneficial in advancing our understanding of these interesting molecules.

## 2 Experimental data: overview of methodologies

X-ray diffraction is a standard method employed in the determination of the structure of new complexes. In the case of transition metal hydride complexes, 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.<sup>4</sup>

The direct measurement of dipolar couplings in solid state  $^1\text{H}$  NMR is a potentially general approach to this problem which requires modest quantities of solid sample. Since dipolar coupling between the bound hydrogen atoms is proportional to  $(d_{\text{HH}})^{-3}$ , this method gives very precise values for  $d_{\text{HH}}$ . The requirement for deuterium substitution of non-hydride hydrogen atoms can be avoided using selective pulse sequences.<sup>5</sup>

A solution  $^1\text{H}$  NMR technique which uses the measurement of dipole–dipole relaxation rates was originally developed to measure  $d_{\text{HH}}$  by Crabtree<sup>6</sup> and co-workers, and later refined by Halpern and

co-workers.<sup>7</sup> This method requires the measurement at various temperatures of the spin lattice relaxation time ( $T_1$ ) of the hydride resonance. If the temperature corresponding to the maximum rate of relaxation (minimum  $T_1$ ) can be reached, a value for  $d_{\text{HH}}$  can be extracted. A drawback to this method (as well as neutron diffraction data) is that the derived values of  $d_{\text{HH}}$  can be affected by the rapid rotational motion of the bound dihydrogen ligand observed in some complexes.

A very useful and general solution NMR method that has been widely employed relies upon the measurement of H–D couplings in the bound dihydrogen ligand. A variety of approaches have been employed to introduce a single deuterium (nuclear spin  $I = 1$ ), the simplest of which is to employ HD gas in the synthesis reaction. In free HD gas, the coupling between H and D ( $^1J_{\text{HD}}$ ) 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 ( $^2J_{\text{HD}}$ ) is typically very small, *ca.* 2–3 Hz. Dihydrogen complexes have  $^1J_{\text{H-D}}$  values between these two limits, and the value of  $^1J_{\text{H-D}}$  is inversely related to the internuclear distance  $d_{\text{HH}}$ . This empirical correlation is anchored by data from solid state NMR and neutron diffraction determinations as outlined above.<sup>8</sup> Quantitatively:

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

An essentially identical linear relationship between  $J_{\text{H-D}}$  and  $d_{\text{HH}}$  was predicted by quantum chemical calculations.<sup>9</sup> A more sophisticated analysis of the relationship between HD coupling and  $d_{\text{HH}}$  recently reported by Chaudret, Limbach and co-workers suggests that the linearity as described in eqn. (1) breaks down at longer distances, but that reliable values for  $d_{\text{HH}}$  can be extracted from H–D coupling.<sup>10</sup> A problem with both of these approaches is the relative paucity of structural data for complexes with values of  $d_{\text{HH}} \geq 1.3$  Å.

An important assumption implicit in the use of the above relationships between H–D coupling and  $d_{\text{HH}}$  is that the interatomic distances are independent of isotope substitution. While this seems reasonable, there are important exceptions, which will be discussed below.

## 3 Overview of computational methods

Despite the success of theoretical calculations in accurately locating the H positions in both dihydrogen and polyhydride compounds,<sup>11</sup> accurate structural modelling of elongated dihydrogen complexes has been a difficult objective for computational chemistry. In this section we will discuss why performing the usual quantum mechanics calculations (resolution of the electronic Schrödinger equation + geometry optimization) is insufficient for accurately determining the position of the H atoms of an elongated dihydrogen ligand.

If the Hamiltonian does not depend on the time, in quantum mechanics the time independent Schrödinger equation contains all the physical information about the state of a chemical system. The corresponding wave function depends simultaneously on both the nuclear and the electronic coordinates, which makes this equation very hard to solve. Taking advantage of the different time scales of the nuclear (slow) and electronic (fast) motions, the Born–Oppenheimer approximation permits separation of these two kinds of coordinates. First, considering that the nuclei are frozen at a given nuclear configuration, the electronic Schrödinger equation is written and solved, providing the electronic wave functions and energy levels, from which, by adding the corresponding internuclear repulsion, the potential energy is obtained. This potential energy is the total energy of the molecule assuming that the nuclei are at fixed positions. The potential energy as a function of the nuclear positions leads to the concept of a potential energy surface. A number of properties of a molecule can be characterized just by analyzing the electronic wave functions and the topology of the potential energy surface. In particular, the well-known concept of equilibrium structure with a fixed geometry is based on the

existence of a minimum energy structure. It must be emphasized that this is merely a static concept.

However, nuclei are not static. Within a classical framework this motion diminishes as the temperature decreases, in such a way that the static point of view would be correct at 0 K. Conversely, a quantum mechanical description preserves a residual vibrational kinetic energy, even at 0 K. This fact is especially important when light nuclei like hydrogen are involved. In these cases the nuclear Schrödinger equation has to be built and solved, which gives the total energy (including now the kinetic energy of nuclei) and the nuclear wave functions. The electronic Schrödinger equation behaves just like an intermediate, auxiliary step to obtain the potential energy term of the nuclear equation, which is the equation that actually contains the most relevant chemical information for the molecule. The nuclei, especially the light ones, no longer define a fixed geometry, but can be extensively delocalized. As a consequence, the experimentally measured geometry does not correspond on a one to one basis to a minimum in the potential energy surface, but to the average of the positions of nuclei weighted according to the nuclear wave function.

Using this procedure, the expectation value of a geometrical parameter  $x$  in a given vibrational state  $i$  can be determined by means of:

$$\langle x_i \rangle = \frac{\langle \Psi_i | \hat{x} | \Psi_i \rangle}{\langle \Psi_i | \Psi_i \rangle} \quad (2)$$

where  $\Psi_i$  is the nuclear wave function in the state  $i$ , and  $\hat{x}$  is the quantum mechanical operator associated to the geometrical parameter  $x$ . If the potential energy surface is harmonic along the variation of  $x$ , the symmetry of the problem gives an expectation value  $\langle x_i \rangle$  that matches the position of the minimum energy structure. In contrast, anharmonicity breaks the symmetry and moves the expectation value away from the minimum, in such a way that the experimental geometry can be quite different from the minimum obtained using only electronic structure calculations.

As we will show below, the potential energy surfaces of the elongated dihydrogen complexes with respect to H–H distance turn out to be quite anharmonic, which leads to a number of interesting properties. In these cases, a combined electronic + nuclear dynamics theoretical treatment is required in order to understand the structure and dynamics of these complexes. A short description of suitable methods to perform such a study follows.

The electronic Schrödinger equation needs to be solved not only to locate the minimum energy structures, but also to build up the reduced potential energy surface over which the nuclear calculations will be carried out later. This requires a method which combines high accuracy and a reasonable computational cost to construct a sizeable portion of the potential energy surface. The density-functional theory (DFT) method meets these two requirements. In particular, the three-parameter hybrid functional of Becke and the correlation functional of Lee, Yang, and Parr, which is widely known as Becke3LYP, is appropriate. This approach has been used with great success to study several organometallic systems, including dihydrogen and polyhydride complexes.<sup>11</sup> To save computational time, the inner electrons of the transition metal atoms are replaced by an effective core operator, the basis set associated with the pseudopotential of Hay and Wadt with a standard valence double- $\zeta$  LANL2DZ contraction being usually employed for the remaining electrons of those atoms.

A discrete variable representation (DVR) is the best choice to solve the nuclear Schrödinger equation for these transition metal complexes. Computationally, the DVR has great advantages over the more traditional variational basis representation, in which the energy levels are obtained by diagonalization of the matrix representation of the projection of the Hamiltonian operator on a given basis set, usually made up of Gaussian functions. Instead, the DVR is a grid-point representation, thus eliminating the need to evaluate the potential energy integrals. The potential energy matrix

representation is diagonal and the kinetic energy matrix representation is very simple, yielding very sparse Hamiltonian matrices which are easier to diagonalize than those coming from a variational basis representation. The DVR method proposed by Colbert and Miller is very appropriate due to its simplicity and accuracy.<sup>12</sup> Very recently a completely different approach, the semiclassical initial value representation method, has been successfully applied to account for the properties of an elongated dihydrogen complex.<sup>13</sup>

## 4 Reported examples of elongated dihydrogen complexes

We will confine our discussion to molecules observable at room temperature with a single dihydrogen ligand and  $d_{\text{HH}}$  values between 1.1 and 1.5 Å. There are several well characterized polyhydride complexes with at least one H–H distance in the range of interest, but complexities introduced by the presence of additional hydride ligands make study of such species more difficult. For example, an H–H distance of 1.357 Å was determined by neutron diffraction for  $\text{ReH}_7\{\text{P}(p\text{-tolyl})_3\}_2$ .<sup>14</sup>

A survey of  $\text{H}_2$  complexes displaying  $J_{\text{H-D}}$  between 25 and 5 Hz, and thus likely containing an elongated dihydrogen ligand, reveals some interesting trends. Although these complexes show considerable structural diversity, some representative structures are depicted in Fig. 1.

Osmium, ruthenium and rhenium are the metals most frequently found in these complexes, and no examples involving first-row transition metals are known. Most of them are cationic and/or contain electronegative N-, O- or halide ligands. With these properties it is likely that the transition metal fragment has low-lying occupied  $d_{\pi}$  orbitals and thus that  $d_{\pi} \rightarrow \sigma^*_{\text{H}_2}$  back donation could not be very strong. Also present are low-lying empty  $d_{\sigma}$  orbitals, responsible for a strong  $\sigma_{\text{H}_2} \rightarrow \text{M}$  donation. This point, that contradicts the traditional description of the transition metal  $-\text{H}_2$  interaction, needs further study. The elongated dihydrogen ligands are usually strongly bonded, making most of the complexes stable toward hydrogen loss. Consistent with this, the calculated dihydrogen binding energies in stretched complexes range from 100 to 190  $\text{kJ mol}^{-1}$ , and are markedly larger than in normal dihydrogen complexes (60–85  $\text{kJ mol}^{-1}$ ).

The conditions that lead to the existence of an elongated dihydrogen complex result from a subtle balance of metal and ligand effects, and can be modified by small changes in the coordination sphere. Changing ligands may drastically affect  $d_{\text{HH}}$ , giving rise in some cases to a series of similar compounds with very different H–H distances.

In the Table below, data for ten representative complexes are tabulated, along with a summary of the available experimental data. Reported values of  $^1J_{\text{H-D}}$  have been converted to  $d_{\text{HH}}$  using eqn. (1) (for distances less than 1.3 Å), or the Chaudret/Limbach correlation (for distances greater than 1.3 Å). In some cases, the derived distances differ slightly from the original reports, where eqn. (1) was used.

Ligand abbreviations: dppm = bis-diphenylphosphinomethane; dppe = bis-diphenylphosphinoethane; dmpm = bis-dimethylphosphinomethane. Cp =  $\text{C}_5\text{H}_5$ ; Cp\* =  $\text{C}_5\text{Me}_5$ ; Cp' =  $\text{C}_5\text{H}_4\text{SiMe}_3$ ; en = ethylenediammine. N–N = *ortho*-( $\text{Me}_3\text{SiN}$ ) $_2\text{C}_6\text{H}_4$

### 4.1 Representative complexes for more detailed discussion

**4.1.1 [Os(en) $_2$ (acetate)(H $_2$ )] $^+$  (1).** In 1991, Taube and Li<sup>26</sup> reported the preparation of a series of cationic hydrogen complexes of the form  $[\text{Os}(\text{NH}_3)_4\text{X}(\text{H}_2)]^+$ , where X is an anionic ligand such as halide. Also reported were dicationic complexes where X was replaced by a neutral ligand L such as pyridine, acetone or acetonitrile. Characterization of these species as elongated dihydrogen complexes was based on the low values of  $^1J_{\text{HD}}$  observed in the corresponding H–D complexes. For example, for L = pyridine,  $^1J_{\text{HD}} = 19.6$  Hz, while for L = acetone,  $^1J_{\text{HD}} = 4.0$  Hz. This data

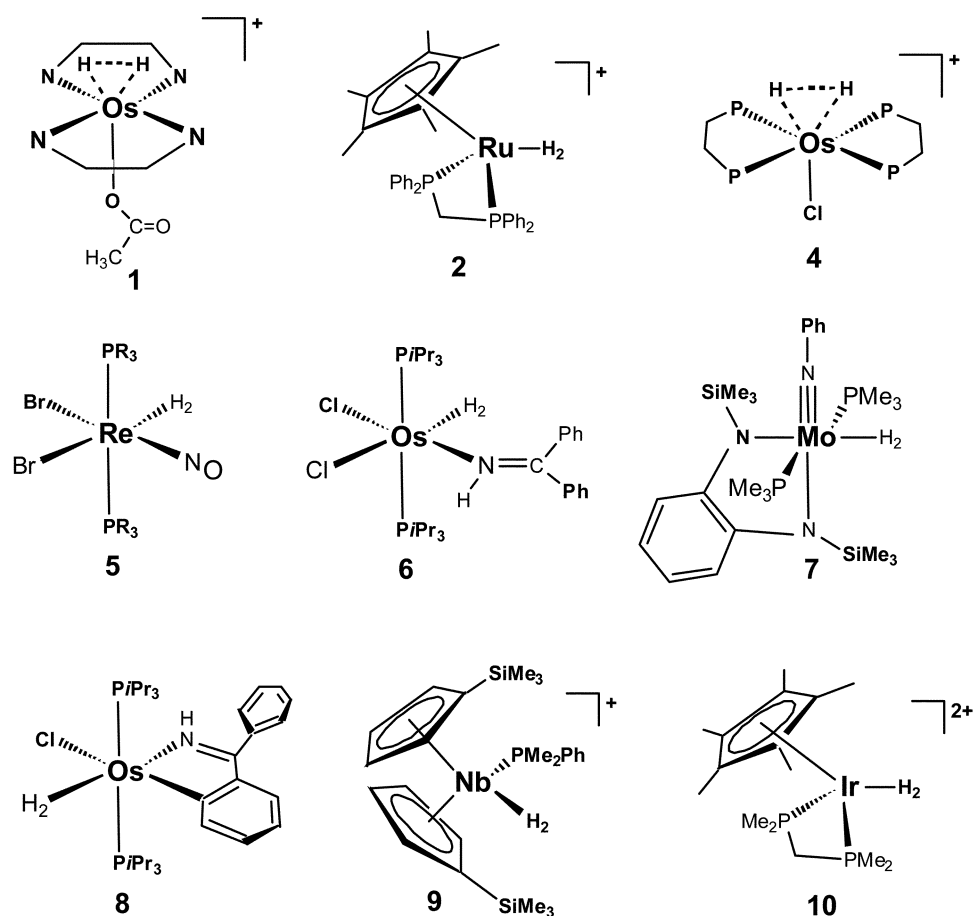


Fig. 1 Schematic representation of some reported elongated dihydrogen complexes.

Table 1 Data for some representative elongated dihydrogen complexes

Compound Number	Formula	$^1J_{\text{H-D}}$ (Hz)	$d_{\text{HH}}$ (Å)	Ref
1	[Os(en) <sub>2</sub> (acetate)(H <sub>2</sub> ) <sup>+</sup>	9	1.31 1.34(N) 1.32(T <sub>1</sub> )	15
2	[Cp*Ru(dppm)(H <sub>2</sub> ) <sup>+</sup>	22.5–21.0	1.06–1.09 1.10(N) 1.10(T <sub>1</sub> )	16,17
3	[CpRu(dmpe)(H <sub>2</sub> ) <sup>+</sup>	23.1–22.3	1.05–1.07	10,18
4	[Os(dppe) <sub>2</sub> Cl(H <sub>2</sub> ) <sup>+</sup>	13.6–14.2	1.21–1.20 1.22(N)	19
5	Re(H <sub>2</sub> )(NO)Br <sub>2</sub> (PiPr <sub>3</sub> ) <sub>2</sub>	12.8	1.23 1.21(T <sub>1</sub> )	20
6	OsCl <sub>2</sub> (H <sub>2</sub> )(NH=CPh <sub>2</sub> )(PiPr <sub>3</sub> ) <sub>2</sub>	10.5	1.26 1.27(T <sub>1</sub> )	21
7	Mo(NPh)(PMe <sub>3</sub> )(N–N)(H <sub>2</sub> )	15	1.19 1.18(T <sub>1</sub> )	22
8	OsCl(NH=C(Ph)C <sub>6</sub> H <sub>4</sub> )(PiPr <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> )	6.8	1.39 1.36(T <sub>1</sub> )	23
9	[Cp' <sub>2</sub> Nb(PMe <sub>2</sub> Ph)(H <sub>2</sub> ) <sup>+</sup>	15	1.17 1.17(T <sub>1</sub> )	24
10	[Cp*Ir(dmpm)H <sub>2</sub> ] <sup>2+</sup>	7.0–9.0	1.38–1.31 1.49(T <sub>1</sub> )	25

$d_{\text{HH}}$  values are derived from H–D couplings. Values from neutron diffraction measurements are indicated by (N); values from relaxation time measurements are denoted by (T<sub>1</sub>).

suggests that a wide range of values of  $d_{\text{HH}}$  are accessible by adjustment of the ligand trans to H<sub>2</sub>. Subsequently, this work was extended to derivatives with two ethylenediamine ligands in place of the NH<sub>3</sub> ligands. In 1994, the structure of complex **1** was determined by neutron diffraction. The H–H distance is  $1.34 \pm .02$  Å.<sup>15</sup>

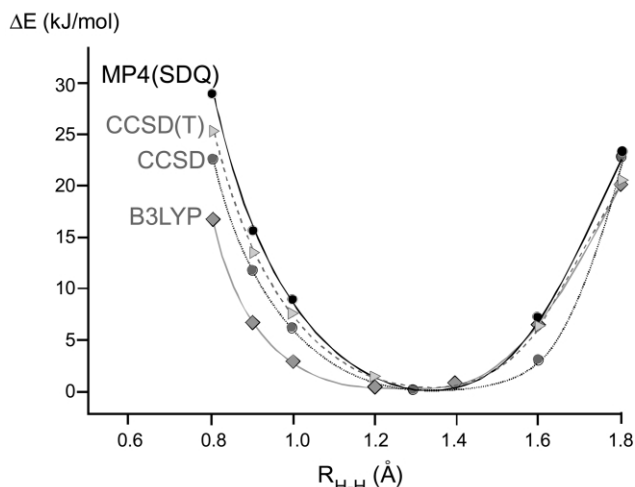
Complex **1** was the first example of a highly elongated dihydrogen complex containing only two “hydride” ligands to be

confirmed by neutron diffraction studies. These results led to considerable activity among theoretical chemists with a view to understanding the bonding situation in complex **1** and related complexes. In 1994 Hush and co-workers performed a quantum mechanical study of the stretched dihydrogen complexes [Os(NH<sub>3</sub>)<sub>4</sub>L<sup>z</sup>(H<sub>2</sub>)]<sup>(z+2)+</sup> (L<sup>z</sup> = (CH<sub>3</sub>)<sub>2</sub>CO, H<sub>2</sub>O, CH<sub>3</sub>COO<sup>-</sup>, Cl<sup>-</sup>, H<sup>-</sup>, C<sub>5</sub>H<sub>5</sub>N and CH<sub>3</sub>CN) using SCF and MP2 methods.<sup>27</sup> These studies revealed an unusually flat potential energy curve for the H–

H stretch. In such a situation small perturbations, such as the substitution of other ligands for  $\text{OAc}^-$ , can lead to large changes in the physical and chemical properties, as indeed has been observed.<sup>26</sup> Another important point is that the potential energy curve has a single minimum. There is no evidence for a double minimum that would suggest the coexistence of the  $\eta^2\text{-H}_2$  and *cis*-dihydride isomers. These two observations are a hallmark of elongated dihydrogen complexes and have now been found in several cases.

**4.1.2  $\text{OsCl}_2(\text{H}_2)(\text{NH}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2$  (**6**).** This complex was reported by Esteruelas *et al.* in 1998.<sup>21</sup> A  $J_{\text{HD}}$  of 10.5 Hz was determined for this compound. Using the standard equation, this value leads to a separation between the H atoms of the dihydrogen ligand of 1.24 Å, intermediate between a normal  $\eta^2\text{-H}_2$  and a dihydride complex.

The optimization of the  $\text{OsCl}_2(\text{H}_2)(\text{NH}=\text{CH}_2)(\text{PH}_3)_2$  model complex with the Becke3LYP method gave a single minimum with an H–H distance of 1.294 Å. The potential energy curve for the H–H stretch was obtained with this method and was then recalculated at the MP4(SDQ), CCSD(T) and CCSD levels of theory. Whatever the methodology employed, the energy cost to move the two hydrogen atoms between 1.00 and 1.60 Å is lower than 4 kJ mol<sup>-1</sup>. As shown in Fig. 2 the energy of complex **6** is practically independent of the H–H separation between 1.00 and 1.60 Å. In this system the  $\text{H}_2$  molecule is coordinated in such a way that oxidative addition/reductive elimination can occur with essentially no activation barrier.



**Fig. 2** Energy profile associated with the H–H stretch in  $\text{OsCl}_2(\text{H}_2)(\text{NH}=\text{CH}_2)(\text{PH}_3)_2$ . (Reprinted with permission from ref. 21. Copyright 1998 American Chemical Society.)

From this result, the description of **6** as a dihydrogen or dihydride complex loses its significance, and it is more appropriate to describe it as a complex containing two H atoms moving freely in a wide region of the coordination sphere of the metal. Further work including the dynamics of the H-nuclei, described in the next section, fully confirms this description. Additional experimental study of complex **6** seems warranted, particularly with respect to measurement of temperature dependence of the HD coupling.

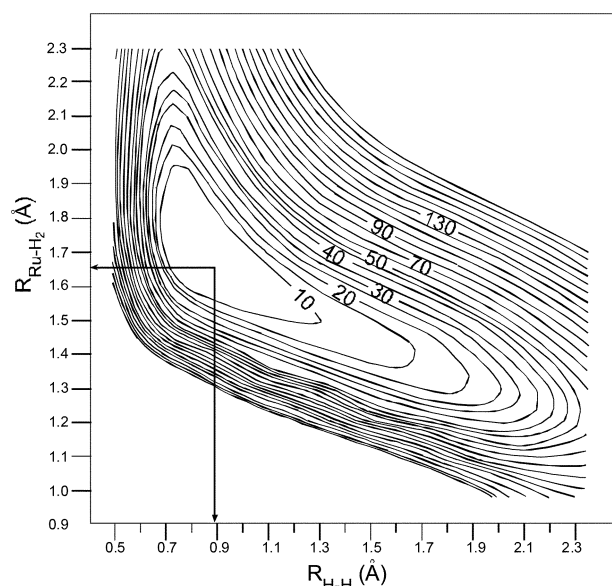
**4.1.3  $[\text{Cp}^*\text{Ru}(\text{dppm})(\text{H}_2)]^+$  (**2**).** This Ru(II) complex is representative of a large class of dihydrogen complexes of the general form  $[\text{Cp}/\text{Cp}^*\text{Ru}(\text{P}-\text{P})\text{H}_2]^+$  (P–P = chelating diphosphine ligand), the first example of which was reported in 1987.<sup>18</sup> These robust cationic complexes can be prepared by a simple protonation reaction starting from the corresponding neutral hydride or by metathesis reactions of the corresponding neutral chloride with  $\text{NaBAR}_4$  under hydrogen gas. The observed H–D coupling in the

bound hydrogen ligand and thus  $d_{\text{HH}}$  varies with the choice of Cp or Cp\* and the phosphine ligand.

The solid state structure of **2** was determined using neutron diffraction by Morris, Koetzle and co-workers in 1994. The value for  $d_{\text{HH}}$  of  $1.10 \pm 0.03$  Å is in good agreement with the distance determined from  $T_1$  measurements and the H–D coupling. Variable temperature <sup>1</sup>H NMR spectra revealed a small decrease in  $J_{\text{HD}}$  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.<sup>16</sup>

In 1997 a theoretical study was reported on the  $[\text{CpRu}(\text{H}_2\text{PCH}_2\text{PH}_2)(\text{H}_2)]^+$  complex, a simplified model system for **2**. This analysis included both electronic structure calculations and quantum treatment of nuclei.<sup>28</sup> The DFT based Becke3LYP method with an extended basis set correctly reproduces the experimental geometry of the complex except for the H–H and Ru–H<sub>2</sub> distances. In particular, a dihydrogen H–H distance of 0.888 Å, which would correspond to a “normal” dihydrogen complex, was found. The same result was obtained with single point energy calculations performed on the Becke3LYP geometries either with an enlarged basis set or with coupled cluster calculations involving single, double, and perturbatively triple excitations (CCSD(T)) and using the original basis set. It was concluded that no minimum potential energy structure corresponding to an elongated dihydrogen structure exists. Thus, the experimental geometry cannot be explained with pure electronic structure calculations, no matter what level of electronic theory is used.

A Becke3LYP two-dimensional potential energy surface was built up as a function of the distance between both hydrogens (H–H) and the distance between the metal center and the point halfway between the two hydrogens (Ru–H<sub>2</sub>) in the dihydrogen ligand. These two parameters behave as orthogonal coordinates, in such a way that no coupled terms between them appear in the nuclear kinetic operator. The resulting potential energy surface is highly anharmonic (Fig. 3). The minimum potential energy structure is

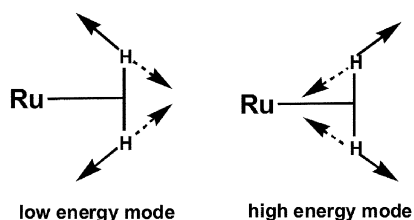


**Fig. 3** Two-dimensional potential energy surface for the  $[\text{CpRu}(\text{H}_2\text{PCH}_2\text{PH}_2)(\text{H}_2)]^+$  complex. Energies of contours are given in kJ mol<sup>-1</sup>. The arrows indicate the position of the minimum potential energy structure. (Reprinted with permission from ref. 28. Copyright 1997 American Chemical Society.)

reached at the deepest point in a long valley with a smooth slope in a direction corresponding mainly to the lengthening of the H–H distance, but with a component of decreasing Ru–H<sub>2</sub> distances. A second, steeper exit of that valley, which is practically parallel to the Ru–H<sub>2</sub> axis, appears for a H–H distance around 0.80 Å. It

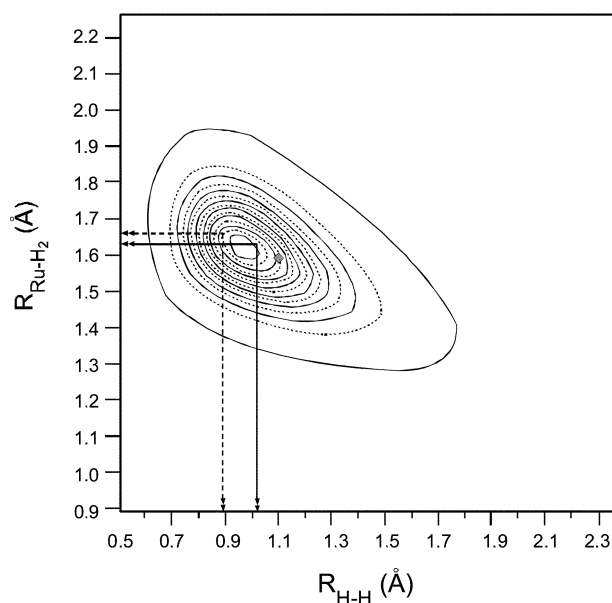
corresponds to the dissociation of the H<sub>2</sub> ligand. A DVR calculation over that surface provided the vibrational wave functions and energy levels.

The analysis of the shape of the vibrational wave functions and the difference among the corresponding energy levels permitted the characterization of two normal modes which correspond to the motion of the hydrogen atoms of the ligand (the dimension of the potential energy surface is just two). Comparison with the experimental Raman spectrum of the complex [CpRu(dppm)(H<sub>2</sub>)]<sup>+</sup> studied by Chopra *et al.* is informative.<sup>29</sup> They found that the frequency that they assigned to the H–H stretch had an unusually low value of 2082 cm<sup>-1</sup>, in contrast to the frequency for free dihydrogen which is 4395 cm<sup>-1</sup>. In addition, another transition at 679 cm<sup>-1</sup> was interpreted as the symmetric Ru–H<sub>2</sub> stretch. When the H<sub>2</sub> ligand was substituted with D<sub>2</sub>, Chopra *et al.* found that the bands shifted to lower energies: 1530 and 460 cm<sup>-1</sup>, respectively. The theoretical results showed that the predicted transitions (2229 and 555 cm<sup>-1</sup> for the complex with the H<sub>2</sub> ligand; 1625 and 466 cm<sup>-1</sup> for the complex with D<sub>2</sub>)<sup>30</sup> were in reasonable agreement with the experimental frequencies. These results suggest that the experimental assignment of these transitions should be reconsidered. In this molecule, it is not possible to separate the H–H and the Ru–H<sub>2</sub> motions as the actual normal modes involve an extended coupling between both degrees of freedom. So, the experimental band at 679 cm<sup>-1</sup> is associated with a normal mode consisting of a motion roughly parallel to the oblique minimum energy path that links the two exits of the potential energy valley (see Fig. 3), in such a way that the stretching of the H–H bond leads to strengthening of the Ru–H bonds, and *vice versa*. Along this normal mode the changes in potential energy are very damped, leading to a low energy transition. Thus, this mode does not correspond to the so-called symmetric Ru–H<sub>2</sub> stretch. On the other hand, the second normal mode involves a motion orthogonal to the previously mentioned oblique path, so leading to significant changes in potential energy, giving a high energy transition (experimental band at 2082 cm<sup>-1</sup>). Along this mode both the H–H bond and the Ru–H bonds stretch (or compress) simultaneously. This transition is not adequately described as an H–H stretch, but actually corresponds to the so-called symmetric Ru–H<sub>2</sub> mode.



On the other hand, the vibrational ground state wave function appears to be notably delocalized, encompassing the whole valley in the potential energy surface with non-negligible values of probability density (see Fig. 4).

This implies that the H<sub>2</sub> ligand is greatly delocalized and can no longer be envisaged as a fixed, rigid block. This fact along with the significant anharmonicity of the potential energy surface lead to expectation values of 1.02 and 1.61 Å for the H–H and Ru–H<sub>2</sub> distances, respectively, closer to the neutron diffraction distances (1.10 and 1.58 Å, respectively) than to the values corresponding to the minimum energy structure (0.89 and 1.66 Å, respectively). When the wave functions of the vibrational excited state were considered it was found that, again due to the anharmonicity of the potential energy surface, the higher the excited state, the greater the H–H distance obtained according to the corresponding expectation value. Assuming a Boltzmann-type equilibrium distribution for all the vibrational states considered, the mean thermal H–H distance could be obtained, which became longer at higher temperatures. This fact explains the experimentally observed decrease in  $J_{\text{HD}}$  upon increasing the temperature, which would be due to the thermal



**Fig. 4** Probability density plot of the vibrational ground-state wave function of the [CpRu(H<sub>2</sub>PCH<sub>2</sub>PH<sub>2</sub>)(H<sub>2</sub>)]<sup>+</sup> complex as a contour plot of  $|\Psi|^2$ . The dashed arrow indicates the position of the minimum potential energy structure, the solid arrow shows the expectation values for this vibrational state, and the square marks the experimentally reported data from neutron diffraction. (Reprinted with permission from ref. 28. Copyright 1997 American Chemical Society.)

population of vibrationally excited states involving longer H–H distances.

This analysis predicts very interesting implications upon isotopic substitution in the dihydrogen unit. The vibrational energy levels are lowered when heavier isotopes are introduced. As a consequence, and again due to the anharmonicity, the H–H distance was predicted theoretically to become significantly shorter when heavier isotopes (deuterium or, even better, tritium) are used in the dihydrogen ligand.

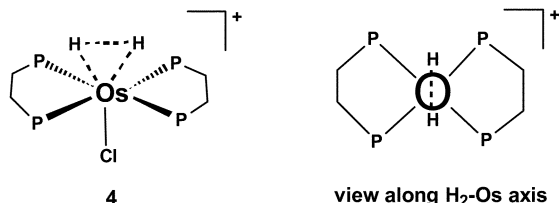
This prediction was subsequently verified experimentally by examination of the coupling in isotopomers of **2** containing bound HD, HT and DT.<sup>17</sup> Since couplings are directly proportional to magnetogyric ratios of the nuclei, it was readily apparent that the bond distances are all temperature dependent and that heavier isotopes lead to significantly shorter bonds between the hydrogen (deuterium, tritium) atoms. For example, a comparison of bound HD *versus* bound DT reveals that  $d_{\text{DT}}$  is 2–3% shorter than  $d_{\text{HD}}$ , 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 **2**. It was found that [CpRu(dmpe)(H<sub>2</sub>)]<sup>+</sup>, a complex with  $d_{\text{HH}} = 1.06$  Å (from  $J_{\text{HD}} = 22$  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<sub>2</sub>)]<sup>+</sup> exhibits a *temperature independent* H–D coupling of 25 Hz, consistent with  $d_{\text{HH}}$  of *ca.* 1.02 Å. Similar temperature independent H–D couplings were observed for [Cp\*Ru(dmppm)(H<sub>2</sub>)]<sup>+</sup> ( $J_{\text{HD}} = 16$  Hz;  $d_{\text{HH}}$  of *ca.* 1.16 Å).<sup>17</sup>

For these Ru(II) complexes, it seems that the potential energy surface (PES) is very sensitive to the nature of the co-ligands. This behavior, related to the very flat potential for the H–H stretch, appears to be characteristic of the elongated dihydrogen complexes. Only Ru complexes with H–H distances of approximately 1.06–1.10 Å show temperature dependent bond distances. Slightly shorter distances seem to give “normal” dihydrogen complexes with stiffer H–H bonds having no measurable temperature dependence of the bond distance. Longer H–H distances correspond to structures perhaps best described as localized dihydrides, again with no temperature dependence. Further calculations are

needed to evaluate the subtle ligand effects on the temperature dependence of the H–H distance.

**4.1.4 [Os(dppe)<sub>2</sub>Cl(H<sub>2</sub>)]<sup>+</sup> (4).** Neutron diffraction measurements on **4** by Koetzle, Morris and co-workers give  $d_{\text{HH}} = 1.22 \pm 0.03 \text{ \AA}$ , consistent with the value derived from  $J_{\text{HD}}$  of ca. 14 Hz. In the representations below, the phenyl rings have been omitted for clarity.



The observed H–D couplings show a modest temperature dependence, increasing slightly with temperature. This leads to the counter intuitive notion that the average bond distance is decreasing at higher temperatures.

An extension of the theoretical study of the [CpRu(H<sub>2</sub>PCH<sub>2</sub>PH<sub>2</sub>)(H<sub>2</sub>)]<sup>+</sup> complex to *trans*-[Os(H<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>)<sub>2</sub>Cl(H<sub>2</sub>)]<sup>+</sup> as a model of the *trans*-[Os(dppe)<sub>2</sub>Cl(H<sub>2</sub>)]<sup>+</sup> shed light on this problem.<sup>31</sup> As for the Ru complex, a Becke3LYP two-dimensional potential energy surface was built up as a function of the distance between both H atoms (H–H) and the distance between the metal center and the point halfway between the two H atoms (Os–H<sub>2</sub>) in the dihydrogen ligand. The minimum energy structure appears at 1.071 and 1.567 Å for the H–H and Os–H<sub>2</sub> distances, respectively, in very poor agreement with the neutron diffraction measurements (1.22 and 1.58 Å for the H–H and Os–H distances, respectively). Again this is due to the fact that the two-dimensional potential energy surface is very flat and anharmonic in the region corresponding to the H–H stretching distance. In this case, to account for the decrease in the H–H distance at high temperatures, it was necessary to add an additional dimension to the potential energy surface: the spinning of the H–H unit around the Os–H<sub>2</sub> axis. In the case of the Ru complex discussed above, a rotational barrier of 17.7 kJ·mol<sup>–1</sup> was calculated for the librational motion of the dihydrogen unit. This relatively high value made it possible to disregard the influence of the librational motion on the dynamics of the H–H unit to explain its properties. However, the rotational potential energy barrier is only 8.5 kJ·mol<sup>–1</sup> for the case of the Os complex **4**. This is consistent with the fact that the Os complex has been classified as intermediate between the fast and slow spinning limits based on relaxation measurements, whereas the Ru complex is in fact a slow spinning dihydrogen complex.

The calculations showed that the value of the librational potential energy barrier depends on the elongation of the H–H distance, becoming higher for longer H–H distances (where the back donation from the metal to σ\* orbital of the bound dihydrogen is more effective). The effects of this behaviour are that the potential energy valley becomes wider in the areas of the three-dimensional potential energy surface in which the H–H distance is small and narrower in those zones of the surface where the H–H distance is longer. There are certain low-energy vibrational states whose nuclear wave functions are able to spread out toward these wide potential energy valleys, which are found in short H–H distances of the surface, in this way leading to short expectation values for the H–H distances. In effect, the Boltzmann averaged DVR calculations showed that on increasing temperature those excited vibrational states with short H–H expectation distances could become populated enough as to lead to a global decrease of the mean thermal H–H distance within some range of temperatures, consistent with the observed increase in  $J_{\text{HD}}$  at higher temperatures. On the other hand, the DVR calculations over the three-dimensional surface gave values of 1.234 and 1.529 Å for the expectation values

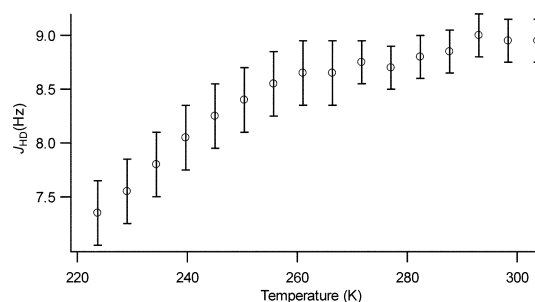
of the H–H and Ru–H<sub>2</sub> distances, respectively, in the vibrational ground state, almost matching the neutron diffraction values.

**4.1.5 [Cp\*<sub>2</sub>Nb(PMe<sub>2</sub>Ph)(H<sub>2</sub>)]<sup>+</sup> (9).** With very few exceptions, rotation of bound dihydrogen ligands is extremely facile, with measured barriers to rotation on the order of 4–15 kJ·mol<sup>–1</sup>.<sup>32</sup> Exceptions to this general rule are provided by a small number of complexes with d<sup>2</sup> configurations. Complex **9** is a rare example of an elongated dihydrogen complex with hindered rotation. An activation energy  $\Delta G^\ddagger$  of ca. 42 kJ mol<sup>–1</sup> was estimated for the H<sub>2</sub> rotation in **9** from variable temperature NMR spectra.<sup>24</sup> High rotational barriers have also been reported for [Cp<sub>2</sub>Ta(H<sub>2</sub>)(CO)]<sup>+</sup><sup>33</sup> and [Cp\*<sub>2</sub>Nb(H<sub>2</sub>)(CNR)]<sup>+</sup>,<sup>34</sup> although the latter species are normal H<sub>2</sub> complexes with shorter values of  $d_{\text{HH}}$ . The high rotational barrier in these d<sup>2</sup> complexes has been attributed to significant reduction in backdonation upon rotation by 90°. In this complex, no temperature dependence of  $J_{\text{HD}}$  on the observation temperature has been reported. When the temperature was increased the complex with L = P(OEt)<sub>3</sub> transformed into its transoid dihydride isomer. For the complex with L = PMe<sub>2</sub>Ph, warming to ambient temperature (20 °C) leads to loss of H<sub>2</sub>.<sup>35</sup>

**4.1.6 [Cp\*Ir(dmpm)H<sub>2</sub>]<sup>2+</sup> (10).** This complex was prepared to serve as a dicationic analog of the Ru complexes described above with the expectation that a formally Ir(III) dihydrogen complex would be favored over an Ir(V) dihydride. The experimental data suggests that complex **10** has a structure intermediate between these limits and is best described as an elongated dihydrogen complex or compressed dihydride.<sup>25</sup>

Examination of the hydride resonance relaxation rates gives a  $T_{1(\text{min})}$  value of 145 ms at 240 K (500 MHz), consistent with  $d_{\text{HH}} = 1.49 \text{ \AA}$  (assuming slow rotation of the bound hydrogen ligand). This value for  $d_{\text{HH}}$  is at variance with the value derived from the H–D coupling at this temperature, where  $J_{\text{H-D}} = 8.1 \text{ Hz}$  gives  $d_{\text{HH}} = 1.34 \text{ \AA}$ , using the distance/coupling correlation reported by Chaudret and co-workers. Surprisingly, in comparison to the directly analogous monocationic Ru analog [Cp\*Ru(dmpm)H<sub>2</sub>]<sup>+</sup>,  $d_{\text{HH}}$  is much longer for the Ir complex. This suggests that the presumed higher Lewis acidity of the dicationic metal center is more important in determining  $d_{\text{HH}}$  than is back donation from the metal to the bound hydrogen.

Measured values of  $^1J_{\text{HD}}$  for **10** exhibit a pronounced temperature dependence (see Fig. 5), which is opposite to that of



**Fig. 5**  $^1J_{\text{HD}}$  as a function of temperature for [Cp\*Ir(dmpm)H<sub>2</sub>]<sup>2+</sup> (**10**) (Reprinted with permission from ref. 25. Copyright 2003 American Chemical Society.)

[Cp\*Ru(dppm)H<sub>2</sub>]<sup>+</sup> (**2**), in that the coupling increases at higher temperatures, suggesting that the bond distance is decreasing. Also in contrast to the behaviour of complex **2**, large and temperature dependent values of the isotope shift ( $\delta_{\text{HD}} - \delta_{\text{HH}}$ ) were also observed. The latter observation may signal non-statistical occupation of more than one distinct structure by deuterium *versus* hydrogen atoms. An equilibrium between a dihydride and a dihydrogen complex was postulated to explain these observations.

## 4.2 Possible further examples

Several literature reports are suggestive of the possibility of elongated dihydrogen complexes. Molecules in which temperature dependent values for  $^1J_{\text{HD}}$  have been reported are promising in this regard.

Jia and co-workers have reported the preparation and properties of  $[\text{CpOs}(\text{dppm})\text{H}_2]^+$ , which is an Os analog of the Ru complexes described above. In this complex, both *cis* and *trans* dihydride isomers were observed, with the *cis* form predominant.<sup>36</sup> A *cis* dihydride structure with  $d_{\text{HH}} = 1.50 \text{ \AA}$  is consistent with the low observed value of  $^1J_{\text{HD}}$  (3.0 Hz) and the relatively long value of  $T_{1(\text{min})}$  of 150 ms (300 MHz). Averaging of  $^2J_{\text{HP}}$  couplings at the lowest reported temperature suggests that there is a rapid dynamic process which interchanges the two hydrogen atoms. No temperature dependence of  $^1J_{\text{HD}}$  was reported, but further investigation at lower temperatures may be warranted.

In 1992, Casey and co-workers reported a study of  $\text{CpRe}(\text{CO})_2\text{H}_2$ , a dihydride complex which exists as a mixture of *cis* and *trans* isomers.<sup>37</sup> The *cis* isomer exhibits  $^1J_{\text{HD}}$  of 6.5 Hz at ambient temperature, decreasing to 5.8 Hz at 238 K. Similar results were reported for the  $\text{Cp}^*$  analog. A modest temperature dependence of the isotope shift ( $\delta_{\text{HD}} - \delta_{\text{HH}}$ ) was also noted. An equilibrium between a *cis* dihydride and a dihydrogen species was postulated, but attempts to directly detect a dihydrogen species by low temperature infrared spectroscopy were not successful. These results are qualitatively similar to the observations discussed above for complex **10**. It seems likely that this Re complex may be another example of an elongated dihydrogen or compressed dihydride species with a very soft PES.

## 5 Conclusions

A key task facing the synthetic chemist is the determination of the structure of a newly prepared molecule. In the case of elongated dihydrogen complexes, this seemingly simple objective is fraught with difficulties. Some but not all of these molecules exhibit temperature and isotope dependent bond distances that are without precedent, rendering the concept of a unique and well defined structure less meaningful. Thus these molecules exhibit a novel type of molecular dynamics not previously available for study. Both experimental and theoretical studies have played an important role in the exploration of the properties of these novel complexes. It is not as yet possible to predict with any certainty the properties of a new hydrogen complex prior to synthesis, demonstrating yet again the rich and sometimes unpredictable variability found in the coordination chemistry of this seemingly simple ligand molecule. A productive synergy between theory and synthetic/spectroscopic work will no doubt continue to be required as we increase our understanding of the binding and activation of hydrogen.

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