The Barrier to Rotation of the Dihydrogen Ligand in the Complexes [MH(η^2-H$_2$)PP$_3$]BPh$_4$ (M = Fe, Ru): Evidence for Stronger Back-Donation in the Iron Complex

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The barrier to rotation of the dihydrogen ligand in the complexes [MH(η^2-H$_2$)PP$_3$]BPh$_4$, M = Fe, Ru, was determined from inelastic neutron scattering studies of the dihydrogen rotational energy levels. Our results demonstrate unambiguously that this barrier is higher in the Fe complex than in the Ru analog. With the assumption of a simple 2-fold barrier our analysis yields heights of 1.82 and 1.36 kcal/mol, respectively, where the rotational constant for the molecular hydrogen ligand ($B = 43$ cm^{-1}) was calculated from a value for the H–H distance of 0.87 Å given by the NMR results of Morris and collaborators on related complexes. Since previous studies have shown that this barrier has its origin primarily in the back-donation from the metal to the antibonding orbital of the dihydrogen, one may conclude that the Fe center is a better back-donor than Ru, contrary to what general trends in the periodic table would lead one to expect. This result provides direct support for a hypothesis made by Morris and collaborators to explain their NMR results on a different series of dihydrogen complexes of the Fe group.

Introduction

Since their original discovery[2] dihydrogen complexes have continued to attract an increasing amount of attention.[3] Recent interest has centered on the electronic details[4,5] of the chemical bond formed between the dihydrogen ligand and the metal center, how these are affected by the other ligands on the metal, and furthermore, complexes[6–8] where the H⋯H separation is so long as to suggest an intermediate state between dihydrogen and dihydride coordination.

We have been able to show[4,5,9] in our previous work that the barrier to rotation for the dihydrogen ligand is to a very large extent a good measure of the dihydrogen–metal bond, or more specifically, indicates the amount of back-bonding dπ(M)–σ*-(H$_2$), as the latter interaction does have a directional property about the M–(H$_2$) axis, whereas the σ-donation does not. Since the H–H bond is likely to be weakened by both of these interactions, the H–H bond length and the value of ν(HH) may also be taken to reflect the degree of bond activation. A combination of experimental results that supply these quantities should therefore provide some insight into the degree to which these bonding interactions affect the binding and stability of the dihydrogen ligand.

With the exception of a few cases[3,5] the observation of ν(HH) has, however, been very difficult. Only for the matrix-isolated species[10] with small inorganic ligands can this band be readily identified. Furthermore, the reliable determination of the HH bond length requires single crystals large enough for a neutron diffraction experiment or solid-state NMR measurements. However, H–H bond lengths obtained from single-crystal data may be biased even at very low temperatures because of the large librational amplitude of this ligand, which may lead to an underestimation of the bond length.

We have, on the other hand, been able to determine the rotational barrier of the dihydrogen ligand in a considerable number of such complexes[9] and have therefore undertaken a program to study the factors that influence metal–dihydrogen binding by this technique and relate it to findings available from other investigations.

Of the factors that control the formation and stability of the metal–dihydrogen bond, the one most easily accessible is the influence of the metal center itself. This would involve complexes with the same ligands and a series of metal centers as in a given group of transition metals. Dihydrogen complexes of the Cr group (Cr, Mo, W) were studied by IR spectroscopy[10] in liquid xenon in the form M(CO)$_5$(η^2-H$_2$) and by inelastic neutron scattering[4,11] in the form M(CO)$_3$(η^2-H$_2$)(PCy$_3$)$_2$ (where Cy = cyclohexyl). The latter compounds are all sufficiently stable in the solid state in which they were examined. For the Co group (Co, Rh, Ir), on the other hand, complexes of the form [M(H$_2$)(PP$_3$)]$^+$ (where PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$) are reported to be nonclassical in the solid state and in solution only for Co, whereas the Rh analog may be nonclassical in solution and the Ir complex is always classical.[12]

An extensive study of a group of transition metal dihydrogen complexes was carried out by Morris and collaborators[5b] on the

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Fe group. Data of various types collected on the series of complexes [MH(η^2-H$_2$)L$_2$]$^+$, where M = Fe, Ru, and Os and L = dppe and depe, led these investigators to the conclusion that the Ru–dihydrogen complex falls out of order in this group, i.e. that it is less stable than its Fe counterpart. The authors used a variety of different experimental techniques, mostly solution NMR studies on both the hydride and dihydrogen ligands, as well as IR spectroscopy. None of the vibrational modes involving the dihydrogen ligand could be observed, however, and only the stretching mode of the hydride could be identified. The latter does, however, provide a measure of the σ bond strength of the metal center. It was found to increase in order down the group of metals, Fe < Ru < Os, as expected.

For the dihydrogen ligand, on the other hand, the metal–hydrogen bond strength was found[5b] to increase in the order Ru < Fe < Os, which is accompanied by a corresponding order of decrease of H–H interactions, Os < Fe < Ru. Morris and collaborators rationalized these sets of findings with the conclusion that Fe must unexpectedly be a better back-donor dπ(M)–σ^*-(H$_2$). No direct evidence for this inference could, however, be obtained with their measurements.

A determination of the barrier to rotation in complexes with different metal centers would, as we pointed out above, provide some evidence for the strength of the back-bonding interaction. Thus we chose to study the complexes[10] [MH(η^2-H$_2$)PP$_3$]$^+$ (M = Fe, Ru), which were crystallized as BPh$_4$ salts.[13]

Indeed, these Fe and Ru complexes exhibit a quite different chemical stability. The Fe(η^2-H$_2$) complex is very stable as it does not decompose in refluxing tetrahydrofuran under Ar and does not undergo H/D exchange when treated in solution with D$_2$ or D$_2$O for several hours.[13a,b] Moreover, when [FeH(η^2-H$_2$)-PP$_3$]BPh$_4$ is used as a homogeneous catalyst for the selective hydrogenation of 1-alkynes to alkenes, a free coordination site for the incoming alkyne molecule is provided by unfastening of a phosphine arm, rather than by H$_2$ coordination.[14] In contrast, the H$_2$ ligand in the Ru derivative can easily be displaced by other ligands such as N$_2$, CO, MeCN, and PR$_3$ in room-temperature solutions.[13c]

Experimental Section

The samples of [MH(η^2-H$_2$)PP$_3$]BPh$_4$, (M = Fe, Ru) were prepared according to the literature method. This involves the reaction of the dihydrides [M(H)2PP3], (M = Fe, Ru)[13c,15] in tetrahydrofuran with 1 equiv of triflic acid under hydrogen pressure. Addition of NaBPh$_4$ in ethanol gave [FeH(η^2-H$_2$)PP$_3$]BPh$_4$ and [RuH(η^2-H$_2$)PP$_3$]BPh$_4$ as yellow and off-white microcrystals, respectively. The yield was about 90%. The dinitrogen complexes [MH(N$_2$)PP$_3$]BPh$_4$, (M = Fe, Ru)[13a,c] were prepared under prepurified N$_2$ by substituting MeOSO$_2$CF$_3$ for HOSO$_2$-CF$_3$ in the procedure described above.

The inelastic neutron scattering experiments were carried out on the cold neutron time-of-flight spectrometer IN5 at the Institut Laue-Langevin, Grenoble (France) and on the FDS instrument at the Manuel Lujan, Jr., Neutron Scattering Center of the Los Alamos National Laboratory. Data were collected at temperatures of 5 and 15 K, respectively. The former experiments yielded the tunnel splitting of the librational ground state[16] of the dihydrogen ligand, whereas the measurements at Los Alamos provided vibrational data including the torsional transition of the molecular hydrogen ligand. Approximately 1 g of each sample was needed, and the phosphine ligands and counterion were not deuterated. In the latter case it was necessary to utilize a spectral difference technique[17] with the aid of analogous samples with a dinitrogen ligand instead of the dihydrogen. Because the scattering cross-section

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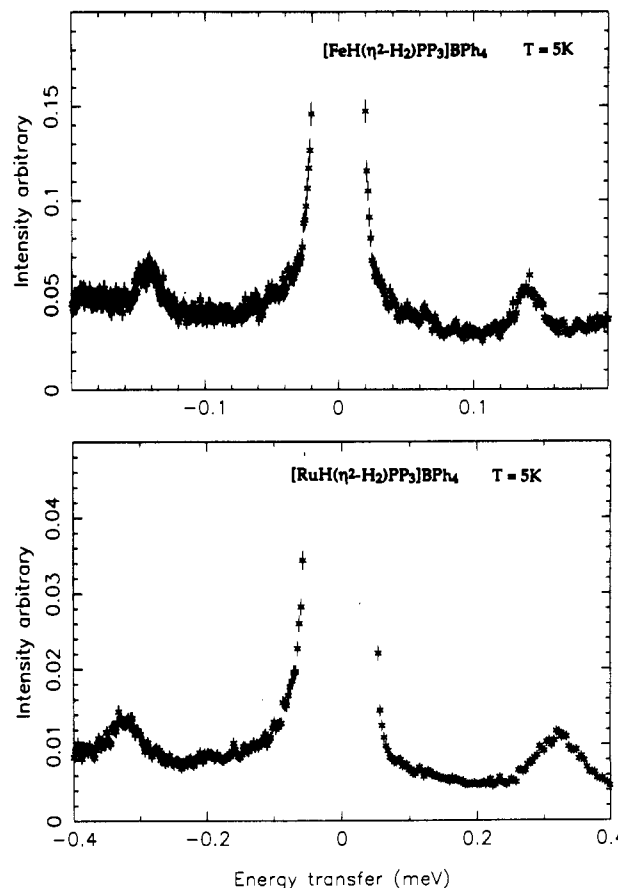
Figure 1. Inelastic neutron scattering data collected at 5K on IN5 at the ILL for [FeH(η^2-H$_2$)PP$_3$)]BPh$_4$ (top) and [RuH(η^2-H$_2$)PP$_3$)]BPh$_4$ (bottom). Incident neutronm wavelengths were 10 and 7 Å, respectively. Note that 0.1 meV = 0.81 cm^{-1}.

for H is more than one order of magnitude greater than that of N, modes involving the latter essentially cannot be "seen" in the presence of many H atoms. A subtraction of the two sets of spectra would then be expected to cancel the modes of all the other ligands, and leave those involving only the dihydrogen–metal fragment. If, however, some dihydrogen modes are mixed with other modes the subtraction will not be complete, and will in fact show evidence for such coupling. Moreover, if the coordination geometry for the N$_2$ and H$_2$ complexes were somewhat different the description of the normal modes of vibration and thus the vibrational spectrum would be affected. We would not, however, expect this to possible difference to be significant on the scale of the resolution of our INS difference spectra. Nonetheless, assignments of the vibrational bands must be regarded as tentative for these reasons.

Results and Discussion

The results of the rotational tunneling data are very clear indeed. Shown in Figure 1are the data obtained on IN5 at the ILL for the Ru and Fe analogs. The tunneling transitions are shown both in neutron energy gain and in energy loss. The elastic peak at the center has an intensity nearly 500 times greater than these inelastic features. The transition occurs at about 2.58 cm^{-1} for Ru and 1.15 cm^{-1} for the Fe complex, which immediately leads to the conclusion that the barrier to rotation of the molecular hydrogen ligand is greater in the latter than the former compound.

In order to extract a value for the barrier height from these results, it is necessary to have a model for the rotation and to know the value of the rotational constant B, i.e. the bond distance d(HH). In all of our previous studies we have successfully employed[9] the simplest picture for the reorientational motion of the dihydrogen ligand, viz. uniaxial (the axis from the metal to the midpoint of the H–H bond) planar rotation in a sinusoidal double-minimum potential well with barrier height V_2. This is the first term in an expansion (see, for example, eq 1 in ref 4)

of the general hindering potential for planar rotation of a dumbbell molecule. The higher order terms V_{2n} serve primarily to modify the shape of the potential well which may arise from the fact that the coordination geometry about the metal center frequency is of low symmetry. This is reflected in some of the theoretical analyses,[4c] which have suggested that the maxima and minima of the rotational potential curve are flattened. In some cases,[4b,5a] it was in fact necessary to add the second term (V_4) in the expansion of the rotational potential for a better fit of the rotational energy levels. Moreover, modeling of the temperature dependence of the solid-state NMR data[18] has also been shown to require a V_4 term for satisfactory agreement with experiment.

Since rotational energy levels are given in units of the rotational constant B, the latter either has to be known independently or be derived in this analysis. In the present case, unfortunately, neither possibility is straightforward. B could be determined from a knowledge of $d(HH)$ obtained by neutron diffraction studies, which has not, however, been carried out on the complexes of the present study. Moreover, even though it is generally assumed that such a study is most likely to give the "best" value for $d(HH)$, the very large librational amplitude of the dihydrogen ligand may require large corrections to the bond length obtained least-squares refinement of single-crystal diffraction studies. These corrections are not usually included in the few such structures that have been published. One indication of this problem is the rather large discrepancy between the values for d(HH) derived from solid-state NMR studies[18] and those from neutron diffraction.[2,5,19] These differ typically by about 0.1 Å, where the NMR value is always larger. The H–H separation in solid-state NMR is derived directly from the spacing of a pair of discontinuities in the observed Pake pattern and can therefore be viewed as a dynamical measurement. It may thus give a more realistic value for the "true" $d(HH)$.

An estimation of the apparent bond shortening caused by the rotation of the H_2 ligand about the $M–H_2$ axis may be obtained by correcting the observed $d(HH)$ for rigid body motion.[20] An attempt to apply this correction to the complex[21] $MoCO(\eta^2-H_2)$-$(dppe)_2$ as well as the cation[22] $[FeH(\eta^2-H_2)dppe_2]^+$ was made using the program THMA.[23] In the former complex the uncorrected value of $d(HH)$ found in the refinement was essentially that of free, uncoordinated H_2 whereas in the latter it was 0.82 (2) Å. The resulting bond length increase was found to be in the range 0.1–0.15 Å, which brings these values into better agreement with those determined from solid-state NMR measurements. It should be noted, however, that rigid body (TLS) treatment is only a very crude approximation in these cases and may result in an overestimation of this correction. Further studies are planned to obtain more reliable answers to this problem.

In the following analysis we have chosen the value $B = 43$ cm^{-1} for both the Fe and Ru complexes. This corresponds to $d(HH)$ $= 0.87$ Å, which is comparable given the esd's to the value obtained for two different Fe–dihydrogen complexes by neutron diffraction studies. This choise is based on the aforementioned work[5b] of Morris and collaborators. Their analysis of solution NMR T_1 data suggested that $d(HH)$ in the complexes $[MH(\eta^2-H_2)$-$(dppe)_2]^+$ (M = Fe, Ru, Os) is about equal for the Fe and Ru analogs, namely 0.87 ± 0.02 Å. It is not unreasonable to relate

this Fe complex of Morris to the one in the present study since the rotational tunnel splitting in the two cases suggests a similar degree of H–H bond activation. Once the choice of B is made, the barrier height for a pure 2-fold barrier can then be computed from the rotational tunnel splitting alone and is found to be 1.82 kcal/mol. The torsional transitions would then be expected to occur at 269 and 291 cm^{-1}.

The sample differential data in the high frequency range for both the Fe and Ru–dihydrogen complexes are shown in Figure 2. The features that remain in these spectra should only be modes involving mainly the dihydrogen ligand. However, in cases where some other skeletal mode of this complex has a significant component of dihydrogen motion, our subtraction procedure involving the dinitrogen analog will leave some intensity at that frequency. In the absence of a more rigorous analysis, our assignments must therefore be regarded as somewhat tentative.

Nonetheless, in both the Fe and Ru complexes the torsions may be assigned as the strongest band in the spectrum, as is normally[24] the case. For the Fe compound, this is the doublet with components at 259 and 276 cm^{-1}. These values do not agree very well with those computed for the purely 2-fold potential barrier (Table I). A very good fit can be obtained with the addition of the next term in the expansion of the rotational potential, V_4, as we discussed above. With the ratio $V_4/V = -0.1$, we find excellent agreement with the experimental data.

At this point one can repeat this same procedure for the Ru analog. Again we take the value of the tunnel splitting (2.58 cm^{-1}) as the basis for the calculation since it can be measured with much greater accuracy than that of the torsions. The values expected for the torsion (209 and 241 cm^{-1}) for only a V_2 term in the potential are in this case in serious diagreement with experiment, where we find a strong peak at 184 cm^{-1} with a broad shoulder at about 225 cm^{-1} (Figure 2). A much larger contribution

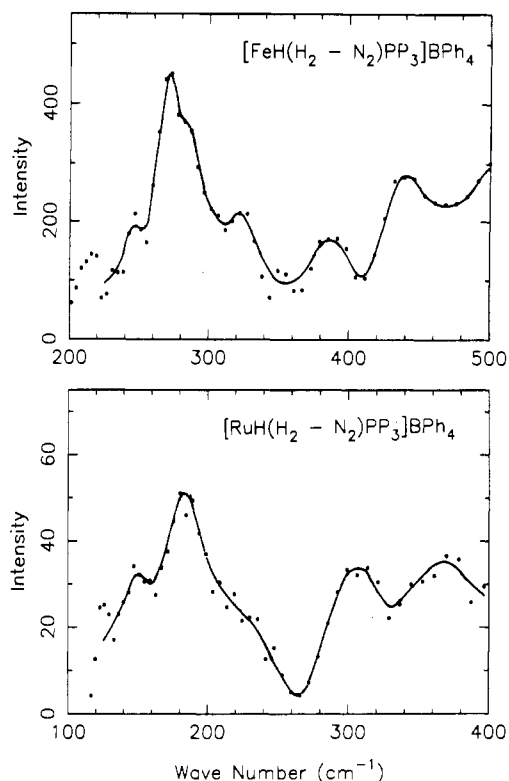**Figure 2.** Differential spectra (see text for a description of this process) for the Fe(η^2-H_2) and Ru(η^2-H_2) fragments obtained on the FDS instrument at LANSCE. $T = 15$ K. The solid lines are drawn to guide the eye.

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Table I. Rotational Transitions (cm⁻¹) and Barrier Heights (kcal/mol) for Metal Dihydrogen Complexes[a]

M = Fe

ω_t	τ(obs)	$V_2 = 1.82$	$V_2 = 1.93$ $V_4/V = -0.1$	$V_2 = 1.73$ $V_4 = 0, B = 41$
			τ(calc)	
1.15 (5)	259 (8)	269	259	266
	276 (8)	291	277	277

M = Ru

ω_t	τ(obs)	$V_2 = 1.36$	$V_2 = 1.59$ $V_4/V = -0.5$	$V_2 = 1.14$ $V_4 = 0, B = 38$
			τ(calc)	
2.58 (6)	184 (7)	209	188	184
	225 (11)	241	209	219

[a] $B = 43$ cm⁻¹ was used (see text) for the values of τ(calc) in the first two columns, and $V = V_2 + V_4$.

of 4-fold symmetry, $V_4/V = -0.5$, is required for the Ru complex in order to achieve reasonable agreement with our observations.

Instead of making an assumption for a value of B, one may attempt to determine B from the rotational energy levels. Because of the small number of observed transitions B (and thus the H–H distance) and V_2 together can only be obtained if the V_4 term to the rotational potential is kept fixed. Analysis of the present rotational data under the assumption that $V_4 = 0$, however, requires (see Table I) that B be *smaller*, i.e. that d(HH) be *longer* for the Ru complex than its Fe analog. Such a result would seem to be at odds with other studies[5b] on dihydrogen complexes of the Fe group, which do suggest that the H–H interaction is *stronger* for the Ru than the Fe complexes. A longer H–H bond (i.e. *weaker* H–H interaction) in the former can therefore be ruled out, a conclusion which is further supported with the aid of the analogy[25] between dinitrogen and dihydrogen complexes. The values of ν(NN) for the present Fe and Ru dinitrogen complexes are 2110 and 2182 cm⁻¹, respectively, which suggests that the N–N bond activation and therefore the metal–ligand (N_2, H_2) interaction is indeed smaller in the Ru complex. It is worth pointing out that the latter value is beyond the region of ν(NN) frequencies for dinitrogen analogs (2060–2150 cm⁻¹) considered indicative of stable dihydrogen binding[25] as has already been

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noted.[26] One might have expected that the shape of the rotational potential (i.e. the value of V_4/V) for dihydrogen in these two complexes would be the same. Theoretical analyses[5a,21] on the barrier to rotation have however clearly shown that this barrier depends on the coordination geometry of the other ligands about the metal center. In the absence of definitive diffraction data on these complexes, one is left with the possibility that there may in fact be slight differences in the phosphine coordination about the metal. In light of the above discussion, where we point out that the higher order terms in the expansion of the rotational potential serve primarily to account for variations in the shape of this potential, one may then conclude that for the less strongly bound dihydrogen ligand (i.e. the Ru complex) the shape of this potential is more distorted from a sinusoidal form with a double-minimum. This would appear to be reasonable as the restoring forces are stronger for the more tightly bound dihydrogen ligand in the Fe complex.

We have therefore demonstrated in this study that in yet another series of dihydrogen complexes of the Fe group Ru falls out of the expected order in the periodic table in terms of its binding strength for the dihydrogen ligand. In addition, we may conclude that it is the better back-donation properties of the Fe center relative to Ru that makes this possible, and thereby support the explanation given by Morris and collaborators[5b] on their observations of different dihydrogen complexes of the Fe triad. We are also continuing our studies of complexes of the Fe triad of Morris to include both the Ru and Os analogs, in order to gain a better understanding of how the metal–dihydrogen bonding interactions and H–H bond activation vary upon changing the metal center. In addition, we should point out that high quality structural results are urgently needed for many of these compounds in order to put many of these conclusions on a firmer basis.

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