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Solvent-Assisted Reversible Proton Transfer within an Intermolecular Dihydrogen Bond and Characterization of an Unstable Dihydrogen Complex

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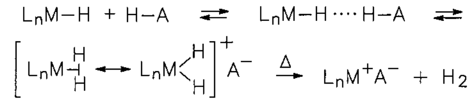
Transition-metal polyhydrides and dihydrogen complexes have received much attention in the past few years as a result of their rich chemistry[1] and physicochemical properties involving in particular interesting intramolecular hydrogen exchange[2] and intermolecular proton-transfer processes.[3] Up to date, little is known about the details of the latter processes. Only recently has it been recognized that transition-metal hydrides can form hydrogen bonds to proton donors.[4] However, the need for the presence of a dihydrogen bond for the proton transfer to occur is still an open question. Few examples of proton transfer within this "dihydrogen bond" have been observed or proposed, the result of which is the protonation of the hydride ligand to give a dihydrogen species which is generally unstable as it may easily release H_2 as shown in Scheme 1.

Scheme 1



During a study of the role of dihydrogen bonds on the chemistry of polyhydride and hydrido dihydrogen complexes[3k,4r,5] some of us observed the particularly interesting case of the ruthenium trihydride complex $Cp^*RuH_3(PCy_3)$ (**1**), $Cp^* \equiv C_5(CH_3)_5$ which exhibits exchange couplings and a classical exchange between the hydride nuclei at low temperatures.[2b,e] In toluene solution **1** formed dihydrogen bonds with weak proton donors leading to a considerable increase of the exchange couplings.[5] By contrast, the interaction of **1** with stronger proton donors such as $HBF_4\cdot Et_2O$ immediately led to extensive dihydrogen evolution and even dehydrogenation of one cyclohexyl ring stabilized by agostic C−H- - -Ru interactions.[6]

In this study we obtained further insights by NMR of the mechanism of proton transfer to transition metal hydrides within dihydrogen-bonded complexes by using the Freon mixture $CDCl_2F/CDF_3$ (2:1) as solvent. This solvent has proven to be useful for NMR studies down to 100 K where the slow hydrogen bond regime can often be reached.[7] Here, we took advantage of another property of this solvent, i.e., that its dielectric constant increases strongly when the temperature is reduced,[8] thus assisting the protonation of **1**.

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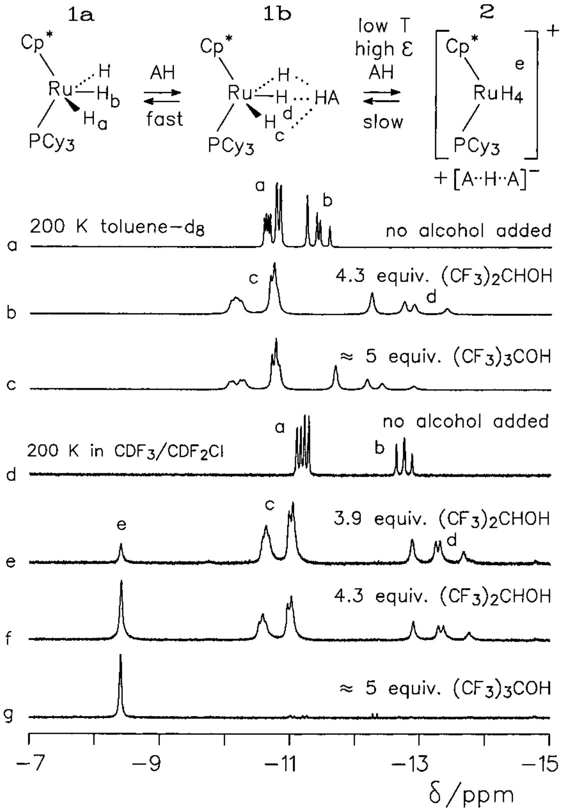

Figure 1. Hydride regions of the 500 MHz ^1H NMR spectra (200 K) of 0.05 M solutions of $Cp^*RuH_3(PCy_3)$ (**1**) in toluene-d_8 (a−c) and $CDClF_2/CDF_3$ (2:1) (d−g) in the presence of varying equivalents of $(CF_3)_2CHOH$ and $(CF_3)_3COH$.

The results of the ^1H NMR measurements are shown in Figure 1. In the absence of an added alcohol the hydride nuclei of **1** give rise to an AB_2X spin system signal pattern due to coupling to ^{31}P. The H−H coupling constant J_{ab} resulting from quantum exchange is of the order of 80 Hz and similar whether measured in toluene-d_8 or in CDF_3/CDF_2Cl. The chemical shifts are also similar in both solvents. When 3.9 equiv of $(CF_3)_2CHOH$ is added as proton donor to a solution of **1** in toluene-d_8, the H−H coupling J_{ab} is strongly increased to about 220 Hz (Figure 1b) as previously reported.[5] Only one signal set is observed which represents an average over the fast exchanging monomer **1a** and the hydrogen bonded complex **1b**. By contrast, when we use the mixture $CDClF_2/CDF_3$ (2:1) as solvent we also obtain an AB_2X signal pattern with an increased exchange coupling J_{ab} but, in addition, we also observe a low-field singlet at −8.4 ppm (Figure 1e) which we assign to the cation $[Cp^*RuH_4(PCy_3)]^+$ (**2**). **2** gives also rise to a CH_3 signal at δ 2.03 ppm in addition to the corresponding signal of **1** at δ 1.97 ppm. Quantitative $^{31}P\{^1H\}$NMR experiments at different temperatures and concentrations gave singlets at 79.8 ppm for **1** and at 65.9 ppm for **2**, where the signal intensity ratios $I(\mathbf{1})/I(\mathbf{2})$ were the same as found for the corresponding methyl group signals. The finding of values of $^3/_4I(\mathbf{1})/I(\mathbf{2})$ for the hydride peaks of **1** and **2** provides strong evidence that **2** is a tetrahydride formed by protonation of **1**.

If we increase the concentration of the alcohol to about 4.3 equiv, J_{ab} increases only slightly indicating that **1** is present almost fully as hydrogen bonded complex **1b** (Figure 1f). By contrast, the concentration of **2** increases indicating a classical slow equilibrium between **1b** and **2**. This is consistent with the assumption that a single alcohol molecule is sufficient for the formation of **1b**, but that the addition of at least a second alcohol molecule is needed for the proton transfer to occur by solvating the anion formed, as illustrated in Figure 1.

If a more acidic alcohol such as $(CF_3)_3COH$ is used the hydrogen bonded species disappears and only **2** is visible (Figure 1g). Additional experiments show that the equilibrium between **1** and **2** is reversible. Longitudinal relaxation time measurements at 500 MHz revealed a minimum value of $T_{1\min} = 18$ ms at 170 K for **2**. This value is in agreement with a dihydrido−dihydrogen structure $[Cp^*RuH_2(H_2)(PCy_3)]^+$ where dihydrogen and dihydride nuclei exchange rapidly, although a bis-dihydrogen structure cannot be excluded.[10]

The observation that the hydride chemical shift of **2** is independent of the type of alcohol is an indication that this species is no longer involved in hydrogen bonding to the anion formed. The fact that **1** is protonated in Freons but not in toluene arises from the dielectric properties of the solvent[8] which favors the ionic form only at low temperature where the solvent is ordered around the ions formed. Because of the associated entropy decrease, this protonation is not possible at high temperatures. By contrast, the dielectric constant (2.5) of toluene remains constant between room temperature and 190 K.[11] Therefore, the Freon mixture is used here for protonation under mild conditions: the reactants can be mixed at room temperature but the proton transfer only occurs when the temperature is sufficiently lowered i.e., the dielectric constant has sufficiently increased. Similar observations were made by using CD_2Cl_2 as solvent which also exhibits an increase of the dielectric constant from 9 at room temperature to about 17 at 170 K.[12]

In conclusion, we have obtained evidence that the protonation of **1** occurs in its hydrogen bonded form to give the novel cationic complex **2**. This transformation is slow within the NMR time scale. As **2** decomposes at room-temperature its synthesis was attempted so far without success.[6] The method described here of low-temperature protonation using a solvent whose polarity increases at low temperatures could therefore be used to characterize reactive intermediates of proton-transfer reactions and to prepare otherwise unaccessible species.

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(8) The dielectric constant of CHF_3/CHF_2Cl (1:1) increases from about 20 at 170 K to 45 at 95 K. A. P. Burtsev, G. S. Denisov, H. H. Limbach, unpublished results.

(9) $Cp^*RuH_3(PCy_3)$ was prepared according to ref 2b. The samples were prepared using standard Schlenk and vacuum techniques[2d,7] employing NMR tubes with an attached Teflon needle valve (Wilmad). The final composition of the samples was checked by integration of the 500 MHz spectra at 200 K.

(10) Shorter relaxation time would have been anticipated for a bis dihydrogen structure (see ref 1b). Couplings of hydrides with ^{31}P were not resolved. An increase of the line width of the hydride signal e from 25 Hz for **2**-h_4 to 29 Hz for **2**-hd_3 was observed indicating nonresolved HD couplings which is compatible with both structures.

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