Proton Transfer to $CpRuH(CO)(PCy_3)$ Studied by Low-Temperature IR and NMR Spectroscopy

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Keywords: Hydrido complexes / Hydrogen bonds / Proton transfer / Kinetics / IR spectroscopy / NMR spectroscopy

The interaction of the ruthenium hydride complex RuH ≡ $CpRuH(CO)(PCy_3)$ (**1**) with various proton donors AH ≡ CF_3CH_2OH (**2a**), $(CF_3)_2CHOH$ (**2b**), $(CF_3)_3COH$ (**2c**), CF_3COOH (**2d**), and HBF_4 (**2e**) has been studied by variable-temperature IR spectroscopy using hexane and CH_2Cl_2 as solvents of different polarity. A low-temperature NMR study of the interaction of **1** with **2c** was performed using [D$_8$]methylcyclohexane, CD_2Cl_2, and a liquefied mixture of CDF_2Cl/CDF_3 (2:1). The first stage of the proton transfer process was found to be the formation of hydrogen-bonded complexes of the type RuH···HA. The hydrogen bonds in these complexes are of medium strength ($-\Delta H° = 5.3–7.6$ kcal mol^{-1}). The second stage is the slow conversion of the H-complex to a dihydrogen complex to which a hydrogen-bonded ion-pair structure $[Ru(\eta^2\text{-}H_2)]^+\cdots A^-$ was assigned. The kinetics of this unusually slow proton transfer reaction was monitored in the case of **2c** at 200 K in CH_2Cl_2. Fast protonation of **1** by **2d** leads additionally to a species assigned as the free cationic complex $[Ru(\eta^2\text{-}H_2)]^+$, whose formation is driven by the formation of the homoconjugated anionic complex $[AHA]^-$. At temperatures above 220 K both the hydrogen-bonded ion pair and the free cationic complex easily release dihydrogen, producing RuA.

Introduction

The protonation of transition metal hydrides by proton donors constitutes an important pathway for the synthesis of cationic non-classical dihydrogen complexes.[1] The elementary steps of this reaction are, however, still unclear up to date. Usually, proton transfer between a neutral proton donor AH and a neutral base is preceded by the formation of a hydrogen-bonded complex of the type A−H···B, which is converted rapidly into the hydrogen-bonded ion pair $A^-\cdots H-B^+$, leading finally to the free ions as reaction products. It has therefore been an exciting discovery that proton donors can form "unconventional" intramolecular[2−7] and intermolecular[8−16] hydrogen bonds to the hydride moieties of transition metal complexes MH, taking the role as proton acceptors. For example, intermolecular hydrogen-bonded complexes were observed in the case of rhenium hydrides in the solid state,[8,9] as well as of tungsten and rhenium hydrides in solution.[11−14] The idea that these complexes constitute important intermediates of transition metal hydride protonation was subsequently proposed in a number of papers,[9,11] although evidence for this idea has been obtained only very recently.[17−21] For example, the application of IR and NMR methods in a wide range of temperatures allowed some of us to establish the existence of an unusually slow equilibrium between M−H···H−A and $M-H_2^+\ A^-$ in the case of $RuH_2(dppm)_2$,[17] and $\{MeC(CH_2PPh_2)_3\}$-$Re(CO)_2H$[19]. NMR alone was used similarly in the case of $Cp^*Ru(PCy_3)H_3$.[21] In the latter study where NMR experiments were performed using both toluene and a liquefied freon mixture CDF_2Cl/CDF_3 (2:1) as solvents − where the latter allows measurements down to 100 K − it was realized that protonation takes place if the solvent polarity is large enough. Interestingly, both the above freon mixture as well as CH_2Cl_2 exhibit similar dielectric constants that increase dramatically by lowering the temperature. As a consequence, protonation is a solvent-assisted process occurring at low temperatures. On the other hand, in the case of nonpolar solvents such as hexane or toluene, only the hydrogen-bonded complex M−H···H−A is formed without subsequent protonation.[21]

In order to study the mechanism of a reaction one usually monitors its kinetics. For the systems mentioned above such experiments have not yet been reported. We are aware only of recent papers of Basallote et al.[22−24] that followed the protonation kinetics of two iron and one ruthenium hydrides with strong acids using electrochemical methods. However, this method does not provide information about the structure of reaction intermediates.

In order to identify the various reaction steps and hence the reaction mechanism we decided to study the interaction of a simple transition metal monohydride with proton donors of different strengths, using a combination of IR and NMR spectroscopy. For this purpose we chose the ruthenium hydride $CpRuH(CO)(PCy_3)$ (≡ RuH, **1**), which was first synthesized by Heinekey et al.[25] and is known to

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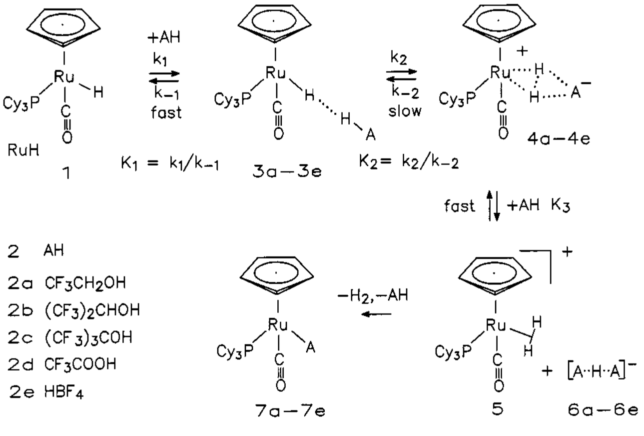
form a stable cationic dihydrogen complex[25,26] under the action of HBF_4. On the other hand this hydride contains a CO group whose stretching band constitutes an excellent IR marker sensitive to hydrogen bond formation and protonation.[11−15,19,27−29]

Thus, in this paper we report the results of variable-temperature IR and NMR studies of interactions of the hydride **1** with CF_3CH_2OH (**2a**), $(CF_3)_2CHOH$ (**2b**), $(CF_3)_3COH$ (**2c**), CF_3COOH (**2d**), and HBF_4 (**2e**) in the nonpolar medium hexane and in the polar media CH_2Cl_2, and CDF_2Cl/CDF_3 (2:1). The results of these experiments will be discussed in terms of the general reaction model depicted in Scheme 1. In addition to free **1**, the hydrogen-bonded complex **3**, and the cationic dihydrogen complex **5**, we have found for the first time, evidence for a further intermediate **4**, a hydrogen-bonded ion pair. We will show that the interconversion between **3** and **4** constitutes the rate-limiting step of the proton transfer. The dissociation of **4** into the free dihydrogen complex **5** is assisted in the case of **2d** by the formation of homoconjugated ions $[AHA]^-$ (**6**). Finally, **5** easily looses a dihydrogen molecule forming the reaction product **7**.



Scheme 1

Results

IR Studies of the Dihydrogen Bonding and Protonation of 1 with Proton Donors

The OH Stretching Region − Dihydrogen Bond of 1 with Weak Proton Donors in Hexane and Dichloromethane

The stretching vibrations ν_{OH} of proton donors at 3600−3000 cm^{-1} are well known to be sensitive to hydrogen bonding. Figure 1 (a) shows the OH stretching region of CF_3CH_2OH (**2a**) at low concentrations in an excess of **1**. We observe a sharp monomer band at 3630 cm^{-1} and a broad bonded band, which is shifted considerably to lower frequencies. Because of the low proton donor concentration and excess of **1**, there are no apparent contributions from complexes $(AH)_n$ or $RuH\cdots(H-A)_n$ involving more than one proton donor molecule. Therefore, the broad band can be assigned to the complex **3a**, and the observed frequency shifts listed in Table 1 are identified as $\Delta\nu_{OH} = \nu_{OH}(AH) - \nu_{OH}(RuH\cdots HA)$, where the position of the broad band corresponds to its center of gravity ($s = \pm 3$ cm^{-1}).

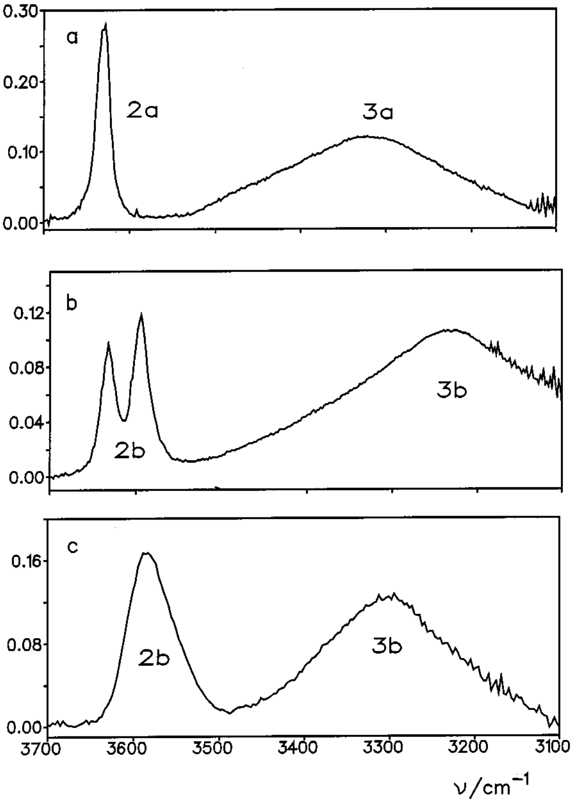


Figure 1. Room-temperature ν_{OH} stretching bands of proton donors (0.02 mol/L) in the presence of a 2.5-fold excess of $CpRu(CO)(PCy_3)H$ (**1**); (a) CF_3CH_2OH (**2a**), hexane; (b) $(CF_3)_2CHOH$ (**2b**), hexane; (c) $(CF_3)_2CHOH$ (**2b**), CH_2Cl_2

When the proton-donating power is increased, $\Delta\nu_{OH}$ increases as illustrated in Figure 1 (b) for the case of complex **2b**. Here, monomeric $(CF_3)_2CHOH$ (**2b**) exhibits two different bands that are due to conformational heterogeneity (two conformers exist) and intermolecular interactions.[30,31] A strong solvent effect is observed in the sense that the hydrogen bond shift $\Delta\nu_{OH}$ is smaller when CH_2Cl_2 is used as solvent (Figure 1, c). In the case of **2c** $\nu_{OH}(RuH\cdots HA)$ was shifted so much that it strongly overlapped with the CH stretching band of the solvent, so that $\Delta\nu_{OH}$ could not be determined properly.

As is known, this region clearly shows the hydrogen bond formation, and is useful for ΔH determination.[11,13,15] It does not, however, give any information on the site of coordination. Therefore, a study of all vibrations should be performed in order to decide whether the hydride atom of **1** is the only hydrogen bond site as assumed in Scheme 1, or whether the oxygen atoms of the CO groups or even the metal center itself acts as proton acceptor site. Unfortunately, the RuH stretching vibration of **1** did not give rise to an observable band, in contrast to the tungsten and rhenium hydrides studied previously.[11,13] Therefore, most of

Table 1. IR data in the ν_{OH} range, formation enthalpies ΔH_l of the formation of the hydrogen-bonded complex RuH···HA and basicity factors E_j of the hydride hydrogen atom

AH	Solvent	ν_{OH}(**3**) [cm^{-1}]	$\Delta\nu_{OH}$ [cm^{-1}]	$\Delta\nu_{1/2}$ [cm^{-1}]	ΔH_l [kcal·mol^{-1}]	E_j
2a	hexane	3327	300	220	−5.3[a]	1.04[b]
2b	hexane	3225	385	350	−6.3[a]	1.03[b]
2b	CH_2Cl_2	3302	285	194	−5.1[a]	1.03[b]
2c	hexane	–	–	–	−7.6[c]	1.0[b]

[a] Obtained using Equation (2). – [b] Obtained using Equation (3). – [c] Obtained from the van't Hoff plot of Figure 4.

the information came from a detailed study of the stretching vibrations of the carbonyl ligand (ν_{CO}) of **1**.

The CO Stretching Region – Dihydrogen Bond Formation and Protonation of 1 by Weak Proton Donors in Hexane and Dichloromethane

The changes in the CO stretching region of **1** observed in the presence of proton donors allowed us to show the formation of the dihydrogen-bonded complexes, and to monitor their following transformations. In Figure 2 (a) we have depicted ν_{CO}(**1**) of pure hydride obtained at 200 K using hexane as solvent. This strong band appears at 1905 cm^{-1} and is quite narrow exhibiting a line width of only 7 cm^{-1}. When a proton donor is added, a new band is observed at slightly larger wave numbers, e.g. at 1920 cm^{-1} in the case of **2c** (Figure 2, a). The new band is shifted by $\Delta\nu_{CO}$ = +12 cm^{-1} in the case of **2b** and +15 cm^{-1} in the case of **2c**. These high-frequency shifts show that the oxygen atom of the CO group does not participate in hydrogen bonding.[11–13] Hence, we assign the new band to the ν_{CO} stretching vibrations of the 1:1 complexes RuH···HA (**3**). As the stretching vibration ν_{RuH} could not be observed, the assignment of the structures **3** containing a dihydrogen bond between the proton donor and the hydride site, and not with the metal atom is then tentative. However, further information supporting this assignment comes from the NMR spectroscopy study, as shown below.

The ν_{CO} band of pure **1**, dissolved in CH_2Cl_2, appears at 1890 cm^{-1} as depicted in Figure 2 (b), again using a sample temperature of 200 K. The band is broader than in hexane and exhibits a half width of 22 cm^{-1}, so in the presence of a proton donor we observe only the summary band of **1** and **3c** with a high-frequency shift of +6 cm^{-1} as depicted in Figure 2 (b) for the case of **2c**. These small changes are not unusual; e.g. we observed similar effects for the dihydrogen bonds with {MeC(CH_2PPh_2)$_3$}Re(CO)$_2$H.[19]

We observed an interesting phenomenon, concerning the spectral changes in time. The intensity of ν_{CO}(**1**+**3c**) band decreases after several minutes, and the new high-frequency band at 1960 cm^{-1} appears and grows in intensity (Figure 2, c). After about 30 min, equilibrium is reached, where both bands are present. We assign this new band to an ion pair of the type **4c**. Arguments for this structure arise from the study of the interaction of **1** with stronger proton donors described below. We do not assign this band to the reaction product **7c**, because upon heating to 250 K the band at 1960 cm^{-1} decreases while a new ν_{CO} band at 1944 cm^{-1} appears. This new band we assign to **7c**.

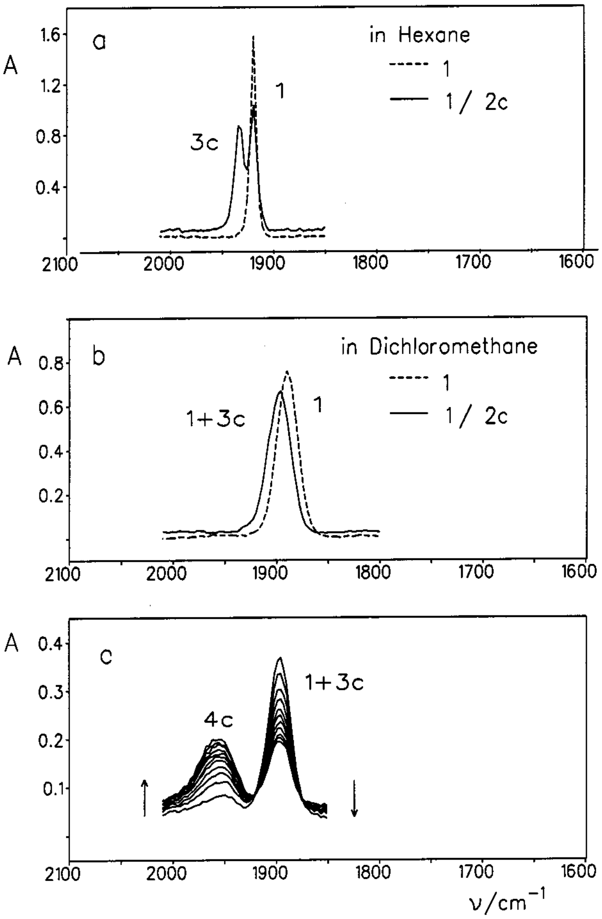


Figure 2. IR spectra in the ν_{CO} range of CpRu(CO)(PCy_3)H (**1**) (0.005 mol/L) at 200 K in hexane (a) and CH_2Cl_2 (b, c) without proton donor (- - - -) and in the presence of 4 equiv. of $(CF_3)_3COH$ (**2c**) (——); (c) time-dependent changes of the sample **1/2c** over a period of 30 min

The CO Stretching Region – Dihydrogen Bond Formation and Protonation of 1 with Strong Proton Donors in Dichloromethane

In principle, the interaction of metal hydrides with strong proton donors will lead to their protonation, constituting a routine procedure for the generation of cationic dihydrogen complexes. However, the choice of acid is crucial for their stability. There are numerous examples where the labile dihydrogen ligand can be easily displaced by anionic ligands.[13,19,32,33] In the present case, the interaction of hydride **1** with proton donors such as fluorinated alcohols and carboxylic acids also leads to unstable (η^2-H_2) complexes due to the high coordinating ability of the corresponding anions (R^FO^- and CF_3COO^-). The elimination of an H_2 molecule and the addition of an anion upon warming results in the formation of organyloxy derivatives **7**. We succeeded in minimizing and even preventing this unwanted process by carrying out the mixing of the reagents and IR measurements at 200 K.

In order to elucidate the protonation of **1** in more detail, we performed various IR studies of **1** with stronger acids, i.e. CF_3COOH (**2d**) and HBF_4 (**2e**). As mentioned in the introduction, the interaction of hydride **1** with HBF_4 results in the formation of the stable dihydrogen complex $[CpRu(CO)(PCy_3)(\eta^2\text{-}H_2)]^+$ (**5**) with BF_4^- as counter ion, exhibiting a ν_{CO} band at 2020 cm^{-1} in the solid state.[26] Here, upon mixing of the hydride **1** with HBF_4 in CH_2Cl_2 at 200 K we observe a similar value. The position of this band does not change with increasing temperature. These results indicate that the ν_{CO} band at 2020 cm^{-1} indeed belongs to the free protonated complex **5** in CH_2Cl_2, formed upon interaction of **1** with HBF_4.

If **5** is not directly involved in an interaction with the counterion it should be possible to generate **5** also with other acids. For this purpose we chose CF_3COOH (**2d**) and carried out experiments at 200 K using again CH_2Cl_2 as solvent. In addition to ν_{CO} of the CO ligand absorbing in the 2100−1850 cm^{-1} range this system exhibits additional CO stretching vibrations ν_{CO} of the acid and the antisymmetric stretching band $\nu_{OCO}{}^{as}$ of trifluroacetate between 1800 and 1600 cm^{-1}.

The ν_{CO} bands of the separate monomeric **1** and the dimeric CF_3COOH molecules (**2d**) in CH_2Cl_2 are represented by the graphs a and b in Figure 3. The band ν_{CO}(**2d**) appears at 1790 cm^{-1}. However, when both reactants are mixed at low concentrations of **1** (10^{-3} mol/L) in the presence of an excess of **2d**, we obtain spectrum c in Figure 3. Again, at 2020 cm^{-1} we observe a new band that coincides with the ν_{CO} band of **5** with BF_4^- as counter anion. Therefore, we can now safely assign this new band to the free protonated ion **5**. Moreover, another new band arises at 1648 cm^{-1}, which we attribute to $\nu_{OCO}{}^{as}$ of the homoconjugated trifluoroacetate.[34−38] The excess of the acid is demonstrated by the band at 1790 cm^{-1}. We note that there is no band arising from the dihydrogen-bonded complex **3d**.

Interesting spectral changes are observed when the ratio of the hydride to the acid is increased, as indicated by the spectral traces d, e, and f in Figure 3. First, we note again ν_{CO} of **5** at 2020 cm^{-1} whose intensity is gradually reduced, then the typical strong band of ν_{CO}(**1**+**3d**) at 1910 cm^{-1} and for hydrogen-bonded acid in **3d** at 1760 cm^{-1}. These species were already identified before. However, in addition, a new band is observed at 1996 cm^{-1}, which is located closer to the band of **5** than of **3d**. We assign this new band to the ionic hydrogen-bonded complex **4d**. The corresponding $\nu_{OCO}{}^{as}$ vibration of the hydrogen-bonded acetate in this complex is assigned to the new sharp band at 1710 cm^{-1}, which is located between the band of dimeric **2d** and of the homoconjugated anion **6d**. This assignment is in agreement with previous studies of molecular and ionic hydrogen-bonded complexes of trifluoroacetic acid with organic and metal-containing bases.[34−38] Finally, before we discuss the spectral changes between spectra d, f, and g in Figure 3 we have to discuss the origin of the remaining two bands that are assigned to the CO ligand and trifluoroacetate group of **7d**. This assignment was confirmed by the experiment depicted by spectra g and h, where spectrum g is identical with spectrum f. Spectrum h was obtained after heating the sample to 260 K. The bands of **7d** are now increased in intensity after elimination of H_2. The spectral changes are irreversible, i.e. lowering of the temperature does not lead to spectrum g.

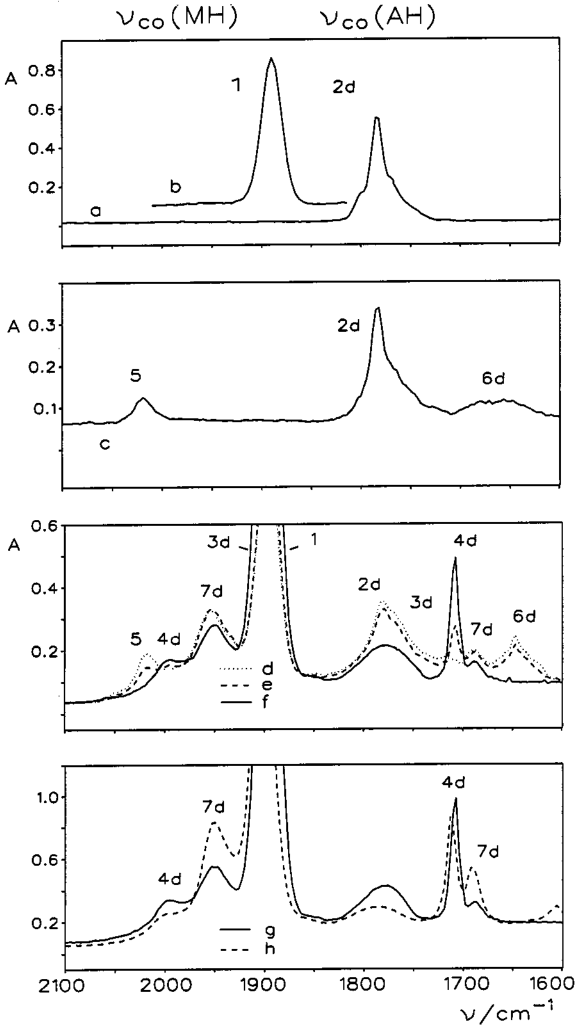


Figure 3. IR spectra of $CpRu(CO)(PCy_3)H$ (**1**) [0.001 mol/L (c), 0.01 mol/L (d−f), 0.03 mol/L (g, h)] in the presence of excess CF_3COOH (**2d**) and a deficiency in CH_2Cl_2; ratio **1/2d** = 1:5 (c), 1:1.5 (d), 1:1 (e), 3:2 (f), 3:1 (g, h); reference spectra of **1** (0.01 mol/L) and of **2d** (0.01 mol/L) are given in b and a, respectively; temperature 200 K (a−g), 260 K (h)

We now consider the series of spectra d, e, and f, where the hydride/acid ratio was increased as indicated by the decrease of the band for dimer **2d**, and the relative increase of the acid band of **3d** at 1760 cm^{-1}. We observe in this series that both the bands of **5** and **6d** are reduced in intensity, and these bands have disappeared in spectrum f. On the other hand, **4d** increases in this series. The structure of this species, indicated in Scheme 1, with two hydrogen bonds to the dihydrogen group is speculative.

Finally, the finding of **4d** as a hydrogen bond stabilized ion-pair intermediate between the dihydrogen-bonded complex **3d** and the free protonated ion **5** allows us to confirm the above assignment of the 1960 cm^{-1} band in Figure 2 (c) to the ion pair **4c**. The lower ν_{CO} band position of **4c** as compared to **4d** is probably associated with a higher basicity of the $(CF_3)_3CO^-$ anion as compared to CF_3COO^-. The assignment of this band to ν_{CO} of the product (**7c**) is excluded since this would result in an irreversible appearance of this band, which is in contrast to the experimental findings.

Thermodynamics of Dihydrogen Bonding of 1 with Proton Donors in Hexane and Dichloromethane

The thermodynamics of dihydrogen bond formation of **1** with **2c** as proton donor in hexane was elucidated by analyzing the relative band intensities of **1** and of **3c** in spectra of the type shown in Figure 2 (a), between 250 K and 290 K. Because the ν_{CO} bands of **1** and **3c** in hexane are reasonably well resolved, the equilibrium concentration of free hydride [**1**] can be easily obtained from the spectra. The [**2c**] and [**3c**] concentrations could then be obtained from the total concentrations of **1** and of the proton donor. Thus, we obtained the values of the equilibrium constant defined in Scheme 1 as a function of temperature [Equation (1)].

$$K_1 = [\mathbf{3c}]/([\mathbf{1}][\mathbf{2c}]) = \exp(-\Delta H_1^0/RT + \Delta S_1^0/R) \quad (1)$$

The corresponding van't Hoff plot is depicted in Figure 4, from which we obtain the values of the enthalpy $\Delta H_1^0 = -7.3\pm0.2$ kcal mol^{-1} and $\Delta S_1^0 = -21.6\pm0.6$ cal K^{-1} mol^{-1}. The entropy value decrease is larger here than in the case of rhenium and tungsten hydrides.[11−13]

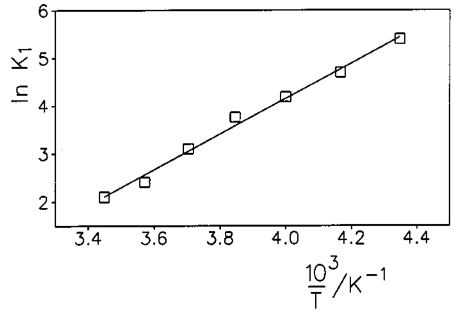


Figure 4. Van't Hoff plot of the hydrogen bonding of CpRu(CO)(PCy$_3$)H (**1**) (0.005 mol/L) in the presence of 4 equiv. of **2c** in hexane

In the case of the other fluorinated alcohols **2a** and **2b** we did not perform extended temperature experiments as we could estimate ΔH_1^0 from the frequency shifts $\Delta\nu_{OH} = \nu_{OH}(\mathbf{2}) - \nu_{OH}(\mathbf{3})$ listed in Table 1 using the correlation proposed for conventional hydrogen bonded complexes[39] according to Equation (2).

$$\Delta H_1^0 = -18\,\Delta\nu_{OH}/(720+\Delta\nu_{OH})\ [\mathrm{kcal\,mol^{-1}}],\ \Delta\nu_{OH}\ \mathrm{in\ cm^{-1}} \quad (2)$$

As has been shown, Equation (2) is perfectly applicable to dihydrogen bonding M−H···H−A.[11,12] The values of ΔH^0 obtained in this way for **2a** and **2b** are included in Table 1. Unfortunately, as mentioned above, we could not determine $\Delta\nu_{OH}$ for **2c**. As expected, the dihydrogen bond is stronger in hexane than in CH_2Cl_2. The basicity factors E_j[15,39] of the hydride atom for hydride **1** were calculated using the "rule of factors" equation [Equation (3)].

$$E_j = \frac{\Delta H_{ij}}{\Delta H_{11} P_i} \quad (3)$$

It is noteworthy that the basicity factor E_j[39,40] values of **1** are constant for all proton donors (Table 1) showing good agreement of enthalpy values obtained from empirical correlation [Equation (2)] and from K_1 temperature dependence [Equation (1)].

Thermodynamics and Kinetics of Protonation of 1 by $(CF_3)_3COH$ (2c) in CH_2Cl_2

In this section we quantitatively analyze the experiment that was illustrated in Figure 2 (c), where protonation of the dihydrogen-bonded complex **3c** slowly leads to an equilibrium with the ion pair **4c**. We studied the kinetics of process at 200 K following in time the ν_{CO}(**4c**) and ν_{CO}(**1**+**3c**) intensity changes at different **1**/**2c** ratios (Table 2). The representative kinetic curve (absorbance A vs. time) for **4c** and its first-order logarithmic plot [$\ln(A_\infty - A_t)$ vs. time] are presented in Figure 5.

Table 2. Rate constants k_{obs} for the reaction of hydride **1** with **2c** and conversion ratios α [Equation (5)]

1/2c ratio	α [%]	k_{obs} [s^{-1}] (**3**)	k_{obs} [s^{-1}] (**1**+**2**)
1:4	37.5	$1.4\cdot10^{-3}$	$1.6\cdot10^{-3}$
1:6	47.5	$1.7\cdot10^{-3}$	$1.5\cdot10^{-3}$
1:8	55.0	$1.5\cdot10^{-3}$	$1.6\cdot10^{-3}$
1:10	62.5	$1.6\cdot10^{-3}$	$1.4\cdot10^{-3}$

The rate constants k_{obs} obtained from intensity changes of the ν_{CO}(**4c**) band are practically the same as those obtained from ν_{CO}(**1**+**3c**) intensity changes. The k_{obs} values do not depend on the alcohol concentration in the concentration range studied, and the average k_{obs} value is $(1.6\pm0.2)\times10^{-3}$ s^{-1} (Table 2). The process in Scheme 1 is a typical reaction with so-called rapid pre-equilibria:

the diffusion-controlled first stage $\mathbf{1} + \mathbf{2c} \xrightleftharpoons{K_1} \mathbf{3c}$

and the rate-limiting step $\mathbf{3c} \xrightleftharpoons[k_{-2}]{k_2} \mathbf{4c}$

The observed rate constant of dihydrogen complex **4c** formation (k_{obs}) can be described by Equation (4).

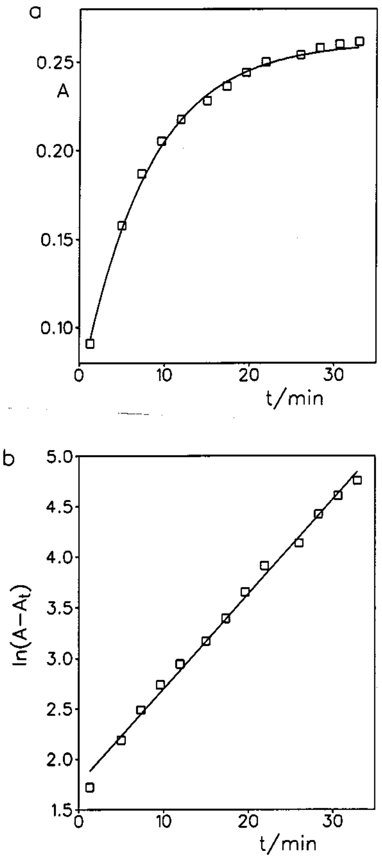


Figure 5. Kinetic curve (a) and its first-order logarithmic plot (b) for the reaction of CpRu(CO)(PCy$_3$)H (**1**) (0.004 mol/L) with 8 equiv. of (CF$_3$)$_3$COH (**2c**) in CH$_2$Cl$_2$ at 200 K

$$k_{obs} = k_2\left(\frac{K_1[HA]}{1+K_1[HA]}\right)+k_{-2} \qquad (4)$$

In the present case the k_{obs} value does not depend on the alcohol concentration, meaning the value in parentheses is approximately 1. In this case, the product of K_1 by [HA] should be >> 1. Lets suggest it is about 10. So, simple calculation using the **2c** concentrations of the order of 10^{-2} mol/L gives $K_1 \approx 10^3$ L/mol, which looks reasonable because the K_1 value in hexane at 200 K is ca. 2300 L/mol.

We were unable to determine the equilibrium constant K_2 (Scheme 1) due to the overlapping of the ν_{CO}(**1**) and ν_{CO}(**3c**) bands, but we could estimate the conversion ratio α [Equation (5)], where C_1 is the total concentration of hydride **1**, based on the ν_{CO}(**1**+**3c**) intensity fall upon the settlement of the equilibrium.

$$\alpha = [\mathbf{4c}]/C_1 \qquad (5)$$

As one can expect, the α value increases as the **2c** concentration increases (Table 2). Although we cannot determine the K_2 equilibrium constant we can estimate its value assuming that at 10-fold alcohol excess and $K_1 \approx 10^3$ L/mol at 200 K, the hydrogen bonding equilibrium should be completely shifted toward **3c**. So, we can determine both **3c** and **4c** concentrations from the corresponding ν_{CO} bands and estimate K_2 = [**4c**]/[**3c**] to be 1.7. The K_2 value estimated seems to be realistic, and the same one has already been observed in other cases.[41] These values correspond to $\Delta G_{200\mathrm{K}} \approx -2.7$ kcal/mol for hydrogen bond formation and only −0.2 kcal/mol for proton transfer, showing that the driving force of the proton transfer reaction in the present case is dihydrogen bond formation.

The Study of the Interaction of Hydride 1 with (CF$_3$)$_3$COH (2c) by NMR Spectroscopy

The measurements in CD$_2$Cl$_2$ and [D$_8$]methylcyclohexane were carried out at 190−270 K. In the presence of hydride **1**, the proton signal of **2c** shifts to low field from δ = 4.5 to δ = 6. A change of the hydride signal position in the ^{1}H NMR spectra (−12.5 ppm) could not be detected, but a substantial shortening of the relaxation time of the hydride signal was observed. In the presence of **2c** T_1 min. of this signal decreases 1.5−2 times from 753 ms to 389 ms in CD$_2$Cl$_2$ and 383 ms in C$_7$D$_8$, at 200 K. Such changes of T_1 min. are typical for MH···HA bond formation.[11,19] The ^{1}H-NMR spectra of **1** in the presence of a 5-fold CF$_3$COOH (**2d**) excess show the signal of the η^2-H$_2$ ligand of **3** at δ = −7.95, with relaxation time T_1 = 11 ms (200 K, 400 MHz). For comparison, an NMR spectrum of [CpRu(η^2-H$_2$)(CO)(PCy$_3$)]BF$_4$ (**5**) in CD$_2$Cl$_2$ was recorded. It shows the signal of the η^2-H$_2$ ligand at δ = −7.95. The T_1 relaxation time of this signal is 9 ms at 210 K (200 MHz) and matches the value found by Heinekey and coworkers.[25,26]

NMR studies in liquid freons have been shown[14,21] as potential tools in obtaining additional information about hydrogen bonds. Therefore, the interaction of hydride **1** with **2c** was studied in a freon mixture (CDClF$_2$/CDF$_3$, 2:1) at different ratios hydride/alcohol.

The OH signal of monomeric alcohol molecules is observed at δ = 4.1. This alcohol is not susceptible to self-association and chemical shift of its proton drifts insignificantly with concentration and temperature changes. In the presence of hydride **1** a strong low-field shift (up to δ = 8.5 at 140 K), characteristic for the hydrogen bond formation, is observed.

The resonance of the hydride ligand in **1** is shifted to high field from δ = −12.5 to −12.7 at 170 K when 12 equiv.

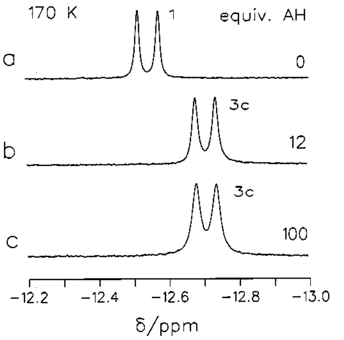


Figure 6. Hydride region of the 500-MHz ^{1}H NMR spectra of CpRu(CO)(PCy$_3$)H (**1**) at 170 K in CDClF$_2$/CDF$_3$ (2:1) (a) without proton donor, (b) in the presence of 12 equiv. of **2c**, (c) in the presence of 100 equiv. of **2c**

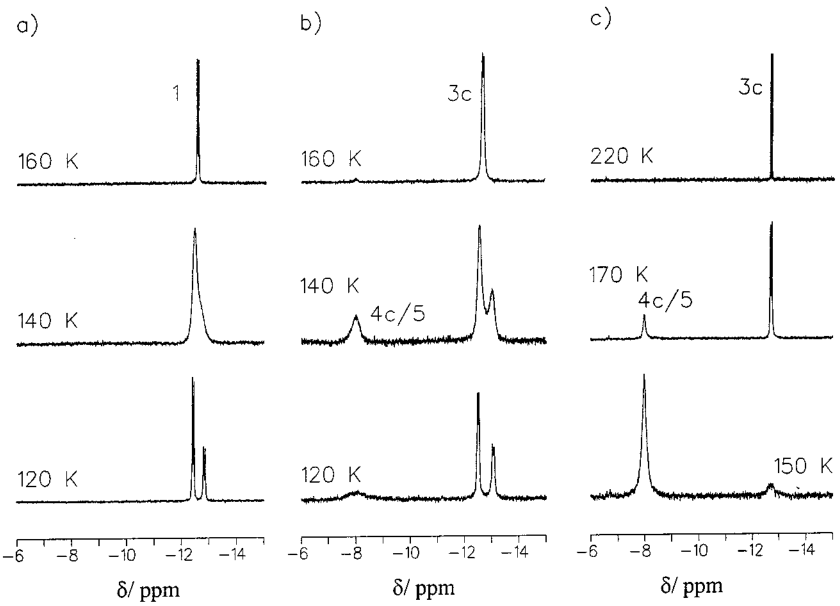


Figure 7. Hydride region of the 500-MHz ^{1}H NMR spectra of CpRu(CO)(PCy$_3$)H (**1**) at different temperatures in CDClF$_2$/CDF$_3$ (2:1) (a) without proton donor, (b) in the presence of 12 equiv. of **2c**, (c) in the presence of 100 equiv. of **2c**

of **2c** is added (Figure 6, a, b). Further increase in alcohol concentration (Figure 6, c) does not change the position of this resonance. A slight high-field shift of the hydride ligand signal ($\Delta\delta = 0.2$ ppm) is normal for RuH···HOR bonding, and has been observed before.[11,14,19,21]

^{1}H NMR spectra of **1** without alcohol at different temperatures show that the position of the hydride signal does not change when the temperature is lowered to 150 K. Below that temperature the signal reversibly splits into two doublets with the intensity ratio 2:1 (Figure 7, a). A similar splitting was observed for Cp*RuH$_3$(PCy$_3$) and is suggested to be due to the frozen motion of cyclohexyl rings.[42]

The η^2-H$_2$ ligand signal at $\delta = -8.0$ appears at 150 K, and increases in intensity down to 140 K in the presence of 12 equiv. of **2c** (Figure 7, b). The broadening of the signal at $\delta = -8.0$ in Figure 7 (b) could be explained by the existence of the equilibrium between forms **4c** and **5**, and fast exchange between them. This suggestion is in accordance with IR-spectroscopic data which showed the formation of ion pair **4c** for this concentration ratio. In the presence of 100 equiv. of **2c** the η^2-H$_2$ ligand signal of **4/5** appears already at 170 K (Figure 7, c). The increase of medium polarity could lead to partial dissociation of **4c**, and the signal becomes narrower. Full proton transfer is already observed at 150 K. At 110 K the signal of the η^2-H$_2$ ligand broadens into the baseline. The increase of the temperature leads to restoration of the initial spectrum revealing the reversibility of the process.

Discussion

The analysis of results obtained by low-temperature IR and NMR studies enables us to propose the stepwise mechanism of reaction between hydride **1** and proton donors **2**, resulting in the formation of the dihydrogen complex **5** according to Scheme 1. The first step of the interaction is the formation of a hydrogen bond between proton donors and hydride hydrogen atom (**3**). The determined thermodynamic characteristics of hydrogen-bonded complexes **3** showed that the ruthenium hydride **1** forms H-bonds of medium strength ($-\Delta H = 5.3-7.6$ kcal mol^{-1}). The $-\Delta H^0$ values increase with ROH proton-donating abilities in the sequence CF$_3$CH$_2$OH (**2a**) < (CF$_3$)$_2$CHOH (**2b**) < (CF$_3$)$_3$COH (**2c**).

The proton-accepting ability E_j of the hydride hydrogen atom in **1** does not depend on the strength of the proton donor or on the media. It equals 1.02±0.02 and is somewhat larger than that in rhenium dihydrides H$_2$Re(NO)(CO)(PR$_3$)$_2$ (0.68−0.79).[13] The increased basicity of the hydride atom is responsible for proton transfer not only from strong proton donors such as CF$_3$COOH (**2d**) and HBF$_4$ (**2e**), but also from weaker proton donors such as (CF$_3$)$_2$CHOH (**2b**) and (CF$_3$)$_3$COH (**2c**) when in excess, as well as in the case of {MeC(CH$_2$PPh$_2$)$_3$}Re(CO)$_2$H ($E_j = 0.97$).[19]

The next step − proton transfer from the H···H complex and generation of the dihydrogen complex − was shown to be an equilibrium process. After proton transfer, the cationic dihydrogen complex forms a contact ion pair **4**, stabilised by hydrogen bonding with the anion. The formation of ion pairs **4**, and the equilibrium between them and free cation **5** was studied using the known very high sensitivity of ν_{CO} vibrations to weak intermolecular interactions. Thus, depending on the ratio **1/2d**, only contact ion pair **4d** ($\nu_{CO} = 1996$ cm^{-1}), only free cation **5** ($\nu_{CO} = 2020$ cm^{-1}), or both forms can exist in solution simultaneously (Figure 3). The concentration dependence of ν_{CO} of **2d** and ν_{OCO}^{as} of **6d** anion bands confirms this conclusion. The existence of the equilibrium between free cation and ion pair $Cp^*M(CO)_2H^+\cdots{}^-OOCCF_3$ was established before for protonation of $Cp^*M(CO)_2$ (M = Rh, Ir) with CF_3COOH (**2d**),[36−38] and the spectral changes were similar to those observed here. The proton transfer to the metal atom has been shown to cause a large high-frequency shift of the ν_{CO} bands ($\Delta\nu$ = +95 to +143 cm^{-1}). Formation of ion pairs $Cp^*M(CO)_2H^+\cdots{}^-OOCCF_3$ resulted in a low-frequency shift of the ν_{CO} band of the cation in the range −20 to −50 cm^{-1}, depending on the nature of the metal atom. Moreover, the low-frequency shift of this band should also depend on the proton-accepting ability of an anion. Indeed, in the present case, the formation of the ion pair of $[Ru(\eta^2\text{-}H_2)]^+\cdots{}^-OC(CF_3)_3$ (**4c**) causes the larger low-frequency shift of the ν_{CO} band of cation **5** than that caused by the CF_3COO^- anion in **4d**. The position of ν_{CO} bands of **4c** is 1960 cm^{-1} compared to 1996 cm^{-1} for **4d**. That is in agreement with the larger proton-accepting ability of $(CF_3)_3CO^-$ compared to that of CF_3COO^-. It is noteworthy that the experimental observation of ion-paired H-complex $[Ru(\eta^2\text{-}H_2)]^+\cdots OR^-$ formation is in accordance with ion-molecular $[Ru(\eta^2\text{-}H_2)]^+\cdots OH_2$ hydrogen bonding determined in DFT calculations.[43]

Thus, the results obtained allow us to believe that proton transfer takes place within dihydrogen-bonded intermediate **3**, leading to complex **4** with a hydrogen bond between the η^2-H_2 ligand and the anion. A series of transition states of similar hydrogen-bonded structures was proposed recently by Basallote et al.[22] on the basis of inverse kinetic isotope effect data for the protonation of *cis*-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ with strong acids. They were, however, unable to provide experimental information on the structure of the intermediates and to elucidate the rate-determining step of the reaction. Here the sensitivity of the IR-spectral method allows us to observe different intermediates and to support such a stepwise proton transfer mechanism.

The proton transfer step appeared to be a slow process − the formation of **4c** and the settling of the equilibrium take about 30 min. Since the hydrogen bond formation is well known to be diffusion-controlled process, we assume that the *intra*-complex conversion of **3c** into **4c** is the rate-determining step in the proton transfer reaction. First-order rate constants obtained (Table 2) do not depend on the concentration of the reagents [k_{obs} = (1.6±0.2) × 10^{-3} s^{-1}] and support this idea.

Very recently,[41] studying the protonation of $\{MeC(CH_2PPh_2)_3\}Re(CO)_2H$ by $(CF_3)_3COH$ (**2c**) we suggested that the proton transfer barrier ($\Delta G^{\#}$) in this system should be about 12 kcal/mol. In the present work the value of k_{obs} obtained gives us an opportunity to estimate the barrier of proton transfer $\Delta G^{\#}$ (14.3 kcal/mol at 200 K). We can suggest that the low rate and high barrier are determined by steric hindrance of the PCy_3 ligand that embarrasses the proton transfer, as well as the accompanying complex reorganization. In this system even H···H hydrogen bonding has substantial steric hindrance and the large change of entropy (ΔS^0 = −21.6±0.6 e.u.) was determined. Such a value is near the highest values of H-complex formation entropy. The steric effects of the ligand and acid perhaps affect the proton transfer. The electronic factors determining the proton transfer barrier height were considered in the theoretical work.[43] The results of the DFT calculations for model hydride $CpRuH(CO)(PH_3)$ show that in the case of a weak proton donor such as H_2O the barrier for proton transfer from the H···H complex to the η^2-H_2 complex reaches about 40 kcal/mol, and proton transfer does not occur. When the strong proton donor H_3O^+ is used as a model the barrier drops significantly. These data are in good agreement with our results. In the case of moderate proton donors like $(CF_3)_2CHOH$ (**2b**) and $(CF_3)_3COH$ (**2c**), the barrier is high and proton transfer yielding the η^2-H_2 complex is slow. In the case of the strong acid CF_3COOH (**2d**) the barrier height becomes negligible, and protonation proceeds immediately.

Conclusions

By varying the proton donor strength, concentration, and temperature (250−140 K) we were able to find experimental evidence of a stepwise mechanism for the protonation of $CpRuH(CO)(PCy_3)$ (**1**). The spectral and thermodynamic characteristics of hydrogen bonding preceding the proton transfer and the formation of a dihydrogen complex were determined. The formation of ion pairs stabilized by hydrogen bonds between dihydrogen complex and anions [CF_3COO^-, $(CF_3)_3CO^-$] was observed in CH_2Cl_2. Low-rate constants and a high barrier of low-temperature protonation were determined for the first time. The results obtained seem to offer good experimental support for the long since suspected mechanism of protonation leading to the cationic dihydrogen complexes. Of course, further studies are required to determine the influence of solvent polarity and proton donor strength on the kinetic and thermodynamic characteristics of this interaction, and to establish the generality of mechanism suggested in this paper.

Experimental Section

$CpRuH(CO)PCy_3$ (**1**) was prepared as previously described.[25,26] IR measurements were carried out with a "Specord M82" spectrometer using 0.1-cm CaF_2 cells. For the low-temperature measurements a cryostat Carl Zeiss Jena was employed in the temperature range 190−300 K using a stream of liquid nitrogen. The accuracy of temperature adjustment was ±0.5 °C. The cell width was 0.04−0.12 cm. The reagents were mixed at low temperatures to prevent the dihydrogen evolution. The cold solution was then transferred into the cryostat pre-cooled to the required temperature. All samples were prepared under dry argon using standard Schlenk techniques. Anhydrous solvents were freshly distilled and degassed prior to use. The ^1H NMR spectra were recorded with Bruker WP-200, AMX 400, and AMX-500 spectrometers. Standard Bruker software was used for the inversion-recovery T_1 determination. The temperature was calibrated externally by a Pt100 thermo device.

The preparation of deuterated freon mixtures and of the samples using high-vacuum techniques were performed according to known procedures.[44–46]

Acknowledgments

We are extremely grateful to Prof. V. I. Bakhmutov and E. V. Vorontsov for NMR measurement in CD_2Cl_2 and C_7D_8, and for useful discussions. Thanks are expressed to P&M company (Moscow, Russian Federation) for providing the fluorinated alcohols. The authors thank RFBR-INTAS (N 95-136) and Russian Foundation for Basic Research (N 96-03-34114, 99-03-33270) for financial support.

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Received October 26, 2000
[I00403]