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Hydrogen bonding and proton transfer involving the trihydride complexes Cp*MH_3(dppe) (M = molybdenum, tungsten) and fluorinated alcohols: the competitive role of the hydride ligands and the metal.

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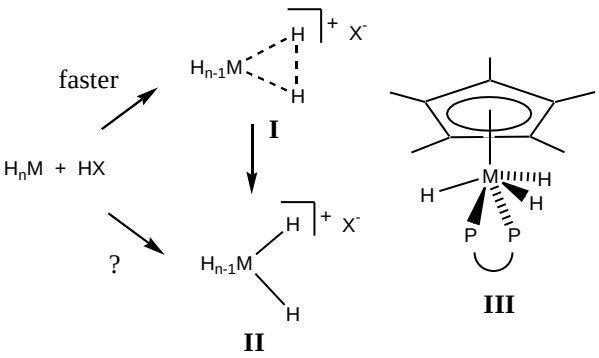
The protonation of complexes Cp*M(dppe)H_3 (M = Mo, **1**; W, **2**) by a variety of fluorinated alcohols of different acid strength (MFE, TFE, HFIP and PFTB) has been investigated experimentally by variable temperature spectroscopic methods (IR, NMR) and by the stopped-flow technique (UV-visible). The structure of the hydrogen bonding and proton transfer products has been probed by DFT studies. In agreement with calculation results the IR data suggest that the initial hydrogen bond is established with a hydride site for **1** and with the metal site for **2**. However, no intermediate dihydrogen complex found theoretically can be detected experimentally on the way to the final classical tetrahydride product.

Key words: transition metal polyhydrides, IR, Uv-vis NMR spectroscopy, hydrogen bonding, proton transfer, theoretical study

Proton transfer to transition metal hydride complexes has been extensively studied as a method to access dihydrogen complexes and for its biological relevance for hydrogenases enzymes.[1] It has been established that hydride ligands are the kinetically preferred protonation sites for hydride complexes; whether direct protonation of the metal center in such complexes can occur under any experimental conditions has been the matter of some debate.[2] Even when the most stable protonation product is a classical complex **II**, *i.e.* the product of formal proton transfer to the metal site, detailed investigations have proven the intermediacy of nonclassical complexes, **I** (see Scheme 1).[3-7] A recent report of the rate ratio between hydride and metal attack for the $CpW(CO)_2(PMe_3)H$ complex is based on indirect measurements and does not demonstrate that a direct metal protonation occurs.[8] Our own recent kinetic investigation of the Cp*Fe(dppe)H protonation provides strong evidence that, at least for this system, a direct protonation at the metal site is not competitive with hydride protonation.[9] The investigation of hydrogen bonding and the determination of the site at which this interaction occurs have also given useful information on the first step of the proton donor approach to the hydride complexes. In addition, theoretical investigations are providing an increasingly accurate description of the energetics and geometry of the molecular interactions in solution, with the consideration of the solvent effect being possible through the use of polarizable continuum models.[10]



Scheme 1

We report here preliminary investigations, comprising spectroscopic, kinetic and theoretical approaches, of the interaction of fluorinated alcohols [FCH_2CH_2OH, MFE; CF_3CH_2OH, TFE; $(CF_3)_2CHOH$, HFIP; $(CF_3)_3COH$, PFTB] with complexes Cp*M(dppe)H_3 (M = Mo, **1**; W, **2**). As shown by X-ray diffraction and confirmed by DFT calculations,[11,12] the geometry of **1** and **2** is as shown in **III** and features the Cp* and dppe ligands in opposite positions, with one hydride ligand on one side and two on the other side with respect to the Cp*(center)-M-P_2 plane. Both complexes yield the classical tetrahydrido product, [Cp*M(dppe)H_4]$^+$, when protonated by strong acids in weakly coordinating solvents (e.g. ether, THF). On the other hand, a difference is noted in MeCN: whereas the W analogue still yields the same cationic tetrahydride product, the Mo complex yields [Cp*Mo(dppe)H_2(MeCN)]$^+$ with loss of H_2.[12]

According to well established protocols,[13] an IR analysis of the ν_{OH} absorption of MFE and TFE in the presence of excess hydride complex shows the hydrogen bond formation. Use of the empirical Iogansen's relationships[14,15] furnishes the enthalpy (ΔH^o) and basicity factor (E_j) data reported in table 1. The E_j values, especially that of compound **2**, are amongst the highest ever reported for a transition metal hydride complex (*cf.* 1.45 for [$ReH_3(\eta^4$-$N(CH_2CH_2PPh_2)_3)$][16] where the site of hydrogen bonding is the metal atom-and 1.66 for [$OsH_2\{P(CH_2CH_2PPh_3)_3\}$][17] where hydrogen bond occurs at hydride ligand. Detailed analysis of the ν_{MH} region of the IR spectrum (see Figure 2) shows low-frequency shifts in the case of the Mo complex, whereas the W system gives rise to small *high* frequency shifts. Following the available literature,[13,18] this represents evidence for H-bonding to the hydride sites in the Mo case and to the metal site in the W case.

In order to analyze the structure of hydrogen bonded complexes more in detail, we have carried out theoretical investigations. The proton donor HFIP was chosen for the investigation, since it gives stronger interactions, and the Cp* and dppe ligands were modeled by Cp and dpe ($PH_2CH_2CH_2PH_2$) for reasons of computational speed. The most important results of the study are summarized in Table 2. Five hydrogen bonded structures have been found for both metals, which can be classified depending on the proton acceptor site: hydride, metal or involving both sites. The coordination geometry of the metal center is not significantly perturbed by H-bonding. Although all structures are close in the energy, the hydrogen bond to the left-hand side hydride ligand (**a**) is least favorable. The analysis of geometry (M…H and H…H distances, M…HO and H…HO angles) helps to distinguish different interactions and allows to compare hydrogen bonding with the hydride (structures a and b) and with the metal (structures **c**) (see Figure 2). Thus, for Mo the most favorable interaction is with hydride ligand (**b**) (almost linear dihydrogen bond ∠H…HO = 169.1°, short H…H distance 1.56Å), while for W that is hydrogen bond to the metal atom (**c**) (∠M…HO = 172.8°, r(M…H) = 2.69Å) with some additional interaction with hydride ligand (H…H distance of 2.03Å is less than the sum of Wan der Waals radii (2.4 Å), but the H…HO angle 133.0° is indistinctive for intermolecular hydrogen bonds).

Another important computational result is the identification of a local minimum for the nonclassical Mo protonation product, $[CpMo(dpe)(H_2)(H)_2]^+$ (3.4 kcal/mol higher than the classical tetrahydride complex), whereas all attempts to locate an analogous W derivative systematically collapsed to the classical tetrahydride product $[CpW(dpe)(H)_4]^+$. The identification of a nonclassical intermediate during the protonation of **1** was attempted by an ^1H and ^{31}P NMR study.

However, even when using the weaker proton donor TFE in CD_2Cl_2, the NMR spectra showed only the resonances of the starting complex and the classical tetrahydride product (–3.57 ppm, T_{1min} = 173 ms at 230K). Thus, proton transfer either occurs directly at the metal or the intermediate nonclassical complex rearranges too rapidly (very small barrier) to be observed, even at 200 K. Nor could a nonclassical intermediate be observed during the protonation of complex **2** by TFE. Additionally, preliminary kinetic investigations by stopped-flow show a single-step process for the protonation of **2** by HFIP and by PFTB, with a first order dependence on the fluorinated alcohol concentration (k = 1300±32 $s^{-1}M^{-1}$ for HFIP; 1250±32 $s^{-1}M^{-1}$ for PFTB). As detailed recently for the analogous investigation of the Cp*Fe(dppe)H-R_FOH system and theoretical calculations of the CpRuH(CO)(PCy_3) protonation,[10] this result shows the involvement of two alcohol molecules, with the formation of a homoconjugate pair (see Equation 1). The theoretical calculations are in support of this interpretation, the energy change associated to the production of the homoconjugate pair from a separate alcoholate and alcohol molecules being -22.3 kcal mol^{-1} in CH_2Cl_2. Analogous kinetic studies for **1** are in progress.

Equation 1

$$Cp^*M(dppe)H_3\cdots HOR_F + R_FOH \rightarrow [Cp^*M(dppe)H_4]^+[R_FO\cdots H\cdots OR_F]^-$$

In conclusion, a combination of spectroscopic, kinetic, and theoretical approaches suggest that the trihydride complexes 1 and 2 undergo proton transfer from fluorinated alcohols directly at the metal center via hydrogen bond to the metal (for **2**) or with hydride ligand and unobservable dihydrogen complex intermediate (for **1**).

Experimental part

Compounds **1** and **2** were prepared according to literature procedures.[11,12] Variable temperature spectral studies were done on "Specord M82" spectrometer (IR) as described. [10, 16]

^{1}H and ^{31}P NMR experiments were carried on Bruker AMX-400 instrument (400.13 and 161.98 MHz respectively). Chemical shifts in ^{1}H NMR spectra were measured related to residual signal of CD_2Cl_2 at 5.31ppm. The conventional inversion-recovery method was used to determine T_1 relaxation times.

All calculations were carried out by the DFT approach with the B3LYP functional, the LANL2DZ basis set for the metal atoms, a double-ζ + polarization basis set for the atoms directly bonded to the metal and the atoms involved in hydrogen bonds, and a double- ζ basis set for the rest of the atoms. Free energies of solvation were calculated with dichloromethane (ε = 8.93) as a solvent by means of the PCM model, using standard options.[19]

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Figures

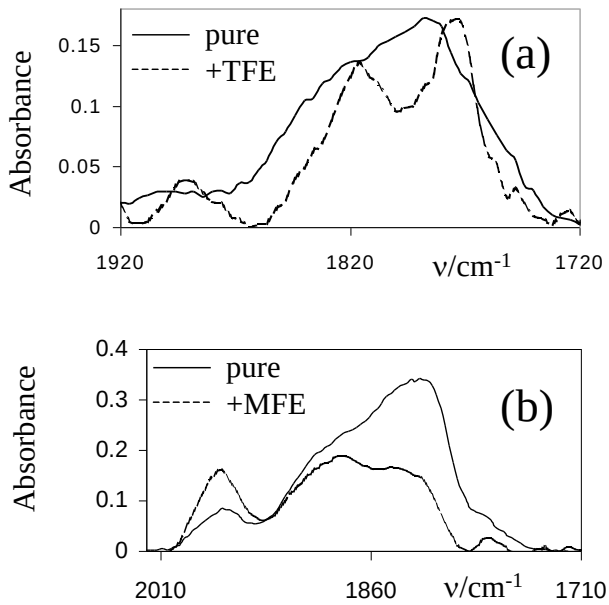

Figure 1. IR spectra in the ν_{MH} stretching region: (a) complex **1** (0.075 mol L^{-1}) (*1*) and product of its interaction with TFE (25 equiv) in THF at 200 K (*2*); (b) complex **2** (0.035 mol L^{-1}) and the product of its reaction with MFE (15 equiv) in CH_2Cl_2 at 200 K (*2*).

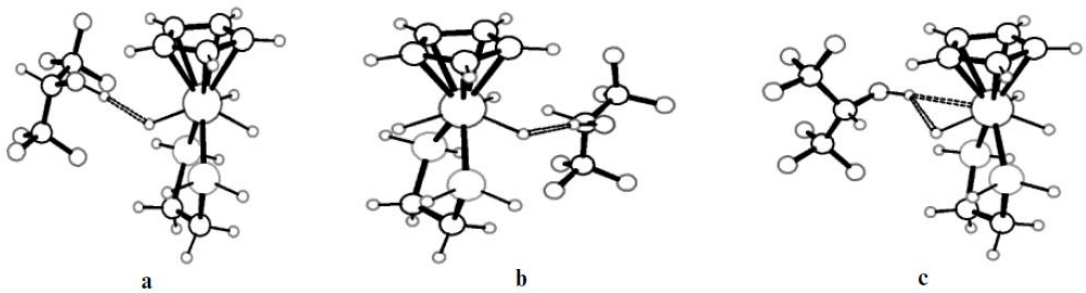

Figure 2. Calculated structures for hydrogen bonded complexes of $CpM(dpe)H_3$ with HFIP (**a**, **b**, **c**).

Table 1. Spectral characteristics and enthalpy values of hydrogen bonds between $Cp^*MH_3(dppe)$ and MFE or TFE in $CH_2\mathbf{Cl_2}$ and of hydrides.

		Cp*Mo(dppe)H_3, **1**				Cp*W(dppe)H_3, **2**			
ROH	$\nu_{OH(free)}$ cm^{-1}	$\nu_{OH(bonded)}$ cm^{-1}	$\Delta\nu$ cm^{-1}	ΔH^{o} [a] kcal/mol	E_j	$\nu_{OH(bonded)}$ cm^{-1}	$\Delta\nu$ cm^{-1}	ΔH^{o} [a] kcal/mol	E_j [b]
MFE	3612	3368	244	-4.9	1.44	3230	364	-6.0	1.65
TFE	3604	3248	364	-5.9	1.41	3136	468	-6.7	1.64

[a] Enthalpies calculated by Iogansen's empirical relationship $-\Delta H^{\circ} = \frac{18\Delta\nu}{\Delta\nu + 720}$.[14] [b] Basicity factors calculated as $E_j = \frac{\Delta H_{ij}}{\Delta H_{11} P_i}$ [15]

Table 2 Calculated H-bonding distances (Å), angles (°) and interaction energies (kcal/mol; ΔH, gas phase, ΔG in dichloromethane)
for several hydrogen bonded adducts of HFIP with CpM(dpe)H_3.

	Mo a	W a	Mo b	W b	Mo c	W c
H…HO	1.649	1.706	1.560	1.578	2.008	2.032
∠H…HO	159.5	151.7	169.1	151.5	134.6	133.0
M…HO	-	-	(>3)	(2.898)	2.717	2.690
∠M…HO	151.7	150.6	161.4	158.9	173.3	172.8
ΔH	-9.07	-9.0	-10.29	-8.67	-9.94	-10.82
ΔG	0.39	0.43	- 0.77	- 0.57	- 0.49	- 1.73