

Hydrogen bonding and proton transfer involving the trihydride complexes $\text{Cp}^*\text{M}(\text{dppe})\text{H}_3$ ($\text{M} = \text{Mo}, \text{W}$) and fluorinated alcohols: the competitive role of the hydride ligands and metal*

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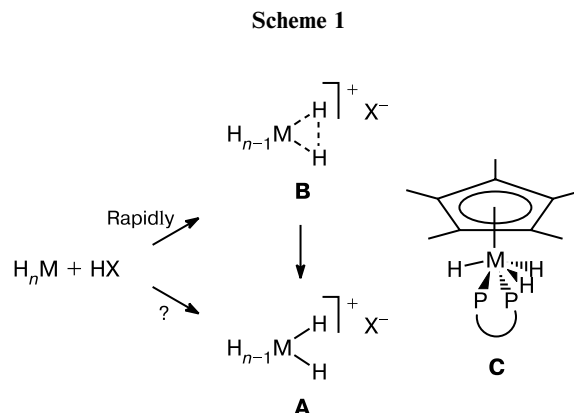
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The protonation of complexes $\text{Cp}^*\text{M}(\text{dppe})\text{H}_3$ (dppe is ethylenebis(diphenylphosphine), $\text{M} = \text{Mo}$ (**1**), W (**2**)) by a variety of fluorinated alcohols of different acid strength ($\text{FCH}_2\text{CH}_2\text{OH}$, $\text{CF}_3\text{CH}_2\text{OH}$, $(\text{CF}_3)_2\text{CHOH}$, and $(\text{CF}_3)_3\text{COH}$) was investigated experimentally by the variable temperature spectroscopic methods (IR, NMR) and stopped-flow technique (UV-Vis). The structures of the hydrogen-bonded and proton transfer products were studied by DFT calculations. In agreement with the calculation results, the IR data suggest that the initial hydrogen bond is established with a hydride site for complex **1** and with the metal site for complex **2**. However, no intermediate dihydrogen complex found theoretically was detected experimentally on the way to the final classical tetrahydride product.

Key words: transition metal polyhydrides, IR spectroscopy, UV-Vis NMR spectroscopy, hydrogen bonding, proton transfer.

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 **A**, *i.e.*, the product of formal proton transfer to the metal atom, detailed investigations proved the intermediacy of nonclassical complexes **B**



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(Scheme 1).^{3–7} A recent report of the rate ratio between the hydride and metal attack for the $\text{CpW}(\text{CO})_2(\text{PMe}_3)\text{H}$ complex is based on indirect measurements and does not demonstrate that a direct metal protonation occurs.⁸ Our recent kinetic investigation of the $\text{Cp}^*\text{Fe}(\text{dppe})\text{H}$ protonation provides strong evidence that, at least for this system, direct protonation at the metal site is not competi-

tive with hydride protonation.⁹ The investigation of hydrogen bonding and the determination of the site at which this interaction occurs also gave useful information on the first step of the proton donor approach to the hydride complexes. In addition, theoretical investigations provide 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

We report here preliminary investigations comprising spectroscopic, kinetic, and theoretical approaches, of the interaction of the fluorinated alcohols (FCH₂CH₂OH, MFE; CF₃CH₂OH, TFE; (CF₃)₂CHOH, HFIP; (CF₃)₃COH, PFTB) with the complexes Cp^{*}M(dppe)H₃ (dppe is ethylenebis(diphenylphosphine), M = Mo (1), W (2)).

Results and Discussion

As shown by X-ray diffraction and confirmed by DFT calculations,^{11,12} the geometry of complexes 1 and 2 is as shown in structure C and features the Cp^{*} and dppe ligands in opposite positions, with one hydride ligand on one side and two hydride ligands on the other side with respect to the Cp^{*}_{center}—M—P₂ plane. Both complexes yield the classical tetrahydrido product [Cp^{*}M(dppe)H₄]⁺, when protonated by strong acids in weakly coordinating solvents (*e.g.*, ether, THF). A difference is noted in MeCN: whereas the W analogue still yields the same cationic tetrahydride product, the Mo complex yields [Cp^{*}Mo(dppe)H₂(MeCN)]⁺ with loss of H₂.¹²

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 (Δ*H*^o) and basicity factor (*E_j*) data (Table 1). The *E_j* values, especially that of compound 2, are among the highest ever reported values for transition metal hydride complexes (*cf.* 1.45 for [ReH₃(η⁴-N(CH₂CH₂PPh₂)₃)]¹⁶ where the site of hydrogen bonding is the metal atom, and 1.66 for [OsH₂{P(CH₂CH₂PPh₃)₃}]¹⁷ where the hydrogen bond

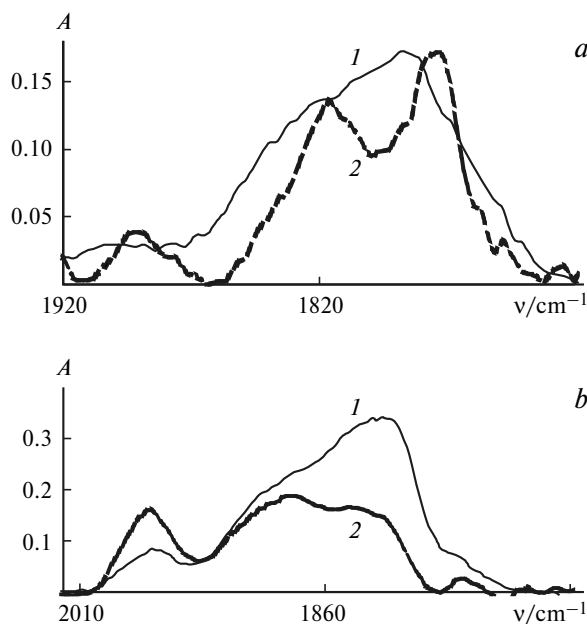


Fig. 1. IR spectra in the ν(MH) region: *a*, complex 1 (0.075 mol L⁻¹) (1) and the product of its interaction with TFE (25 equiv.) in THF at 200 K (2); *b*, complex 2 (0.035 mol L⁻¹) and the product of its reaction with MFE (15 equiv.) in CH₂Cl₂ at 200 K (2).

occurs at hydride ligand). Detailed analysis of the ν(MH) region of the IR spectrum (Fig. 1) 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 carried out theoretical investigations. The proton donor HFIP was chosen for analysis, since it gives stronger interactions, and the Cp^{*} and dppe ligands were modeled by Cp and dpe (PH₂CH₂CH₂PH₂) for reasons of computational speed. The most important results of the study are summarized in Table 2. Five hydrogen-bonded structures were found for both metals, which can be classified depending on the

Table 1. Spectral characteristics and enthalpies of formation of hydrogen bonds between Cp^{*}M(dppe)H₃ and MFE or TFE in CH₂Cl₂

Alcohol ROH	ν(OH _{free}) /cm ⁻¹	Cp [*] Mo(dppe)H ₃ (1)				Cp [*] W(dppe)H ₃ (2)			
		ν(OH _{bonded})	Δν	−Δ <i>H</i> ^o ^a	<i>E_j</i> ^b	ν(OH _{bonded})	Δν	−Δ <i>H</i> ^o ^a	<i>E_j</i> ^b
		/cm ⁻¹	/cm ⁻¹	/kcal mol ⁻¹		/cm ⁻¹	/cm ⁻¹	/kcal mol ⁻¹	
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 Calculated by Iogansen's empirical relationship¹⁴: −Δ*H*^o = 18Δν/(Δν + 720), where Δν = ν_{free} − ν_{bonded}.

^b Basicity factors calculated as *E_j* = Δ*H*_{ij}/(Δ*H*₁₁*P_i*)¹⁵, where Δ*H*_{ij} is the enthalpy of the H-complex, Δ*H*₁₁ is the enthalpy of the standard phenol—diethyl ether H-complex (Δ*H*₁₁ = −4.6 kcal mol⁻¹ in CH₂Cl₂), *P_i* is the acidity factor of the proton donor.

Table 2. Calculated H-bonded distances (*d*), angles (ω), and enthalpies of formation for H-bonded CpM(dpe)H₃ complexes with HFIP

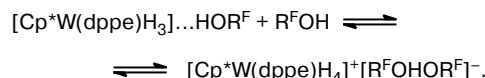
M	Structure	<i>d</i> /Å		ω /deg		$-\Delta H^a$	ΔG^b
		H...H—O	M...H—O	H...H—O	M...H—O	kcal mol ⁻¹	
Mo	a	1.649	—	159.5	151.7	9.07	0.39
	b	1.560	(>3)	169.1	161.4	10.29	-0.77
	c	2.008	2.717	134.6	173.3	9.94	-0.49
W	a	1.706	—	151.7	150.6	9.00	0.43
	b	1.578	(2.898)	151.5	158.9	8.67	-0.57
	c	2.032	2.690	133.0	172.8	10.82	-1.73

^a Enthalpy of formation of the complex in the gas phase.^b Free energy of complex formation in CH₂Cl₂.

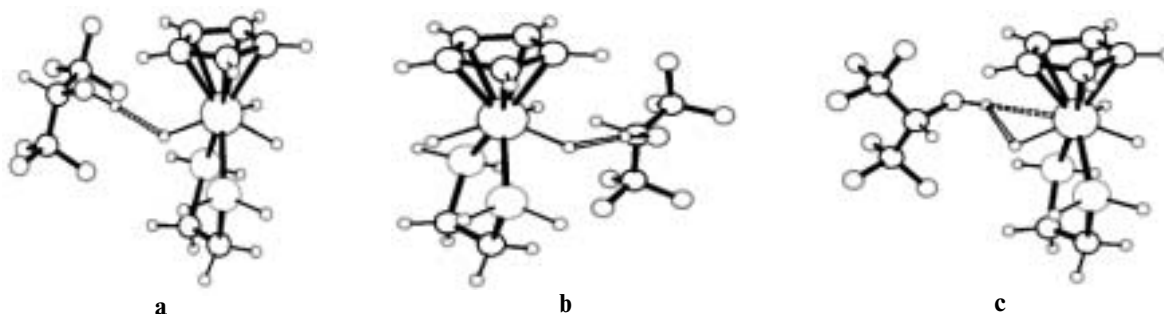
proton acceptor site: hydride, metal, or involving both sites. The coordination geometry of the metal center is not significantly perturbed by H-bonding. Although all the structures are close in energy, the hydrogen bond to the left-hand side hydride ligand (Fig. 2, structure **a**) is least favorable. The analysis of geometry (M...H and H...H distances, M...H—O and H...O—H angles) helps to distinguish different interactions and allows one to compare hydrogen bonding with the hydride (structures **a** and **b**) and with the metal (structures **c**) (see Fig. 2). Thus, for Mo the most favorable interaction is with the hydride ligand (**b**) (almost linear dihydrogen bond, H...H—O angle is 169.1°, short H...H distance 1.65 Å), while for W that is hydrogen bond to the metal atom (**c**) (M...H—O angle is 172.8°, M...H distance is 2.69 Å) with some additional interaction with the hydride ligand (H...H distance of 2.03 Å is less than the sum of van der Waals radii (2.4 Å), but the H...H—O 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)(H₂)(H)₂]⁺ (3.4 kcal mol⁻¹ 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 complex **1** was attempted by an ¹H and ³¹P NMR study. However, even

when using the weaker proton donor TFE in CD₂Cl₂, the NMR spectra showed only the resonances of the starting complex and classical tetrahydride product (-3.57 ppm, *T*_{1min} = 173 ms at 230 K). Thus, proton transfer 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 stopped-flow investigation showed a single-step process for the protonation of **2** by HFIP and by PFTB. Together with finding of hydrogen bond to the metal atom only, this suggests that direct attack of the metal atom takes place for tungsten hydride. The rate constants obtained have first order dependence on the fluorinated alcohol concentration (*k* = 1300 ± 32 L mol⁻¹ s⁻¹ for HFIP; 1250 ± 32 L mol⁻¹ s⁻¹ for PFTB). As detailed recently¹⁰ for the analogous investigation of the Cp*Fe(dppe)H—R_FOH⁹ system and theoretical calculations of the CpRuH(CO)(PCy₃) protonation, this result shows the involvement of two alcohol molecules, with the formation of a homoconjugate pair



Our theoretical calculations are in support of this interpretation. The energy change associated to the production of the homoconjugate pair from a separate alcoholate

**Fig. 2.** Calculated structures for hydrogen-bonded complexes of CpM(dpe)H₃ with HFIP (**a**, **b**, **c**).

and alcohol molecules is $-22.3 \text{ kcal mol}^{-1}$ in CH_2Cl_2 . Analogous kinetic studies for **1** are in progress.

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

Experimental

Compounds **1** and **2** were prepared according to literature procedures.^{11,12}

Variable temperature spectra were recorded on a Specord M-82 spectrometer (IR) as described.^{10,16}

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

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

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