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Nature of the Rh−H_2 Bond in a Dihydrogen Complex Stabilized Only by Nitrogen Donors. Inelastic Neutron Scattering Study of $Tp^{Me_2}RhH_2(\eta^2\text{-}H_2)$ (Tp^{Me_2} = Hydrotris(3,5-dimethylpyrazolyl)borate)

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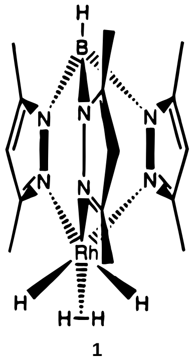
The tunnel splitting of the librational ground state and the torsional frequencies of the dihydrogen ligand in $Tp^{Me_2}RhH_2(\eta^2\text{-}H_2)$ (Tp^{Me_2} = hydrotris(3,5-dimethylpyrazolyl)borate) were measured using inelastic neutron scattering spectroscopy. The barrier for the rotation of the H_2 ligand and its H−H separation, calculated from these data, are 0.56(2) kcal/mol and 0.94 Å, respectively. These values indicate that π-back-donation from the $Tp^{Me_2}RhH_2$ fragment to H_2 is relatively weak and/or the interaction between the coordinated dihydrogen molecule and the two *cis*-hydride ligands significantly lowers the barrier for H_2 rotation.

Introduction

Since the original discovery by Kubas et al.[1] of transition metal complexes containing coordinated molecular hydrogen, these compounds have attracted increasing attention[2,3] as they are likely to provide a better understanding of the nature of the dihydrogen−metal interactions and, therefore, of the fundamental process of dihydrogen activation at a metal center and of the role of dihydrogen complexes in homogeneous catalysis.

Schematic representations of the $M(H_2)$ and MH_2 interactions in their complexes are shown in Figure 1.



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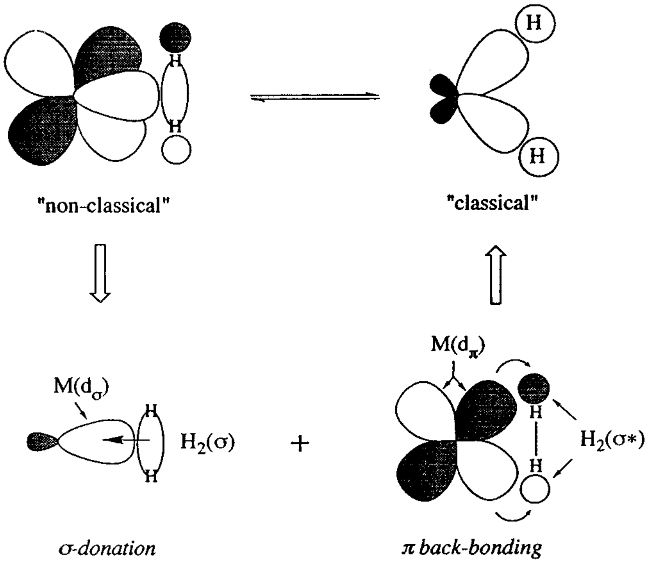

Figure 1. Schematic representation of the MH_2 and $M(H_2)$ interactions.

Most of these complexes contain phosphine, cyclopentadienyl, or organometallic donors as coligands, and it has been assumed that the high electron density at the metal center induced by the presence of these ligands strengthens the $M(H_2)$ bond by π-back-donation. However, the compound $Tp^{Me_2}RhH_2(\eta^2\text{-}H_2)$ (**1**) (Tp^{Me_2} = hydrotris(3,5-dimethylpyrazolyl)borate), the first example of a dihydrogen complex which contains only nitrogen donors as coligands, was recently prepared and extensively characterized by NMR studies as well as IR spectroscopy.[4,5] A space-filling model of molecule **1**, viewed along the pseudo-C_3 axis, is shown in Figure 2. The H−H interaction within the coordinated dihydrogen ligand in this compound appears to be relatively weak and, therefore, close to the limit of an oxidatively added dihydrogen molecule. This is indicated by the value of the IR band at 2238 cm^{-1}, tentatively assigned to the H−H stretching frequency, and relative stabilities of related compounds. Thus, only a slight increase in the electron-donating ability of the pyrazolyl ligand used, i.e., Tp^{Me_3} (Tp^{Me_3} = hydrotris(3,4,5-trimethylpyrazolyl)borate) instead of Tp^{Me_2}, makes the resulting dihydogen complex less stable, while the presence of an electron-withdrawing CF_3 group in $Tp^{CF_3,Me}$ ($Tp^{CF_3,Me}$ = hydrotris(3-trifluoromethyl-5-methylpyrazolyl)bo-

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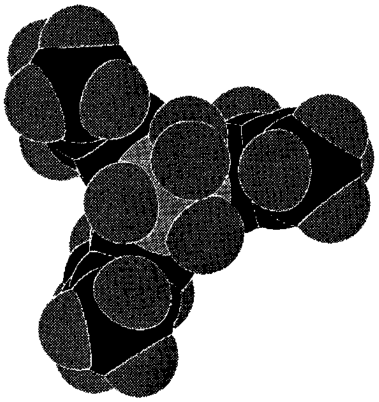

Figure 2. Space-filling model of molecule **1** viewed along the pseudo-C_3 axis.

rate) improves the stability of the corresponding dihydrogen complex.[4b]

The dihydrogen and hydride ligands in **1** are highly fluxional on the NMR time scale and, therefore, the measured J(H,D) of 4.7 Hz is an average resulting from the dynamic H,D exchange between the H$_2$ molecule and the two hydride ligands. Similar effects have been observed in related complexes such as FeH$_2$(η^2-H$_2$)(PEtPh$_2$)$_3$[6] and Tp^{Me_2}RuH(η^2-H$_2$)$_2$.[7]

Considerable insight into dihydrogen−metal interactions has been obtained by studying the barrier to rotation of coordinated dihydrogen by inelastic neutron scattering (INS) techniques.[8] This barrier arises primarily from the variation in the back-bonding interaction between d_π(M) and the σ^*(H$_2$) orbitals (see Figure 1) as the dihydrogen ligand is rotated around the σ-bond to the metal. Therefore, the barrier height, derived from measurements of the rotational transitions, provides an indication of the strength of the back-bonding interaction. In addition to the direct σ- and π-interactions between the metal center and dihydrogen (which depends on the coligands), EHMO and *ab initio* calculations have shown that, in the case of the above iron complex, the barrier height is also affected by the presence of hydride ligands *cis* to coordinated dihydrogen (*cis* effect).[6,9]

Therefore, INS measurements of the rotational and vibrational transitions of the dihydrogen ligand in **1** were performed in order to carry out a detailed study of its rotational barrier.

Experimental Section

The data collected on the cold neutron time-of-flight spectrometer IN5 at the Institut Laue-Langevin, Grenoble, France, at temperatures of 5 K, yielded the tunnel splitting of the librational ground state of the coordinated dihydrogen.[10] Another set of data, obtained at 15 K, on the FDS instrument at the Manuel Lujan Jr. Neutron Scattering Center of Los Alamos National Laboratory, provided vibrational data including transitions to the excited librational states ("torsions") of the dihydrogen ligand.

Compound **1** and its deuteride were prepared as described elsewhere.[4,5] Approximately 1 g samples, sealed under a helium atmosphere, were used for these experiments. The vibrational spectra were obtained with the aid of a "difference technique"[11] using two samples, one of the hydride and the other of the corresponding complex, in which the two H and the H$_2$ ligands were replaced by D and D$_2$, respectively.

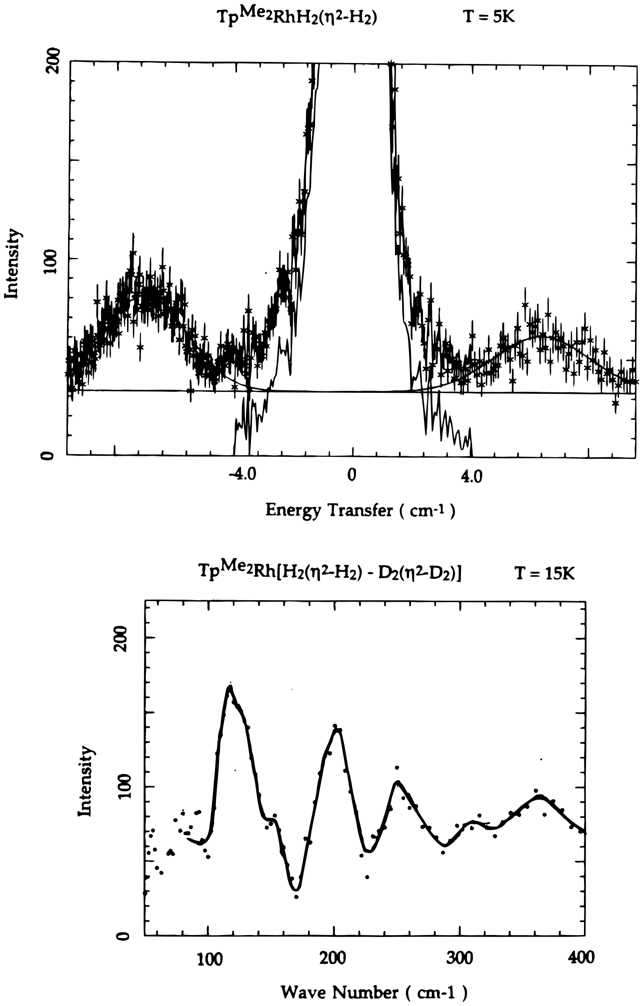

Figure 3. INS spectra of Tp^{Me_2}RhH$_2$(η^2-H$_2$) (**1**): (a, top) low-frequency spectrum collected at T = 5 K, on IN5 at the ILL using an incident neutron wavelength of 5 Å; (b, bottom) sample difference spectrum, at T = 15 K, obtained on FDS at LANSCE.

Results and Discussion

The rotational tunneling spectrum, obtained on IN5 at 5 K, is shown in Figure 3a, and the two peaks at ± 6.7 cm^{-1} are assigned[12] to the rotational tunneling of the bound dihydrogen. The vibrational difference spectrum of the RhH(H$_2$) fragment is shown in Figure 3b.

The two peaks at *ca.* 120 and 200 cm^{-1} are assigned to the dihydrogen torsions because of their high intensities and the weaker peaks at higher frequencies to the skeletal deformation modes involving the (H)$_2$/(H$_2$) motions. Data from both experiments are summarized in Table 1.

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(12) Assignment of the peaks at ±6.7 cm^{-1} to rotational tunneling of the methyl groups of the 3,5-dimethylpyrazolyl ligands can be ruled out for the following reasons: The constant B for rotation of a methyl group about its 3-fold axis is 5.3 cm^{-1}, and therefore, the observed transition at ±6.7 cm^{-1} would correspond to a B value of 1.25 for uniaxial methyl rotation. However, the largest possible value of B for the lowest transition (J = 0 to J = 1) for uniaxial rotation is 1.[10] Therefore, the observed transitions must be attributed to the dihydrogen ligand for which B is in the order of 40−50 cm^{-1}. In addition, a rough estimate of the rotational tunnel splitting for the methyl groups in 3,5-dimethylpyrazole may be obtained from the observed torsional frequency at about 110 cm^{-1} (Jayasooriya, U. A.; Stride, J.; Eckert, J. Unpublished work). From this transition one can calculate that the rotational tunnel splitting would have been ca. 0.04 cm^{-1}.[10]

Table 1. Tunneling Frequency, ω_t (cm^{-1}), Observed and Calculated Rotational Transitions, τ (cm^{-1}), and Barrier Heights, V_n (kcal/mol), for Dihydrogen in [TpMe$_2$RhH$_2$(η_2-H$_2$)]

		τ (calc)		
ω_t	τ (obs)	$V_2 = 1.1$ $B = 49.7$	$V_2 = 0.68$ $B = 37.1$	$V_2 = 0.60$ $V_4 = 0.26$ $B = 37.1$
6.7(5)	118, 126		121	123
	194	188	180	195
	203	255	219	204

The barrier height can be calculated using the equation for a hindered rotor:

$$[-B(\delta^2/\delta\phi^2)] + \sum_{2n} V_n(1 - \cos n\phi)]\Psi = E\Psi$$

where ϕ is the angle of rotation about the N−Rh−H$_2$ axis and B is the rotational constant ($B = \hbar^2/2I \times r$, and $I \times r$ = moment of inertia) under the assumption of planar rotation and negligible coupling with vibrational modes.[8] However, in the present case, the value of B (which must be lower than that for the free hydrogen molecule, i.e., 59.3 cm^{-1}) is not known, as a single-crystal neutron diffraction study of this compound, to obtain the value of the H−H distance, could not be carried out.[13] Therefore, initially, the barrier height was calculated using a value of $B = 49.7$ cm^{-1}, as this corresponds to d(HH) = 0.81 Å, a typical distance in coordinated unstretched dihydrogen, obtained by neutron diffraction.[14]

This value yielded a barrier height V_2 of 1.1(1) kcal/mol. However, the agreement with the observed rotational transitions was not satisfactory when only the V_2 term was used (see Table 1). Even the inclusion of the next term in the Fourier expansion of the rotational potential, V_4, did not result in significantly better agreement with the observed transitions.

Thus, the rotational constant B, and, consequently, the H−H distance, was allowed to vary. This approach is reasonable as both the chemistry and the spectroscopic data for compound **1** indicate that the H−H distance in the coordinated dihydrogen is significantly longer than 0.81 Å. Much better agreement was obtained using a potential where $V_2 = 0.60$ and $V_4 = 0.26$ kcal/mol. This potential had a maximum well depth of 0.56(2) kcal/mol and a set of secondary minima at 90° to those of the equilibrium orientation of the dihydrogen. The resulting rotational constant was 37.1 cm^{-1}, giving an H−H distance of 0.94 Å. This value is qualitatively in accord with the fact that **1** is a fairly stable dihydrogen complex, i.e., that the M−H interaction is rather strong and the H−H interaction weak. The latter conclusion is also consistent with the assignment of the very low energy band at 2238 cm^{-1} to ν(HH).

It should be noted that the rotational tunneling peaks and some of the torsional peaks appear to be split. The magnitude of this effect, approximately 0.8 cm^{-1}, implies a splitting of the first torsional state of about 7 cm^{-1} (close to what is indeed observed—see Table 1) and leads to two very close barrier heights of 0.54 and 0.58 kcal/mol. While different sites might experience different crystal fields for complexes containing bulky ligands, it can be assumed that electronic effects and intramolecular nonbonded interactions are considerably stronger than those with neighboring molecules. Indeed, crystal field effects should be small as (a) the packing distances in related compounds are longer or comparable with van der Waals distances and (b) the dihydrogen ligands are "shielded" by the organic ligand (see Figure 2). Thus, the most likely explanation for this effect is (i) the crystals contain two inequivalent independent molecules and, therefore, two inequivalent dihydrogen ligands or (ii) there is a slight disorder of the molecular structure.

The very low value obtained for the barrier to rotation of dihydrogen in this compound would appear to be somewhat surprising in view of the spectroscopic evidence for a weak H−H interaction with its attendant enhanced Rh-H interaction. The most plausible explanations for this low value are as follows: (i) the strong metal−H$_2$ bond is mainly due to a σ-interaction which does not directly contribute to the barrier to rotation, (ii) the direct interaction of dihydrogen with the *cis*-hydrides[5] has the effect of lowering the barrier to rotation, and (iii) the $d_\pi(M) \rightarrow \sigma(H_2)$ back-bonding does not vary much as a function of dihydrogen rotation because the arrangement of the coligands is highly symmetrical. In the absence of structural data, one can only reach tentative conclusions for this problem. However, it is likely that one can rule out an effect such as (iii), as this is important[15] only in more symmetrical compounds, e.g., *trans*-Mo(H$_2$)(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$, where the H$_2$ molecule is parallel to plane defined by the metal and the four P atoms which are practically coplanar. In the present case, however, the corresponding plane contains the metal, two *cis*-H, and two N donor atoms. One may, therefore, conclude that π-back-donation from the Tp^{Me_2}RhH$_2$ fragment to H$_2$ is relatively weak and/or that the dihydrogen/*cis*-hydride interaction significantly lowers the barrier for H$_2$ rotation. While the qualitative stability trend for the complex containing CF$_3$-substituted pyrazolylborates indicates that σ effects are not negligible, the fast exchange between coordinated hydride and dihydrogen observed by NMR[5] provides a clear indication of significant H$_2$···H interactions and thus indicates that *cis*-H effects may also play a significant role.

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