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Effect of the nature of the metal atom on hydrogen bonding and proton transfer to [Cp*MH₃(dppe)]: tungsten vs. molybdenum

Natalia V. Belkova,^[a] Maria Besora,^[b] Miguel Baya,^[c] Pavel A. Dub,^[a] Lina M. Epstein,^[a] Agustí Lledós,^{*[b]} Rinaldo Poli,^[c] Pavel O. Revin,^[a] and Elena S. Shubina^{*[a]}

Abstract: The hydrogen bonding and proton transfer pathway to complex [Cp*W(dppe)H₃] (Cp* = η⁵-C₅Me₅; dppe = Ph₂PCH₂CH₂PPh₂) has been investigated experimentally by IR, NMR, UV-vis spectroscopy in the presence of fluorinated alcohols, p-nitrophenol and HBF₄, and using DFT calculations for the [CpW(dhpe)H₃] model (Cp = η⁵-C₅H₅; dhpe = H₂PCH₂CH₂PH₂) and for the real system. A study of the interaction with weak acids (CH₂FCH₂OH, CF₃CH₂OH, (CF₃)₂CHOH) allowed the determination of the basicity factor, E_j = 1.73 ± 0.01, making this compound the most basic hydride complex reported to date. A

computational investigation reveals several minima for the [CpW(dhpe)H₃] adducts with CF₃CH₂OH, (CF₃)₂CHOH and 2(CF₃)₂CHOH and confirms that these interactions are stronger than those established by the Mo analogue. Their geometries and relative energies are closely related to those of the homologous Mo systems, with the most stable adducts corresponding to H bonding with M-H sites, but the geometric and electronic parameters reveal that the metal center plays an increased role in the tungsten systems. Proton transfer equilibria are observed with the weaker proton donors, the proton transfer step for the system

[Cp*W(dppe)H₃]/HOCH(CF₃)₂ in toluene having ΔH = -3.9 ± 0.3 kcal mol⁻¹ and ΔS = -17 ± 2 cal mol⁻¹ K⁻¹. The thermodynamic stability of the proton transfer product is greater for W than for Mo. Contrary to the Mo system, the protonation of the [Cp*W(dppe)H₃] appears to involve a direct proton transfer to the metal center without a non-classical intermediate, although assistance is provided by a hydride ligand in the transition state.

Keywords: Tungsten, Hydride complexes, Phosphine ligands, Proton transfer, Hydrogen bonding

Introduction

Hydrogen bonds involving transition metal mono- and polyhydrides as proton acceptors have attracted considerable attention in recent years, since they are involved in intermediates of fundamental processes such as enzymatic dihydrogen evolution and catalytic ionic hydrogenation.^[1-6] As proton acceptors, M-H moieties offer a relatively unencumbered site of attack, where the proton accepting orbital σ_{MH} (mostly constituted by the spherically symmetrical 1s orbital of the H atom)^[7] is less sensitive to angular limitations for the best interaction with the proton donor (Chart 1). Spectroscopic manifestations of hydrogen bonding in (M)-H...H-A complexes are

similar to those found in the case of classical hydrogen bonding.^[8] Accordingly, the (M)H...H-A angles tend to be linear in dihydrogen bonded complexes.^[9] On the other hand, the dihydrogen bonded complexes of metals with a dⁿ (n ≥ 2) configuration (namely, possessing at least one metal-based lone pair) often feature the non-linear M-H...H(A) arrangement, such that the proton donor A-H bond approaches the M-H unit in a side-on direction.^[10] A typical H...M distance in such a case was found to be 2.8 Å leading to a possible ambiguity, because a metal's d_π nonbonding orbital, if pointing between the ligands, could, in principle, interact with the A-H proton (Chart 2). Providing the hydrogen bonding involving metal lone pairs as proton acceptors is very well established for metal complexes that do not contain hydride ligands (e.g. L_nM...HA with L ≠ H),^[11-16] this may not only be an additional interaction

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but may ultimately lead to the proton donor coordination to the metal center. Yet, many examples are known where the protonating reagent attacks a hydride position, yielding a dihydrogen complex as the kinetically controlled protonation product, even when the classical di- or polyhydride product is thermodynamically favoured.^[17-22]

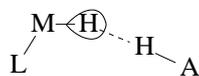


Chart 1.

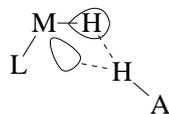
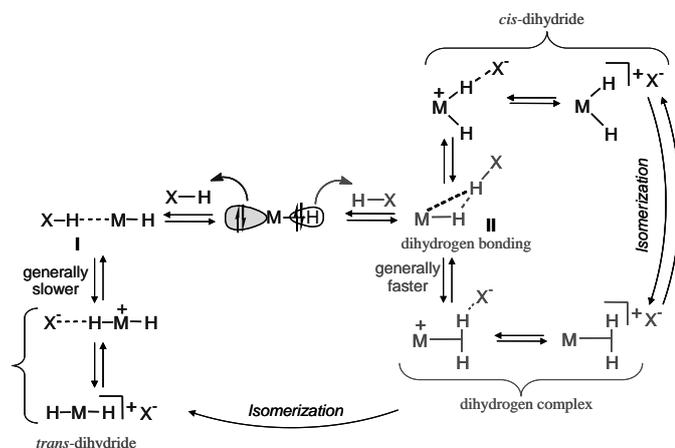


Chart 2.

This general behaviour for the protonation of hydride complexes may be summarized as shown in Scheme 1, where the initial competition between a metal lone pair and a hydride unit leads to the hydrogen bonded adducts **I** and **II**, respectively. In the second case, however, both the hydride ligand and the metal atom could contribute to the interaction and may lead to either a dihydrogen complex or a *cis*-dihydride depending on the relative energy of these isomers. Note that the isomerization process interconverting a dihydrogen complex and a *cis*-dihydride, in cases where a double minimum may exist, is predicted to have a very small activation barrier,^[23] whereas much larger activation barriers are associated to processes where a more severe ligand rearrangement occurs, such as in *cis*/*trans* isomerizations.^[24-28]



Scheme 1. Two pathways of proton transfer to transition metal hydrides

Given the above scenario, it may be reasonably expected that the kinetic preference for attack at an M-H site vs. the metal lone pair should be greater for a polyhydride compound, relative to a monohydride compound. Recently, we have reported detailed investigations^[29, 30] on the hydrogen bonding and proton transfer to complex $[\text{Cp}^*\text{Mo}(\text{dppe})\text{H}_3]$, an electron-rich half-sandwich trihydride complex of Mo^{IV} .^[31] The protonation product observed by the use of either strong (HBF_4 , CF_3COOH) or moderate (perfluoro-*tert*-butanol or PFTB, hexafluoroisopropanol or HFIP, *p*-nitrophenol) acids is the classical tetrahydrido derivative, $[\text{Cp}^*\text{Mo}(\text{dppe})\text{H}_4]^+$, without detection of any nonclassical intermediate, even upon working at 200K. On the other hand, use of even weaker proton donors (2,2,2-trifluoroethanol or TFE, 2-fluoroethanol or MFE) and low temperatures (200K), backed up

by a theoretical investigation, revealed that the most likely site of attack is a hydride ligand. The calculations, which were carried out in the $[\text{Cp}^*\text{Mo}(\text{dhpe})\text{H}_3]$ model system ($\text{dhpe} = \text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2$), could also locate the nonclassical protonation product, $[\text{Cp}^*\text{Mo}(\text{dhpe})(\eta^2\text{-H}_2)\text{H}_2]^+$, in a shallow energy minimum and showed that its rearrangement to the more stable (by 1.5 kcal mol⁻¹ in the gas phase, 1.7 kcal mol⁻¹ in CH_2Cl_2 solution) classical tetrahydrido product occurs with an extremely small activation barrier of 1.8 kcal mol⁻¹ in the gas phase (1.3 kcal mol⁻¹ by use of the PCM in CH_2Cl_2).^[29] Thus, it appears that this complex undergoes a kinetically favored protonation of a hydride ligand, but the resulting dihydrogen complex does not accumulate at sufficiently high concentration for detection before rearranging to the final tetrahydrido product.

It is of interest to investigate trends of fundamental properties for series of compounds with the same stoichiometry for metals within the same group. This kind of knowledge for hydrogen bonding and proton transfer to transition metal hydrides is still scarce, the only two series of hydrides studied up to date being PP_3MH_2 ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$; $\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$)^[32, 33] and $\text{Cp}^*\text{MH}(\text{dppe})$ ($\text{M} = \text{Fe}, \text{Ru}$).^[24, 25, 27] Thus, we have proceeded to investigate the behavior of $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ hydride^[31] in terms of hydrogen bonding and proton transfer. The results of this investigation and a comparison with those previously described for the Mo analogue are reported here.

Results

The investigation of hydrogen bonding and proton transfer to complex $[\text{Cp}^*\text{WH}_3(\text{dppe})]$ followed a combined spectroscopic and theoretical protocol, similar to that used previously for complexes $[\text{Cp}^*\text{M}(\text{dppe})\text{H}]$ ($\text{M} = \text{Fe}, \text{Ru}$),^[24, 25, 27] $[\text{Cp}^*\text{Mo}(\text{dppe})\text{H}_3]$,^[29, 30] and $\text{CpRuH}(\text{CO})(\text{PCy}_3)$.^[34]

1. Study of the starting trihydride complex

The synthesis and full characterization of this compound has been reported previously.^[31, 35] An X-ray structure was reported for the Mo analogue and the similarity of the spectroscopic properties and chemical behavior leave no reason to suspect that the structure may be different for the W trihydride complex. It must be underlined that $[\text{Cp}^*\text{Mo}(\text{dppe})\text{H}_3]$ adopts a pseudo-trigonal prismatic structure (once the Cp^* ligand is idealized as occupying a single coordination position coinciding with the ring centroid), instead of the much more common pseudo-octahedral arrangement. However, the same geometry has since been observed for other isoelectronic half-sandwich hydride complexes of Group 6 metals, i.e. $[(\text{C}_5\text{H}_6\text{Pr}_4)\text{Mo}(\text{PMe}_3)_2\text{H}_3]$ ^[36, 37] and $[\text{WCp}^*(\text{CO})_2\text{H}_2(\text{SiH}_2\text{Ph})]$.^[38] The adoption of the same structure by $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ was also suggested by subsequent DFT geometry optimizations, which were run at the B3LYP/LANL2DZ level, on the smaller $[\text{Cp}^*\text{W}(\text{dhpe})\text{H}_3]$ model system in which the methyl groups of the cyclopentadienyl ring and the phenyl rings of the dppe ligand were substituted by hydrogens.^[39]

In order to compare the structure of the trihydride compound with those of the hydrogen bonded adducts and proton transfer products, and in order to analyze the computational results in greater details, the optimization of the same model complex $[\text{Cp}^*\text{WH}_3(\text{dhpe})]$ has been repeated with a more extensive basis set (see Computational Details) and has included the frequency calculations. Furthermore, selected calculations have been carried

out on the real complex to check the appropriateness of the smaller model. Cartesian coordinates of all optimized geometries are available in the Supporting Information.

As expected, the calculated structural parameters closely match those obtained with the previous calculations and experimentally obtained for the Mo analogue, while the spectroscopic parameters resemble those found for the molybdenum congener.^[29] A view of the optimized geometry is shown in Figure 1. As is perhaps best appreciated from the top view on the right hand side, the three hydride ligands are asymmetrically disposed, one on one side and two on the opposite side of the plane that contains the two P donors and the Cp* ring centroid. Atoms H1 and H2, although being situated rather symmetrically across the ideal plane that contains atoms W, H3 and the ring centroid, are not equivalent in terms of the W-H distances and Mulliken charges, H1 being closest to the metal atom and possessing a higher negative charge than H2. The unique H3 atom exhibits the longest W-H distance and bears the highest negative charge, thus clearly appearing as the most hydridic site.

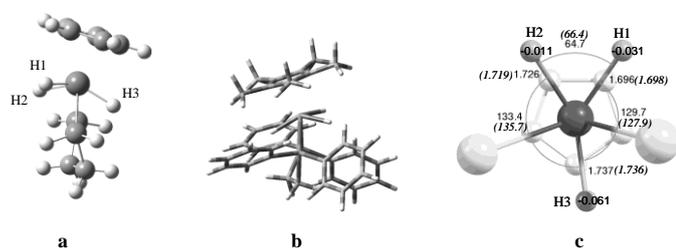


Figure 1. Optimized geometry of [CpW(dhpe)H₃] (a), [Cp*W(dppe)H₃] (b) and main geometrical parameters (distances in Å, angles in degrees) for the WH₃ moiety (c). The values in parentheses correspond to those optimized for the full system. The numbers on the three H atoms are the computed Mulliken charges.

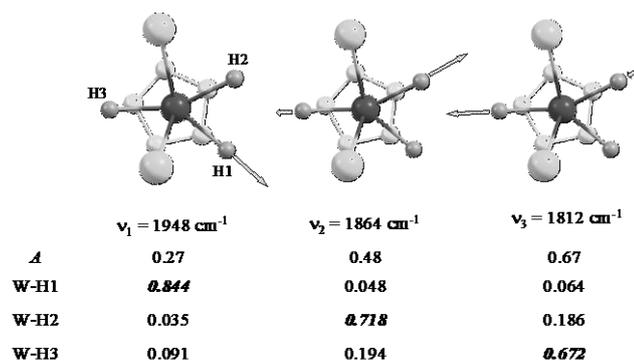


Figure 2. The W-H normal modes of the DFT optimized [CpW(dhpe)H₃] with their frequency, intensity (A, 10⁴ L mol⁻¹cm⁻²), and potential energy distribution (major components are in **bold italic**). The Cp- and P-bonded H atoms and ethylene backbone have been omitted for clarity.

An IR study of complex [Cp*WH₃(dppe)] was also previously reported,^[39] although the low spectral quality prevented an unambiguous assignment of the three expected normal modes for the WH₃ moiety. Therefore, a higher quality spectrum has now been obtained. Like its molybdenum analogue, [Cp*WH₃(dppe)] displays a wide ν_{MH} band of complex shape, which is superimposed with a few weaker features belonging to overtones of the phenyl group vibrations. A band decomposition, performed after subtraction of the dppe spectrum, shows the presence of three ν_{MH} vibrations: 1964w, 1882m, 1846s cm⁻¹ in THF; 1959w, 1873s, 1822s cm⁻¹ in CH₂Cl₂

(see Figure 1S in the Supporting Information). These were assigned on the basis of the computation of the W-H normal modes, which are represented schematically in Figure 2. Thus, the higher-energy normal mode (ν_1) is essentially a pure stretching vibration of the hydride ligand H1, which shows the shortest (and therefore strongest) bond. The other two vibrations are relatively close to each other in frequency and are a mixture of the other two M-H bond vibrations, the higher-frequency one (ν_2) being an in-phase combination with the major contribution from the shorter bond to H2, and the lower-frequency one (ν_3) being an out-of-phase combination with the major contribution from the longer bond to H3. The intensities of the ν_{MH} bands increase as the temperature is decreased. The absorbance of the strongest band changes upon cooling from 270 to 200 K from 59.5 to 75.9 L mol⁻¹ cm⁻¹ in THF and from 60.5 to 85.5 L mol⁻¹ cm⁻¹ in CH₂Cl₂.

2. Hydrogen bonding to [Cp*W(dppe)H₃] – Experimental information

The IR study of the interaction of [Cp*WH₃(dppe)] with MFE and TFE in CH₂Cl₂, carried in the ν_{OH} range, shows the appearance of the expected low-frequency shifted and quite broad ν_{OH} band for the hydrogen-bonded OH group. It is important to underline that these measurements are carried out with excess hydride, thus favoring the formation of 1:1 adducts. From the analysis of the ν_{OH} region of the spectrum, the hydrogen bond enthalpies, $-\Delta H^\circ$, were obtained by two independent methods, *i.e.* the empirical correlation outlined in Equation 1 and by the *Van't Hoff* method (Table 1).^[8, 40] Subsequent use of the Iogansen relationship^[41-43] gives the basicity factor E_j reported in Table 1, making [Cp*WH₃(dppe)] the most basic transition metal hydride compound reported so far.^[9] This justifies the observation that even the weakest fluorinated alcohol MFE is sufficiently acidic to afford equilibrium amounts of the proton transfer product in CH₂Cl₂ (*vide infra*).

Table 1. Parameters of the hydrogen bonding between Cp*WH₃(dppe) and MFE or TFE, basicity factors of the hydride complex.

ROH	$\nu_{\text{OH}}(\text{free})$ cm ⁻¹	$\nu_{\text{OH}}(\text{bonded})$ cm ⁻¹	$\Delta\nu$ cm ⁻¹	$\Delta\nu_{1/2}$ cm ⁻¹	ΔH^{a} [a] kcal mol ⁻¹	ΔH^{b} [b] kcal mol ⁻¹	ΔS^{b} [b] cal mol ⁻¹ K ⁻¹	E_j
MFE ^[c]	3608	3248	360	261	-6.0			1.74
TFE ^[c]	3604	3140	464	251	-7.1	-6.5±0.6	-18±2	1.72
HFIP ^[d]	3535					-7.6±0.9	-19±3	1.77

[a] ΔH^{a} parameter calculated by the empirical relationship of equation 1. [b] ΔH^{b} and ΔS^{b} parameters calculated by the *Van't Hoff* method. [c] in CH₂Cl₂. [d] in toluene. In this solvent maximum of $\nu_{\text{OH}}(\text{bonded})$ band is masked by ν_{CH} absorptions.

$$-\Delta H^\circ = \frac{18\Delta\nu}{\Delta\nu + 720} \quad (1)$$

In an attempt to establish which of the four possible sites, namely the W atom and the three hydride ligands, is used as proton acceptor site for hydrogen bonding, the IR spectra were analyzed in the ν_{MH} stretching vibration region in the presence of proton donors. Following previous studies, dihydrogen bonding (*i.e.* H bonding to a hydride site) results in a low frequency shift of the corresponding M-H stretching vibration band, whereas hydrogen bonding to a metal lone pair causes a high frequency shift.^[8, 9, 40] However, the mixing of bond vibrations in the normal modes for polyhydride

compounds makes the analysis of frequency shifts much more complicated. This was clearly demonstrated for the $[\text{Cp}^*\text{MoH}_3(\text{dppe})]\cdot\text{alcohol}$ system,^[29] where the interaction (excess MFE, CH_2Cl_2 , 200K) leads to broadening and to a small (-5 cm^{-1}) low-frequency shift of the ν_{MoH} band, attributed to the effect of dihydrogen bonding. For the present compound, similar and even more pronounced spectroscopic changes would be expected, due to the higher basicity of the tungsten hydride complex, if the H bonding site was the same as for the Mo analogue. Instead, a gradual high-frequency shift and an intensity decrease for the major ν_{WH} band of $[\text{Cp}^*\text{WH}_3(\text{dppe})]$ were observed in the presence of the increasing amounts of MFE in CH_2Cl_2 at 200K the (Figure 3). However, no unambiguous band deconvolution was possible for these spectra because of the occurrence of partial proton transfer, even under these mild conditions. These spectroscopic changes underscore a difference between the nature of the H-bonded adduct for the homologous Mo and W trihydrides complexes, but the above mentioned problem of possible M-H vibration mixing in the normal mode requires caution for the extrapolation of these observations to a structural assignment.

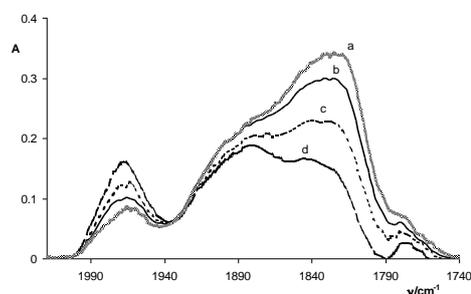


Figure 3. IR spectra of $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ (0.04 M) in the $\nu_{\text{W-H}}$ stretching region in the presence of MFE at the following concentrations: 0 M (a); 0.2 M (b); 0.4 M (c); 0.6 M (d). CH_2Cl_2 , 200K.

Additional experimental evidence was sought by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy using the interaction of $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ with HFIP in $[d_8]$ toluene. In the absence of proton donor the hydride signal of $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ (δ -5.99, 210K) exhibits a $T_{1\text{min}}$ of 0.425 s at 250 K (500 MHz). Upon addition of ca 2 equiv HFIP this signal does not significantly shift and its $T_{1\text{min}}$ is only ca. 10% lower (0.391 s at 250K). A summary figure of all T_1 measurements is available in the Supporting Information (Figure 2S). For unambiguous cases of hydrogen bonding to hydrides, an upfield shift and a significant (e.g. 20% or more) lowering of $T_{1\text{min}}$ is observed for the hydride resonance even for polyhydrides. For example, the magnitude of the high-field signal shifts and T_1 relaxation time measurements show preferential coordination of the alcohol to the central hydride of Cp_2NbH_3 .^[44] Similarly, upfield shift and $T_{1\text{min}}$ shortening found for one of the two hydride signals of PP_3OsH_2 ^[32] or $\text{H}_2\text{Re}(\text{CO})(\text{NO})(\text{PME}_3)_2$ ^[45] in the presence of fluorinated alcohols was interpreted as the evidence for dihydrogen bonding to the more hydridic hydride ligand. Thus, the NMR data, like the IR data, reported herein do not allow an unambiguous assignment of the H-bonding site. For these reasons, we have turned to a computational investigation of the H-bonding interaction.

3. Hydrogen bonding to $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ – a computational insight

The formation of hydrogen bonded adducts has been investigated with both TFE and HFIP, using the model $[\text{CpW}(\text{dhpe})\text{H}_3]$ system

for most investigations. Since previous studies have shown the importance of the cooperative effect of two proton donor molecules for the subsequent proton transfer process, selected calculations have also been carried out on bis-alcohol adducts. The evaluation of the interaction energies is subject to the basis set superposition errors (BSSE), especially in cases such as this one where the interaction is weak and the basis sets used are not very large.^[44] The typical counterpoise correction has been applied.^[46] In addition, the interaction energies were evaluated in dichloromethane solution by running single point calculations on the gas-phase optimized geometries with the polarizable continuum model (PCM).^[47, 48]

Four isomers, differing by the site of the hydrogen bond, were located for the $[\text{CpW}(\text{dhpe})\text{H}_3]\cdot\text{TFE}$ adduct (Figure 4). The greater complexity of the HFIP molecule leads to a greater number of stable configurations (Figure 5), which can however be related to those already found for the TFE adduct. Furthermore, all these structures can be related to those found earlier for $[\text{CpMo}(\text{dhpe})\text{H}_3]$ complexes with TFE and HFIP^[29] and thus they are given similar codes. The main structural and energetic results are collected in Table 2 (TFE) and Table 3 (HFIP). The calculated changes of stretching frequencies reflect the complexity of the structural and electronic changes upon H-bond formation for this polyhydride complex, at variance with the simpler trends exhibited in general by monohydride complexes.^[25, 49] Because of mixing of the W-H vibrations in the normal modes, no clear trend emerges as to the influence of the H-bonding site on the frequency shift of each mode. Therefore, these frequencies will not be analyzed in detail and are presented in the Supporting Information.

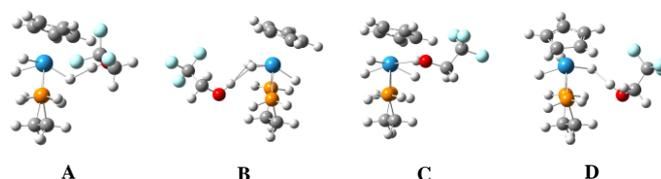


Figure 4. The optimized structures of the $[\text{CpW}(\text{dhpe})\text{H}_3]\cdot\text{TFE}$ adducts.

For complex **A** (TFE) / **A'** (HFIP), the proton donor interacts with the unique hydride ligand H3. These adducts are those showing the longest distance of the proton from the W atom. For adducts **B/B'**, the proton donor is on the other side of the P-W-P plane close to the hydride ligands H1 and H2. It interacts simultaneously with both W-H bonds, more strongly with one of the two (H2 for **B** and **B2'**, H1 for **B1'**), and the separation from the W atom is also relatively short. The O-H...H(W) angles are between 154° and 162° , and the O-H...W angles are in the 160 - 167° range. Notably, the W...H(O) distance in these adducts is shorter than in the related Mo complexes, thus suggesting the significant participation of the metal atom to H bonding.^[29] The **C** (TFE) and **C1'**, **C2'** (HFIP) isomers feature a nearly linear O-H...W moiety (172 - 177°) and the shortest (O)H...W distances and, thus, the strongest hydrogen bonds with the metal centre. The **C2'** isomer also shows a relatively short distance to H3 (1.809) and a relatively wide O-H...H3 angle (142.1°). The main interaction, however, is with the metal centre. Thus, it seems that a metal lone pair contributes the most to the interaction in these adducts. Finally, species **D/D'** feature very short W-H3...H(O) “dihydrogen bonds”. At a first glance, they should be considered together with adducts **A/A'**. However, an additional interaction with the tungsten atom in **D/D'** is evident from the rather short W...H(O)

distances and from the wide O-H...W angles, closer to linearity than O-H...H3. Species **C2'** and **D/D'** also show a significant tilting of the dhpe ligand toward the Cp ring, relative to free [CpW(dhpe)H₃]. Hydrogen bond formation also leads to an electron density shift, increasing the absolute value of the negative charge on the hydride ligand and/or tungsten atom involved in the interaction (see Tables 2, 3).

Table 2. Main energetic, structural, and charge parameters of the [CpW(dhpe)H₃]-TFE adducts. Energies are given relative to the separated reactants.

	A	B	C	D
$\Delta E_{\text{gas phase}} / \text{kcal mol}^{-1}$	-9.7	-11.9	-11.0	-8.5
$\Delta E_{\text{BSSE}} / \text{kcal mol}^{-1}$	-5.0	-8.4	-6.4	-4.1
$\Delta E_{\text{DCM}} / \text{kcal mol}^{-1}$	-1.3	-3.4	-3.3	-2.4
Dist. (O)H...H(W)/Å	1.742	2.126(H1) 1.771(H2)	2.273	1.673
Dist. (O)H...W / Å	3.040	2.882	2.816	2.925
$\angle \text{O-H}\cdots\text{H(W)}$	151.5	139.8 (H1) 161.8 (H2)	138.1	157.6
$\angle \text{O-H}\cdots\text{W}$	152.9	159.6	173.8	162.5
$r_{\text{W-H1}} / \text{\AA}^{[a]}$	1.693 (-0.003)	1.704 (0.008)	1.696 (0.000)	1.740 (0.044)
$r_{\text{W-H2}} / \text{\AA}^{[a]}$	1.733 (0.007)	1.718 (-0.008)	1.738 (0.012)	1.725 (-0.001)
$r_{\text{W-H3}} / \text{\AA}^{[a]}$	1.742 (0.005)	1.737 (0.000)	1.739 (0.002)	1.725 (-0.012)
$\Delta q_{\text{W}}^{[b]}$	-0.005	-0.106	-0.163	0.016
$\Delta q_{\text{H1}}^{[b]}$	0.002	-0.015	0.015	0.007
$\Delta q_{\text{H2}}^{[b]}$	0.003	-0.041	0.011	-0.040
$\Delta q_{\text{H3}}^{[b]}$	-0.064	0.011	0.003	-0.036

[a] Value of Δr ($r_{\text{compl}} - r_{\text{free}}$) in parentheses. [b] $\Delta q = q_{\text{compl}} - q_{\text{free}}$.

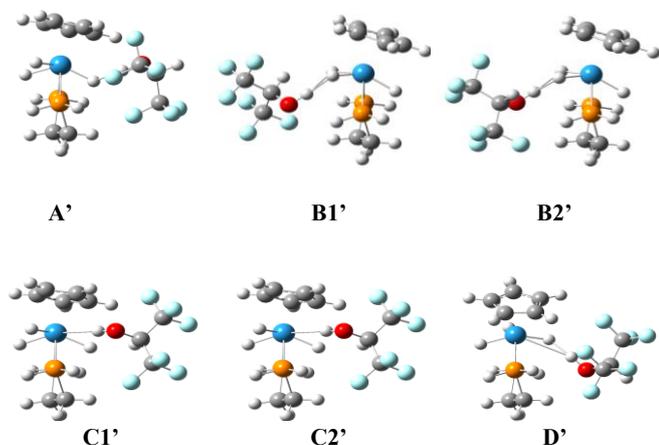


Figure 5. The optimized structures of the [CpW(dhpe)H₃]-HFIP adducts.

In order to have an insight on the proton transfer process, which requires the addition of two proton donor molecules (see kinetics section below), calculations were also carried out on bis-HFIP adducts, still using the smaller [CpW(dhpe)H₃] model. The details of these calculations are given in the Supporting Information. As expected,^[29, 34] the second HFIP molecule further stabilizes energetically the hydrogen bonded species by stabilizing the partial negative charge on the oxygen atom via the additional hydrogen bond with the second proton donor molecule. This O-H...O hydrogen bond further strengthens the primary [CpW(dhpe)H₃]-HFIP interaction, leading to shorter (W)H...H(O) and W...H(O) distances in structures **A''-D''** and to nearly linear W...H-O angles in structures **B''-D''**, illustrating the effect of cooperativity in hydrogen bonding.

The most stable adducts are **B** for TFE (-11.9 kcal mol⁻¹ relative to the separated species) and **B1'** for HFIP (-12.8 kcal mol⁻¹), involving the main interaction with a hydride ligand and the metal. However, the isomers involving the main interaction with the metal atom (**C** for TFE and **C1'** for HFIP) are only marginally less stable, whereas the adducts where the proton donor interacts mostly with the H3 site (**A/A'** and **D/D'**) are significantly less stable, in spite of the fact that this hydride ligand appears the most hydridic in the trihydride ground state structure (see Figure 1). Note that, for each pair of structurally related adducts, HFIP shows a stronger interaction than TFE by ca. 1 kcal mol⁻¹, in agreement with the stronger acidity of the former. In quantitative terms, the uncorrected gas phase values are too high, the gas-phase BSSE-corrected values are closer, whereas the values calculated using the polarizable continuum model for the solvent are too small. The ordering of the two most stable species is preserved upon introducing the BSSE correction and the PCM.

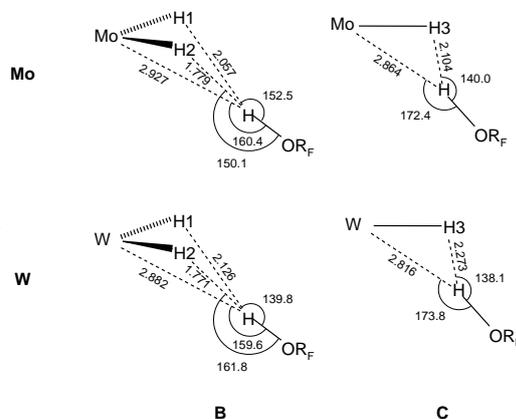


Figure 6. Comparison of H bond distances and angles for the [CpM(dhpe)H₃]-TFE adducts **B** and **C** (M = Mo, W).

The energy ordering found for the [CpW(dhpe)H₃]-TFE adducts parallels that previously observed for the corresponding [CpMo(dhpe)H₃]-TFE adducts.^[29] For each pair of structurally related adducts, the W complex shows a stronger interaction than the Mo analogue, in agreement with the stronger basicity of the former. The preference for **B** vs. **C** is nearly the same for the two metal systems. However, it is interesting to note that the relative contribution of the metal atom to the H-bonding interaction increases on going from Mo to W in both adducts **B** and **C** (see Figure 6). For both species, the H...H distance only marginally shortens (for H2 in **B**) or lengthens (for H1 in **B** and for H3 in **C**),

whereas significant shortening would be expected for dihydrogen bonding to a stronger base. At the same time, the M...H distance becomes significantly shorter on going from Mo to W. In conclusion, the calculations suggest that the preferred H-bonded species for the

[CpM(dhpe)H₃] (M = Mo, W) model complexes feature bifurcate interactions with both M and H, rather than with either a metal lone pair or hydride ligand solely. However, the metal atom contribution increases on going from Mo to W.

Table 3. Main energetic, structural, and charge parameters of the [CpW(dhpe)H₃]-HFIP adducts. Energies are given relative to the separated reactants.

	A'	B1'	B2'	C1'	C2'	D'
$\Delta E_{\text{gas phase}} / \text{kcal.mol}^{-1}$	-10.4	-12.8	-12.6	-12.3	-10.9	-9.6
$\Delta E_{\text{BSSE}} / \text{kcal.mol}^{-1}$	-4.9	-8.6	-8.1	-6.6	-5.3	-3.5
$\Delta E_{\text{DCM}} / \text{kcal.mol}^{-1}$	0.4	-3.0	-2.5	-1.7	-1.9	-0.6
Dist. (O)H...H(W) / Å	1.706	1.812 (H1) 1.919 (H2)	2.066 (H1) 1.688 (H2)	2.032	1.809	1.725
Dist. (O)H...W / Å	3.020	2.792	2.822	2.690	2.612	2.898
\angle O-H...HW	151.7	154.0 (H1) 140.8 (H2)	139.2 (H1) 158.0 (H2)	133.0	142.1	151.5
\angle O-H...W	150.6	166.9	164.2	172.8	176.7	158.9
$r_{\text{W-H1}} / \text{Å}^a$	1.694 (-0.002)	1.706 (0.010)	1.715 (0.019)	1.696 (0.000)	1.723 (0.027)	1.739 (0.043)
$r_{\text{W-H2}} / \text{Å}^a$	1.734 (0.008)	1.718 (-0.008)	1.708 (-0.018)	1.734 (0.008)	1.734 (0.008)	1.723 (-0.003)
$r_{\text{W-H3}} / \text{Å}^a$	1.743 (0.006)	1.736 (-0.001)	1.737 (0.000)	1.739 (0.002)	1.728 (-0.009)	1.724 (-0.013)
Δq_{W}^b	-0.005	-0.130	-0.102	-0.189	-0.149	0.024
Δq_{H1}^b	0.003	-0.014	-0.039	0.016	-0.002	0.012
Δq_{H2}^b	0.006	-0.067	-0.065	0.012	0.003	-0.038
Δq_{H3}^b	-0.084	0.016	0.014	-0.018	-0.037	-0.067

[a] Value of Δr ($r_{\text{compl}} - r_{\text{free}}$) in parentheses. [b] $\Delta q = q_{\text{compl}} - q_{\text{free}}$ [c] Calculated intensity in parentheses (A , $10^4 \text{ L mol}^{-1} \text{ cm}^{-2}$)

4. The proton transfer product, [Cp*W(dppe)H₄]⁺

The quantitative protonation of complex [Cp*W(dppe)H₃] by HPF₆ and the X-ray structure of the resulting product, [Cp*W(dppe)H₄]⁺PF₆⁻, have previously been described.^[31] The product adopts a classical tetrahydride structure. In the present study, we have investigated the proton transfer processes using fluorinated alcohols of different strength and *p*-nitrophenol, as well as the strong acid HBF₄. NMR investigations carried out at low temperature reveal that in all cases the tetrahydride product is formed directly, without the detection of any intermediate (notably non-classical species). This behavior is identical to that of the Mo analogue.^[29] Before discussing the details of the interaction with the weaker acids, we analyze in more detail the nature of the proton transfer product from the experimental and computational points of view.

The optimized geometry of the model [CpW(dhpe)H₄]⁺ complex (Figure 7) is in agreement with the X-ray data presented earlier for [Cp*W(dppe)H₄]⁺PF₆⁻.^[31] An even closer agreement is obtained by optimization of the system with the real ligands (Figure 7). This geometry is also very close to that optimized for the analogous Mo complex.^[29] A second, higher-energy isomer has also been located (see details in the Supporting Information). On the other hand, at variance with the Mo analogue, no stable minimum could be located for a nonclassical isomer, namely a dihydrogen complex of type [CpW(dhpe)(η^2 -H₂)H₂]⁺. This is in line with the preference of (early) third row transition metal polyhydrides to exist as classical species.^[50,51]

The only previous theoretical work addressing the metal influence on hydrogen bonding is the study of dihydrogen bonded complexes of MH(CO)₂(NO)(PH₃)₂ (M = Mo, W) with HF by Orlova and Scheiner.^[49] Their B3PW91 computations revealed the dihydrogen bonded complex of tungsten hydride being only 0.3 kcal mol⁻¹ more stable than that of molybdenum. The presence of strong π -accepting ligands, CO and NO, makes the metal atom in these hydride complexes a poor proton acceptor, hence the relatively short M...H(F) contact found is only an additional interaction, which, in contrast to the trihydrides discussed herein, lengthens on going from MoH...HF to WH...HF adduct.

The coordination geometry of the energy minimum can be viewed as a distorted pentagonal bipyramid, with four hydride ligands and one of the phosphorus atoms describing the pentagonal plane and the second phosphorus atom and the Cp* ring centroid in the axial positions. The hydride ligands bear similar small positive Mulliken charges of ca. 0.06 units, but are different in terms of distance to the metal (Figure 7). Correspondingly, the frequency calculations give two pairs of normal modes, which can be described as symmetric and asymmetric stretching vibrations involving pairs of equivalent hydrides (Figure 8). This is in good agreement with the experimentally observed spectrum of [Cp*W(dppe)H₄]⁺BF₄⁻, which features two lower and two higher intensity bands after the subtraction of dppe overtones (see Figure 3S in the Supporting Information).

The proton affinity of the tungsten trihydride, calculated as $-\Delta H$ (298 K) for the reaction with H⁺, is 255.1 kcal mol⁻¹ in respect to more stable [CpWH₄(dhpe)]⁺ isomer, being only 15 kcal mol⁻¹ higher than that for the analogues molybdenum complex (240.3 kcal mol⁻¹). When taking into account the real system, the proton affinities of the metal hydrides increase by about 20 kcal mol⁻¹ for both the tungsten and the molybdenum complexes, being 274.5 kcal mol⁻¹ and 263.2 kcal mol⁻¹ respectively.

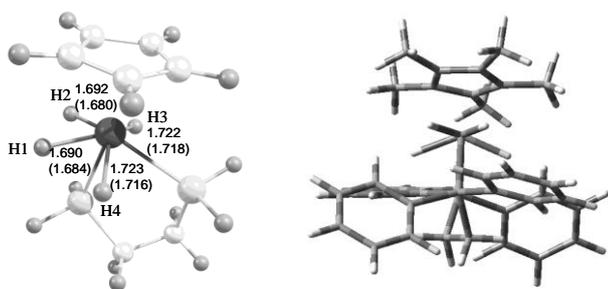


Figure 7. Optimized geometry of the $[\text{Cp}^*\text{WH}_4(\text{dppe})]^+$. W-H bond lengths are in Å. The values in parentheses correspond to those optimized for the real cation (structure on the right).

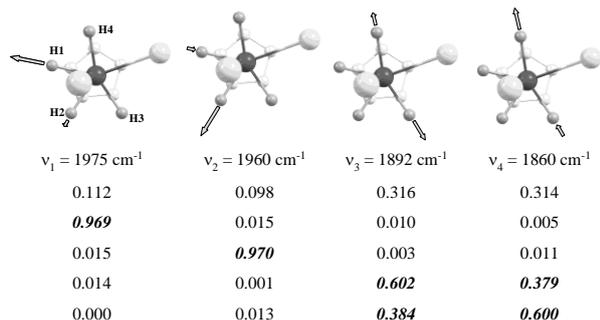


Figure 8. W-H normal modes of the DFT optimized $[\text{Cp}^*\text{WH}_4(\text{dppe})]^+$ with their frequency, intensity (A, $10^4 \text{ L mol}^{-1} \text{ cm}^{-2}$), and potential energy distribution (major components are in **bold italic**). The Cp- and P-bonded H atoms and ethylene backbone have been omitted for clarity.

5. Experimental study of the proton transfer thermodynamics

As mentioned above, the interaction of $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ with fluorinated alcohols results in partial protonation, whose extent depends on the proton donor strength and amount. The proton transfer equilibrium for the $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]/\text{HFIP}$ system was investigated in toluene by UV spectroscopy in the 190-240 K range. The trihydride complex shows a wide band at 425 nm ($\Delta\lambda_{1/2} = 100 \text{ nm}$) with an extinction coefficient of $2128 \text{ M}^{-1} \text{ cm}^{-1}$, whereas the tetrahydride complex has a negligible absorption in this region (Figure 9). The UV-visible properties of the hydrogen-bonded complexes are essentially indistinguishable from those of the free hydride complex.^[24, 29] Upon addition of 3 equiv HFIP at 190 K, 90% of the complex converts to the tetrahydride product, leading to a decrease of the absorption intensity. This intensity slowly increases upon heating, demonstrating the reversibility of the proton transfer process, the equilibrium shifting toward the trihydride complex as the temperature increases. These spectral changes allowed the calculation of the proton transfer equilibrium constants (Equation 2) assuming that the ionic complex has the same 1:1 composition as determined for *p*-nitrophenol (*vide infra*).

Taking into account the K_1 constants determined by IR spectroscopy for the hydrogen bond formation (*vide supra*), the van't Hoff analysis yielded the proton transfer equilibrium constant in toluene, K_2 , at each temperature and consequently $\Delta H_2 = -3.9 \pm 0.3 \text{ kcal mol}^{-1}$ and $\Delta S_2 = -17 \pm 2 \text{ cal mol}^{-1} \text{ K}^{-1}$. Unfortunately, no direct comparison can be made to thermodynamics of hydrogen bonding and proton transfer of other systems ($[\text{Cp}^*\text{FeH}(\text{dppe})] + \text{HFIP}$,^[25] or $[\text{Cp}^*\text{MoH}_3(\text{dppe})] + \text{TFE}$ ^[29]) because the latter have been obtained in a more polar solvent – CH_2Cl_2 . Yet, considering that the less polar toluene solvent should disfavor proton transfer, the present

system – $[\text{Cp}^*\text{WH}_3(\text{dppe})] + \text{HFIP}$ – gives the highest proton transfer enthalpy value in agreement with the greater basicity of the trihydride complex.

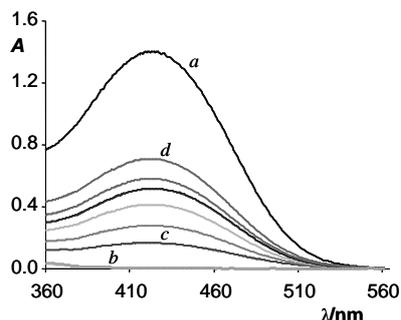


Figure 9. UV-visible spectra of $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ (0.0015 M in toluene, 0.22 cm cell): (a), alone; (b) $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]^+[\text{OCH}(\text{CF}_3)_2]^-$ obtained by addition of 30 equiv HFIP and (c-d) in the presence of HFIP (0.0045 M) every 10 K temperature increments in the 190 – 240K range.



The $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ protonation was also investigated using *p*-nitrophenol (PNP). This proton donor has the advantage of being a convenient chromophore, with an absorption band centered at quite different positions in the visible region as a function of protonation state (neutral phenol, H-bonded phenol, H-bonded or free anion). The exact band positions and extinction coefficients are solvent and temperature dependent: e.g. *p*-nitrophenol (PNP) absorbs at 309-318 nm ($\ln \varepsilon = 9.36-9.57$) in THF, at 305-312 nm ($\ln \varepsilon = 8.99-9.21$) in CH_2Cl_2 ,^[25] and at 300-310 nm ($\ln \varepsilon = 7.50-7.67$) in toluene in the 290-200K range. The *p*-nitrophenolate anion (as Bu_4N^+ salt) shows a band at 430-425 nm ($\ln \varepsilon = 10.22-10.24$) in THF, and at 433-428 nm ($\ln \varepsilon = 10.21-10.22$) in CH_2Cl_2 in the same range.

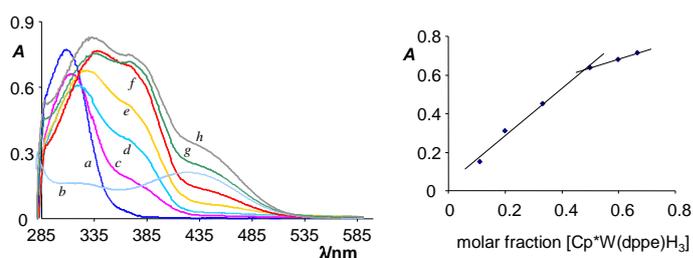


Figure 10. Left: UV-visible spectra (toluene solution, 200 K, 0.12 cm cell) of: (a) *p*-nitrophenol ($3 \cdot 10^{-4} \text{ M}$); (b) $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ ($3 \cdot 10^{-4} \text{ M}$); (c-h) *p*-nitrophenol in the presence of increasing amount of $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$: $3.7 \cdot 10^{-5} \text{ M}$ (c), $7.5 \cdot 10^{-5}$ (d), $1.5 \cdot 10^{-4}$ (e), $3 \cdot 10^{-4}$ (f), $4.5 \cdot 10^{-4}$ (g), $6 \cdot 10^{-4}$ (h). Right: intensity changes at 380 nm.

As was previously observed for other hydrides interacting with *p*-nitrophenol ($[\text{Cp}^*\text{FeH}(\text{dppe})]$,^[25] $[\text{Cp}^*\text{MoH}_3(\text{dppe})]$,^[29] and $[\text{PP}_3\text{MH}_2]$ ^[33] with $\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ and $\text{M} = \text{Fe}, \text{Ru}$ and Os), the UV-visible spectra of PNP/ $[\text{Cp}^*\text{WH}_3(\text{dppe})]$ mixtures at 200K in toluene exhibit a wide band of a complex shape, resulting from the overlap of three bands of PNP in its different forms: free phenol (310 nm), hydrogen-bonded phenol (339 nm), phenolate (376 nm), as well as the broad band of the trihydride complex at 425 nm. The phenolate band is blue-shifted from the free *p*-nitrophenolate band by 36 nm, because of hydrogen bonding to $[\text{Cp}^*\text{WH}_4(\text{dppe})]^+$. A

titration experiment (Figure 10) allowed to establish the 1:1 stoichiometry of hydrogen-bonded ion pair $[\text{Cp}^*(\text{dppe})\text{WH}_4]^+\cdots[\text{OAr}]^-$.

Note that an analogous study of complex $[\text{Cp}^*\text{Fe}(\text{dppe})\text{H}]$ showed instead a 1:2 bonding stoichiometry, suggesting formation of a hydrogen bonded ion pair between the non-classical cation and the homoconjugated anion $[\text{Cp}^*\text{Fe}(\eta^2\text{-H}_2)(\text{dppe})]^+\cdots[\text{ArOHOAr}]^-$,^[25] whereas the molybdenum analogue $[\text{Cp}^*\text{Mo}(\text{dppe})\text{H}_3]$ shows again formation of a 1:1 ion pair with the *p*-nitrophenolate, $[\text{Cp}^*(\text{dppe})\text{MoH}_4]^+\cdots[\text{OAr}]^-$.^[29]

The interesting solvent effect was noted for this system then THF was used. The equilibrium between PNP and $[\text{Cp}^*\text{WH}_3(\text{dppe})]$ or PNP-anion and $[\text{Cp}^*\text{WH}_4(\text{dppe})]^+\text{BF}_4^-$ (at 1:1 ratios) appeared to be completely shifted to the left in this solvent (envelop of the overlapping bands of “free” PNP and $[\text{Cp}^*\text{WH}_3(\text{dppe})]$ were observed in both cases), probably due to highly favored specific solvation of the phenol (hydrogen bonding PNP·THF).

6. Kinetics of the proton transfer process

The kinetics of $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ protonation was investigated by stopped-flow with UV-visible detection in CH_2Cl_2 and toluene. The kinetics was studied at variable WH_3/HOR^F ratios under pseudo-first order conditions (large alcohol excess). The reaction with TFE, HFIP and PFTB was explored, but only the data obtained for PFTB lead to the reliable results. The representative plots are shown in Figure 11. Surprisingly, a non linear dependence on the HOR^F concentration was found for the observed rate constant, k_{obs} , in contrast to our previous kinetics studies on $[\text{Cp}^*\text{Fe}(\text{dppe})\text{H}]$.^[24]

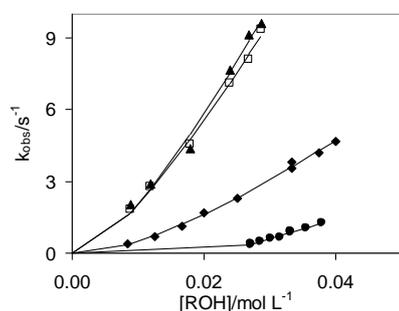
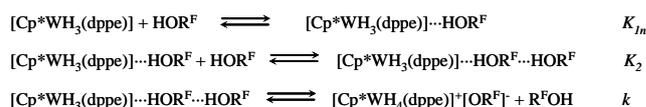


Figure 11. Dependence of the observed rate constant for the $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ protonation on the ROH concentration. ROH = HFIP in toluene at 293 K (circles), PFTB in toluene at 293 K (diamonds), CH_2Cl_2 at 288K (triangles), and CH_2Cl_2 at 283 K (open squares). The solid lines correspond to the fitting according to Equation 4 (see text).

A straightforward rationalization of this behavior is possible on the basis of the previously established kinetic model, which is shown in Scheme 2. The resulting expression for the observed rate constant is in Equation 3. The last term (proportional to the 1:2 adduct) can reasonably be neglected to yield Equation 4. According to this model, the $[\text{R}^F\text{OH}]$ dependence is function of the hydrogen bonding equilibrium: under conditions in which the dominant species is free hydride, the expression simplifies to yield a second order dependence on $[\text{R}^F\text{OH}]$, whereas a first order behavior is expected if the dominant species is the 1:1 adduct, $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]\cdots\text{HOR}^F$. The observed behavior is consistent with Equation 4, where the two terms in the denominator (proportional to

free hydride and 1:1 adduct) are equally important, which allows a reasonable fit of the kinetics data, as shown in Figure 11.



Scheme 2. Kinetic model for the proton transfer to $\text{Cp}^*\text{WH}_3(\text{dppe})$.

$$k_{\text{obs}} = \frac{K_1 K_2 k [\text{R}^F\text{OH}]^2}{1 + K_1 [\text{R}^F\text{OH}] + K_1 K_2 [\text{R}^F\text{OH}]^2} \quad (3)$$

$$k_{\text{obs}} \sim \frac{K_1 K_2 k [\text{R}^F\text{OH}]^2}{1 + K_1 [\text{R}^F\text{OH}]} \quad (4)$$

The two independent parameters adjusted by the least-squares fitting are K_1 (in L mol^{-1}) and $(K_2 k)$ (in $\text{s}^{-1} \text{L mol}^{-1}$), which are given in Table 4. The $K_2 k$ parameter can be treated as an effective rate constant since the individual values of K_2 and k are highly dependent on each other making it impossible to derive them on the basis of these data. The values resulting from the data fitting for HFIP carry large uncertainties; no reasonable values could be obtained for the reaction with this alcohol in CH_2Cl_2 . However, we include herein the data in toluene to discuss them at the qualitative level.

The values of hydrogen bond formation constants, K_1 , are in agreement with those estimated using H-bond enthalpy and entropy values obtained from IR data. Their increase on going from HFIP to PFTB is consistent with the greater proton donor ability in H-bonding of PFTB. The K_1 values also increase from toluene to dichloromethane, as one could expect basing on the ability of toluene to bind proton donors and therefore to lower their activity in hydrogen bonding.^[45, 52] The effective rate constants, $K_2 k$, are higher for PFTB than for HFIP in agreement with the stronger acidity of the former. The reaction rate substantially increases in more polar dichloromethane, the $K_2 k$ values being more than 2 times higher in this solvent than in toluene even at slightly lower temperatures.

It is also interesting to compare the above results with those obtained in the corresponding proton transfer by HFIP and PFTB to $[\text{Cp}^*\text{Fe}(\text{dppe})\text{H}]$.^[24] For the Fe system, more marked first order behaviour was observed for both proton donors. This is probably not related to greater K_1 values, because the iron hydride complex is a weaker base ($E_j = 1.36 \pm 0.02$) than the tungsten trihydride complex. Rather, it is related to the greater $[\text{R}^F\text{OH}]$ used in that study (in the 0.05-0.2 M range). The effective rate constants, $K_2 k$, are higher for $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ than for $[\text{Cp}^*\text{Fe}(\text{dppe})\text{H}]$ in agreement with higher basicity of the tungsten complex and stronger interaction at the first reaction step – hydrogen bonding. The other notable difference between the two systems is that for the iron compound $K_2 k$ changes by more than one order of magnitude on going from PFTB to HFIP in CH_2Cl_2 (156 and $5.4 \text{ s}^{-1} \text{L mol}^{-1}$, respectively), whereas the values are more similar for the tungsten trihydride complex and are markedly higher at that. This difference could be due to a smaller discrimination of the proton donor strength in the case of more basic W compound.

Table 4. Hydrogen bond formation and proton transfer rate constants for the reaction of [Cp*W(dppe)H₃] with alcohols.

R ^F OH	solvent	T/ K	K ₁ / L mol ⁻¹	K ₂ k/ s ⁻¹ L mol ⁻¹	ΔG [‡] / kcal mol ⁻¹
HFIP	toluene	293	13	165	14.2
PFTB	toluene	293	31	214	14.0
PFTB	CH ₂ Cl ₂	288	62	528	13.3
PFTB	CH ₂ Cl ₂	283	75	463	13.1

The values of k_{obs} do not greatly change with temperature (see e.g. Figure 11). This is probably due to simultaneous dependence of K_1 , K_2 and k on temperature: whilst the two equilibrium constants are expected to decrease with a temperature increase (the H-bond formation is exothermic), the proton transfer rate constant increases. Thus two effects cancel each other. The activation free energy, ΔG^\ddagger , values calculated from the rate constants in Table 4 are notably lower than those for the above mentioned [Cp*Fe(dppe)H] system in CH₂Cl₂ ($\Delta G^\ddagger_{298\text{ K}} = 14.5$ kcal mol⁻¹ for PFTB and 16.5 kcal mol⁻¹ for HFIP).

7. Computational study of the proton transfer process

In order to estimate the energy barrier and the energy gain associated to the proton transfer process, the reaction coordinate leading from the hydrogen bonded species to the tetrahydride product has been studied both in gas phase and in CH₂Cl₂ by computational methods. The calculations explain how several factors, namely ion-pairing, alcohol strength, substituent (Me, Ph) and solvent effects, contribute to the product stabilization, resulting in the net exothermic proton transfer process observed for the real system.

As mentioned in section 4, [CpWH₃(dhpe)] possess quite high proton affinity (energy of the reaction with H⁺ is highly negative). But then two neutral species (the trihydride and the alcohol) are converted to two isolated charged species in the gas phase the proton transfer products are highly destabilized because of the charge separation (Table 5). This energy penalty, ΔE_{PT} , is lowered when considering the effect of a second alcohol molecule, which affords a hydrogen-bonded (ROH)₂ species on the side of the reactants and a homoconjugate anion, (RO⁻H⁺OR⁻) on the side of the product. As the presence of the methyl substituents on the Cp ring and the phenyl one on the P-ligands allows a better stabilization of the positive charge, these energies appeared being substantially lower for the real system. As may be expected, the acidic strength of the proton donor also affects considerably the thermodynamics of the proton transfer, making it more favourable on going from TFE to HFIP. Finally, the solvent plays a major role in stabilizing the charged species: calculations with the polarizable continuum model (PCM) in CH₂Cl₂ show the markedly reduced the endothermicity. As the result for the reaction of Cp*WH₃(dppe) with two HFIP molecules in CH₂Cl₂ the separated ions are found 11.5 kcal mol⁻¹ below the neutral reactants.

Until now we have considered separated anion and cation as the product, but ion-pair formation between the tetrahydride cation and the anion may be expected in CH₂Cl₂ solution. Thus, ion pairs with one and two HFIP units were optimised for the model and real cations (for the latter structures see Figure 5S in Supporting Information). Formation of hydrogen bonded ion pair with HFIP-

anions is highly favourable not only in the gas phase, but in solution as well (Table 5). Note that the ion pairing energy, ΔE_{IP} , is lower for the homoconjugate anion, [(CF₃)₂CHO⁻⋯H⁺⋯OCH(CF₃)₂]⁻, in agreement with its lower basicity relative to simple [(CF₃)₂CHO]⁻. This can also be appreciated from the (W)H⁺⋯O distances (with one HFIP the H⁺⋯O distance is 2.460 Å, and with two, the distance from the two oxygen atoms are 3.143 and 3.166 Å) As the result of the ion pairing stabilization, the proton transfer reaction energy, $\Delta E'_{\text{PT}}$, becomes less endothermic and even exothermic and remains such in solution. Notably, despite the destabilization of all the species, passing from the gas phase to solution makes the proton transfer reaction more favorable.

Table 5. Calculated proton transfer reaction energies (in kcal mol⁻¹)

	ion pairing energy, ΔE_{IP} ^[a]		proton transfer energy, ΔE_{PT} ^[b]		proton transfer energy, $\Delta E'_{\text{PT}}$	
	ion pair	in CH ₂ Cl ₂	separated ions	in CH ₂ Cl ₂	Ion pair	in CH ₂ Cl ₂
CpWH ₃ (dhpe)						
TFE			118.9	36.2		
(TFE) ₂			88.7	22.9		
HFIP	-95.7	-15.1	98.0	22.0	13.3 (2.3) ^[c]	8.7 (6.9)
(HFIP) ₂	-74.0	-7.0	61.0	1.3	1.7 (-13.0) ^[d]	-3.1 (-5.7)
Cp*WH ₃ (dppe)						
(TFE) ₂			99.2	28.6		
HFIP	-81.8	-13.5	78.4	14.3	8.7 (-3.4) ^[e]	4.7 (0.8)
(HFIP) ₂	-65.0	-8.4	41.4	-11.5	-7.4 (-23.6) ^[e]	-11.4 (-19.9)

[a] Relative to the separated ions. [b] Relative to the separated neutral reactants. [c] Ion pair relative to the H-bonded adduct C2' presented in the reaction coordinates (Figure 12) and, in parentheses, to the separated neutral reactants. [d] Ion pair relative to the H-bonded adduct D'' presented in the reaction coordinates (Figure 13) and, in parentheses, to the separated neutral reactants. [e] For the structures see Figure 5S in Supporting Information.

In order to estimate the energy barrier associated to the proton transfer process, the reaction coordinate leading from the hydrogen bonded species to the tetrahydride product has been studied both in gas phase and in CH₂Cl₂ by computational methods. The proton transfer process from HFIP to the model complex, [CpWH₃(dhpe)], has been the subject of a more complete investigation along the proton transfer pathway, using the O-H distance of the HFIP molecule as the key parameter. Species C2', featuring the interaction with the W and H3 atoms, was chosen for the proton transfer coordinate study by analogy to the previous Mo study.^[29] The results obtained in the gas phase and in dichloromethane are presented in Figure 12. The coordinate presents a maximum at 18.7 kcal mol⁻¹ in gas phase, and of 14.9 kcal mol⁻¹ in CH₂Cl₂, for an O-H distance of 1.7 Å. The W-H distance is 1.786 Å and the distance between the transferring proton and the closest hydride is 1.855 Å. Thus, there is no indication for the formation of a nonclassical H₂ complex along this proton transfer pathway.

The minimum located at the end of the reaction coordinate presents a close geometry to that of the isolated tetrahydride complex, the W-H distances being 1.695, 1.693, 1.693 and 1.724 Å (cf. 1.690, 1.692, 1.722, and 1.723 for the isolated tetrahydride complex). The deprotonated base of the proton donor is still in proximity and interacts with the ligands. Instead of the expected (W)H \cdots O(R_F) bond, the oxygen atom is located near a phosphine group, (P)H \cdots O(R_F) = 2.457 Å, while the newly formed W-H bond is in close proximity of one of the anion C-H bonds, (W)H \cdots H(C) = 2.084 Å. This result is obviously related to the use of the dhpe model. The barriers calculated for this process are sensibly lower than those for the same process occurring at the analogous Mo complex (24.7 and 22.8 kcal mol⁻¹ in the gas phase and in CH₂Cl₂, respectively).^[29]

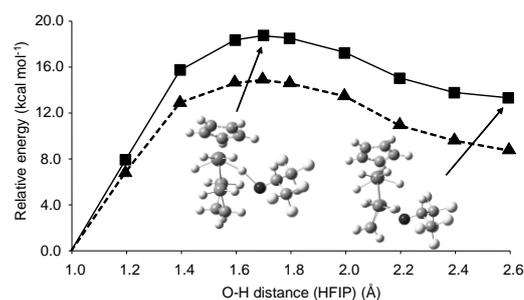


Figure 12. Proton transfer reaction coordinate for species **C2*** in the gas phase and in dichloromethane. Plain curve and squares: in the gas phase; dashed line and triangles: in dichloromethane solution. The O-H length of the transferring proton has been taken as the reaction coordinate.

Since the proton transfer reaction from fluorinated alcohols was shown to involve the active participation of a second proton donor molecule (vide supra) we have also investigated the reaction coordinates considering two HFIP molecules. Two [Cp*W(dhpe)H₃] \cdot 2(HFIP) minima (**C2*** and **D***), see Supporting Information) were chosen for this study. **C2*** is configurationally related to that of above described investigation with a single HFIP molecule, except that the interaction is stronger with W and weaker with H₃, whereas **D*** exhibits a much stronger interaction with H₃ ligand and a weaker one with W. Both pathways yield an earlier maxima on the proton transfer reaction coordinates and lower energy barriers than the pathway involving a single HFIP molecule, paralleling the results reported previously for the (Cp*Fe(dppe)H+2CF₃COOH) and (Cp*Mo(dppe)H₃+2HFIP) systems.^[29] The lower energy pathway is that resulting from adduct **D***, the results being presented in Figure 13 (those obtained from **C2*** are presented in the Supporting Information). The maximum of the potential energy curve is located at 8.7 kcal mol⁻¹ in the gas phase and 8.8 kcal mol⁻¹ in dichloromethane, for an O-H distance of 1.3 Å (cf. 10.6 and 9.0 kcal mol⁻¹, respectively, for the **C2*** pathway). These barriers are lower than those calculated for the Mo system (11.2 and 9.4 kcal mol⁻¹ in the gas phase and in dichloromethane, respectively). The geometry of the maximum shows a small H-H distance of 1.102 Å and a W-H distance for the transferring proton of 2.215 Å. Thus, this structure may be described as an asymmetric nonclassical species. However, no stable minimum corresponding to a nonclassical intermediate could be located along the proton transfer pathway. The product of the proton transfer shows once again the geometry of the stable tetrahydride minimum, with W-H distances of 1.725, 1.698, 1.686, 1.710 Å, with weak interaction with the anionic group through the transferred

hydride ligand, (W)H \cdots O = 2.384 Å, and the phosphine H atom, (P)H \cdots O = 2.083 Å.

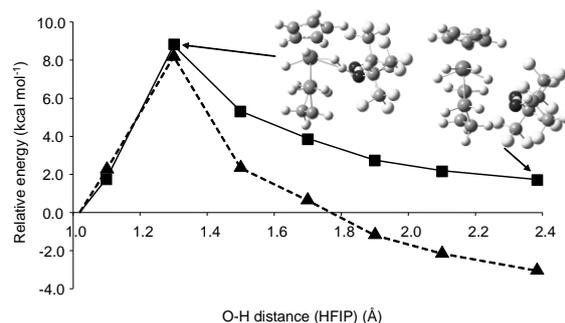


Figure 13. Proton transfer reaction coordinate for species **D*** in the gas phase and in dichloromethane. Plain curve and squares: in the gas phase; dashed line and triangles: in dichloromethane solution. The O-H length of the transferring proton has been taken as the reaction coordinate.

Discussion

The main interest of this work resides in the comparison of basicity, hydrogen bonding, and proton transfer mechanism of the two homologous complexes [Cp*M(dppe)H₃] (M = Mo, W). The two compounds adopt an identical structure and are reversibly protonated to yield an identical classical tetrahydrido product, [Cp*M(dppe)H₄]⁺, without the detection of a nonclassical intermediate. However whereas the Mo complex can lose H₂ in coordinating solvents or in the presence of coordinating anions,^[30, 31] the W complex is stable under the same conditions.^[31] Thus, a reasonable question is whether the preferred position of hydrogen bonding and proton transfer may be the metal site and whether the reaction mechanism may be different for two metal hydrides. For the Mo species, the experimental results^[29] suggest that the hydrogen bonding occurs at a hydride ligand, and an additional interaction with the metal atom is revealed by calculations. But this H-bonded intermediate leads to the final classical tetrahydride product without an experimental detection of an intermediate dihydrogen complex, [Cp*Mo(dppe)(η^2 -H₂)H₂]⁺. Calculations on the proton transfer pathway for the model [CpMo(dhpe)H₃] system revealed the existence of the dihydrogen complex [CpMo(dhpe)(η^2 -H₂)H₂]⁺ in a shallow local minimum, while the rearrangement to the classical tetrahydrido isomer occurs with an extremely small barrier.

The present [Cp*W(dppe)H₃] system displays a record high basicity in hydrogen bonding ($E_j = 1.74 \pm 0.03$ vs. the value of 1.42 ± 0.02 for the Mo analogue). Thus one could expect similar but more pronounced spectroscopic changes if the hydrogen bonding sites would be the same for two metal systems. But this is not the case; the different IR spectroscopic results observed for the hydrogen bonding to two hydrides suggest difference in the structure of H-complexes. The DFT calculations of the hydrogen bonded complexes reproduce the experimental finding of the stronger interactions in the order W > Mo and HFIP > TFE. The geometry optimization in gas phase reveals also that for either metal system the preferred H-bonded structures feature interactions with both metal atom and hydride ligand, but a M \cdots HO contribution increases and a M-H \cdots HO contribution decreases on going from Mo to W.

A second important difference is that no $[\text{Cp}^*\text{W}(\text{dhpe})(\eta^2\text{-H}_2)\text{H}_2]^+$ intermediate was located along the proton transfer pathway by the DFT calculations, but one of the possible reaction coordinate maxima (the lowest-energy one) has a nonclassical character. It may be stated that the protonation process involves a direct transfer to the metal site, involving however assistance by a hydride ligand. The absence of non-classical minimum is also suggested qualitatively by experimentally observed differences in reactivity. Whereas the Mo complex loses H_2 in coordinating solvents or in the presence of coordinating anions,^[30, 31] the W complex is stable under the same conditions.^[31]

As hydrogen bonding can be regarded as the incipient stage of a proton transfer, the protonation occurs easier, i.e. the proton transfer barrier becomes lower as the base becomes stronger. Indeed, the proton transfer barrier estimated from the stopped flow kinetic data for $[\text{Cp}^*\text{WH}_3(\text{dppe})]$ is lower than for $[\text{Cp}^*\text{FeH}(\text{dppe})]$ with the same alcohols (HFIP or PFTB) in agreement with the greater basicity of the tungsten complex. It involves the active participation of the second alcohol molecule, which as shown by theoretical calculations for this and other systems^[24, 25] strengthens the primary hydrogen bond via a cooperative effect and lowers proton transfer barrier. However, the 1:1 composition was determined for the proton transfer product, the hydrogen bonded ion pair $[\text{Cp}^*\text{WH}_4(\text{dppe})]^+\cdots[\text{OR}]^-$, whereas a 1:2 stoichiometry was found for the protonation of $[\text{Cp}^*\text{MH}(\text{dppe})]$ ^[25, 27] and PP_3MH_2 hydrides,^[33] yielding $[\text{L}_n\text{M}(\eta^2\text{-H}_2)]^+\cdots[\text{ROHOR}]^-$. A possible rationalization of this phenomenon could be the weaker acidity of classical polyhydride species vs non-classical ones, so it can be stabilized by stronger interaction with $[\text{OR}]^-$ and withstand a deprotonation.^[34] This rationalization finds support in the computational results.

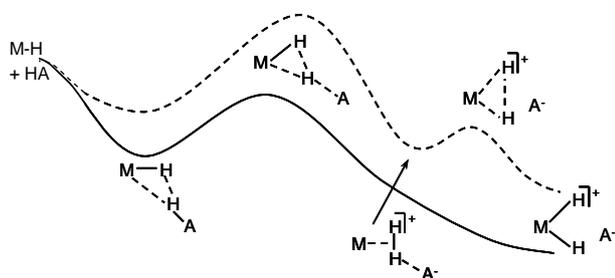


Figure 14. Qualitative energy profile for the proton transfer to $[\text{Cp}^*\text{M}(\text{dppe})\text{H}_3]$ (M = Mo, dashed curve; W, plain curve).

According to both experimental and theoretical results the protonation reaction is more exothermic for the W system, in agreement with its greater basicity in hydrogen bonding and proton affinity. The thermodynamic parameters of hydrogen bonding and proton transfer were obtained for $[\text{Cp}^*\text{WH}_3(\text{dppe})] + \text{HFIP}$ in toluene. Due to the solvent effect^[45, 52] they are lower than they would be in CH_2Cl_2 (the solvent used for other studies, $[\text{Cp}^*\text{FeH}(\text{dppe})] + \text{HFIP}$,^[25] or $[\text{Cp}^*\text{MoH}_3(\text{dppe})] + \text{TFE}$ ^[29]). Still they exceed other systems in agreement with the greater basicity of the tungsten trihydride complex.

The cumulative experimental and theoretical results allow drawing different reaction energy profiles for the Mo and W system, as shown in Figure 14. The stronger H-bonding, greater stability of the tetrahydrido protonation product and lower activation barrier for

proton transfer step are the salient features of the tungsten system in respect to the molybdenum congener. The stronger participation of the metal in hydrogen bonding assists the direct proton transfer to the tungsten atom, and the dihydrogen complex found for molybdenum disappears as a minimum along the reaction pathway in the case of tungsten. Such difference in the proton transfer mechanism and the character of the energy profile could be expected for hydride complexes of electron rich metals bearing donor ligands descending the group (from 2nd to 3rd transition row).

Conclusion

Basic knowledge that has been accumulated over the last two decades suggests that a direct proton transfer to a metal lone pair is an unlikely event in the presence of hydride ligands, which are considered to be the kinetic site of the proton attack even if a classical di-(poly)hydride would be a thermodynamic protonation product. According to both experimental and theoretical results presented herein the greater metal basicity for tungsten in $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ leads to stronger H-bonding, and to the more exothermic protonation reaction having lower activation barrier, relative to Mo analogue. In this work the evidence was obtained for the first time for stronger (relative to the proton-hydride interaction) participation of the metal in hydrogen bonding affecting the subsequent proton transfer profile, which involves a direct proton transfer to the metal centre without the formation of a nonclassical intermediate.

Experimental Section

General. All manipulations were performed under an argon atmosphere by standard Schlenk techniques. All solvents were dried over appropriate drying agent (Na/benzophenone for toluene or THF, CaH_2 for CH_2Cl_2) and freshly distilled under an argon atmosphere prior to use. The NMR solvents (Aldrich) were degassed by three freeze-pump-thaw cycles, and then purified by vacuum transfer at room temperature. Compound $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ was synthesized according to literature.^[31]

Spectroscopic studies. (a) **NMR investigations.** Samples of the hydride $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$ in toluene- d_6 were prepared under an argon atmosphere in 5 mm NMR tubes. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ data were collected with a Bruker AV500 spectrometer, operating at 500.3 MHz and 202.5 MHz, respectively. The temperature was calibrated using a methanol chemical shift thermometer; the accuracy and stability was ± 1 K. All samples were allowed to equilibrate at every temperature for at least 3 min. The spectra were calibrated with the residual solvent resonance (^1H) and with external 85% H_3PO_4 (^{31}P). The conventional inversion-recovery method (180- τ -90) was used to determine the variable-temperature longitudinal relaxation time T_1 . Standard Bruker software was used for the calculation of the longitudinal relaxation time.

(b) **IR and UV-visible Investigations.** The IR measurements were performed on the "Infracalum 801" FT-IR spectrometer using CaF_2 cells of 0.04 – 0.22 cm path length. The UV measurements were performed on Specord M-40 and Varian Cary 5 spectrophotometers. All measurements were carried out by use of a home-modified cryostat (Carl Zeiss Jena) in the 190-290 K temperature range. The cryostat modification allows operating under an inert atmosphere and transferring the reagents (premixed either at low or room temperature) directly into the cell pre-cooled to the required temperature. The accuracy of the temperature adjustment was ± 1 K.

Computational details. Calculations were performed with the Gaussian98^[53] package at the DFT/B3LYP level.^[54-56] Effective core potentials (ECP) were used to represent the innermost electrons of the tungsten atom as well as the electron core of phosphorous atoms.^[57, 58] The basis set for the W and P atoms was that associated with the pseudopotential,^[57, 58] with a standard double- ζ LANL2DZ contraction,^[53] supplemented in the case of P with a set of d-polarization functions.^[59] The carbon and hydrogen atoms of the transition metal complexes that are not bonded to the metal atom, together with the atoms of proton donor molecules (C, F, H) that are not involved in hydrogen bonds, were described with a 6-31G basis set.^[60] The carbon and hydrogen atoms directly bonded to the metal and the proton donor molecules hydrogen and oxygen atoms involved in hydrogen bonding were described with a 6-31G(d,p) set of basis functions.^[61] Geometry optimizations were carried out without symmetry restrictions.

Given the impossibility of locating the transition states in solution for technical reasons, the potential energy curves were explored from reactants to products by series of partial optimizations in gas phase. All the parameters were optimized except for the O-H distance that was increased by 0.2 Å at each step. The energy corresponding to each O-H distance was then evaluated in solution, and the maximum energy obtained along the resulting curve was taken to give the maximum point of the coordinate. Solvent effects were taken into account by means of polarized continuum model (PCM) calculations,^{147, 481} using standard options.¹⁵³¹ The solvation free energies were computed in dichloromethane ($\epsilon = 8.93$) at the gas phase optimized geometries. The gas phase complexation energies were corrected from the basis set superposition error according to the counterpoise method of Boys and Bernardi.¹⁴⁶¹

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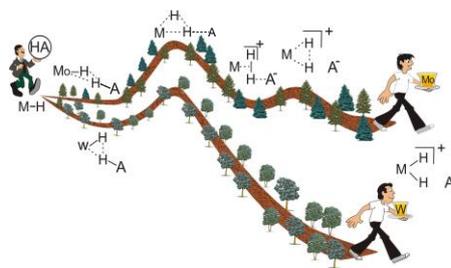
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M-H protonation: Mo vs W

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**Effect of the metal atom nature on
hydrogen bonding and proton
transfer to [Cp*MH₃(dppe)]:
tungsten vs. molybdenum**



Analysis of hydrogen bonding and proton transfer for Cp*MH₃(dppe) complexes of Mo and W, featuring many similarities, shows the delicate balance between the H...H and M...H interactions. Direct H...M bonding prevails for the electron-richer W system.

