J. Am. Chem. Soc. 1993, 115, 7533–7534 7533

Mechanism of Hydride Scrambling in a Transition-Metal Dihydrogen Dihydride As Studied by Solid-State Proton NMR

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Received September 22, 1992

Since the discovery of Kubas[1] of the first stable dihydrogen complex, there has been a flurry of activity by synthetic,[2] theoretical,[3-7] and physical chemists[8,9] in investigating the wide array of new structures and dynamic phenomena displayed by transition-metal polyhydrides. The fluxional behavior of these molecules is of particular interest and can involve quantum exchange or rotational tunneling.[8,9] Furthermore, theoretical studies have identified novel rearrangement mechanisms[3-5] which do not formally involve oxidative addition of H_2 followed by a reductive elimination in which it reappears. This paper reports on some rather unexpected results of a single crystal ^1H NMR study of $Ir(P^iPr_3)_2(Cl)(\eta^2\text{-}H_2)(H)_2$ (**1**). Surprisingly, it is found that the facile rearrangement which renders all the hydrides equivalent in the solution ^1H NMR[10] of **1** does not scramble them between every position in the solid state.

The initial motivation for studying compound **1** by solid-state ^1H NMR was to see if the presence of an H_2 ligand could be confirmed. Solution NMR of partially deuterated isotopomers had failed to provide a measureable J_{HD}, and neutron diffraction[11] was unable to locate a distinct H_2 ligand. Previous work in this laboratory[8] has demonstrated that solid-state ^1H NMR of powder samples is an especially effective method for detecting an H_2 ligand and for determining the H–H bond length. A solid-state ^1H NMR study[12] did indeed confirm the presence of the H_2 ligand in **1** ($r_{HH} < 1.1$ Å).

In the course of this study, it was noted that the powder pattern line shape displayed a very unusual temperature dependence due to thermally activated molecular motion. Motional models such as a hindered rotation of the dihydrogen ligand in a plane[8] were unsuccessful at accounting for our observations. This motion is apparently quite facile in the solid since it does not appear to be slowed on the NMR time scale even at 77 K. It was reasoned that this facile motion was very probably related to the fluxional process observed by solution NMR.[10] A clearer picture of the nature of this motion was made possible by the availability of large single crystals of **1** synthesized with perdeuterated phosphines.[10] The solid-state NMR spectrum of a single crystal sample is greatly simplified since one has only a single orientation of the magnetic field with respect to the crystal axes. A typical spectrum of one of these crystals sealed under an atmosphere of $H_2(g)$ is shown at the top of Figure 1. This example was acquired at 7.05 T using a dipolar echo sequence.[13] The intense central resonance is due to uncoordinated H_2 and residual ligand protons. A portion of this line and the next upfield line arise from the residual dihydride precursor[10] to **1** which has not coordinated H_2. This assignment is supported by the observation that the spin lattice relaxation times T_1 are quite different for these signals than for the four outermost lines attributed to **1**.

A single crystal neutron diffraction study[11] shows that all the molecules in the unit cell are chemically and magnetically equivalent, in the sense that they should give the same NMR spectrum. One hydride is located trans to the Cl, and a proton density of ~1.5 is found in each of the two cis positions. This indicates the presence of either a static or a dynamic disorder of the H_2 ligand between these two sites. Normally a static disorder of a ligand has the effect of doubling the lines in a single crystal NMR spectrum. In this crystal, doubling is not expected, as the H–H bond should have basically the same orientation with respect to the magnetic field in either site. However, the spectra clearly show that **1** is not static. If **1** were static, then the spectrum would consist of two equal-intensity hydride resonances (with small dipolar splittings) flanked by a single wide dipolar coupled doublet for the η^2-H_2 ligand.[8] This is not observed; regardless of the crystal orientation or temperature, there are no resonances that can be assigned to the terminal hydrides in **1**. Therefore, the spectra are inconsistent with **1** having a static structure on the NMR time scale, regardless of any complications due to the disorder. The spectrum observed is instead a pair of strongly coupled dipolar doublets, as shown by the connectivity in the COSY[14] spectrum at the bottom of Figure 1.

We will report later on a detailed study of how the dynamically averaged dipolar splittings change with both temperature and the orientation of the crystal with respect to the magnetic field.[12] The principal conclusion of the rotation study is that the two dipolar tensors are the same except for their orientation in the molecular frame. Similar results have been obtained for several crystals, demonstrating that none of these data can be interpreted as a consequence of crystal twinning.

The only motional model identified to date that is consistent with all these data is a rapid equilibrium between the isomeric forms **A** and **F** of **1**. Scheme I depicts several possible mechanisms[3-5] for this interconversion. In intermediate **B**, the η^2-H_2 ligand appears trans to the Cl. The heptacoordinate transition state **C** has two hydrides in a plane containing the Ir, the Cl, and the phosphines and two hydrides out of this plane. The bis-η^2-H_2 complex **D** and the pentagonal bipyramid structure **E** with axial phosphines are also possible intermediates. Although chemically different, the pathways involving **D** and **E** are actually quite similar topologically. In **D** the new H–H bond is made before the old one is broken, while in **E** the old bond is broken first. Rapid rotation of the H_2 ligand in **B** or the symmetry of **C** would require the hydrides to scramble between all four positions if either were involved. In the mechanisms invoking **D** and **E**, the hydrides instead occur in distinct pairs which do not cross the Cl–Ir–phosphine plane. These latter two pathways do not allow the hydrides to scramble between all four sites on the NMR time scale. This is, in fact, the case for **1** as demonstrated by the absence of cross peaks interconnecting the two doublets in the COSY spectrum. Therefore, the rearrangement of $\mathbf{A} \rightleftharpoons \mathbf{F}$ must

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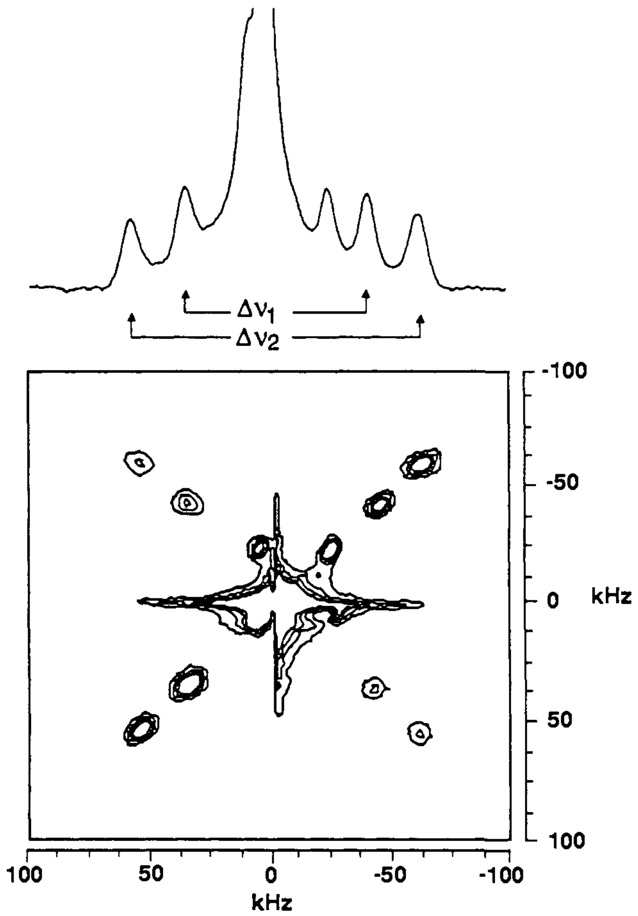


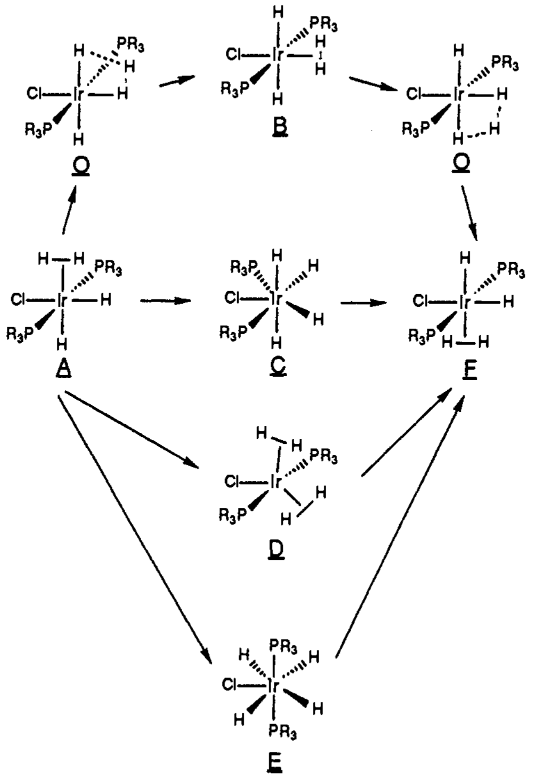
Figure 1. (Top) Single crystal ^1H spectrum of **1** as described in the text. The two dipolar coupled doublets for **1** are indicated. (Bottom) Contour plot of COSY spectrum for **1**. The connectivity of the pairs of lines comprising the dipolar doublets is evident.

involve a process similar to the two paths depicted at the bottom of Scheme I.

The dipolar couplings observed in the single crystal spectra are the result of the dynamic averaging[8] of the large coupling in the H_2 ligand in **A**, for example, with that of the much smaller coupling in the associated pair of terminal hydrides in **F**. This averaging results in the dipolar tensors for the two distinct pairs of protons having different orientations in the molecular frame but the same principal values. Thus, although all molecules in the unit cell are equivalent, the two halves within a single molecule are rendered magnetically inequivalent in the solid state, and the spectrum generally consists of two doublets at any one orientation of the crystal.

In a recent computational study[4] of a model $Fe(PR_3)_4(H_2)H$ system, Maseras *et al.* found that hydride rearrangement via an open direct transfer mechanism[3] was energetically more favorable than a route consisting of an oxidative addition followed by reductive elimination. An open direct hydride transfer in **1** would presumably pass through **O** and thereby lead to formation of **B**.

Scheme I



The combination of two cis hydrides and a trans Cl apparently so destabilizes **B** that this pathway is not easily accessible to **1**. **B** could, however, be involved in the much slower process which eventually does equilibrate all of the hydrides, as found in isotope studies[10] of **1**. Determining whether **D**, **E**, or a more exotic intermediate[6] provides a good description of the reaction coordinate will have to await additional computational investigations. In this vein, it will be important to explain the rapid rate of this isomerization even at 77 K, implying either tunneling or a barrier substantially under 3 kcal mol^{-1}.

This study provides a classic example of how the anisotropy of the solid state allows one to probe mechanistic details of dynamic molecular processes by NMR which cannot be followed in isotropic solutions. It is expected that further NMR studies of this type will be helpful in addressing many of the mechanistic questions being raised by computational studies[3-5] of fluxional transition-metal polyhydrides. The observation here of a rapid isomerization in a transition-metal polyhydride which does not interchange all of the chemically equivalent hydrides is unprecedented to our knowledge.

Acknowledgment. This work was supported at Yale in part by a grant from the National Science Foundation (CHE-9018455) and at the University of Hawaii by the National Renenewable Energy Laboratory. L.L.W. acknowledges support by a Department of Education graduate fellowship.