An Extremely Low Barrier to Rotation of Dihydrogen in the Complex $IrClH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$

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Received July 12, 1993

Since the original discovery by Kubas et al.[1] of coordinated molecular hydrogen in metal complexes, these compounds have attracted an increasing amount of attention[2,3] both because of their fundamental significance and for their potential applications in catalysis. The isolation and characterization of the iridium nonclassical polyhydride complex $IrClH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**1**) was recently reported.[4] The presence of dihydrogen in this complex has been indicated by both solution[4] and solid-state NMR.[5] The solid-state studies indicate that the barrier to intramolecular conversion of the dihydrogen and hydride ligands is surprisingly small, namely "substantially under 3 kcal mol^{-1}." [5] In addition, studies by Oro et al.[6] have indicated that **1** is an intermediate in the hydrogenation of benzylideneacetone by $IrCl_2H(P^iPr_3)_2$. An increased understanding of the nature of the dihydrogen-metal interaction in **1** should help in elucidating the fundamental process of activation of dihdyrogen at iridium centers as well as the role of dihydrogen complexes in homogeneous catalysis.

A considerable amount of insight into the dihydrogen-metal interaction has been obtained through studies of the barrier to rotation of the dihydrogen ligand[7,8] by use of inelastic neutron scattering (INS) techniques. Apart from the direct interaction between the metal center and the dihydrogen ligand (which strongly depends on the spectator ligands), an effect of a hydride *cis* to dihydrogen has also been demonstrated.[9]

This dihydrogen-hydride interaction must also play an important role in the exchange between these two ligands. The extremely rapid intramolecular dihydrogen-hydride exchange[5] observed in **1** would therefore be expected to have a pronounced effect on the barrier to rotation as well, especially since the barrier to that exchange appears to be of similar magnitude[7,8] to the rotational barrier for many dihydrogen complexes.

We have accordingly performed INS measurements of the rotational transitions of the dihydrogen ligand in **1** to determine the height of its rotational barrier. This barrier was also calculated by an *ab initio* method.

Experiments were carried out on the cold neutron time-of-flight spectrometers MIBEMOL at the Orphee Reactor of the Laboratoire Leon Brillouin as well as IN5 and IN6 at the Institut Laue-Langevin, Grenoble, France, and on the FDS instrument at the Manuel Lujan Jr. Neutron Scattering Center of Los Alamos National Laboratory. Data were collected at temperatures of 1.7, 5, and 15 K, respectively, at the three sites. The former experiments yielded the tunnel splitting of the librational ground state[10] of the dihydrogen ligand, whereas the measurements at Los Alamos provided vibrational data including the transition to the excited librational state ("torsion") of the dihydrogen ligand.

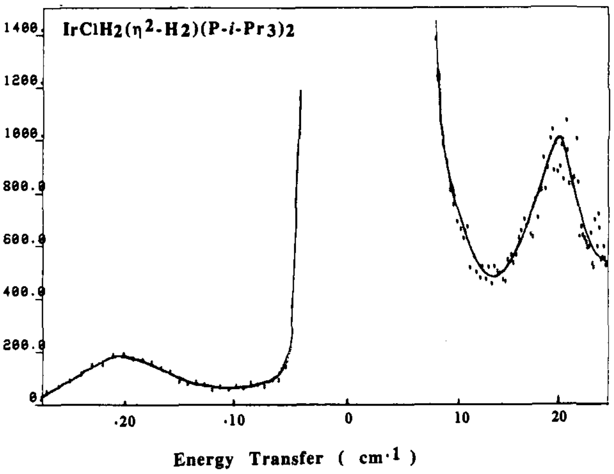

Figure 1. Inelastic neutron scattering spectrum on $IrClH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ obtained at $T = 1.7$ K on MIBEMOL using an incident neutron wavelength of 4.5 Å. Rotational tunneling peaks appear at approximately ±20 cm^{-1}. Similar results were obtained on IN5 and IN6.

Table I. Rotational Transitions (cm^{-1}) and Barrier Heights (kcal/mol) for Dihydrogen in $IrClH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$[a]

		τ(calc)	
ω_t	τ(obs)	$V_2 = 0.51$	$V_2 = 0.46$ $V_4 = 0.46$ $B = 53.3$
19.9(5)	127(6)	127	135
	221(5)	215	211
	270(7)	233	272

[a] $B = 50$ cm^{-1} was used (see text) for the values of τ(calc) in the first two columns.

Approximately 1 g of sample sealed under hydrogen atmosphere was used in these experiments with phosphine ligands that were not deuterated. The vibrational spectra were obtained with the aid of a spectral difference technique[11] which utilizes two samples in which the dihydrogen and hydride ligands were H and D, respectively. The rotational tunneling spectrum obtained on MIBEMOL at 1.7 K is shown in Figure 1. Data from both low- and high-frequency experiments are summarized in Table I.

The barrier height can be derived from the transitions of the hindered dihydrogen rotor under the assumption of planar rotation[7,8] in a potential of the form $V = {}^1/_2\sum V_{2n}(1 - \cos 2n\phi)$ if the value of the rotational constant B is known. In the present case, however, B (which must be lower than that of the free hydrogen molecule, i.e., 59.3 cm^{-1}) is undetermined since a single crystal neutron diffraction study[12] on this compound did not yield a value for d(HH) on account of the disorder between dihydrogen and hydride ligands.

We have, therefore, in the following analysis of the barrier height first used the value of d(HH) = 0.81 Å (i.e., B = 49.7 cm^{-1}), which is the result of several neutron diffraction studies on other dihydrogen complexes. This yields a barrier height V_2

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0002-7863/93/1515-11056$04.00/0

of 0.51(2) kcal/mol, which is the lowest value for a barrier to dihydrogen ligand rotation observed to date. Agreement with the transition frequencies of the excited states is, however, not satisfactory when only the V_2 term is used (see Table I). Upon including the next term in the Fourier expansion of the potential, V_4, and varying the rotational constant as well, a much better agreement can be achieved with a potential where $V_2 = V_4 = 0.46$ kcal/mol. This potential has a maximum well depth of 0.65 kcal/mol and a set of secondary minima at 90° to those of the equilibrium orientation of the dihydrogen. The rotational constant was found to be 53.3 cm^{-1}, which implies that d(HH) = 0.78 Å. This value is qualitatively in accord with the fact that this is an extremely labile dihydrogen ligand, i.e., that the M–H interaction is rather weak and the H–H interaction strong.

The structure and rotational barrier for dihydrogen in the model compound $IrClH_2(H_2)(PH_3)_2$ were computed with core pseudopotential *ab initio* calculations at the RHF/MP2 level. The basis set is identical to that used for[13] $IrCl_2H(H_2)(PH_3)_2$. The geometry of the heavy atoms in $ICl_2H(H2)(PH_3)_2$ was held fixed to the values obtained by X-ray diffraction[4] (Ir–H = 1.575 Å, H–Ir–H = 90°, P–H = 1.42 Å, Ir–P–H = 115°). The Ir–(H_2) and H–H distances were optimized and found to be 1.7 and 0.9 Å, respectively, when the H–H axis eclipses Cl–Ir–H and 1.7 and 0.8 Å when H–H eclipses P–Ir–P. The former is the most stable conformation, and the difference in energy between the two orientations is calculated to be 2.2 kcal/mol.

The discrepancy between this calculated value for the barrier to rotation and the experimental value of $V_2 = 0.5$ kcal/mol may at least in part be attributed to the very limited geometrical optimization carried out in our calculation and the assumption of a metal fragment that is frozen as the dihydrogen reorients.

A comparison with results[13] on the isoelectronic $IrCl_2H(H_2)P_2$ (P = P^iPr_3 and PH_3 for the calculations) is most instructive. In this case, the calculated (observed) values for d(HH) were 1.4 Å (1.1 Å) and for the barrier to rotation 6.5 kcal/mol (>2 kcal/mol). First, we may conclude that our value of 0.78 Å derived from the rotational transitions for d(HH) in the title compound is qualitatitively in accord with the trend found in the calculation (0.9 Å), which overestimates both d(HH) and the barrier to rotation. Second, the increase in barrier height on going from the monochloro to the dichloro analogue is clearly associated with a dramatic lengthening of the H–H bond. The large *trans* influence of the replacement of the chloride ligand with the hydride opposite to dihydrogen stems from a dimished interaction between the vacant orbital of the metal fragment $IrClH_2P_2$ and $\sigma(H_2)$. This reduces back-donation (and therefore the rotational barrier) since dihydrogen remains farther from the metal center.

Both the very low value of the observed rotational barrier and the very pronounced fourfold component in the shape of the barrier in **1** may be related to the very rapid dihydrogen–hydride exchange. On the basis of the solid-state NMR study as well as theoretical work on related compounds, we propose that a bis-dihydrogen form is the most likely intermediate in the observed pairwise dihydrogen–hydride exchange and that the unavailability of such an Ir(I) intermediate could account for the much higher barriers to dihydrogen–hydride exchange and dihydrogen rotation found for the monohydride dichloro analogue. If the equilibrium orientation of this intermediate has the H–H axes aligned with P–Ir–P, a rotation through 90° is required of each dihydrogen ligand which corresponds to the location of the secondary set of potential minima. Rotation and exchange thereby become strongly coupled and their respective barriers of similar magnitude. This is an unprecendented situation in the solid state, and further experiments using the quasielastic neutron scattering technique are planned to elucidate details of the exchange reaction.

Acknowledgment. The authors would like to thank L. A. Diebolt and G. Coddens for assistance with the data collection and M. Mediati for assistance with preliminary studies. We would also like to express our gratitude to the Institut Laue-Langevin and the Laboratoire Leon Brillouin for the use of their facilities. This work has also benefitted from the use of facilities at the Manuel Lujan Jr. Neutron Scattering Center, a national user facility funded as such by the U.S. Department of Energy, Office of Basic Energy Sciences.

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