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Notes

Kinetics of Formation of Dihydrogen Complexes by Protonation of CpRuHL Complexes (L = DPPM, DPPE, 2 PPh_3) with $HBF_4·Et_2O$ in THF and the Failure To Observe Dihydrogen Complexes in the Reactions with Other Acids

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Summary: The second-order rate constants for the reactions of the title complexes with HBF_4 in THF do not correlate with the previously reported pK_a's of these complexes. The lack of formation of dihydrogen complexes in their reactions with HCl, HBr, or CF_3COOH in THF and acetone solutions indicates the limited validity of predictions based on aqueous pK_a scales.

Introduction

The properties of dihydrogen complexes and their comparison with classical metal hydrides have been the subject of great interest in recent years.[1,2] Although there is now a reasonable understanding of the synthetic and structural aspects of the chemistry of dihydrogen complexes, the kinetics and mechanisms of their reactions are still far from being well understood. We have recently proposed that protonation of metal hydrides with acids to form dihydrogen complexes occurs through a series of dihydrogen-bonded structures with a transition state that closely resembles the final reaction product.[3] For the reactions of $MH_2(phosphine)_4^+$ complexes (M = Fe, Ru) there is also a correlation between the rate constants for protonation with several acids, and the correlation leads to two parameters (R and S) that can be used as a measure of the intrinsic reactivity and selectivity of the metal hydride toward acids.[4,5] To see if the previous findings can be extended to complexes with very different steric and electronic requirements, we decided to study the kinetics of protonation of CpRuHL complexes where L is a bidentate phosphine or two monodentate phosphines, and the results are reported in the present paper.

Table 1. Signals in the NMR Spectra of the Starting Hydride Complexes and Their Products of Reaction with $HBF_4·Et_2O$ in Acetone-d_6 Solution[a]

	CpRuHL			$CpRu(H_2)L^+$		$CpRu(H)_2L^+$		
L	δ_H	δ_P	J_{HP}	δ_H	δ_P	δ_H	δ_P	J_{HP}
2 PPh_3	−11.6(t)	68.0	35	−7.3(s)	49.1	−7.1(t)	59.3	24
DPPM	−11.7(t)	20.1	32	−7.4(s)	5.5			
DPPE	−13.6(t)	91.8	35	−9.2(s)	79.3	−8.6(t)	68.4	29

[a] The chemical shifts are expressed in ppm and the coupling constants in Hz. The values reported correspond to the hydridic or dihydrogen signals referenced to external TMS (δ_H), and the singlet in the phosphorus spectra is referenced to external H_3PO_4 (δ_P).

Experimental Section

Both the preparative and the kinetic work were carried out under an argon atmosphere using standard Schlenk and syringe techniques. The solvents were obtained from SDS and dried by refluxing them from appropriate drying agents; they were also deoxygenated by bubbling Ar through them immediately before use. The complexes $CpRuH(PPh_3)_2$, CpRuH(DPPM), and CpRuH(DPPE) were obtained using literature procedures[6−9] and characterized by ^1H and $^{31}P\{^1H\}$ NMR (DPPM = $Ph_2PCH_2PPh_2$, DPPE = $Ph_2PCH_2CH_2PPh_2$). Hydrogen chloride and HBr were generated from methanol and chloro- or bromotrimethylsilane, respectively. The acids $HBF_4·Et_2O$ and CF_3COOH and other reagents were obtained from Aldrich. The NMR spectra were obtained with a Varian Unity 400 spectrometer, and the experimental procedure for the NMR monitoring of the reactions of the complexes with acids at different temperatures has been previously described.[3] The positions of the hydride and phosphorus signals for the starting compounds and the dihydrogen complexes and classical dihydrides formed in the protonation reactions (Table 1) do not differ significantly from those previously reported.[6−8]

The kinetic experiments were carried out at 25.0 °C using an Applied Photophysics SX17MV stopped-flow spectropho-

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tometer. All the experiments were carried out at 340−350 nm under pseudo-first-order conditions (acid excess), and kinetic traces could be always satisfactorily fitted by a single exponential using the standard software of the instrument. The HBF_4 solutions used in the kinetic work were used within 2 h from preparation, and the concentration of acid was determined in every case by dilution of an aliquot of the THF solution with water followed by titration with KOH using phenolphthalein indicator.

Results

Low-temperature NMR experiments showed that the initial reaction products of $HBF_4{\cdot}Et_2O$ with CpRuH(PPh_3)$_2$, CpRuH(DPPM), and CpRuH(DPPE) in acetone-d_6 are the corresponding dihydrogen complexes. In the case of the PPh_3 complex protonation is followed of tautomerization to give the corresponding classical dihydride, whereas a mixture of the dihydrogen compound and the classical dihydride are formed from the DPPE complex. No classical dihydride was observed for the DPPM complex. These results are in agreement with previous observations for these and related complexes,[6,8,10−12] and the mechanistic aspects of the tautomerization process have been discussed.[6]

The kinetics of reaction of the three CpRuHL complexes (L = DPPM, DPPE, 2 PPh_3) with HBF_4 in THF[13] was studied by monitoring an absorbance decrease at 340−350 nm. The absorbance changes associated with tautomerization are smaller and much slower than those corresponding to protonation, and so, they do not affect the determination of the k_{obs} values for dihydrogen complex formation (Table S1, Supporting Information). The observed rate constants show a linear dependence on the acid concentration (see Figure 1), and the values derived for the second-order rate constant k_{HX} are given in Table 2.

Surprisingly, the metal hydrides do not react to an appreciable extent with HCl or HBr after several hours at room temperature in THF and acetone solutions. Thus, both the NMR and the stopped-flow experiments showed that there is no evidence for the formation of dihydrogen complexes or classical dihydrides in these reactions. The reactions with CF_3COOH were also monitored, and the NMR spectra (acetone-d_6) showed the disappearance of the starting complex without evolution of any new signal, whereas the stopped-flow traces (THF solutions) showed that the reactions occur with irreproducible kinetics. Again, no evidence was obtained for the formation of the dihydrogen complexes, and since there is no formation of any precipitate in the NMR tubes, we concluded that these reactions lead to uncharacterized paramagnetic species and did not attempt further characterization or kinetic work.

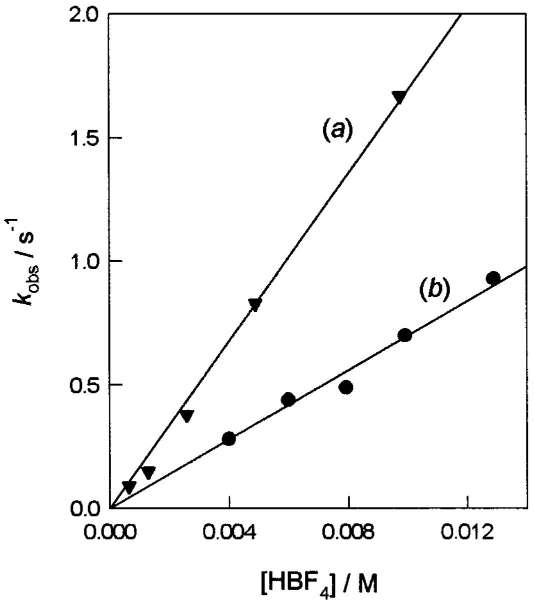

Figure 1. Dependence of the pseudo-first-order rate constant on the acid concentration for the reaction of HBF_4 with the complexes CpRuH(PPh_3)$_2$ (a) and CpRuH(DPPE) (b) at 25.0 °C in THF solution. The points for CpRuH(DPPM) are close to those of CpRuH(PPh_3)$_2$ and have not been included for clarity.

Table 2. Second-Order Rate Constants for the Reaction of CpRuHL Complexes with $HBF_4{\cdot}Et_2O$ To Give the Corresponding Dihydrogen Complexes (THF solution, 25.0 °C, Ar atmosphere)[a]

L	k_{HX}/M^{-1} s^{-1}	log k_{HX}	pK_a
2 PPh_3	169(4)	2.23	<5[b]
DPPE	70(2)	1.84	7.2
DPPM	186(8)	2.27	7.5

[a] The numbers in parentheses indicate the standard deviation in the last significant digit. [b] A pK_a of 8.0 has been reported for CpRu(H)$_2$(PPh_3)$_2^+$ in THF solution; as the equilibrium constant for the tautomerization of the dihydrogen complex to the corresponding dihydride is higher than 10^3 (equilibrium displaced toward the dihydride complex), the pK_a of the dihydrogen species can be estimated to be lower than 5.

Discussion

The formation of a dihydrogen complex through protonation of a metal hydride with acids can be represented in a simplified way by eq 1, which is formally an acid−base reaction in which a proton is transferred from HX to L_nMH. So, the pK_a values of the HX/X$^-$ and $L_nM(H_2)^+/L_nMH$ conjugated pairs can be used to determine the extent of protonation in every case, and the reaction is expected to be displaced toward formation of the dihydrogen complex when the pK_a of the dihydrogen complex is higher than that of HX.

$$L_nMH + HX \rightleftarrows L_nM(H_2)^+ + X^- \qquad (1)$$

The pK_a scale proposed by Morris[1] is now widely accepted to measure the acidity of dihydrogen complexes, and the values reported for the CpRuHL complexes are included in Table 2. As these values are referenced to an aqueous scale, one would then expect protonation of the hydrides with all the four acids tested, but our experimental observations indicate that there is no protonation of CpRuHL with acids as strong

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(13) The THF solutions were prepared from commercial $HBF_4{\cdot}Et_2O$. Although the exact nature of the acid under these conditions is not well-known, comparison with other acids indicates that the solutions must contain essentially (H^+, BF_4^-) ion pairs, with both ions being solvated.[14] The solutions of HBF_4 and other acids used for the kinetic work were always freshly prepared dilute solutions in order to avoid possible polymerization problems; actually, titration of older solutions leads to different and erratic values of the proton concentration.

as HCl or HBr, which suggests a much higher acidity of the $CpRuL(H_2)^+$ species. Actually, the closely related CpRuHL complex with $L = PR_2CH_2CH_2PR_2$ ($R = C_2F_5$) is so acidic that it is not protonated by HBF_4, and conversion to a mixture of the corresponding dihydrogen complex and the classical dihydride is only achieved using triflic acid.[11] However, there are also literature reports showing formation of the dihydrogen complexes upon protonation of CpRuHL (L = DPPM, DPPE, 2 PPh_3) complexes with acids both stronger (HBF_4, CF_3SO_3H) and weaker ($CpRuHL'_2$, HPR_3^+) than HCl or HBr.[7,15]

The lack of formation of dihydrogen complexes in the reactions with a large excess of HCl, HBr, or CF_3COOH is unlikely to be due to kinetic reasons because we have observed that protonation of other metal hydrides with these acids is usually faster than with HBF_4.[3−5] Thus, the lack of formation of dihydrogen complexes in our experiments with acids other than HBF_4 must be related to the thermodynamics of the process and clearly indicate the limited validity of simple pK_a scales to measure the acidity in a solvent such as THF.

In THF solutions, eq 1 is an oversimplification of the chemical processes that actually take place in solution because the low dielectric constant favors the formation of ion pairs (eq 2) and homoconjugated species (eq 3) that affect equilibrium 1.[16] The values of the equilibrium constant for ion pair formation (K_{ip}) can be as high as 10^5-10^7 M^{-1} in THF solution,[14] and a significant difference between the values for $A^+ = H^+$ and $L_nM(H_2)^+$ can make reaction 1 go in the opposite direction.

$$A^+ + X^- \rightleftarrows (A^+,X^-); \quad K_{ip} \tag{2}$$

$$HX + X^- \rightleftarrows HX_2^-; \quad K_{hc} \tag{3}$$

As a consequence of the large values possible for both K_{ip} and K_{hc}, the effective acidity of a species in THF and other organic solvents is very different from its acidity in water, which becomes especially important when comparing the acidity of two species. For example, CF_3SO_3H and picric acid have extremely different acidity in water, but their pK_a values in THF differ by less than 4 units.[14,17] Thus, the pK_a values of dihydrogen complexes in the aqueous scale maintain their utility to measure the relative tendency of these compounds to deprotonate, but they do not appear to be valid for the comparison with acids of a very different nature whose acidity has not been directly measured in the same solvent. Probably, it would be preferable to use a nonaqueous scale including exclusively the dihydrogen complexes and those species such as HPR_3^+ that have been used in the equilibrium measurements required for the determination of their pK_a.

The dependence of the rate constants for proton transfer on the difference of acidity between the reagents was recognized long ago, and it is usually expressed by the Bronsted correlation.[18] The operation of a Bronsted-type correlation for proton transfer involving acidic metal hydrides was demonstrated years ago by Norton and co-workers,[19−21] and we have shown more recently a similar correlation for the formation of dihydrogen complexes from basic metal hydrides.[4,5] According to this correlation, the values of log k_{HX} for the reaction of a series of metal hydrides with a common acid to form the corresponding dihydrogen complexes are expected to show a linear dependence with the pK_a of the dihydrogen complexes.

The values in Table 2 for the DPPE and DPPM complexes show that a modest increase in the pK_a leads to a small increase of log k_{HX}, but the values for the PPh_3 complex do not appear to follow this trend. Although the pK_a of the dihydrogen complex cannot be measured in this case, the quantitative conversion to the dihydride species ($pK_a = 8.0$) indicates a significantly smaller value, probably close to 5, which places this complex clearly out of the tendency observed for the DPPE and DPPM complexes.

We are unable at this time to explain satisfactorily the lack of correlation between the pK_a and log k_{HX} values, but there is the possibility that it is caused by a different kinetic selectivity of the complexes toward acids. Actually, we have shown that two parameters (R and S) are required to express the correlation between the kinetic and the acidity data for the reaction of a series of complexes with several acids.[4,5] The impossibility of obtaining kinetic data for the reaction of the Cp complexes with the other acids tried hinders a detailed analysis of the problem, and comparison of kinetic data for reactions with a single acid would be meaningless if the complexes have a very different selectivity.

An alternative interpretation to the lack of $k_{HX}-pK_a$ correlation would be that protonation of the CpRuHL hydrides does not lead directly to the dihydrogen complexes. If the latter compounds are formed through a mechanism of the type shown in eqs 4 and 5, with the rate-determining step being formation of an unstable and undetectable intermediate A that converts rapidly into the dihydrogen complex, the values of log k_{HX} would correlate with the acidity of the intermediate. In that case, the absence of correlation with the pK_a of the dihydrogen complexes would simply reflect a mechanistic change with respect to that proposed for the $MH_2(phosphine)_4$ complexes. Several possibilities of proton attack at a metal hydride are possible and have been discussed in the literature,[8,10,22] including attacks at the hydride ligand, at the metal center, and at an ancillary ligand.

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$$\mathrm{CpRuHL + HX \rightarrow A;} \quad k_{\mathrm{HX}} \tag{4}$$

$$\mathrm{A \rightarrow CpRu(H_2)L^+;} \quad \text{fast} \tag{5}$$

Attack at the hydride is not compatible with the mechanism in eqs 4 and 5 because it would lead directly to the dihydrogen complex without the need of any intermediate. Attack at the metal would lead to a metal dihydride as intermediate, and the NMR observations in this work and previous literature reports clearly show that the classical dihydrides are slowly formed from the dihydrogen complexes, so ruling out this interpretation. Thus, the only possibility is that the intermediate results from proton attack at an ancillary ligand, either the phosphine or the Cp ring. For the CpRuHL complexes, phosphine protonation requires the opening of a chelate ring, whereas protonation of the cyclopentadienyl ring requires a ring slippage process. Although both of these processes have been observed or proposed for other compounds,[23−25] there is no experimental evidence favoring their operation in the reactions of the CpRuHL complexes. In any case, with the information available at this time, we think that a mechanistic change in the protonation reaction or a different selectivity of the CpRuHL complexes toward acids appears as the most reasonable explanation for the lack of correlation between log k_{HX} and pK_a values.

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Supporting Information Available: A table including pseudo-first-order rate constants for the reactions of CpRuHL complexes with HBF_4 in THF at 25.0 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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